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Struktura a magnetismus reálných systémů nanočástic

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Obsah

1	Úvod	9
2	Vybrané partie z magnetismu, struktury a metod	13
2.1	Magnetismus monodoménových částic	13
2.1.1	Magnetická anizotropie nanočástic	13
2.1.2	Superparamagnetismus ideálního systému monodoménových částic . .	16
2.1.3	Superparamagnetismus v reálných systémech	25
2.1.4	Typické experimenty pro studium systémů monodoménových částic .	33
2.2	Strukturní a magnetické uspořádání ve vybraných oxidech	46
2.3	Metody přípravy magnetických nanočástic a nanokompozitů	51
3	Soubor publikací a komentáře	55
3.1	Nanočástice a nanokompozity ternárních spinelů	55
3.1.1	Nanočástice a nanokompozity feritu kobaltnatého	55
3.1.2	Nanočástice a nanokompozity dopovaného feritu kobaltnatého	109
3.1.3	Nanočástice feritu hořečnatého	122
3.1.4	Nanokrystaly chromitu kobaltnatého	131
3.2	Nanomateriály s oxidy železa	146
3.2.1	Nanokompozity na bázi oxidu železitého	146
3.2.2	Izolované nanočástice magnetitu a maghemitu	183
3.3	Další systémy s magnetickými nanočásticemi	215
3.3.1	Granulární multivrstvy $\text{SiO}_2-(\text{Co}/\text{Fe}/\text{CoFe}_2)$	215
3.3.2	Magnetické částice v uhlíkových nanotubách	225
4	Závěr	243

Seznam obrázků

2.1	Vývoj doménové struktury nanočástic ve srovnání s typickou magnetizační izotermou pro danou velikost.	17
2.2	Konvence pro popis koherentní rotace magnetizace v rámci SW modelu a znázornění SW astroidu.	18
2.3	Simulace volné energie v rámci SW modelu.	22
2.4	Schématické znázornění hysterezní smyčky pro různé směry aplikovaného vnějšího magnetického pole.	23
2.5	Schématické znázornění vývoje volné energie pro monodoménovou částici o dané velikosti a efektivní anizotropii v nulovém a externím magnetickém poli. Význam symbolů, zavedených pro potřeby popisu SW a Néelova-Arrheniova modelu je vysvětlen v souvisejícím textu.	24
2.6	Srovnání log-normálních rozdělení teplot blokace, které byly určeny pomocí SQUIDové magnetometrie a feromagnetické rezonance.	24
2.7	Důsledek distribuce velikosti částic na tvar ZFC křivky společně s histogramy velikosti částic určenými na základě transmisní elektronové mikroskopie. . . .	27
2.8	Znázornění kladného posunu teploty blokace, nárustu koercivity a saturace FC křivky v důsledku vzrůstajících dipolárních interakcí.	29
2.9	Průběh normalizované energie pro superferomagnetický systém o různých poměrech interakční a anizotropní energie.	31
2.10	Schéma možného spinového neuspořádání v systémech magnetických nanočástic a výsledného průběhu hysterezní smyčky v blokováném stavu.	32
2.11	Ilustrace časové škály relaxačních procesů v systémech superparamagnetických částic a možných experimentálních metod studia v dané oblasti frekvencí. . .	34
2.12	Typická teplotní závislost magnetizace v režimech ZFC a FC společně s magnetizačními izotermami v blokováném a superparamagnetickém stavu.	35
2.13	Typické protokoly pro studium kolektivních jevů s souborech nanočástic. . . .	36

2.14	Původ hyperjemných interakcí v jádru ^{57}Fe společně s typickými průběhy Mössbauerovských spekter.	39
2.15	Paralelní a kolmé experimentální uspořádání Mössbauerovy spektroskopie v externím magnetickém poli.	44
2.16	Možné spinové a strukturní uspořádání nanočástic.	46
2.17	Typické příklady studovaných nanomateriálů zobrazených pomocí transmisní nebo skenovací elektronové mikroskopie.	54

Seznam tabulek

2.1	Přehled strukturního uspořádání v oxidech železa a vybraných spinelech. . .	49
2.2	Přehled magnetických parametrů vybraných spinelů.	50

Kapitola 1

Úvod

Nanomateriály s přechodnými kovy představují atraktivní systémy z hlediska výzkumu fundamentálních fyzikálních jevů i široké škály aplikací. Narozdíl od makroskopických materiálů identického složení preferují odlišná strukturní uspořádání [1] a vykazují specifické transportní a optické vlastnosti spojené s restrikcí elektronových stavů [2, 3]. U magneticky uspořádaných fází dochází k významným změnám magnetokrystalové anizotropie [4], vzniku monodoménového stavu [5], k odlišné konfiguraci magnetických struktur až ke ztrátě dlouhodosahového magnetického uspořádání [6, 7] nebo naopak k jeho stabilizaci [8, 9].

Mezi nejvíce studované systémy patří nanorozměrové magnetické nanočástice, tj. objekty o typické velikosti¹ v řádu jednotek až desítek nanometrů sestávající se z materiálu vykazujícího dlouhodosahové magnetické uspořádání. Důsledkem redukce rozměrů objemových magnetik je vznik tzv. monodoménového stavu, který implikuje specifické chování souboru částic [10, 11, 12]. Tyto nanočástice nachází již v dnešní době široké uplatnění zejména v biomedicínských aplikacích jako vektorové nosiče léčiv, magnetické kontrastní látky, nosiče pro separaci a detekci biomolekul nebo účinné lokální generátory tepla pro hypertermické terapie nádorových tkání [13, 14]. V posledních letech je společným jmenovatelem biomedicínského výzkumu magnetických nanočástic tzv. teragnostika, jejímž cílem je vývoj multifunkčních nanomateriálů pro multimodální terapie nejčastěji nádorových onemocnění. Vhodně modifikovaný nanomagnet slouží zároveň jako synergický detektor, hypertermický element a nosič selektivně se vázajících nebo terapeuticky aktivních biomolekul. Magnetické nanočástice a systémy od nich odvozené vykazují potenciální využití i jako multifunkční katalyzátory, záznamová média nebo komponenty vysoce citlivých senzorů v mikro- až nano-rozměrovém

¹Pokud není explicitně zmíněno, význam termínu velikost částice obecně odpovídá jejímu průměru za předpokladu sféricky symetrické částice, resp. délce hlavní poloosy elipsoidu pro sferoidální částice. U rektangulárních částic se velikost specifikuje vzhledem ke tvaru částice.

měřítku.

Významným příspěvkem fyziky pevných látek v této mezioborové oblasti je korelace strukturních a magnetických parametrů nanočástic s jejich maximální efektivitou ve výše zmíněných aplikacích. Detailní pochopení fyzikálních mechanismů funkcionality magnetických částic umožňuje konvergenci k optimálnímu chemického složení, strukturnímu uspořádání a magnetickým parametrům nanočástic a od nich odvozených systémů. V prvním přiblížení je magnetická odezva nanočástic funkcí jejich velikosti, která přímo souvisí s celkovou magnetizací nanočástice tzv. superspinem, a magnetokrystalové anizotropie příslušného materiálu. Četné experimenty, jak čistě fyzikální tak biomedicínské, ukazují, že tzv. reálné jevy pozorované ve vzorcích nanočástic dramaticky ovlivňují jejich fyzikální vlastnosti, a tedy potenciální efektivitu v souvisejících aplikacích.

Předkládaná habilitační práce se věnuje problematice magnetického a strukturního uspořádání ve vybraných nanomateriálech na bázi přechodných kovů a zahrnuje 25 publikací uveřejněných se spoluautory v letech 2005 - 2014. Převážná část práce (21 publikací) je zaměřena na studium izolovaných nanočástic a nanokompozitů s oxidy železa a spinelovými ferity. Důraz je kladen na popis reálných faktorů: distribuce velikosti částic, sklonění spinu a strukturního resp. spinového neuspořádání. Dále jsou zahrnuty výsledky studií dipolárních interakcí mezi superparamagnetickými částicemi v granulárních multivrstvách oxidu křemičitého a železa resp. kobaltu. Důsledek velikosti částic na magnetické uspořádání v multiferoickém spinelu diskutuje práce zabývající se monodisperzními nanočásticemi chromitu kobaltnatého. V závěrečných dvou publikacích je demonstrováno, jak aplikace teorie silně interagujících superparamagnetů ve spojení s korektní analýzou velikosti částic a fázového složení pomocí synchrotronového záření umožňuje určení struktury reziduálního kovového katalyzátoru v jednotěnných uhlíkových nanotubách, podrobených různým purifikačním postupům.

V první kapitole (1. Úvod) je stručně popsána motivace předkládaného výzkumu a struktura habilitační práce.

Ve druhé kapitole (2. Vybrané partie z magnetismu, struktury a metod studia a přípravy magnetických nanočástic) je zařazen stručný přehled modelů popisujících ideální a interagující superparamagnety společně s dalšími aspekty reálných systémů jako je distribuce velikosti částic a spinové neuspořádání. Část je věnována typickým experimentálním přístupům pro studium vlastností souborů reálných nanočástic. V další sekci jsou stručně shrnuta specifika jednotlivých studovaných systémů včetně metod přípravy.

Třetí kapitola (3. Soubor publikací a komentáře) obsahuje soubor 25 publikací s komentáři, které jsou rozdělené tématicky do tří částí, a to: 2.1. Nanočástice a nanokompozity

ternárních spinelů, 2.2. Nanomateriály s oxidy železa a 2.3. Další systémy s magnetickými nanočásticemi.

Poslední kapitola (4. Závěr) shrnuje a vzájemně koreluje výsledky uveřejněné v souboru publikací, které jsou součástí této habilitační práce. Dále stručně popisuje možné výzkumné směry v této oblasti, zejména v souvislosti s aktuálně řešenou problematikou ve skupině.

Na závěr jsou uvedeny použité reference. Kromě publikací, na jejichž základě vznikla tato práce, jsou zařazeny i citace souvisejících prací dalších autorů, zejména pro potřeby kapitoly č. 2.

Vzhledem k charakteru úvodní části habilitační práce lze předpokládat, že poslouží nejen svému primárnímu účelu, ale bude užitečná i pro studenty (zejména bakalářského a magisterského studia), kteří se chtějí se zde diskutovanou tematikou seznámit a nedostatek přehledových publikací, případně odborných textů v českém jazyce je často odradí od hlubšího zájmu o tuto problematiku.

Tato práce by nikdy nevznikla bez významné podpory kolegů, přátel a mých nejbližších. V prvé řadě bych chtěla poděkovat RNDr. Danielu Nižňanskému, Ph.D., který mne seznámil s problematikou, jeho slovy 'malých částic', a po několik let se společně se svou skupinou intenzivně věnoval rozvoji metod přípravy nanomateriálů a jejich detailní charakterizaci pomocí Mössbauerovy spektroskopie, vždy byl vtřícný k vědeckým i přátelským diskuzím. Zásadní podíl na této práci mají úžasné členky skupiny magnetických nanosystémů: RNDr. Barbara Pacáková (Bittová), RNDr. Simona Kubíčková (Burianová) a RNDr. Alice Mantlíková, které se v rámci svých bakalářských, diplomových a dizertačních prací intenzivně věnovaly problematice nejen superparamagnetických částic, ale i příbuzným tématům. Bez jejich kontinuálního úsilí, kreativního přístupu a nadšení pro vědeckou práci by většina fyzikálních problémů nebyla nikdy vyřešena a výsledky publikovány. Mé díky patří také kolegům z Matematicko-fyzikální fakulty UK, katedry fyziky kondenzovaných látek (prof. RNDr. Vladimíru Sechovskému, Dr.Sc., prof. RNDr. Václavu Holému, Dr.Sc. a doc. RNDr. Stanislavu Danišovi, Ph.D.), kteří mi poskytli zázemí a pomocnou ruku při zavedení této problematiky v naší skupině. Romaně Pohořalé děkuji za ochotu a pomoc při zpracování administrativní stránky habilitační práce. Závěrem bych chtěla vyjádřit upřímné díky svému manželovi, RNDr. Ing. Martinu Kalbáčovi, Ph.D. který mi svou velkorysou podporou v profesním i osobním životě umožnil po několika letech rezignace zdárné dokončení této práce a přesvědčil mě, že má smysl alespoň se pokusit nadále pokračovat ve výzkumu a výuce studentů v této oblasti.

Kapitola 2

Vybrané partie z magnetismu, struktury a metod přípravy a studia magnetických nanočástic

2.1 Magnetismus monodoménových částic

Magnetické vlastnosti monodoménových částic lze v prvním přiblížení popsat s využitím dobře zavedených modelů, které budou stručně shrnuty v první části této kapitoly. Důvodem je fakt, že v souhrnné podobě jsou tyto informace obtížně dostupné i v dosud publikované přehledové literatuře [15, 16]. Nejprve bude nastíněn koncept magnetické anizotropie nanorozměrových částic a diskutovány jednotlivé příspěvky, které jsou charakteristické pro sféroidální částice. Navazuje část, která shrnuje vybrané partie z teorie superparamagnetismu pro ideální soubor monodisperzních nanočástic. Bude stručně zaveden model Stonera a Wohlfartha pro koherentní rotaci magnetizace a model Néela a Browna, který zavádí charakteristický relaxační čas superspinu vzhledem k efektivní magnetické anizotropii a velikosti nanočástice. V navazující části jsou zmíněny tzv. reálné efekty projevující se v systémech nanočástic, které vedou až ke vzniku různého typu kolektivního chování. Poslední část je věnována typickým experimentům, které jsou využívány pro studium magnetické odezvy a struktury souborů reálných nanočástic.

2.1.1 Magnetická anizotropie nanočástic

Magnetická anizotropie je pro formulaci modelů popisujících chování magnetických nanočástic stěžejním parametrem. Vyjadřuje závislost vnitřní energie systému (nanočástice) na

směru spontánní magnetizace (superspinu), která je určena energetickým rozdílem pro orientaci magnetizace ve snadném a nesnadném směru. Typicky dosahuje hodnot $10^2 - 10^7$ J/m³, což odpovídá energii $10^{-8} - 10^{-3}$ eV na atom. Obecně lze očekávat, že bude nabývat vyšších hodnot pro méně symetrické mříže. Magnetická anizotropie je důsledkem dvou mikroskopických příspěvků, a to spin-orbitální interakce a dlouhodosahové dipolární vazby mezi magnetickými momenty.

Příspěvek do magnetické anizotropní energie souboru identických neinteragujících nanočástic lze souhrnně vyjádřit pomocí následujícího vztahu:

$$E_a = E_{mc} + E_{sh} + E_{ms} + E_{surf}, \quad (2.1)$$

kde jednotlivé členy odpovídají:

- magnetokrystalové anizotropii, E_{mc} ,
- tvarové anizotropii, E_{sh} ,
- magnetoelastické energii (magnetostrikci), E_{ms} ,¹
- povrchové anizotropii, E_{surf} .

Zatímco magnetokrystalová a povrchová anizotropie jsou determinovány spin-orbitální interakcí, tvarová anizotropie a magnetostrikce jsou magnetostatického původu, tj. důsledkem dipolární interakce. V následující části budou stručně popsány jednotlivé příspěvky.

Magnetokrystalová anizotropie, E_{mc} vykazuje symetrii prostorové, resp. Laueho grupy daného materiálu. Pro jednoosý (uniaxiální) systém je obecně definována pomocí rozvoje:

$$E_{mc}^{uni} = \sum_n K_n V \sin^{2n} \theta, \quad (2.2)$$

kde K_n je anizotropní konstanta n -tého řádu a θ odpovídá úhlu mezi snadnou osou magnetizace a vektorem magnetizace. V případě běžných feromagnetů je příspěvek 1. řádu dominantní, dle konvence kladný a další členy rozvoje nejsou pro většinu interpretací významné. Proto se často uvádí ve tvaru:

¹V případě objemových materiálů, epitaxních vrstev a nanomateriálů s preferenční orientací je tento příspěvek signifikantní. U sferoidálních částic v uvažovaném rozmezí velikostí je však nevýznamný. Je nutné ho uvažovat pouze ve speciálním případě, že je nanočástice tvořena materiálem, u kterého dochází ke strukturnímu fázovému přechodu, který je spojený se změnou objemu, resp. tvaru částice (příkladem mohou být spinelové chromity).

$$E_{\text{mc}}^{\text{uni}} = K_1 V \sin^2 \theta, \quad (2.3)$$

kde K_1 odpovídá konstantě jednoosé magnetokrystalové anizotropie 1. řádu.

Pro krystaly s kubickou symetrií, což je případ většiny materiálů studovaných v rámci této habilitační práce, je možné vyjádřit magnetokrystalovou anizotropní energii ve tvaru:

$$E_{\text{mc}}^{\text{cub}} = K_1 V (\alpha_1 \alpha_2 + \alpha_2 \alpha_3 + \alpha_3 \alpha_1) + K_2 V (\alpha_1 \alpha_2 \alpha_3 + \dots), \quad (2.4)$$

kde α_1 , α_2 a α_3 jsou definovány výrazy $\alpha_1 = \sin \theta \cos \phi$, $\alpha_2 = \sin \theta \sin \phi$ a $\alpha_3 = \cos \theta$, θ odpovídá úhlu mezi osou z souřadného systému a vektorem magnetizace a ϕ je azimutální úhel.

Tvarová anizotropie, E_{sh} je důsledkem nehomogenního rozložení indukovaných magnetických dipólů na povrchu, je-li symetrie částice odlišná od sférické (pak je tento příspěvek nulový). Pro sferoidální částice je snadný směr orientace magnetizace podél hlavní rotační osy, protože v této orientaci je hodnota demagnetizačního pole minimální. Pro popis tvarové anizotropie se zavádí tzv. demagnetizační faktor, který bude diskutován v sekci věnující se obecnému odvození Stonerova-Wohlfarthova modelu. Lze říci, že pro protáhlý elipsoid bude preferována jednoosá anizotropie, zatímco pro sploštělý se bude snadná orientace magnetizace nacházet v rovině kolmé na význačnou rotační osu symetrie.

Magnetostrikce, E_{ms} představuje sekundární efekt, který souvisí s vlivem symetrie povrchu a je důsledkem indukovaného mechanického napětí ve směru vektoru magnetizace. Může být formulován ve tvaru:

$$E_{\text{ms}} = -\frac{3}{2} \lambda_s \sigma S \cos^2 \theta, \quad (2.5)$$

kde λ_s odpovídá saturované magnetostrikci, σ hodnotě mechanického napětí vztaženému na jednotku plochy, S povrchu nanočástice a θ úhlu mezi vektorem magnetizace a význačnou osou tenzoru napětí.

Povrchová anizotropie, E_{surf} je důsledkem nárůstu orbitálního příspěvku k celkovému momentu hybosti elektronů v povrchové vrstvě atomů z důvodu vzniku asymetrie v rozložení elektronové hustoty oproti objemovému materiálu. V nanočásticích, zejména o velikosti pod 10 nm, tvoří významný příspěvek do celkové magnetické anizotropie, který může převážet předchozí zmíněné. Celková magnetická anizotropie nanočástic se tedy často uvádí ve tvaru, kde je oddělen povrchový člen:

$$E_a = K_{\text{eff}} V \sin^2 \theta = (K_V + \frac{6}{d} K_{\text{surf}}) V \sin^2 \theta, \quad (2.6)$$

kde K_{eff} reprezentuje tzv. efektivní anizotropní konstantu, K_V postihuje objemovou anizotropii (souhrnný příspěvek magnetokrystalové a tvarové anizotropie, případně magnetostriktce) a K_{surf} odpovídá výhradně povrchovému příspěvku.

2.1.2 Superparamagnetismus ideálního systému monodoménových částic

Stonerův-Wohlfarthův model

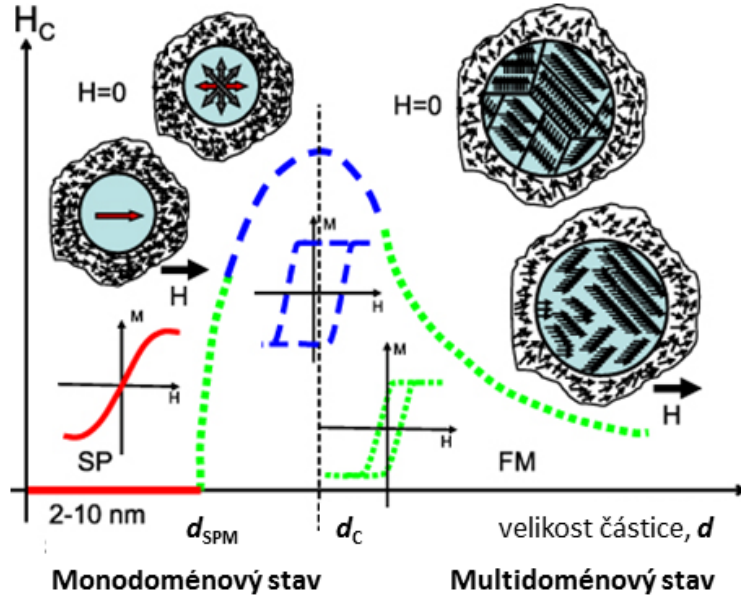
V případě, že je velikost systému s feromagnetickým uspořádáním redukována pod tzv. kritickou, dochází ke vzniku monodoménového stavu, tj. příslušný systém, typicky o velikosti jednotek až desítek nm, figuruje jako jedna magnetická doména reprezentovaná celkovým vektorem magnetizace, tzv. superspinem. V případě sférické částice závisí hodnota kritického poloměru, r_c dle vztahu [10]:

$$r_c \approx 9 \frac{\sqrt{AK_1}}{\mu_0 M_s^2} \quad (2.7)$$

kde A je tzv. výměnná konstanta, K_1 je konstanta magnetokrystalové anizotropie 1. řádu, M_s je saturovaná magnetizace a μ_0 permeabilita vakua. Jako příklad lze uvést následující hodnoty pro běžné feromagnety: Fe - 15 nm, Co - 35 nm, maghemit - 30 nm, SmCo_5 - 750 nm. Odpovídající hodnoty superspinu se pohybují v rozmezí 10^2 - $10^5 \mu_B$ v závislosti na velikosti a typu materiálu.

Kritická velikost nanočástice je zásadním parametrem pro predikci jejích magnetických vlastností při dané teplotě, jak je schematicky znázorněno na Obr.2.1 pro materiál s Curiovou teplotou $> 300K$ při $T \sim 300K$. V případě multidoménového režimu jsou vlastnosti srovnatelné s objemovým materiálem, v blízkosti kritické velikosti (d_c) dochází ke vzniku monodoménového stavu, což je spojeno se vznikem hystereze, zatímco se snižující se velikostí a dosažením tzv. superparamagnetické limity (d_{SPM}) vymizí koercivita i remanence.

Statický model pro popis rovnovážného chování superspinu, μ ve vnějším magnetickém poli vychází z konceptu Stonera a Wohlfartha (dále SW) pro koherentní rotaci magnetizace v homogenní feromagnetické doméně. Model tedy předpokládá souhlasně zmagnetované jednodoménové částice o sféroidální geometrii s jednoosou anizotropií podle význačné rotační osy (znázorněno na Obrázku 2.2). Tento přístup lze aplikovat pro neinteragující superparamagnetické částice se všemi dílčími spiny, resp. magnetizacemi podmřížek orientovanými paralelně.



Obrázek 2.1: Vývoj doménové struktury nanočástic ve srovnání s typickou magnetizační izotermou pro danou velikost.

Pro obecné zavedení SW modelu vyjdeme z předpokladu, že celková volná energie fero-magnetické látky je plně reprezentována vztahem:

$$G(\mathbf{M}, \mathbf{H}_a) = F_{\text{ex}} + F_{\text{an}} + F_{\text{m}} + G_a + F_{\text{ms}} \quad , \quad (2.8)$$

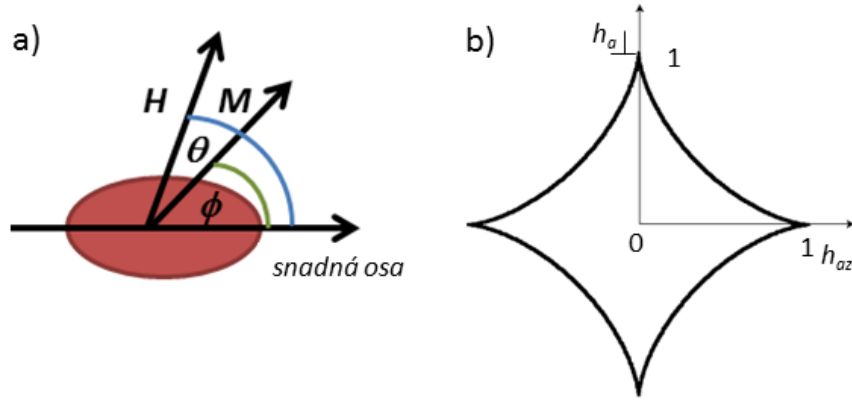
kde F_{ex} odpovídá výměnné energii, F_{an} anizotropní energii, F_{m} magnetostatické energii, G_a příspěvku vlivem vnějšího magnetického pole (Zeemanův člen) a F_{ms} magnetoelastické energii.

S vyloučením příspěvku magnetoelastické energie, který je pro popis superparamagnetického režimu nevýznamný, lze jednotlivé příspěvky vyjádřit následujícím vztahem:

$$G(\mathbf{M}, \mathbf{H}_a) = \int_{\Omega} \left\{ A[(\nabla m_x)^2 + (\nabla m_y)^2 + (\nabla m_z)^2] + f_{\text{an}} + -\frac{1}{2}\mu_0 \mathbf{M} \cdot \mathbf{H}_m - \mu_0 \mathbf{M} \cdot \mathbf{H}_{\text{ext}} \right\} dV \quad (2.9)$$

Příspěvek výměnné energie, F_{ex} pro izotropní systém (např. s kubickou prostorovou grupou) vychází z odvození Landau a Lifshitze publikovaného v [17] a zahrnuje součin výměnné konstanty, A (typicky v řádu 10^{-11} J/m) s rozvojem gradientu složek magnetizace

(m_x, m_y, m_z) . Hustota anizotropní energie, f_{an} , která figuruje v příspěvku F_{an} ² definuje orientaci snadné a nesnadné osy ve svém minimu a maximu. Magnetostatická energie, F_{m} reprezentuje nelokální interakce magnetizace, $\mathbf{M}$ s magnetostatickým polem, $\mathbf{H}_{\text{m}}$ a lze ji interpretovat jako práci k překonání působení magnetického pole na přenesení elementárního magnetického momentu z nekonečna do daného bodu v rámci kontinuální distribuce magnetických momentů v daném objemu. Zeemanův člen dle konvencí vyjadřuje interakci s externím magnetickým polem, $\mathbf{H}_{\text{ext}}$. Detailní odvození a interpretace výše uvedených veličin lze nalézt např. v [17, 18].



Obrázek 2.2: Konvence pro popis koherentní rotace magnetizace v rámci SW modelu (a) společně se schématickým znázorněním SW astroidu v jednotkách K_{eff} (b).

Za předpokladu elipsoidální geometrie nanočástice je již snadné zavést vztah mezi magnetizací a magnetostatickým polem s využitím tenzorové reprezentace:

$$\mathbf{H}_{\text{m}} = -\mathcal{N} \cdot \mathbf{M} \quad (2.10)$$

kde $\mathcal{N}$ je tzv. demagnetizační tenzor³. Pokud vyjádříme $\mathcal{N}$ ve tvaru vzhledem k souřadným osám, které koincidují s osami symetrie elipsoidální částice, získáme:

$$\begin{pmatrix} H_x \\ H_y \\ H_z \end{pmatrix} = \begin{pmatrix} N_x & 0 & 0 \\ 0 & N_y & 0 \\ 0 & 0 & N_z \end{pmatrix} \begin{pmatrix} M_x \\ M_y \\ M_z \end{pmatrix} \quad (2.11)$$

² $F_{\text{an}}(\mathbf{m}) = \int_{\Omega} f_{\text{an}}(\mathbf{m}) dV$

³Vždy pozitivně semidefinitní forma.

kde N_x, N_y, N_z reprezentují složky demagnetizačního faktoru, pro které platí: $N_x + N_y + N_z = 1$. V případě, že z odpovídá snadné ose magnetizace, anizotropní energii lze vyjádřit jako:

$$F_{\text{an}}(\mathbf{m}) = K_1(1 - m_z^2)V, \quad (2.12)$$

kde V je objem sféroidní částice a K_1 odpovídá v prvním přiblížení konstantě magneto-kryсталové anizotropie 1. řádu. Důsledkem platnosti rotační symetrie je zjednodušení vztahu 2.11:

$$N_x = N_y = N_{\perp}, \quad (2.13)$$

což vede k vyjádření volné energie ve tvaru:

$$G(\mathbf{m}, \mathbf{H}_a) = K_1(1 - m_z^2)V + \frac{1}{2}\mu_0 M_s^2 \mathbf{m} \cdot \mathcal{N} \cdot \mathbf{m}V - \mu_0 M_s \mathbf{m} \cdot \mathbf{H}_a V \quad . \quad (2.14)$$

Pro zjednodušení zavedeme bezrozměrné veličiny⁴, což umožní explicitní vyjádření magnetostatické energie, čímž vztah přechází na:

$$g(\mathbf{m}, \mathbf{h}_a) = \frac{K_1}{\mu_0 M_s^2} + \frac{1}{2}N_{\perp} + \left(\frac{1}{2}N_{\perp} \dots \mu_0 M_s^2 - \frac{1}{2}N_{\perp} \right) m_z^2 - \mathbf{m} \cdot \mathbf{h}_a \quad . \quad (2.15)$$

Po minimalizaci volné energie a faktorizaci získáme vztah pro celkovou volnou energii ve tvaru:

$$g(\mathbf{m}, \mathbf{h}_a) = -\frac{1}{2} \left(N_{\perp} + \frac{2K_1}{\mu_0 M_s^2} - N_z \right) m_z^2 - \mathbf{m} \cdot \mathbf{h}_a \quad . \quad (2.16)$$

S platností vztahu pro efektivní anizotropní konstantu:

$$K_{\text{eff}} = N_{\perp} + \frac{2K_1}{\mu_0 M_s^2} - N_z \quad (2.17)$$

přechází vztah 2.16 na jednoduchý tvar⁵:

$$g(\mathbf{m}, \mathbf{h}_a) = -\frac{1}{2}K_{\text{eff}}m_z^2 - \mathbf{m} \cdot \mathbf{h}_a \quad . \quad (2.18)$$

⁴Obě strany rovnice vydělíme výrazem, který představuje redukované jednotky magnetické anizotropní energie: $\mu_0 M_s^2 V$ a využijeme platnosti vztahu $1 - m_z^2 = m_x^2 + m_y^2$.

⁵Je nutné si uvědomit, že pro rotačně symetrickou částici je magnetostatická energie kvadratickou formou v m_z stejně jako anizotropní energie (pro jednoosý případ, kde z je význačná osa symetrie). Z toho důvodu se často objevuje tvrzení, že K_{eff} zahrnuje tvarovou a magnetokrystalovou anizotropii, ačkoliv mají velmi odlišný fyzikální význam.

Důsledkem symetrie problému je, že v rovnovážném stavu leží magnetizace v rovině definované snadnou osou $\mathbf{e}_z$ a směrem aplikovaného magnetického pole $\mathbf{h}_a$, proto je užitečné zavést sférické souřadnice s úhly θ, θ_h mezi $\mathbf{m}, \mathbf{h}_a$ a $\mathbf{e}_z$. Výsledný vztah pro směr vektoru magnetizace je tedy:

$$m_z = \cos \theta \quad , \quad \mathbf{m} \cdot \mathbf{h}_a = h_a \cos(\theta_h - \theta) \quad (2.19)$$

a výraz pro celkovou volnou energii pak přechází do tvaru:

$$g(\theta, \theta_h) = -\frac{1}{2}K_{\text{eff}} \cos^2 \theta - h_{az} \cos \theta - h_{a\perp} \sin \theta, \quad (2.20)$$

kde h_{az} a $h_{a\perp}$ jsou paralelní a kolmá složka vnějšího magnetického pole vzhledem k ose z .

Nyní krátce diskutujeme získaný výsledek. V případě, že není aplikováno externí magnetické pole a částice je zmagnetovaná ve směru snadné osy ($\theta = 0$), nachází se v rovnovážném stavu, stejně tak jako v případě $\theta = \pi$, energetické maximum nastává v případě $\theta = \pm\pi/2$. Aplikujeme-li malé externí magnetické pole ve směru opačném než je počáteční magnetizace, křivka volné energie stále vykazuje dvě minima a maxima. Zvyšujeme-li vnější magnetické pole až ke kritické hodnotě $h_a = h_{\text{SW}}$, dojde k vymizení jednoho minima a maxima a pro magnetická pole vyšší než toto kritické pole $h_a > h_{\text{SW}}$ existuje už jen jedno minimum, resp. maximum. Tento vývoj v externím magnetickém poli lze snadno interpretovat tak, že pro $h_a < h_{\text{SW}}$ zůstane magnetizace orientovaná v původním směru podle osy z , zatímco pro $h_a > h_{\text{SW}}$ dojde k přemagnetování.

V obecném případě je ovšem kritické pole, h_{SW} funkcí θ_h . Proto je *de facto* hlavním výstupem SW modelu definice bifurkační křivky v kontrolní rovině (h_a, θ_h v polárních souřadnicích nebo $h_{az}, h_{a\perp}$ v kartézských souřadnicích), která odděluje oblasti existence dvou minim a jednoho minima. Bifurkační křivka je analyticky dána vztahem:

$$\frac{\partial g}{\partial \theta} = 0 \quad , \quad \frac{\partial^2 g}{\partial \theta^2} = 0 \quad , \quad (2.21)$$

který určuje sedlové body volné energie v rovině $h_{az}, h_{a\perp}$.

Uvažujeme-li výše uvedené podmínky, získáme následující soustavu rovnic:

$$\frac{h_{a\perp}}{\sin \theta} - \frac{h_{az}}{\cos \theta} = K_{\text{eff}}; \quad \frac{h_{a\perp}}{\sin^3 \theta} + \frac{h_{az}}{\cos^3 \theta} = 0 \quad (2.22)$$

jejíž řešení vede k parametrickému popisu bifurkační křivky, známé jako Stonerův-Wohlfarthův astroid (schématicky znázorněný na Obrázku 2.2):

$$h_{az} = -K_{\text{eff}} \cos^3 \theta; h_{a\perp} = K_{\text{eff}} \sin^3 \theta. \quad (2.23)$$

Pokud vnější magnetické pole obsahuje složky takové, že v bodě $(h_{az}, h_{a\perp})$ leží mimo astroid, existuje pouze jedno minimum volné energie a výsledná orientace magnetizace bude odpovídat tomuto stavu. Např. bude-li počáteční magnetizace orientována ve směru snadné osy, $\mathbf{m} = \mathbf{e}_z$, aplikace magnetického pole s amplitudou $h_a h_{\text{SW}} >$ ve směru $\mathbf{e}_z$ způsobí změnu orientace magnetizace do konfigurace $\mathbf{m} = -\mathbf{e}_z$, která je reprezentována jediným energetickým minimem. Oproti tomu pokud bod $(h_{az}, h_{a\perp})$ leží uvnitř astroidu, existují dvě minima a které bude preferováno záleží na dynamice magnetizačního procesu, která je nad rámec konceptu SW modelu.⁶ Proto lze říci, že změna orientace je možná, ale ne jistá. Simulace limitních případů ve smyslu volné energie jako funkce θ a vnějšího magnetického pole, h_a je znázorněna na Obrázku 2.3.

Přímým experimentálně pozorovatelným důsledkem výsledků SW modelu je výrazná závislost tvaru hysterezní smyčky monodoménové částice na úhlu mezi vnějším magnetickým polem a snadnou osou magnetizace (θ), což je znázorněno na Obrázku 2.4.

Néelův-Arrheniův model

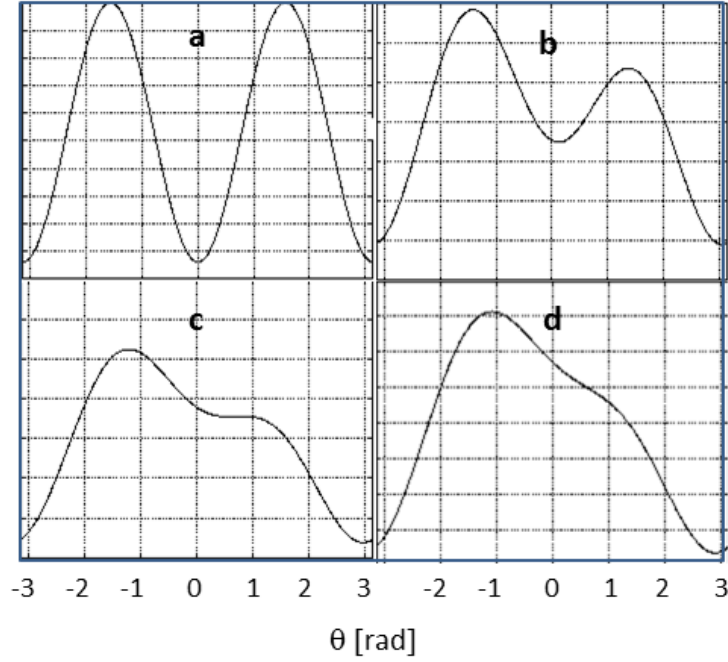
SW model plně popisuje mechanismus změny orientace superspinu homogenní sferoidální částice, nezahrnuje ovšem vliv teploty a s ním související relaxační procesy superspinu. Nejjednodušší přístup pro popis relaxačního procesu při konečné teplotě byl zaveden Néelem a Brownem na základě Arrheniova vztahu pro tepelně aktivované procesy.

Vychází z předpokladu, že energetická bariéra, která odděluje přechod mezi dvěma minimy v nulovém externím magnetické poli (znázorněno na Obrázku 2.5), je reprezentována vztahem:

$$E \approx K_{\text{eff}} V \sin \theta \approx k_B T_B. \quad (2.24)$$

V případě, že $K_{\text{eff}} V$ převažuje příspěvek energie teplotních fluktuací, je možná spontánní změna orientace superspinu z jedné rovnovážné polohy do druhé i bez aplikace vnějšího magnetického pole a systém se nachází v tzv. superparamagnetickém režimu. V tomto stavu

⁶V případě částic v limitě přechodu mezi monodoménovým a vícedoménovým stavem často dochází k jinému mechanismu změny orientace superspinu přes nekoherentní módy různého typu (tzv. fanning nebo curling). Ještě složitější mechanismy zahrnují nukleaci a následný pohyb doménových stěn, což je typický mechanismus pozorovaný u nanodrátů.



Obrázek 2.3: Simulace volné energie v rámci SW modelu jako funkce θ ($K_{\text{eff}} > 0$). (a) V nulovém vnějším magnetickém poli. $h_a = 0$ existují dvě minima pro $\theta = 0, \pi$ dvě maxima pro $\theta \pm \pi/2$. (b) Pro malá vnější magnetická pole jsou zachována dvě minima, resp. maxima. (c) Vznik sedlového bodu z důvodu dosažení kritické hodnoty vnějšího magnetického pole h_{SW} . (d) Pro $h_a > h_{\text{SW}}$ existuje jen jedno maximum, resp. minimum.

je střední hodnota magnetizace nulová a chování magnetické susceptibility lze popsat pomocí modifikace Curiova zákona pro superparamagnet:

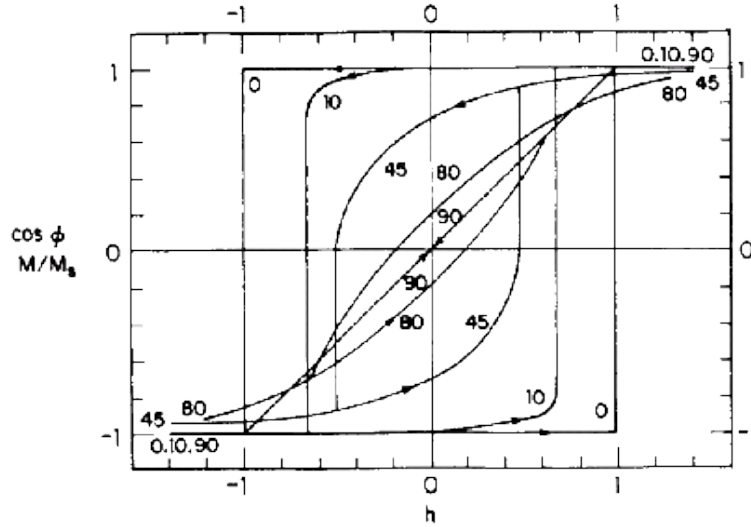
$$\chi_{\text{SPM}} = \frac{C_{\text{SPM}}}{T}, \quad (2.25)$$

kde C_{SPM} je Curiova konstanta ve tvaru: $C_{\text{SPM}} = \frac{\mu_B^2}{3k_B T} N g^2 \mu (\mu + 1)$.

Předchozí vztah jasně demonstruje původ termínu superparamagnetismus, kdy chování systému monodoménových částic vystihuje popis pro paramagnetický systém, kde místo magnetického momentu jednotlivých paramagnetických atomů figuruje celkový magnetický moment, tj. obří spin monodoménové částice.

V kontextu Curiova zákona lze vyjádřit chování superspinu v rovnováze s teplotou a vnějším magnetickým polem pomocí Langevinovy funkce:⁷

⁷Kvantový popis chování spinu v rovnováze s vnějším magnetickým polem a teplotou popisuje Brillouinova



Obrázek 2.4: Schématické znázornění hysterezní smyčky pro různé směry aplikovaného vnějšího magnetického pole. Převzato z [19].

$$L(x) = \coth(x) - \frac{1}{x}; x = \frac{\mu_0 \mu H}{k_B T}. \quad (2.27)$$

Při konečné teplotě magnetizace nanočástice fluktuuje s charakteristickou frekvencí, resp. relaxačním časem, τ :

$$M(t) = M_0 \exp(-t/\tau), \quad (2.28)$$

který souvisí s velikostí energetické bariéry dle Néel-Arrheniova vztahu:

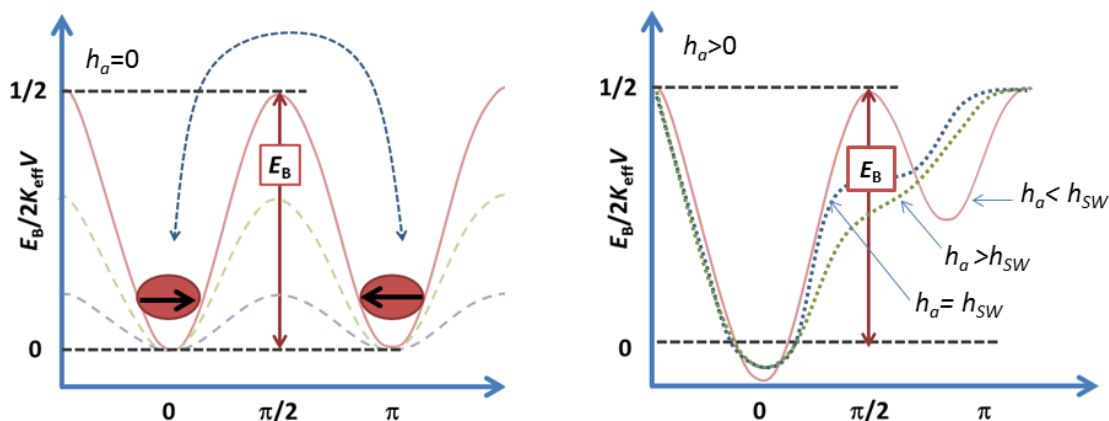
$$\tau = \tau_0 \exp\left(\frac{K_{\text{eff}} V}{k_B T}\right). \quad (2.29)$$

V případě, že snižujeme teplotu až na kritickou hodnotu, tzv. teplotu blokace, T_B kdy platí $K_{\text{eff}} V = k_B T_B$, nastává přechod do blokováného stavu. Tento režim je charakteristický otevřením hysterezní smyčky a dalšími projevy, které budou stručně popsány v části věnující se experimentálním postupům studia magnetických nanočástic. Definici blokováného stavu, resp. hodnoty teploty blokace, je vzhledem ke vztahu 2.28 nutné uvažovat vždy v kontextu příslušné experimentální metody studia, která operuje v určité časové škále (τ_m) a systém tak

funkce:

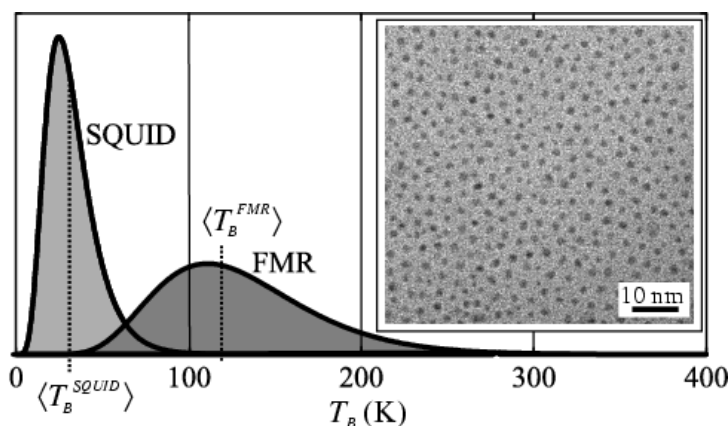
$$B_J(y) = \left(\frac{2J+1}{2J}\right) \coth\left(\frac{2J+1}{2J}y\right) - \left(\frac{1}{2J}\right) \coth\left(\frac{1}{2J}y\right); y = \frac{g_J \mu_B \mu_0 J H}{k_B T}, \quad (2.26)$$

která v limitním případě $\lim_{J \rightarrow \infty} B_J(y) \rightarrow L(y)$ přechází na klasický výsledek Langevina.



Obrázek 2.5: Schématické znázornění vývoje volné energie pro monodoménovou částici o dané velikosti a efektivní anizotropii v nulovém a externím magnetickém poli. Význam symbolů, zavedených pro potřeby popisu SW a Néelova-Arrheniova modelu je vysvětlen v souvisejícím textu.

'sleduje' buď v termodynamické rovnováze ($\tau \ll \tau_m$), kdy se jeví jako superparamagnetický nebo nerovnovážném stavu ($\tau > \tau_m$), což odpovídá režimu blokace. Z tohoto pohledu lze přechod mezi blokováním a superparamagnetickým stavem definovat právě při teplotě, kdy $\tau = \tau_m$. Obrázek 2.6 uvádí příklad, kde je srovnáno rozdělení efektivních teplot blokace pro systém nanočástic o střední velikosti 10 nm, získané pomocí měření magnetizace ($\tau > \tau_m$) a feromagnetické rezonance ($\tau \ll \tau_m$). Rozdíl mezi charakteristickými škálami těchto metod je cca 10 řádů.



Obrázek 2.6: Srovnání log-normálních rozdělení teplot blokace, které byly určeny pomocí SQUIDové magnetometrie a feromagnetické rezonance.

Rigorózní popis pomalé dynamiky s využitím mistrovské rovnice zavádí Sasaki a kol. [20]:

$$\frac{d}{dt}p_1(t) = -W_{1\rightarrow 2}(t)p_1(t) + W_{2\rightarrow 1}(t)\{1 - p_1(t)\}, \quad (2.30)$$

kde $W_{1\rightarrow 2}$, $W_{2\rightarrow 1}$ reprezentují pravděpodobnost přechodu mezi dvěma stavy superspinu, definovanými vztahy 2.31, 2.32 pro libovolné hodnoty magnetického pole a teploty ($h(t)$, $T(t)$) za daných počátečních podmínek.

$$W_{1\rightarrow 2}(t) = \frac{1}{2}\tau_0^{-1} \exp[-K_{\text{eff}}V/T(t)]\{1 - M_s V h(t)/T(t)\} \quad (2.31)$$

$$W_{2\rightarrow 1}(t) = \frac{1}{2}\tau_0^{-1} \exp[-K_{\text{eff}}V/T(t)]\{1 + M_s V h(t)/T(t)\}, \quad (2.32)$$

Pro soubor částic o objemu V a zavedení $h(t)=h$, $T(t)=T$, získáme výsledný tvar pro magnetizaci ve tvaru:

$$M(t; V) = M(t = 0; V) \exp(-t/T) + \frac{(M_s V)^2 h}{T} \{1 - \exp(-t/\tau)\}, \quad (2.33)$$

kde $\tau \equiv \tau_0 \exp(K_{\text{eff}}V/T)$.

Relaxační procesy jsou bezesporu výrazně ovlivněny aplikací vnějšího magnetického pole, nicméně detailní diskuze přesahuje rámec této kapitoly. Detailní rozbor lze nalézt např. v [21].

2.1.3 Superparamagnetismus v reálných systémech

Jak již bylo několikrát uvedeno, modely uvedené v předchozí sekci lze aplikovat na ideální soubor superparamagnetických částic, tj. homogenních monodoménových částic o stejné velikosti, které vzájemně neinteragují. Reálné vzorky se více či méně odlišují od ideálního stavu, a proto je nutné při analýze experimentálních dat uvažovat tzv. reálné efekty, mezi které lze zahrnout:

- distribuci velikosti částic,
- mezičásticové interakce,
- spinové neuspořádání.

V následující části je nastíněn původ reálných jevů a stručně zmíněny možné přístupy, jak je lze korektně popsat a kvantifikovat na základě analýzy experimentálních výsledků.

Distribuce velikosti částic

Distribuce velikosti částic se v experimentálních výsledcích projevuje jako distribuce charakteristických parametrů jako je teplota blokace, superspin nebo relaxační čas. Vyskytuje se ve větší či menší míře u všech typů nanočástic a je přirozeným důsledkem různého mechanismu růstu částic. Ve většině případů lze uvažovat o log-normálním rozdělení. Možnou variantou, jak zahrnout distribuci velikostí je adaptovat log-normální rozdělení objemů určené pomocí analýzy velikosti částic z transmisního elektronového mikroskopu. Tento přístup má zásadní nedostatek v tom, že tzv. fyzická velikost částice, určená pomocí mikroskopie je často velmi odlišná od tzv. magnetické velikosti částice, která odpovídá efektivnímu magneticky aktivnímu objemu, jež je reprezentativním parametrem pro popis magnetických vlastností souboru částic (bude diskutováno dále). Proto je korektnějším postupem zavést log-normální rozdělení superspinů dle vztahu:

$$f(\mu) = \frac{N}{\sqrt{2\pi}} \exp \left[\frac{-\ln^2(\mu/\mu_m)}{2\sigma^2} \right], \quad (2.34)$$

kde N odpovídá počtu částic, σ je šířka distribuce a μ_m je medián distribuce, ze kterého lze určit superspin, μ dle vztahu:

$$\mu = \mu_m \exp \left(\frac{-\sigma}{2} \right). \quad (2.35)$$

Typickým postupem určení této distribuce je analýza magnetizačních izoterm v superparamagnetickém stavu při teplotách » T_B . S využitím Langevinova škálování M/M_s vs. H/T izotermy splývají v generalizovanou křivku (v případě zanedbatelných mezičásticových interakcí). Saturovanou magnetizaci M_s souboru N částic s magnetickým momentem (superspinem) μ lze pak vyjádřit pomocí Langevinovy funkce následovně:

$$M = M_s \cdot L(x); x = \frac{\mu_0 \mu_B H}{k_B T}. \quad (2.36)$$

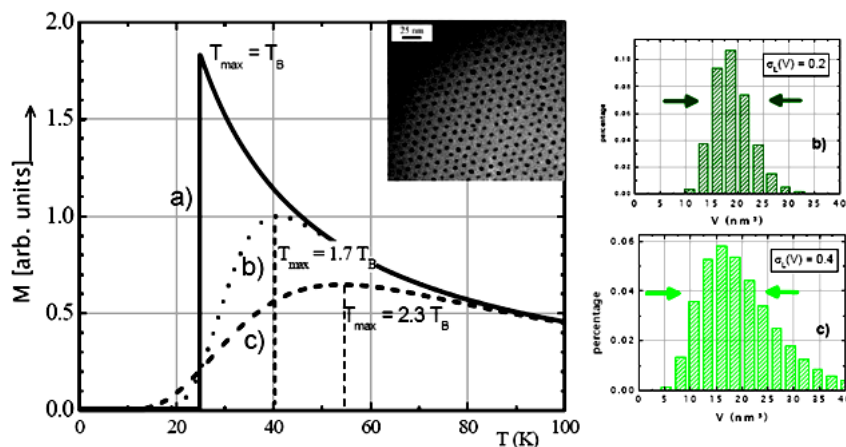
Vážená suma Langevinových funkcí, která popisuje magnetizaci systému neinteragujících částic s log-normálním rozložením superspinů, je pak definována vztahem:

$$M(H, T) = \int_0^\infty L(\mu) M_s d\mu = \int_0^\infty \mu L(x) f(\mu) dx. \quad (2.37)$$

Na základě znalosti μ_m , magnetického momentu a objemu základní buňky μ_Z , Z , je možné určit tzv. magnetickou velikost nanočástice, ve smyslu průměru d_{mag} :

$$d_{\text{mag}} = \sqrt[3]{\frac{3V}{4\pi}}; V = \frac{\mu_Z}{\mu} V_Z. \quad (2.38)$$

Typický příklad je uveden na Obrázku 2.7, kde jsou srovnány dva průběhy teplotní závislosti magnetizace měřené v režimu ZFC v identickém externím magnetickém poli pro dva vzorky s různou distribucí velikosti částic. Pro názornost je uveden i teoretický případ monodisperzního systému, kde dochází ke skokové blokaci.



Obrázek 2.7: Důsledek distribuce velikosti částic na tvar ZFC křivky společně s histogramy velikosti částic určenými na základě transmisní elektronové mikroskopie.

Mezičásticové interakce

Magnetickou odezvu systémů reálných nanočástic výrazně ovlivňují jejich vzájemné interakce. V závislosti na koncentraci nanočástic v systému, tj. jejich vzálenosti při dané velikosti částic, a tedy velikosti superspinu dochází v principu ke dvěma druhům interakcí, a to dipolárním nebo výměnným [22, 23]. Mezičásticové interakce způsobují změnu hodnot charakteristických parametrů blokováného, resp. superparamagnetického stavu, ovlivňují relaxační procesy a spinovou strukturu zúčastněných nanočástic. V systémech, kde nejsou jednotlivé nanokrystaly fixované, vedou ke vzniku aglomerátů či řetězců s odlišným chováním oproti individuálním částicím. Známým důsledkem výměnných interakcí na rozhraní feromagneticky a antiiferomagneticky uspořádané látky je pak asymetrie hysterezní smyčky a nárůst koercitivního pole, známá jako výměnně-zesílený režim (v angl. exchange-bias) [24]. Nejčastěji je pozorován v povrchové vrstvě kovových nanočástic, která je tvořena oxidem příslušného kovu.

Ve velmi koncentrovaných systémech nanočástic dochází ke vzniku kolektivního uspořádání, které lze označit jako tzv. superspinové sklo (v analogii se spinovým sklem) [25, 26, 27]

nebo tzv. superferomagnetický stav (v analogii s feromagnetickým uspořádáním) [28, 29]. V materiálech, které jsou předmětem studia této práce, hrají klíčovou roli interakce dipolárního původu, nicméně v následujícím textu budou stručně shrnuta specifika obou typů kolektivního uspořádání a možné přístupy k jejich teoretickému popisu využitelné pro analýzu experimentálních dat.

Dipolární interakce, superspinová skla

Dipolární interakce jsou důsledkem dlouhodosahového vzájemného působení magnetických dipólů, potenciální energii, E_d v případě dvou dipólů ve vzdálenosti r lze uvažovat ve tvaru:

$$E_d = \frac{\mu_0}{4\pi r^3} \left[\mu_1 \mu_2 - \frac{3}{2} (\mu_1 r)(\mu_2 r) \right] \approx \frac{\mu_0 \mu^2 h}{4\pi r^3}, \quad (2.39)$$

kde μ_1 , μ_2 , resp. μ odpovídají superspinům zúčastněných částic.

Zatímco pro jednoatomové spiny ($\sim 1 \mu_B$) ve vzdálenosti odpovídající typickým rozměrům vazebných délek (0.1 nm) se hodnoty E_d pohybují v řádu 10^{-23} J ~ 1 K, pro charakteristické hodnoty superspinů 10^{-5} - $10^{-3} \mu_B$ s mezičásticovými vzdálenostmi srovnatelnými s jejich rozměry (1 - 10 nm) dosahujeme dipolárního uspořádání pro teploty v řádu desítek K. Přibližnou teplotu dipolárního uspořádání, T_d můžeme odhadnout ze vztahu:

$$T_d \approx \frac{E_d}{k_B}. \quad (2.40)$$

Pokud dochází ke vzniku řetízků nanočástic, je teplota uspořádání v rámci aproximace středního pole dána vztahem [30]:

$$T_d = 1.202 \frac{\mu_0 \mu^2}{3\pi d^3 k_B}. \quad (2.41)$$

Obecně lze očekávat, že dipolární interakce vedou k potlačení superparamagnetické relaxace, resp. zvýšení teploty blokace, nicméně pro systémy se slabou interakcí bylo pozorováno snížení energetické bariéry spojené s poklesem teploty blokace a relaxačního času [34].

V případě slabých interakcí lze modifikovanou superparamagnetickou relaxaci systému popsat s využitím Vogelova-Fulcherova zákona [31], [32]:

$$\tau_m = \tau_0 \exp \left[\frac{K_{\text{eff}} V}{k_B (T - T_{\text{VF}})} \right], \quad (2.42)$$

kde T_{VF} reprezentuje sílu dipolárních interakcí a τ_0 odpovídá charakteristickému relaxačnímu času superspinu neinteragujícího systému.

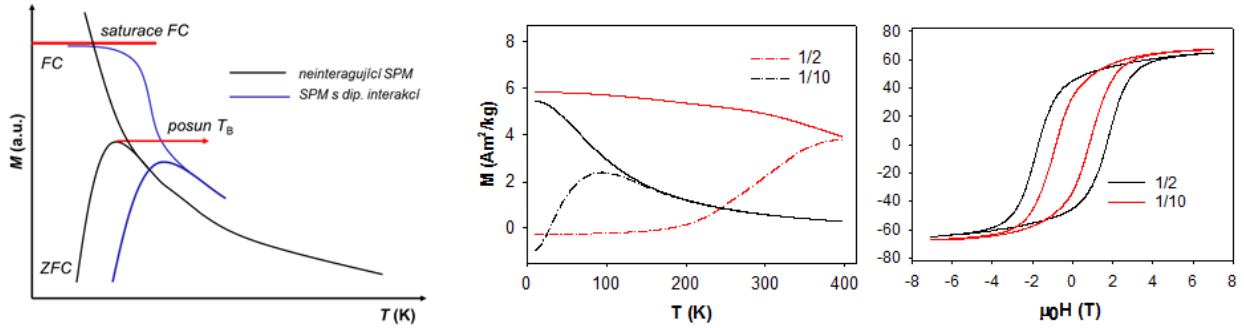
Dochází-li ke vzniku kolektivně blokováného stavu, tzv. **superspinového skla** (SSG) vyhovujícím popisem pro divergenci relaxačního času je vztah pro kritickou dynamiku zavedený

pro spinová skla [33]:

$$\tau_m = \tau_0 \exp \left(\frac{T}{T_g - 1} \right)^{zv}, \quad (2.43)$$

kde T_g odpovídá teplotě přechodu do skelného stavu a zv reprezentuje tzv. kritický exponent, který nabývá hodnot v řádu jednotek až desítek.

Důsledek mezičásticových interakcí je přímo pozorovatelný na změně charakteru teplotní závislosti magnetizace, jak je znázorněno na Obrázku 2.8. Interakce mezi částicemi se typicky projevuje jako saturace větve FC (přesný význam popsán dále) a její charakter lze odhadnout na základě analýzy magnetické susceptibility v superparamagnetickém režimu. Obecně lze říci, že se vzrůstající dipolární interakcí také dochází ke zvyšování teploty blokace a nárůstu koercivity.



Obrázek 2.8: Schématické znázornění kladného posunu teploty blokace a saturace FC křivky v důsledku vzrůstajících dipolárních interakcí. Vpravo je uveden příklad nepublikovaných výsledků pro systém nanokrystalů feritu kobaltnatého v matrici SiO_2 , kde 1/2 resp. 1/10 odpovídá molárnímu poměru Fe k Si.

Superspinová skla se vyznačují náhodným kooperativním uspořádáním spinů při teplotách menších než T_g . Kolektivní dynamika v metastabilním skelném stavu je důsledkem silné dipolární interakce mezi superspiny a náhodnou orientací snadných os magnetizace v náhodných pozicích, kde se nacházejí příslušné nanočástice. Kolektivní projevy superspinů lze v prvním přiblížení popsat s využitím velmi dobře definového konceptu pro spinová skla. V závislosti na typu a symetrii dominantní výměnné interakce rozlišujeme (super)spinová skla typu RKKY s izotropní výměnnou interakcí (tzv. kanonická nebo Heisenbergova) a re-entrantní (super)spinová skla, která jsou charakteristická vznikem mezistavu (super)klastrového skla při přechodu mezi feromagnetickým a paramagnetickým stavem.

Výměnné interakce, superferomagnetický stav

V analogii s definicí výměnných interakcí mezi individuálními spiny rozlišujeme dle mechanismu několik druhů **výměnných interakcí** v systémech nanočástic. K přímé výměnně dochází v případě, že jsou povrchy zúčastněných nanočástic v přímém kontaktu. Tzv. tunelovací výměnnou interakci lze pozorovat v systémech, kde jsou nanočástice separované na velmi malou vzdálenost, typicky menší než je jejich velikost. Speciálním případem je tzv. RKKY výměnná interakce v systémech s vodivou maticí, kde je vazba mezi superspiny zprostředkovaná pomocí polarizace elektronového plynu kovové matrice. K tzv. supervýměnně dochází u systémů, kde jsou nanočástice umístěné v dielektrické matici a na rozhraní částic a matrice dochází ke kovalentní vazbě. Nejvíce diskutovaným uspořádáním je superferomagnetický režim, diskutovaný v následující části.

Superferomagnetický stav (SFM) vzniká v souborech nanočástic, kde koncentrace částic převyšuje tzv. perkolační mez. Chování superferomagnetu lze přirovnat k objemového feromagnetu, nicméně vznik superferomagnetických domén, jako typické analogie s objemovými feromagnety, nebyl dosud jednoznačně experimentálně potvrzen. Proto lze tento typ kolektivního uspořádání chápat jako systém superspinů se silnými korelacemi feromagnetického charakteru. Energii takového systému lze popsat pomocí následujícího vztahu [35, 36]:

$$E_{\text{SFM}} = K_{\text{eff}} V \sin^2 \theta - \sum_{i,j} J_{ij} \mathbf{S}_i \mathbf{S}_j, \quad (2.44)$$

kde první člen popisuje magnetickou anizotropní energii a druhý reprezentuje interakční energii, J_{ij} je výměnní konstanta a $\mathbf{S}_i$, $\mathbf{S}_j$ reprezentuje sousední superspiny v přímém kontaktu, např. v povrchové vrstvě nanočástic. S využitím aproximace středního pole přechází vztah do tvaru:

$$E_{\text{SFM}} = K_{\text{eff}} V \sin^2 \theta - J_{\text{eff}} \mathbf{M}(T) \langle \mathbf{M}(T) \rangle, \quad (2.45)$$

kde $\mathbf{M}(T)$ je magnetizaci podmříže, J_{eff} reprezentuje efektivní výměnnou konstantu a $J_{\text{eff}} \langle \mathbf{M}(T) \rangle$ odpovídá efektivnímu interakčnímu (střednímu) poli.

V případě, že je orientace anizotropního a interakčního pole paralelní, lze energii systému vyjádřit ve tvaru:

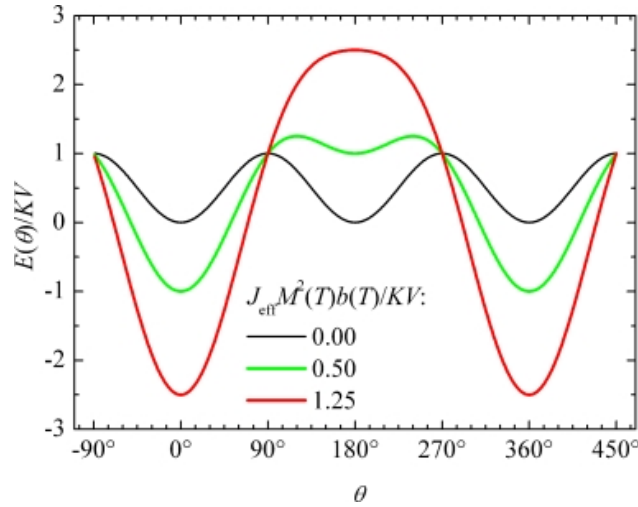
$$E_{\text{SFM}} \approx K_{\text{eff}} V \sin^2 \theta - J_{\text{eff}} M^2(T) b(T) \cos \theta, \quad (2.46)$$

kde $M(T)$ je magnetizace podmříže s vyloučením magnetických fluktuací a $b(T)$ je parametr uspořádání zavedený jako:

$$b = \frac{|\langle (M)(T) \rangle|}{M(T)}. \quad (2.47)$$

Typický průběh magnetické energie systému pro různé poměry interakční a magnetické energie je znázorněn na Obrázku 2.9. Uvažujeme-li dominantní interakční člen, lze charakteristickou teplotu stabilizace superferomagnetického stavu odhadnout ze vztahu:

$$T_{SFM} \approx \frac{J_{\text{eff}} M^2(T_{SFM})}{3k_B}. \quad (2.48)$$



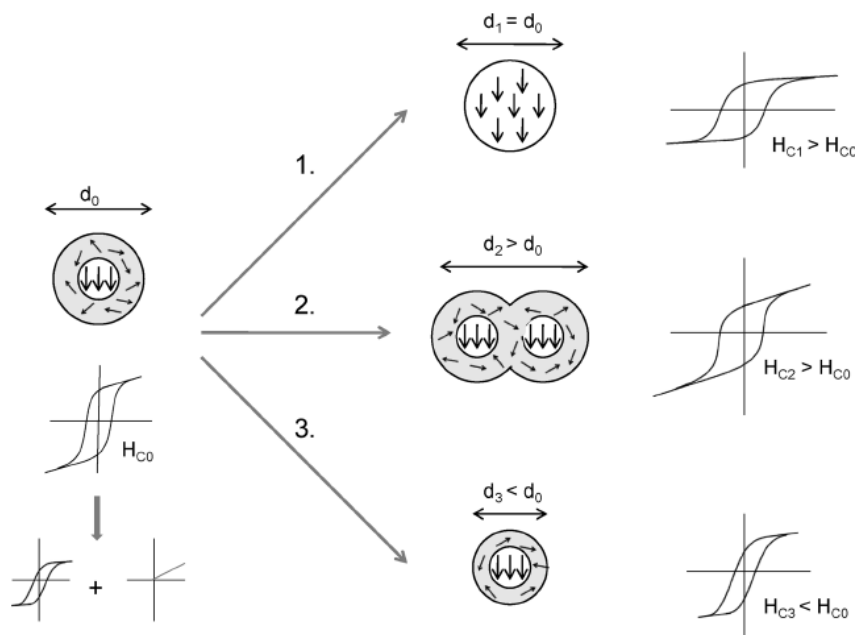
Obrázek 2.9: Průběh normalizované energie pro superferomagnetický systém o různých poměrech interakční a anizotropní energie. Převzato z [35].

Spinové a strukturní neuspořádání

Důsledkem nanorozměrové velikosti částic je vznik tzv. magneticky mrtvé vrstvy u povrchu nanočástice, tj. efektivní objem částice, který se projevuje jako homogenní magnetická doména, je menší než fyzická velikost částice. Podíl povrchové magneticky, a často i krystalograficky, neuspořádané vrstvy závisí na způsobu přípravy nanomateriálu a přímo souvisí s krystalinitou částice, která je daná podílem mikronapětí, nestechiometrií fáze, koncentrací defektů apod. Dle zjednodušeného konceptu tzv. struktury jádro-slupka (v angl. core-shell), zavedeného Coeym [37], je uvažováno ostré rozhraní mezi magneticky uspořádaným jádrem a zcela neuspořádanou slupkou. Problematice povrchové vrstvy nanočástic se věnuje monografie [38].

V reálných vzorcích je situace složitější, protože povrchová vrstva může vykazovat gradient strukturního a spinového neuspořádání, projevuje se aglomerace částic v sintrovaných vzorcích nebo velmi koncentrovaných ferrofluidech. Na základě jednoduché analýzy výsledků magnetických a strukturních experimentů nelze vždy zcela jednoznačně určit, jaká je skutečná krystalografická a spinová struktura reálné nanočástice, nicméně lze ji poměrně dobře odhadnout (bude diskutováno v části zaměřené na experimentální metody studia nanočástic). Příklad charakteristické struktury částečně neuspořádaných částic a typický průběh hysterezních smyček v blokováném stavu je uveden na Obrázku 2.10.

Uvažujeme-li, že spinová struktura povrchové vrstvy nabývá rovnovážné konfigurace z důvodu minimalizace energie systému, je očekáváno sklonění dílčích spinů vzhledem ke snadné ose magnetizace díky dominantnímu vlivu povrchové anizotropie. Proto je často definován tzv. úhel sklonění spinu, který odráží pokles celkového superspinu částice vzhledem k ideálně uspořádanému stavu.⁸



Obrázek 2.10: Schéma možného spinového neuspořádání v systémech magnetických nanočástic a výsledného průběhu hysterezní smyčky v blokováném stavu. Převzato z [39].

⁸Tento koncept má své limity, zejména pro vysoce krystalické částice s charakteristickými krystalografickými poruchami, jak je popsáno např. v [40].

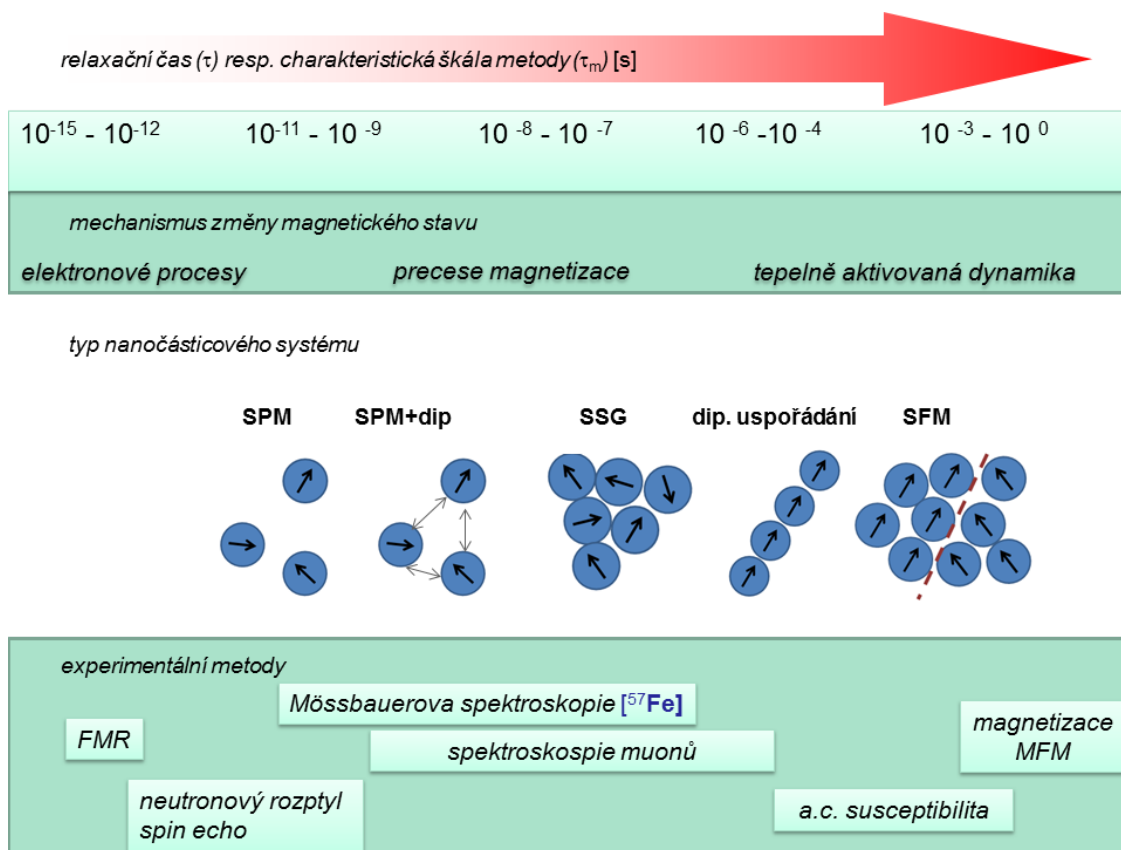
2.1.4 Typické experimenty pro studium systémů monodoménových částic

Magnetické a strukturní vlastnosti monodoménových částic jsou typicky studovány pomocí objemových i mikroskopických metod. V této sekci budou stručně shrnuty tři nejdůležitější z nich společně s typickými experimentálními protokoly a nástinem možné analýzy výsledků v kontextu teoretických přístupů diskutovaných v částech 2.1.2. a 2.1.3.. Cílem této části není detailní popis principu měřících metod, potažmo technických detailů zařízení, které jsou specifické pro konkrétní aparatury a lze je nálezt v běžně dostupné literatuře. Účelem je nastínit specifika typových experimentů a analýzy experimentálních dat pro studium souborů reálných nanočástic.

Je vhodné připomenout, že experimentálně zjištěná teplota blokace superparamagnetického systému je vázaná na charakteristický čas příslušné experimentální metody, kterou je studován, proto je časová škála metody velmi důležitým faktorem. Typické časové škály experimentálních metod se pohybují v následujících rozmezích: 10^{-12} - 10^{-10} s pro nepružný rozptýl neutronů, 10^{-10} - 10^{-7} s pro Mössbauerovu spektroskopii (dáno dobou života excitovaného stavu u jaderného přechodu, pro $^{57}\text{Fe} \sim 8 \times 10^{-8}$ s), 10^{-10} - 10^{-5} s pro spektroskopii muonů (doba života muonu je typicky 2,2 ms), 10^{-1} - 10^{-5} s pro střídavou susceptibilitu, 10^{-14} - 10^{-11} s pro feromagnetickou rezonanci aj. Schéma, které koreluje typické relaxační časy systémů monodoménových částic a charakteristické časy metod studia je znázorněno na Obrázku 2.11.

Magnetizace

Prvotním experimentem, který slouží pro odhad základních parametrů superparamagnetického, resp. blokováného stavu, je měření teplotní závislosti magnetizace. Typicky se provádí v tzv. režimu zero field-cooled, ZFC a field-cooled, FC. V režimu ZFC je vzorek nejprve ochlazen na nízkou teplotu, následně je aplikováno magnetické pole v řádu 0.1 mT a změřena magnetizace do pokojové, případně maximální dostupné teploty. V režimu FC se experiment opakuje při ponechání vnějšího magnetického pole. Typická křivka reálného vzorku je znázorněna na obrázku 2.12. V případě, že soubor částic neinteraguje, je důsledkem přechodu do blokováného stavu odchylka ZFC křivky od Curiova zákona, objevuje se maximum, které koinciduje s bifurkačním bodem. Průběh závislostí ZFC a FC a jejich koincidence závisí v nejjednodušším přiblížení na velikosti částic, nicméně vlivem reálných efektů jsou obě křivky významně modifikovány. Na Obrázku 2.12 je znázorněn i typický průběh ZFC křivky pro na-



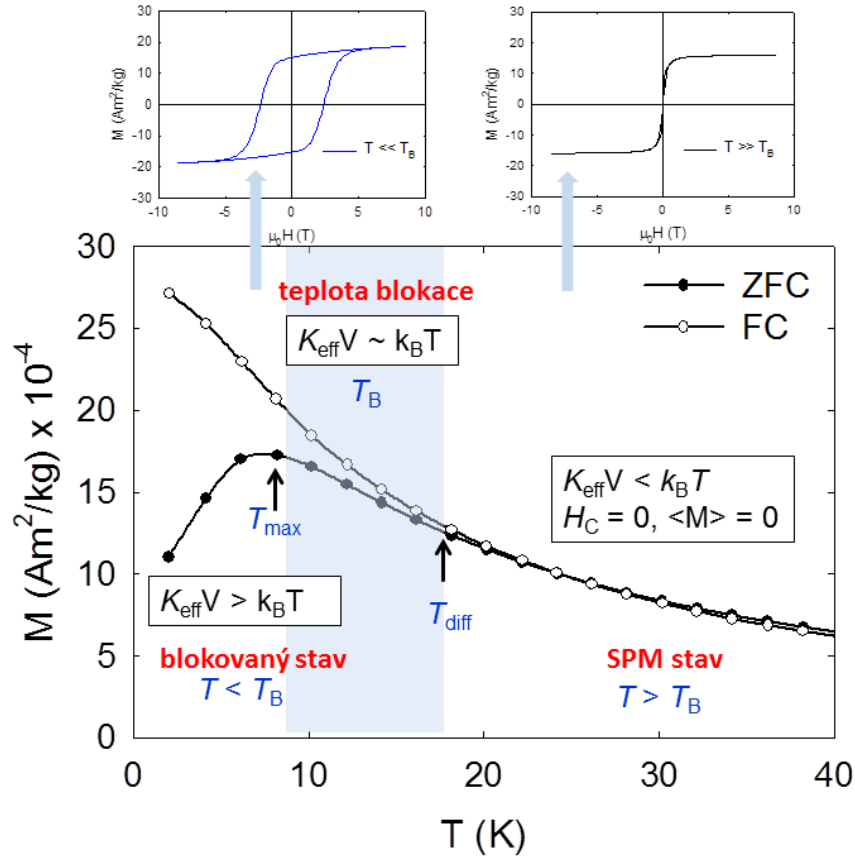
Obrázek 2.11: Ilustrace časové škály relaxačních procesů v systémech superparamagnetických částic a možných experimentálních metod studia v dané oblasti frekvencí.

nočástice s různou distribucí velikostí. Teplota blokace určená buď z maxima na křivce ZFC nebo z bifurkačního bodu křivek ZFC a FC je tedy pouze orientační. Jako odhad distribuce teploty blokace lze využít jednoduchého vztahu:

$$\frac{dT_B}{dT} = \frac{d(\mu_{ZFC} - \mu_{FC})}{dT}, \quad (2.49)$$

který udává odhad rozložení teploty blokace v rovnovážném režimu za předpokladu zanedbatelných mezičásticových interakcí.

Pro studium kolektivních jevů je možné využít rozšířených přístupů. Jednou z možností je tzv. termoremanentní protokol (z angl. thermoremanence, TRM), při kterém je systém ochlazen ve vnějším magnetickém poli na teplotu T_{wait} , kde je ponechán k relaxaci po dobu t_{wait} . Následně je odstraněno vnější magnetické pole a je sledován pokles magnetizace. Charakteristickým projevem je maximum na křivce TRM v okolí efektivní teploty blokace (korelované k objemu příslušné dynamicky aktivní frakce nanočástic), které se posouvá k vyšším



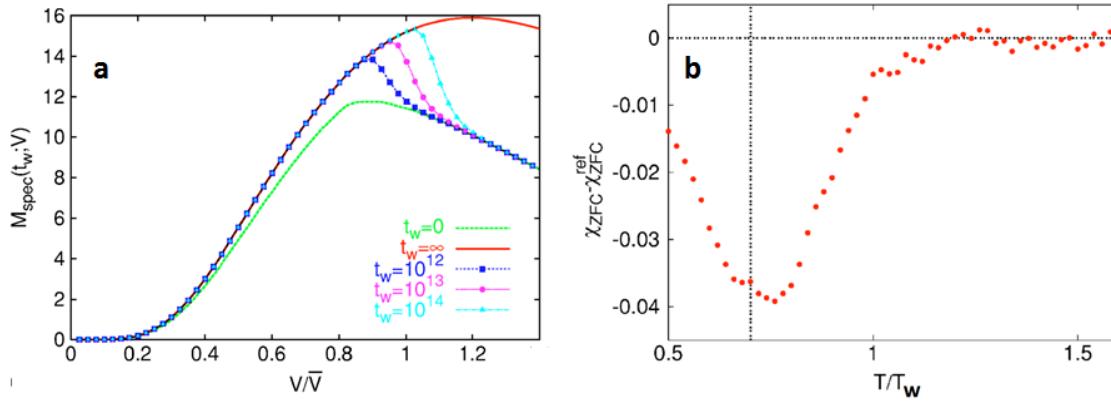
Obrázek 2.12: Typická teplotní závislost magnetizace v režimech ZFC a FC (vysvětleno v textu) společně s magnetizačními izotermami v blokovaném a superparamagnetickém stavu.

teplotám, resp. objemům s rostoucím t_{wait} , jak je znázorněno na Obrázku 2.13. Pro teplotní závislost termoremanetní magnetizace, M_{TRM} platí součtové pravidlo ve tvaru:

$$M_{TRM}(t, t_{wait}) = M_{FC}(t + t_{wait}) - M_{ZFC}(t). \quad (2.50)$$

Dalším typickým experimentem využívajícím měření teplotní závislosti magnetizace je tzv. stárnutí (agging), kdy je systém ponechán v nulovém magnetickém poli při teplotě $T_{wait} < T_B$ po dobu t_{wait} , následně je změřena křivka ZFC v běžném teplotním rozsahu. Rozdíl křivky ZFC měřené standardním postupem a křivky ZFC s relaxací poskytuje v případě signifikantní kolektivní dynamiky anomálii v okolí T_{wait} .

Teplotní závislost magnetizace lze také analyzovat ve smyslu Curie-ova zákona modifikovaného pro superparamagnety a získat odhad velikosti superspinu, případně informaci o



Obrázek 2.13: Typické protokoly pro studium kolektivních jevů s souborech nanočástic. (a) Termoremanentní protokol v redukované reprezentaci, (b) studium vlivu stárnutí systému. Přepočítáno na základě [20].

charakteru možných interakcí mezi částicemi.⁹ Je-li závislost výrazně ovlivněna distribucí velikosti částic a silnými dipolárními interakcemi, odchyluje se od předpokládaného průběhu a tuto jednoduchou analýzu není možné v běžně dostupném teplotním rozsahu aplikovat.

Dalším důležitým experimentem je měření magnetizačních izoterm v blokovaném a superparamagnetickém stavu. Z křivek v blokovaném stavu lze určit charakteristické parametry (koercitivní pole, H_c , remanenci, M_r a saturovanou magnetizaci, M_s), případně vyhodnotit jejich teplotní závislost s využitím výše popsaných modelů. Analýzou magnetizačních izoterm v superparamagnetickém stavu lze určit magnetický moment (superspin) částice, případně superspinovou distribuci aplikací příslušné distribuční funkce (pro log-normální rozdělení bylo popsáno v předchozí části). Analýza křivek v režimu saturace poskytuje odhad příspěvku spinově neuspořádané frakce, který se projevuje jako lineární (paramagnetický) příspěvek způsobující nesaturaci magnetizačních křivek do vysokých magnetických polí. Pro korektní analýzu magnetizačních izoterm je vždy nutné data korigovat na tento příspěvek.

Střídavá susceptibilita

Střídavá susceptibilita je velmi užitečná metoda pro studium superspinové dynamiky, protože umožňuje studium systému v poměrně široké časové škále, která koinciduje s charakteristickými relaxačními časy. Při experimentu je na vzorek aplikováno střídavé magnetické pole, které lze vystihnout vztahem:

⁹V případě mezičásticových interakcí je nutné rozšířit vztah do tvaru Curie-Weissova zákona $\mu/H = C^{\text{SPM}}/(T - \theta_P^{\text{SPM}})$, který mezičásticové interakce postihuje.

$$H(t) = H_{ac} \sin(2\pi ft), \quad (2.51)$$

kde H_{ac} je amplituda (tzv. stejnosměrná komponenta) typicky v řádu mT a f odpovídá frekvenci v intervalu 10^{-2} - 10^4 Hz.

Časově, resp. frekvenčně závislou odezvu magnetizace lze vystihnout pomocí rozvoje:

$$M(t) = H_{ac} \sum_{n=1}^{\infty} \text{Im}(\chi_n e^{in2\pi ft}) = H_{ac} \sum_{n=1}^{\infty} [\chi'_n \sin(2n\pi ft) + \chi''_n \cos(2n\pi ft)], \quad (2.52)$$

kde χ_n odpovídá magnetické susceptibilitě n -tého řádu a χ'_n , χ''_n její reálné, resp. imagi-nární komponentě svázané jednoduchým vztahem:

$$\chi = \chi' + \chi''. \quad (2.53)$$

Ve frekvenční doméně lze jednotlivé složky vyjádřit pomocí níže uvedených vztahů.

$$\chi'_n = \frac{2}{H_{ac}} \int_0^{2\pi} M(t) \sin(2nt) df t, \quad (2.54)$$

$$\chi''_n = \frac{2}{H_{ac}} \int_0^{2\pi} M(t) \cos(2nt) df t. \quad (2.55)$$

Pro soubor monodoménových částic v teplotním oboru koincidujícím s přechodem mezi superparamagnetickým a blokováným stavem, lze jednotlivé příspěvky vyjádřit ve tvaru:

$$\chi(\omega) = \frac{\chi_{sp} + i\omega\tau\chi_b}{1 + i\omega\tau*}, \quad (2.56)$$

kde χ_{sp} odpovídá susceptibilitě v superparamagnetickém stavu, χ_b susceptibilitě v blokováném stavu a $\tau*$ reprezentuje střední relaxační čas ($\tau* = \tau/2$).

Pro první odhad charakteru relaxačního procesu a typu magnetického stavu systému se často využívá empirický vztah:

$$\phi = \left(\frac{\Delta T_f}{T_f \Delta \ln f} \right), \quad (2.57)$$

kde T_f odpovídá efektivní teplotě blokace pro danou časovou škálu (frekvenci). Pro ideální superparamagnetický systém je očekávána hodnota 0,1, zatímco pro superspinová skla a systémy s kolektivními relaxacemi se hodnoty pohybují v intervalu 10^{-3} - 5×10^{-2} .

Výsledky teplotní závislosti magnetické susceptibility 1. řádu jsou analyzovány s využitím modelů popsanych v částech 2.1.2. a 2.1.3..

Studium vyšších členů rozvoje slouží jako komplementární metoda k potvrzení existence kooperativních jevů. Při teplotě do skelného stavu (T_g) dochází k divergenci susceptibility vyššího řádu, jak je uvedeno pro složky 3. a 5. řádu:

$$\chi_3 = \chi_3^0 \left(\frac{T}{T - T_g} \right)^{-\gamma}, \quad (2.58)$$

$$\chi_5 = \chi_5^0 \left(\frac{T}{T - T_g} \right)^{-(\beta - 2\gamma)}, \quad (2.59)$$

kde β a γ jsou kritické exponenty.

Pro ověření kritické dynamiky se využívá univerzálního škálování pro imaginární složku, $\chi''(f, T)$:

$$\frac{\chi''}{\chi_{eq}} = \left(\frac{T}{T - T_g} \right)^{\beta} Y(f, t), \quad (2.60)$$

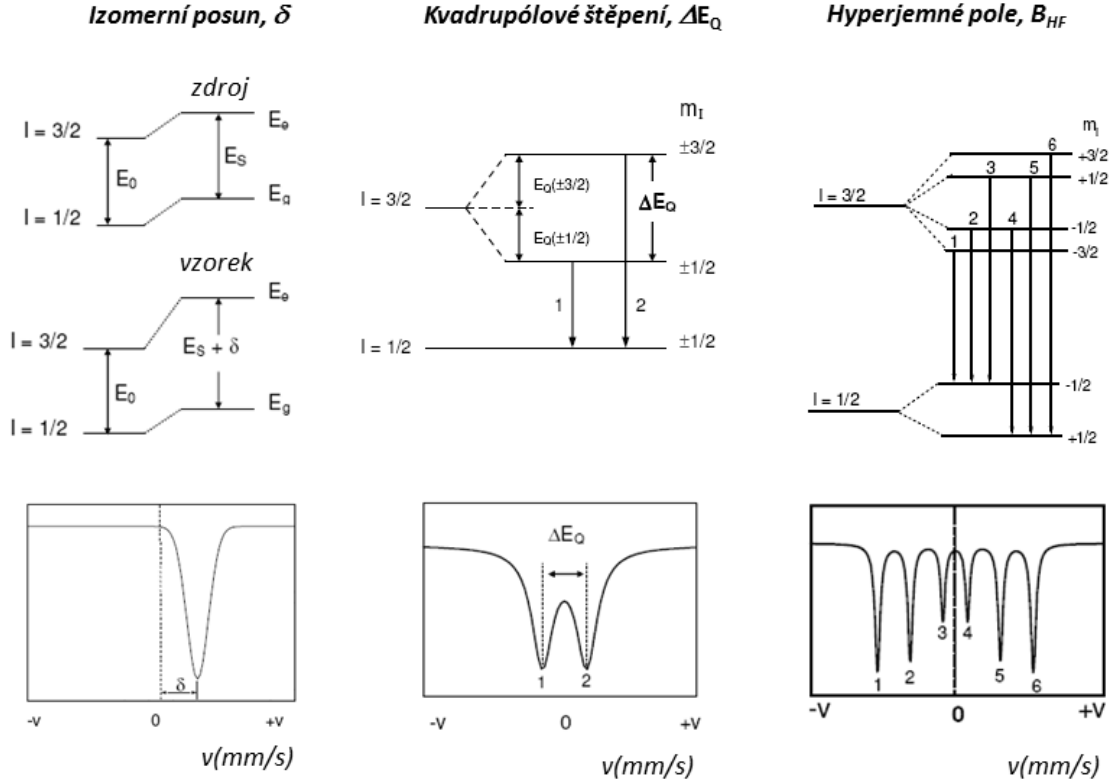
kde χ_{eq} odpovídá rovnovážné susceptibilitě v limitě nulové frekvence.

Mössbauerova spektroskopie - fyzikální principy

Tato metoda patří mezi lokální sondy struktury a spinového stavu atomů a iontů v pevných látkách a je založena na bezodrazové rezonanční absorpci záření γ jádrem studovaného atomu. Experimentálně je plynulé změny energie γ záření emitovaného zdrojem dosaženo s využitím Dopplerova jevu, kdy se zdroj a vzorek (absorbér) pohybují vůči sobě plynule se měnící rychlostí, typicky v řádu mm/s. Pro potřeby výzkumu v rámci této habilitační práce byla využita výhradně spektroskopie jader ^{57}Fe pro stanovení zastoupení $\text{Fe}^{2+}/\text{Fe}^{3+}$ kationtů v oxidovaných částicích magnetitu, určení stupně inverze ve spinelových feritech a odhad sklonění spinu, resp. spinového neuspořádání. Detailní popis principu, experimentálního uspořádání a široké škály aplikací této metody lze nalézt v několika rozsáhlých monografiích [41, 42, 43]. Proto se tato část sestává pouze ze stručného shrnutí fyzikální podstaty metody a využití Mössbauerovy spektroskopie při aplikaci externího magnetického pole.

Výstupem analýzy Mössbauerovských spekter je v prvním přiblížení informace o strukturním uspořádání a magnetickém stavu pevné látky, které jsou reflektovány v tzv. parametrech hyperjemných interakcí. Celkovou energii systému v důsledku působení hyperjemných interakcí, E_{hf} lze vyjádřit ve tvaru:

$$E_{\text{hf}} = E_e + E_m, \quad (2.61)$$



Obrázek 2.14: Původ hyperjemných interakcí v jádru ^{57}Fe společně s typickými průběhy Mössbauerovských spekter.

kde E_e odpovídá elektrostatické interakci a E_m magnetické interakci s okolní elektronovou hustotou.

Elektrostatický příspěvek lze vyjádřit ve tvaru:

$$E_e = E_I + E_Q, \quad (2.62)$$

kde E_I odpovídá interakční energii sféricky symetrické hustoty jaderných stavů s okolními elektronovými stavy a způsobuje tzv. izomernímu posunu a E_Q reprezentuje elektrostatické interakce vyššího řádu z důvodu asymetrického rozložení jaderné, resp. elektronové hustoty vedoucí k tzv. kvadrupólovému štěpení.

Na základě Poissonovy rovnice lze vyjádřit E_I jako:

$$E_I = \frac{1}{6} \sum_{i,k} V_{i,k} \int r^2 \rho^2(\mathbf{r}) d^3\mathbf{r}, \quad (2.63)$$

kde $V_{i,k}$ odpovídá Taylorově rozvoji tenzoru interakčního potenciálu v místě jádra. S využitím pravděpodobnosti výskytu elektronů v místě, $|\Psi(0)|^2$ jádra přechází vztah na:

$$E_I = \frac{2\pi}{3} e^2 Z |\Psi(0)|^2 \langle R^2 \rangle, \quad (2.64)$$

kde $\langle R^2 \rangle$ reprezentuje střední průměr jádra. Tato interakční energie tedy vyadřuje Coulombickou interakci mezi sféricky rozloženým nábojem jádra a okolní elektronovou hustotou, která způsobuje posun jaderné energie vzhledem k energii jádra v případě, že je uvažováno jako bodový náboj. Obecně jsou hodnoty $|\Psi(0)|^2$ a $\langle R^2 \rangle$ rozdílné pro základní a excitovaný stav, stejně tak jako pro zdroj a vzorek. Proto vzniká tzv. izomerní (chemický) posun, definovaný jako:

$$\delta = \frac{4\pi}{5} e^2 Z \frac{2(R_e - R_g)^2}{R_e^2 - R_g^2} \left[\frac{R_e^2 - R_g^2}{2(R_e - R_g)} \right]^2 (|\Psi(0)_a|^2 - |\Psi(0)_z|^2), \quad (2.65)$$

kde R_e a R_g odpovídají jaderným poloměrům excitovaného a základního stavu a $|\Psi(0)_a|^2$, $|\Psi(0)_z|^2$ pravděpodobnosti výskytu elektronů v absorbéru (vzorku), resp. zdroji. Typické hodnoty δ pro možné oxidační stavy Fe ve spinelových feritech a známých oxidech se pohybují v rozmezí : 0,1 - 0,4 mm/s pro Fe^{3+} a 0,8 - 1,5 mm/s pro Fe^{2+} [44].

Důsledkem od sférické symetrie rozložení náboje jádra je vznik tenzoru gradientu elektrického pole, $V_{i,k}$ v místě jádra (v literatuře označován jako EFG angl. electric field gradient tensor):

$$E_Q = \frac{1}{6} \sum_{i,k} V_{i,k} \int (3X_i X_k - \delta_{ik} r^2) \rho(\mathbf{r}) d^3 \mathbf{r}, \quad (2.66)$$

Ve standardní reprezentaci jsou členy mimo diagonálu nulové a pro diagonální členy platí: $|V_{xx}| < |V_{yy}| < |V_{zz}|$ a $V_{xx} + V_{yy} + V_{zz} = 0$. Interakce jaderného elektrického kvadrupólu s principální složkou V_{zz} diagonalizovaného tenzoru vede k sejmutí degenerace $(2I+1)$ hladin pro jádra s $I > 1/2$. Pro ^{57}Fe s $I = 3/2$ vznikají dva stavy o vlastní energii:

$$E_Q^n = \pm \frac{1}{4} Q V_{zz} \left(1 + \frac{\eta}{3} \right)^{1/2}, \quad (2.67)$$

kde η odpovídá parametru asymetrie EFG ve tvaru:

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}. \quad (2.68)$$

Energetický rozdíl mezi dvěma nedegenerovanými stavy odpovídá kvadrupólovému štěpení. Typické hodnoty kvadrupólového štěpení se pohybují v rozmezí (-0,05) - (-0,20) mm/s pro kationty Fe^{3+} ve spinelových strukturách, kladné hodnoty lze pozorovat u hematitu v

antiferomagnetickém stavu (0.41 mm/s) nebo superparamagnetických částicích (0.9 - 1.1 mm/s) [45].

Zatímco izomerní posun a kvadrupólové štepení souvisí s elektrostatickou interakcí hustoty náboje jádra a elektronů, magnetická dipolární interakce, resp. magnetické hyperjemné pole je důsledkem interakce nenulového jaderného spinu, $\mathbf{I}$ s externím magnetickým dipólovým momentem ve smyslu efektivního magnetického pole, $\mathbf{B}_{\text{eff}}$ v místě jádra. Lze ji vyjádřit ve tvaru:

$$E_m = -g_N \mu_j \mathbf{I} \mathbf{B}_{\text{eff}}, \quad (2.69)$$

kde g_N je jaderný Landauův g-faktor a μ_j jaderný magneton. Důsledkem této interakce je sejmutí $(2I+1)$ -násobné degenerace jaderného stavu. Pro povolené jaderné přechody pak platí výběrové pravidlo ve tvaru $\Delta m_I = 0, \pm 1$, kde m_I odpovídá magnetickému kvantovému číslu jadernému spinu dle vztahu pro vlastní hodnoty energií:

$$E_m^n = -g_N \mu_j m_I B_{\text{eff}}. \quad (2.70)$$

Příspěvky do magnetického hyperjemného pole lze v nulovém vnějším magnetickém poli vyjádřit jako superpozici vnitřního iontového dipolárního pole, $\mathbf{B}_d$ orbitálního pole, $\mathbf{B}_o$ a Fermiho kontaktního pole, $\mathbf{B}_c$.

Dipolární pole je způsobeno interakcí spinového příspěvku magnetického momentu valenčních elektronů atomu a jaderného magnetického momentu. Za předpokladu slabé spin-orbitální interakce lze tento příspěvek vyjádřit ve tvaru:

$$\mathbf{B}_d = -2\mu_B \left\langle \frac{3\mathbf{r}(\mathbf{S}\mathbf{r}) - r^2\mathbf{S}}{r^5} \right\rangle. \quad (2.71)$$

Velikost dipolárního příspěvku závisí na symetrii elektronové hustoty daného atomu, nicméně typicky dosahuje hodnot v řádu desetin až jednotek T. V případě sféricky symetrického rozložení náboje je tento příspěvek nulový (např. elektronová konfigurace d^5 pro Fe^{3+}).

Orbitální příspěvek je indukován orbitálním pohybem valenčních elektronů a pro zcela nebo z poloviny zaplněné orbitály je nulový. Je vyjádřen následujícím vztahem:

$$\mathbf{B}_o = -2\mu_B \left\langle \frac{\mathbf{L}}{r^3} \right\rangle. \quad (2.72)$$

Nejvýznamnějším příspěvkem do hyperjemného pole je Fermiho kontaktní člen:

$$\mathbf{B}_c = -\frac{8\pi}{3}\mu_{BG} (|\Psi_1(0)|^2 - |\Psi_2(0)|^2). \quad (2.73)$$

kde $|\Psi_1(0)|$ a $|\Psi_2(0)|$ odpovídají hustotě s -elektronů v místě jádra pro spiny s opačnou orientací. Tento příspěvek je důsledkem polarizace s -elektronů vlivem valenčních elektronů ($3d$) a okolních atomů. Díky antisymetrii vlnové funkce jsou repulzivní interakce silnější pro s a $3d$ elektrony s opačně orientovanými spiny, proto jsou s -elektrony s antiparalelními spiny vypuzeny blíže k jádru. Výsledné kontaktní pole je dáno superpozicí příspěvků vnitřních (záporný) a vnějších (kladný) s -stavů. Např. pro Fe^{3+} platí: $B_c = (-3) \text{ T [1s]} + (-131) \text{ T [2s]} + (79) \text{ T [3s]} = -55 \text{ T}$. Typické experimentálně určené hodnoty pro ionty Fe^{3+} ve spinelových feritech a hematitu se pohybují v rozmezí 48 - 55 T, nižší hodnoty lze nalézt např. u $\epsilon\text{-Fe}_2\text{O}_3$ (25 - 46 T) [45].

Pro spinelové ferity a známé fáze oxidu železitého se tedy výsledné spektrum skládá z několik podspekter, které odpovídají rezonanční absorpci kationtů Fe^{3+} nebo Fe^{2+} v symetricky neekvivalentních polohách v elementární, resp. magnetické buňce.

Dalšími důležitými parametry, které primárně definují charakter spekter, je rozšíření spektrálních linií, Γ a pravděpodobnost přechodu. Γ je principiálně dáno Heisenbergovými relacemi neurčitosti a souvisí se střední dobou života excitovaného jaderného stavu, τ_j dle vztahu:

$$\Gamma\tau_j \geq h. \quad (2.74)$$

Pravděpodobnost rezonančního přechodu v rámci harmonické aproximace reprezentuje tzv. bezodrazový faktor, definovaný vztahem:

$$f = \exp(-k_y^2 \langle x^2 \rangle), \quad (2.75)$$

kde k_y odpovídá vlnovému vektoru záření a $\langle x^2 \rangle$ je střední kvadratická výchylka jádra v rezonanci ve směru šíření záření.

S využitím Debyeova modelu přechází do tvaru:

$$f = \exp - \frac{6E_R}{k_B\Theta_D \left[\frac{1}{4} + \left(\frac{T^2}{\Theta_D^4} \right) \int_0^{\Theta_D/T} \frac{x}{e^x - 1} dx \right]}, \quad (2.76)$$

kde Θ_D je Debyeova teplota a E_R odpovídá bezodrazové energii jádra.¹⁰

¹⁰Při absolutní nule je faktor nedosahuje hodnoty 1 z důvodu pohybu jader:

$$f(T=0) = \exp - \frac{3E_R}{2k_B\Theta_D}. \quad (2.77)$$

Bezodrazový faktor je v obecném případě směrově závislý díky anizotropii vibračních projevů jádra, což může vést k asymetrii integrálních intenzit jednotlivých spektrálních linií.

Mössbauerova spektroskopie v externím magnetickém poli

Při aplikaci vnějšího magnetického pole v řádu T obecně dochází k zásadním změnám ve spektrech. V případě, že daný materiál vykazuje při působení magnetického pole spinovou reorientaci, resp. metamagnetický fázový přechod, případně z důvodu magneto-elastické vazby dochází ke změně krystalové struktury, je charakter spektra dán symetrií polem indukované magnetické, případně i krystalové struktury. V případě spinelových feritů a některých fází oxidů železa k takovým změnám magnetického ani strukturního uspořádání v běžně dostupném oboru magnetických polí nedochází. Důsledkem aplikace magnetického pole, $\mathbf{B}_{\text{ext}}$ je však rozdílná hodnota hyperjemného pole $\mathbf{B}_{\text{hf}}$ pro různé podmříže ve spinelové struktuře, což umožňuje např. přesnější určení stupně inverze spinelu. Dále je možné určit orientaci magnetizace dané podmříže (v daném magnetickém poli). Pro vektorovou analýzu orientace jednotlivých příspěvků platí jednoduchý vztah:

$$\mathbf{B}_{\text{eff}} = \mathbf{B}_{\text{ext}} + \mathbf{B}_{\text{hf}}, \quad (2.78)$$

kde $\mathbf{B}_{\text{eff}}$ odpovídá tzv. efektivnímu (magnetickému) poli.

Experiment lze provádět v paralelní nebo kolmé (perpendikulární) geometrii, jak je znázorněno na Obrázku 2.15. V případě, že je magnetické pole $\mathbf{B}_{\text{ext}}$ aplikováno paralelně ke směru šíření γ záření, $\mathbf{B}_{\text{eff}}$ preceduje ve směru vlnového vektoru γ záření pod úhlem θ . Úhel mezi $\mathbf{B}_{\text{eff}}$ a magnetizací podmříže lze snadno určit z poměru integrálních intenzit prostřední a vnitřní linie na základě vztahu ¹¹

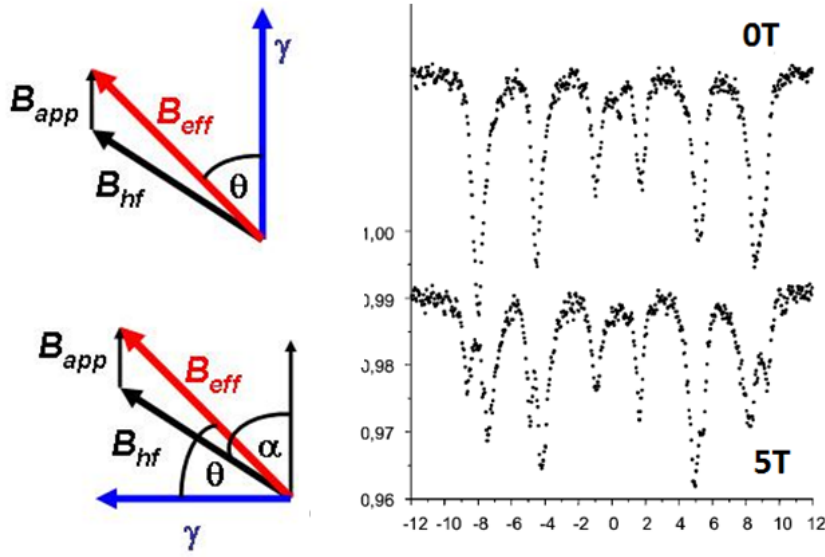
$$4 \left(\frac{2}{\sqrt{1 + \sin^2 \theta}} - 1 \right) : 1. \quad (2.80)$$

V případě kolmé geometrie je situace komplikovanější, protože $\mathbf{B}_{\text{eff}}$ preceduje okolo směru $\mathbf{B}_{\text{ext}}$ a úhel θ pak není konstantní.

Úhlu sklonění spinu, resp. magnetizace podmříže, α je možné určit několika způsoby. První možnost využívá vztahu 2.79, nicméně tento výpočet je velmi nepřesný. Důvodem je

¹¹Pro poměr integrálních intenzit krajní, prostřední a vnitřní linie platí:

$$3 : \left(\frac{4 \sin^2 \theta}{\sqrt{1 + \cos^2 \theta}} \right) : 1. \quad (2.79)$$



Obrázek 2.15: [Paralelní a kolmé experimentální uspořádání Mössbauerovy spektroskopie v externím magnetickém poli. Vpravo je znázorněno typické spektrum nanokrystalů feritu kobaltnatého, měřené při 4,2 K v nulovém a v externím magnetickém poli 5 T vykazující jasné rozlišení jednotlivých podspekter.

horší rozlišení poměru integrálních intenzit paralelní geometrie (možné hodnoty nabývají 4:1 - 1.657:1 ve srovnání s 4:1 - 0:1 pro kolmé uspořádání). Spektra jsou často zatížena artefakty (saturace, preferenční orientace, distribuce hyperjemných parametrů, demagnetizační faktor aj.), které výrazně ovlivňují intenzitu jednotlivých linií.

Proto je možné využít alternativního přístupu k určení úhlu sklonění spinu, který je založen na srovnání spekter v kolmé geometrii pro $\mathbf{B}_{\text{ext}} = 0$ a $\mathbf{B}_{\text{ext}} = n\text{T}$, kde n je v jednotkách T. $\mathbf{B}_{\text{hf}}$ je určeno ze spektra v nulovém magnetické poli a $\mathbf{B}_{\text{eff}}$ ze spektra v externím magnetickém poli. Úhel sklonění spinu, α je pak možné určit na základě vztahu:

$$\cos \alpha = \frac{B_{\text{eff}}^2 - B_{\text{app}}^2 - B_{\text{hf}}^2}{2B_{\text{app}}^2 B_{\text{hf}}^2}. \quad (2.81)$$

V případě nanorozměrových částic je situace složitější, protože často dochází k odlišné orientaci magnetizace podmříží v jádře a slupce částice, případně dochází ke kontinuální změně orientace spinů. Proto je určení sklonění spinů ovlivněno zejména distribucí hyperjemných parametrů a snadných os magnetické anizotropie nanočástic. Jak bylo ukázáno v [40], je tato metoda neselektivní pro objemové a povrchové spiny v nanočásticích a bez komplementárních experimentů není možné sklonění spinu přiřadit pouze povrchové vrstvě.

Vzhledem ke srovnatelné časové škále Mössbauerovy spektroskopie a typických relaxačních časů superparamagnetických systémů lze využít studia teplotní závislosti Mössbauerových spekter k odhadu teploty blokace a podílu superparamagnetické, resp. blokové frakce, tedy odhadnout i distribuci velikosti částic (resp. jejich relaxačních časů). Charakteristickým projevem superparamagnetického stavu ve spektru je dublet s výrazně rozšířenými liniemi. Typickým projevem přechodu do blokového stavu je široký sextet (často asymetrický z důvodu superpozice distribucí velikosti částic, hyperjemných parametrů, koordinačních okolí aj.), jehož intenzita kontinuálně roste na úkor dubletu. Z poměru integrálních intenzit pak lze odhadnout podíl superparamagnetické frakce ve vzorku.

Odhad strukturního a spinového uspořádání nanočástic

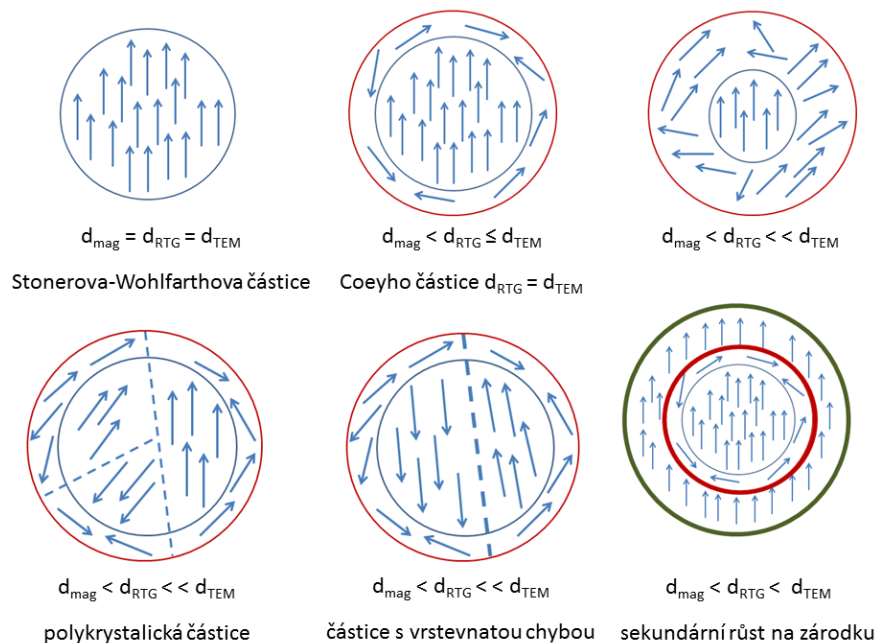
Korektní určení strukturního a magnetického uspořádání individuálních nanočástic tak vyžaduje součinnost různých experimentálních metod. Pro velmi dobrý odhad lze využít srovnání velikosti částic, získaných pomocí transmisní elektronové mikroskopie, RTG difrakce a na základě analýzy magnetických měření. U všech zmíněných metod je možné zahrnout i distribuci velikostí. Možná uspořádání v nanočásticích znázorňuje Obrázek 2.16, pro zjednodušení jsou zobrazené částice sférické.

První případ odpovídá izotropní částici v rámci Stonerova-Wohlfarthova modelu, která je strukturně i magneticky homogenní v celém objemu. Druhý případ je nejtypičtější pro reálné vzorky a lze jej vystihnout jako strukturně a magneticky uspořádané jádro a neuspořádanou slupku, kdy krystalograficky uspořádaný objem je větší než magnetický. Idealizovaná struktura jádro-slupka (core-shell) zavedená Coeyem odpovídá částici, pro kterou je $d_{\text{RTG}} = d_{\text{TEM}}$. Rozporuplné výsledky magnetických měření lze často snadno vysvětlit jako důsledek struktury velmi špatně krystalické částice, kdy je v interpretacích chybně uvažována fyzická velikost částic, nikoliv magnetická, tj. platí $d_{\text{RTG}} \ll d_{\text{TEM}}$.

Složitější je interpretace v případě polykrystalických částic nebo v podstatě velmi dobře krystalických částic s různými defekty, např. vrstevnatými chybami. Pro tyto případy je nutné mít k dispozici pozorování transmisním mikroskopem s vysokým rozlišením, protože výsledky objemových metod budou v podstatě totžné s předchozími případy.

Speciálním případem jsou částice, které vznikají metodou růstu na zárodku. Přirůstání stejné fáze na původní částici vede ke vzniku různě neuspořádaného rozhraní, takže výsledná částice nemusí nutně vykazovat největší stupeň neuspořádání na povrchu. Tento případ znázorňuje poslední obrázek, zesílená červená čára odpovídá nárůstu neuspořádané vrstvy na rozhraní, zelená reprezentuje neuspořádanou povrchovou vrstvu, která může být zanedba-

telná vůči neuspořádané frakci na rozhraní. Proto obecně akceptovaný model jádro-slupka nemusí v některých případech vystihovat reálnou strukturu nanočástic.



Obrázek 2.16: Možné spinové a strukturní uspořádání nanočástic společně s typickou relací pro velikost částice získanou pomocí transmisní elektronové mikroskopie, d_{TEM} , RTG difrakce, d_{RTG} , a magnetických měření, d_{mag} . Komentář k jednotlivým strukturám je v textu.

2.2 Strukturní a magnetické uspořádání v oxidech železa a vybraných spinelech

Fázové složení magnetických nanokrystalů a nanokompozitů studovaných v této práci je poměrně úzce definováno, jedná se převážně o některou ze známých fází oxidů železa nebo spinelových feritů. V této sekci budou krátce shrnuty jejich strukturní a magnetické vlastnosti, detailní rozbor strukturního a magnetického uspořádání lze nalézt v řadě přehledových článků a monografií, např. [46, 45, 47].

V současné době jsou známy dvě stabilní a dvě metastabilní fáze oxidu železitého, Fe_2O_3 a podvojný oxid železnato-železitý, Fe_3O_4 (magnetit). Nízkoteplotní fáze $\gamma\text{-Fe}_2\text{O}_3$, maghemit je tvořena strukturou defektního spinelu odvozenou od inverzního spinelu.

Obecně lze strukturu spinelu vystihnout jako $(X_\delta Y_{\delta-1})_{Td}[X_{1-\delta} Y_{1+\delta}]_{Oh}O_4$, kde X, Y od-

2.2. STRUKTURNÍ A MAGNETICKÉ USPOŘÁDÁNÍ VE VYBRANÝCH OXIDECH 47

povídá kationtům dvoj- a trojmocným, Td a Oh značí oktaedrické a tetraedrické pozice ve spinelové struktuře a parametr δ reprezentuje tzv. stupeň inverze, který nabývá hodnot od 0 (inverzní spinel) do 1 (normální spinel). Struktura maghemitu vytváří tři možné strukturní varianty v závislosti na stupni uspořádání vakancí Fe^{2+} iontů v oktaedrických polohách (uvedeno v Tabulce 2.1). Nejběžnější je varianta defektního spinelu s prostorovou grupou $P4_332$, kterou lze vystihnout pomocí krystalochemického vzorce: $(Fe)_{Td}[Fe_{5/3}\square_{1/3}]_{Oh}O_4$, kde $\square$ značí vakanci v oktaedrické poloze.

Inverzní spinelovou strukturu vykazuje v objemovém stavu i magnetit. V nanočásticích magnetitu, nicméně i v povrchové vrstvě objemového materiálu, dochází k téměř okamžité topotaktické oxidaci na maghemit, proto není možné za běžných podmínek dlouhodobě stabilizovat magnetit v nanočásticích s velikostí pod 20 nm [48]. Tato změna je snadno pozorovatelná jako změna barvy prášku či ferrofluidu z černé na hnědou a spolehlivě detekovatelné např. pomocí Mössbauerovy spektroskopie nebo metod absorpce synchrotronového záření (EXAFS, z angl. Edge X-Ray Absorption Fine Structure). Validace přítomnosti magnetitu pomocí RTG difrakce srovnáním hodnot kubického mřížového parametru (8,369 Å- magnetit vs. 8,342 Å- maghemit) je naopak zcela neprůkazná, nicméně často využívaná.

V magnetitu dochází k distorzi krystalové struktury při tzv. Verweyově přechodu typu kov-izolátor, který v objemovém materiálu nastává při $T_V = 124$ K. V případě malých částic dochází k poklesu T_V zejména z důvodu strukturního neuspořádání a nárustu podílu vakancí v oktaedrických polohách, tj. kontinuálně se zvyšujícím podílem maghemitu. Odchylku od stechiometrického složení magnetitu lze vystihnout pomocí vzorce $Fe_{3(1-x)}O_4$, pro $x > 0,004$ nastává přechod 2. druhu.¹²

Vysokoteplotní fáze oxidu železitého - hematit, $\alpha-Fe_2O_3$ krystalizuje ve struktuře tvořené nejtěsnějším hexagonálním uspořádáním kyslíků, se strukturním typem korundu.

Metastabilní fáze $\beta-Fe_2O_3$ vzniká při oxidaci maghemitu za specifických podmínek a krystalizuje ve strukturním typu bixytu s kubickou tělesově centrovanou mříží. Atomy Fe obsazují dvě neekvivalentní polohy s kubickou symetrií (uvedeno v Tabulce 2.1).

Neobvyklé strukturní uspořádání vytváří i druhá známá metastabilní fáze $\epsilon-Fe_2O_3$, která je izostrukturní s $\kappa-Al_2O_3$ a $GaFeO_3$. Anionty kyslíku vytvářejí nejtěsnější uspořádní typu ABAC a atomy železa obsazují 4 neekvivalentní polohy se symetrií koordinačního polyedru:

¹²Detailní přehled modelů neobvyklých fyzikálních procesů spojených s uspořádáním náboje a přeskoky elektronů poskytuje přehledový článek [49]. Zahrnuje popis pomocí konceptu Wignerova skla-krystalu dle Motta, Ihle-Lorentzův model a diskuzi nízkoteplotního chování defektního magnetitu, kde je pozorováno tzv. víceelektronové tunelování.

Fe1 - T_d , Fe2, Fe3 - distortovaný O_h , Fe4 - regulární O_h .¹³

Magnetické vlastnosti výše diskutovaných fází lze shrnout následovně. Maghemit a magnetit vykazují v objemovém stavu kolineární ferrimagnetické uspořádání (magnetické parametry jsou uvedeny v Tabulce 2.2). α -Fe₂O₃ je tzv. slabý ferrimagnet (resp. antiferomagnet se skloněnými spiny) s Néelovou teplotou, $T_N = 955$ K. Pod tzv. Morinovou teplotou, $T_N = 250$ K dochází k reorientaci magnetických momentů paralelně s osou c (spin-flop) a vzniku antiferomagnetického uspořádání. β -Fe₂O₃ je antiferomagnet s $T_N(\alpha)$ reportovanou v rozmezí 100 - 120 K.

ϵ -Fe₂O₃ vykazuje magnetické uspořádání ferrimagnetického typu ($T_C = 480$ K), které podléhá magnetické fázové transformaci do nesouměřitelné struktury (spinové vlny) při teplotě 150 K.¹⁴ Aplikacně zajímavým aspektem vysokoteplotní magnetické fáze ϵ -Fe₂O₃ je enormně vysoká hodnota koercitivního pole (až 2 T při pokojové teplotě) a rezonanční absorpce elektromagnetického záření v oblasti GHz laditelná substitucí Fe [50].

Strukturní uspořádání spinelů o složení MFe₂O₄, M = Co, Ni, Mg odpovídá inverznímu spinelu, případně spinelu s částečnou inverzí, jak je uvedeno v Tabulce 2.1. Tyto spinelové ferity jsou, obdobně jako magnetit a maghemit, ferrimagnetické. Parametry magnetického uspořádání jsou shrnuty v Tabulce 2.2, nicméně je nutné poznamenat, že magnetické parametry v reálných vzorcích, zejména v případě malých částic, významně závisí na stupni inverze.

Vyjímkou mezi spinely studovanými v rámci této práce je chromit kobaltnatý. Narozdíl od výše popsanych feritů tvoří normální spinelovou strukturu a vykazuje multiferoické vlastnosti, v tomto případě koexistenci netriviálního ferrimagnetického a feroelektrického

¹³Za nízké teploty údajně dochází ke strukturní transformaci, nicméně výsledky původní práce citované v [45] nejsou jednoznačné. Nedávná studie pomocí nízkoteplotní RTG difrakce s vysokým rozlišením a Ramanové spektroskopie tento jev vyloučily.

¹⁴V literatuře je uvedeno několik možných modelů magnetické struktury vysokoteplotní fáze. Obecně přijatý je model z roku 2006, který navrhuje kolineární ferrimagnetické uspořádání s extrémně nízkou hodnotou magnetického momentu na Fe v tetraedrické poloze. Tento výsledek je zdánlivě podpořen experimentem magnetického cirkulárního dichroismu, kde byl na základě neadekvátní aplikace součtových pravidel určen nenulový příspěvek orbitálního momentu, navíc teplotně závislý (důsledek změny projekce složek magnetizace při magnetickém fázovém přechodu, nikoliv změna magnitudy orbitálního momentu). Dosud platný model magnetické struktury ovšem nevyhovuje žádné povolené ireducibilní reprezentaci magnetické grupy a je důsledkem opomenutí obecné orientace magnetických momentů, tj. předpokladem kolinearity ve směru os souřadného systému. Revize výsledků neutronové difrakce poskytla nový model magnetické struktury (ferrimagnet se skloněnými magnetickými momenty) a hodnotami magnetických momentů na atomech Fe v očekávaném rozmezí. Tento model odpovídá i pozorované změně magnetické struktury z důvodu polem indukovaného magnetického fázového přechodu.

<i>fáze</i>	<i>strukturní typ</i>	PG	Z/Wyckoffovy pozice
α -Fe ₂ O ₃	korund	$R\bar{3}c$	6 Fe: 12c, O: 18e
β -Fe ₂ O ₃	bixbyt	$Ia\bar{3}$	16 Fe: 8b, 24d, O: 48e
γ -Fe ₂ O ₃	inv. spinel, $\delta = 0$,	$Fd\bar{3}m$	8
	neusp. $\square$		Fe ³⁺ (Td, A): 8a, ,Fe ³⁺ , $\square$ (B, Oh): 16d, O: 32e
	částečně usp. $\square$	$P4_332$	12 Fe: 12d, 4b, 8c, O: 8c, 24e
	usp. $\square$, $c/a \approx 3$	$P4_12_12$	12 Fe: 8b, 4a, 8b, O: 8c, 24e
ϵ -Fe ₂ O ₃	κ -Al ₂ O ₃	$Pna2_1$	8 Fe: 4a, O: 4a
Fe ²⁺ Fe ₂ ³⁺ O ₄	inv. spinel, $\delta = 0$	$Fd\bar{3}m$	8 Fe ³⁺ (Td, A): 8a, Fe ²⁺ , Fe ³⁺ (B, Oh): 16d, O: 32e
MFe ₂ O ₄ ,	inv. spinel, $\delta = 0$	$Fd\bar{3}m$	8 Fe ³⁺ (Td, A): 8a, Fe ³⁺ , M ²⁺ (B, Oh): 16d, O: 32e
CoCr ₂ O ₄	norm. spinel, $\delta = 1$	$Fd\bar{3}m$	8 Co(Td, A): 8a, Cr(B, Oh): 16d, O: 32e

Tabulka 2.1: Přehled strukturního uspořádání v oxidech železa a ve vybraných spinelech, uvedeno pro objemové materiály. PG - prostorová grupa, Z - počet vzorcových jednotek na elementární buňku.

<i>fáze</i>	$n_B^{\text{teor}} (\mu_B)$	$n_B^{\text{exp}} (\mu_B)$	$K_1 (\text{J/m}^3)$	$M_s (\text{Am}^2/\text{kg})$	$T_C (\text{K})$	C	$\theta_P (\text{K})$
Fe_3O_4	4	4,03 - 4,20	-(11 - 13)	92	847 - 858	14,2	869
$\gamma\text{Fe}_2\text{O}_3$	2,5 - 3,3	2,39 - 2,90	-(4,6 - 5,0)	76 - 82	850 - 950	15,0	-
CoFe_2O_4	3	3,30 - 3,94	180 - 300	80	769; 793	13,9	812
NiFe_2O_4	2	2,22 - 2,40	-(6,2 - 6,8)	50	858; 870	19,5	896
MgFe_2O_4	0	0,86 - 2,15	-(2,5 - 4,5)	27	588; 713	-	635

Tabulka 2.2: Přehled magnetických parametrů vybraných spinelů, uvedeno pro objemové materiály. K_1 a M_s odpovídají hodnotám za pokojové teploty. Převzato z [47, 51, 52].

uspořádání. Jedná se o vzácný příklad multiferoického systému tzv. spinového původu, protože vykazuje extrémně silnou vazbu mezi feroelektrickou polarizací a magnetizací [53]. Jeho magnetický fázový diagram je poměrně složitý, k ferrimagnetickému uspořádání dochází při teplotě 93 K, přechod do magnetické fáze s kónickou spinovou konfigurací nastává při 26 K a pod 15 K se objevuje magnetická struktura základního stavu, což je spojeno s velmi malou změnou propagačního vektoru (tzv. lock-in přechod) [54]. Nedávno publikovaná práce [55] popisuje strukturní fázový přechod ve vysokých magnetických polích v teplotním oboru 6 - 17 K, při kterém dochází k uspořádání longitudinální složky magnetizace zatímco spirální komponenta magnetické struktury zůstává neuspořádaná. Vzhledem ke složitému charakteru výměnných interakcí, magnetoelektrické a magnetoelastické vazbě lze očekávat významné změny ve fyzikálních vlastnostech tohoto systému v případě nanorozměrových částic. Např. studie nanokrystalů příbuzného systému, chromitu manganatého, MnCr_2O_4 [56] ukazuje anomální hodnotu Blochova koeficientu 3,5, která při klesající velikosti částic limituje k obvyklé hodnotě 1,5, nicméně kolaps magnetického uspořádání nebyl pozorován, ačkoliv se velikost částic blíží charakteristické koherentní délce magnetické.

V nanomateriálech, které jsou předmětem studia prací v sekci 2.3., se nachází nanočástice železa, kobaltu a karbidu triželeza (cementitu).

Fe a Co v objemovém stavu krystalizují v nejtěsnějším uspořádání kubickém (fcc, z angl. face-centered cubic), resp. hexagonálním (hcp, z angl. hexagonal close packed). V případě směsné CoFe_2 je preferována mříž hcp [57], [58]. Fe a Co jsou archetypální feromagnety, kde vzniká spontánní spinová polarizace pásového původu dle Stonerova kritéria. K fero-magnetickému uspořádání dochází pod Curiovou teplotou, $T_C(\text{Co}) = 1043 \text{ K}$ a $T_C(\text{Fe}) 1388 \text{ K}$, hodnoty saturovaného magnetického momentu při absolutní nule, určené z extrapolace Blochova zákona, jsou $\mu_s(\text{Fe}) = 2,22 \mu_B$ a $\mu_s(\text{Co}) = 1,72 \mu_B$ [58]. Další důležité magnetické

2.3. METODY PŘÍPRAVY MAGNETICKÝCH NANOČÁSTIC A NANOKOMPOZITŮ⁵¹

parametry reprezentuje anizotropní konstanta, $K_1(\text{Fe}) = 0,48 \text{ J/m}^3$ a $K_1(\text{Co}) = 5 \text{ J/m}^3$, satureovaná magnetizace při pokojové teplotě, $M_s(\text{Fe}) = 2,16 \text{ T}$ a $M_s(\text{Co}) = 1,82 \text{ T}$ a výměnná konstanta, $A(\text{Fe}) = M_s(\text{Co}) = 1.5 \times 10^{-11} \text{ J/m}$. Limitní dosah magnetického uspořádání definuje výměnná délka, l_{ex} ¹⁵ která činí 2,8 nm pro Fe a 3,4 nm pro Co.

Fe_3C krystalizuje v ortorombické soustavě (strukturní typ $D0_{11}$) s prostorovou grupou $Pnma$ a $Z = 4$. Atomy Fe obsazují dvě neekvivalentní Wyckoffovy pozice: 4c a 8d, okolí atomu C tvoří hexagonální prisma šesti atomů Fe ($2 \times 4c$, $4 \times 8d$). V objemovém materiálu dochází k feromagnetickému uspořádání při $T_C = 486 \text{ K}$, Fe_3C vykazuje satureovaný magnetický moment, $\mu_s = 1,78 \mu_B$. V paramagnetickém stavu je charakterizován efektivním magnetickým momentem, $\mu_{\text{eff}} = 3,89 \mu_B$ a paramagnetickou Curiovou teplotou, $\theta_P = 506 \text{ K}$ [58].

2.3 Metody přípravy magnetických nanočástic a nanokompozitů

V této sekci jsou velmi stručně shrnuty metody přípravy magnetických nanočástic a nanokompozitů, které jsou předmětem studia předkládaného souboru prací.

Izolované nanočástice lze připravit různými postupy, pro větší množství částic je využíváno převážně chemických metod na mokré cestě. Mezi nejvíce používané patří koprecipitace ve vodném prostředí, mikroemulzní metoda, dekompozice organického prekursoru a hydrotermální metoda. Detaily o preparativních postupech magnetických nanočástic obsahuje např. přehledový článek [59].

Koprecipitace je jednoduchá metoda, při které dochází k vyloučení nanokrystalů z vodného roztoku příslušných solí působením silné báze, např. amoniaku [60]. Nevýhody této metody jsou velká distribuce velikosti částic, omezená možnost kontroly jejich velikosti a tvaru, a v podstatě okamžitá aglomerace nanočástic po jejich vyloučení. Omezeně lze parametry nanočástic řídit poměrem kationtů v reakční směsi, teplotou reakce nebo iontovou silou a koncentrací báze [59, 61, 62, 63, 64]. Protože metoda poskytuje velké výtěžky a nevyžaduje speciální vybavení, je v současné době velmi rozšířená i přes svá omezení. V našem případě byla využita pro přípravu nanočástic magnetitu a maghemitu.

Mikroemulzní metoda je založena na výměnné reakci uvnitř normální nebo inverzní mi-

$$l_{\text{ex}} = \sqrt{\frac{2A}{\mu_0 M_s^2}} \quad , \quad (2.82)$$

cely, která figuruje jako tzv. nanoreaktor, ve kterém dochází k nukleaci a následnému růstu nanočástice, jejíž velikost je tak omezena velikostí micely [65]. V našem případě bylo pro přípravu nanočástic využito hydrolýzy mikroemulze alkoxidů příslušných kovů v suchém etanolu. Tato metoda poskytuje poměrně dobře krystalické částice, nicméně jejich velikost je limitovaná vlastnostmi dané mikroemulze, a proto je obecně vhodné výsledné nanoprášky dodatečně žíhat, typicky na 800 - 1000 °C.

Dekompozice organického prekurzoru je metoda, která umožňuje přípravu vysoce krystalických nanočástic s velmi úzkou distribucí velikosti [66, 67]. Je založena na rozkladu komplexu příslušného kovu (nejčastěji acetylacetonátu nebo oleátu) ve vysokovroucím rozpouštědle (fenyléter, oktyléter, oktadecen) v přítomnosti mastné kyseliny, nejčastěji olejové. Vhodným poměrem reaktantů a volbou rozpouštědla lze poměrně přesně řídit velikost částic v intervalu 9 - 22 nm [68]. V této práci je to stěžejní metoda přípravy vysoce krystalických nanočástic maghemitu a magnetitu.

Hydrotermální metoda v systému voda - alkohol - mastná kyselina je univerzální syntézou pro přípravu monokrystalických nanočástic kovů, jejich oxidů, případně sulfidů, selenidů aj. [69]. Nanokrystaly vykazují úzkou distribucí velikosti, nicméně není možné měnit jejich velikost v širším intervalu jako u dekompozice. V našem případě byla metoda modifikována pro přípravu feritu a chromitu kobaltnatého [70, 71]. Speciálním případem je tzv. kontinuální hydrotermální metoda za superkritických podmínek, popsána v práci [72].

Nanokompozity, jejichž magnetické vlastnosti byly studovány v této práci, byly připraveny metodou sol-gel a jejími modifikacemi. Většina nanokompozitů je tvořena nanokrystaly zabudovanými v amorfní matici SiO_2 [73, 74, 75]. Principem metody sol-gel je hydrolýza alkoxidů křemičitých v přítomnosti alkoholů (v kyselém nebo bazickém prostředí) a následné kondenzaci za vzniku tzv. gelu. V závislosti na postupu sušení gelu vznikají kompozity o různé hustotě a velikosti pórů. Pro přípravu nanokompozitů studovaných v této práci bylo pro tvorbu matrice SiO_2 použito kyselé hydrolýzy tetra-ethyl-ortosilikátu (TEOS) v metanolu za přítomnosti formamidu, zdrojem kationtů byly dusičnany Fe, Co, Ni nebo Mg.

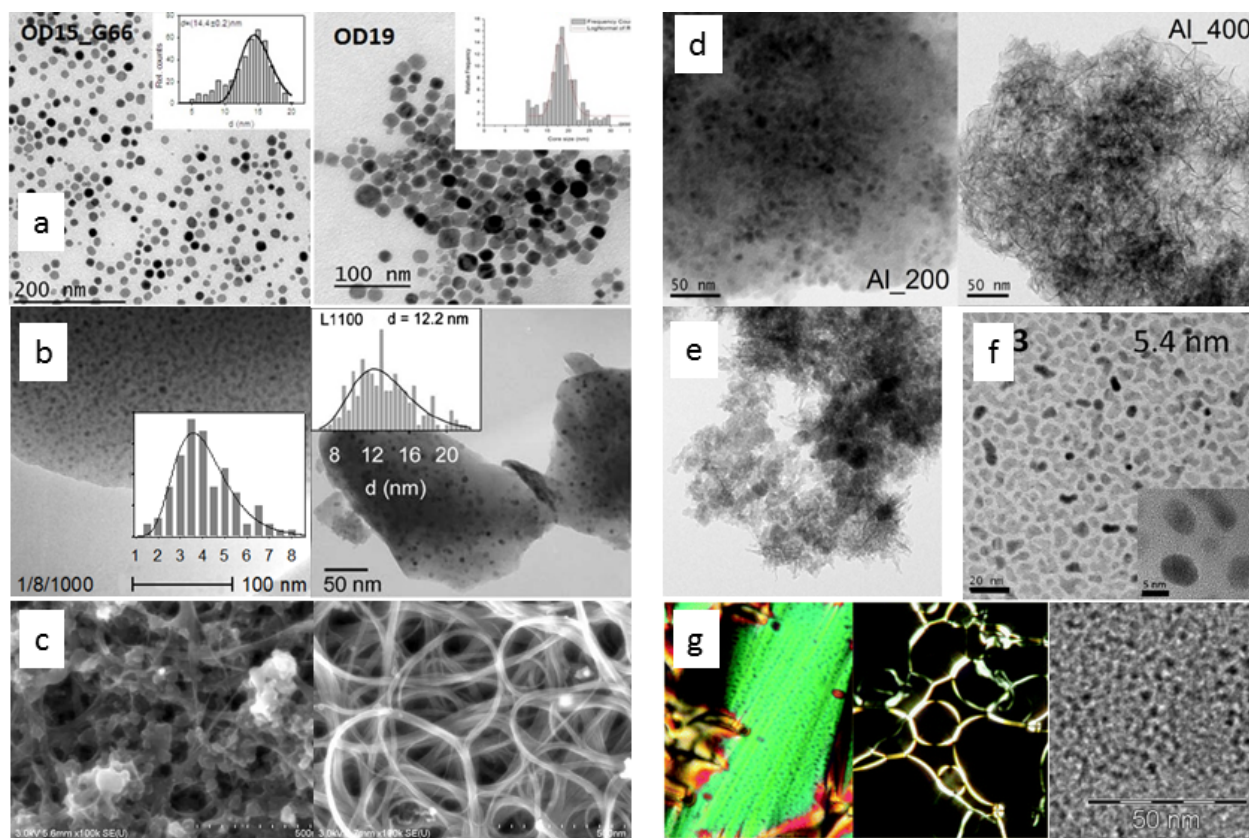
Alternativním typem přípravy nanokompozitů jsou víceetapové syntézy, při kterých jsou nanočástice připraveny v prvním kroku a následně jsou zabudovány do matrice nebo pokryty jinou fází. V našem případě byl připraven kompozit $\text{Fe}_2\text{O}_3\text{-TiO}_2$ heterogenní precipitací oxidu titaničitého z roztoku síranu titanylu pomocí močoviny na povrchu nanočástic maghemitu modifikovaných kyselinou citrónovou [76, 77]. Zcela novou metodu přípravy nanokompozitů monodisperzních nanočástic v maticích oxidů přechodných kovů na bázi sol-gel jsme popsali v [78]. Nejprve byly připraveny monodispersní částice pomocí hydrotermální metody nebo

2.3. METODY PŘÍPRAVY MAGNETICKÝCH NANOČÁSTIC A NANOKOMPOZITŮ⁵³

dekompozice organického prekurzoru, převedeny do reakční směsi s alkoxidy a následně inkorporovány do dielektrické matrice, která vzniká hydrolýzou alkoxidů. Další alternativou je zabudování hydrofilních nanočástic připravených surfaktantem asistovanou koprecipitací do matrice SiO_2 v mikroemulzi, jak bylo využito pro přípravu nanokompozitu $\text{CoFe}_2\text{O}_4\text{-SiO}_2$ [79].

Metody přípravy dalších nanomateriálů budou zmíněny jen okrajově. Multivrstvy obsahující nanočástice Fe, Co a CoFe_2 byly připraveny metodou radiofrekvenčního magnetronového naprašování, detailní popis této fyzikální metody depozice lze najít např. v [80]. Vysoce kvalitní jednotěnné uhlíkové nanotuby byly získány od komerčního dodavatele a byly připraveny metodou HiPco (tzv. HiPco, z angl. high-pressure carbon mono-oxide), tj. depozicí chemických par (CVD, z angl. chemical vapor deposition) za vysokého tlaku oxidu uhelnatého. V této metodě figuruje CO jako zdroj uhlíku a $\text{Fe}(\text{CO})_5$ jako katalyzátor, resp. zdroj nanokrystalů Fe jako templátů pro růst nanotub [81].

Na obrázku 2.17 jsou uvedeny příklady nanočástic a nanokompozitů studovaných v rámci této práce.



Obrázek 2.17: Typické příklady studovaných nanomateriálů zobrazených pomocí transmisní nebo skenovací elektronové mikroskopie. a - nanočástice oxidu železitého pokryté kyselinou olejovou připravené pomocí dekompozice organického prekursoru, b - nanokompozit feritu kobaltnatého v matrici amorfního oxidu křemičitého s vysokou koncentrací nanočástic připravený metodou molekulárního prekursoru (vlevo) ve srovnání s nanokompozitem feritu kobaltnatého a oxidu ceričitého v matrici amorfního oxidu křemičitého připraveném klasickou metodou sol-gel, c - jednotěnné uhlíkové nanotuby připravené metodou HiPco (vlevo) ve srovnání se stejným vzorkem po čištění (vpravo), d - nanokompozit feritu kobaltnatého v matrici oxidu hlinitého žíhaný při 200 a 400 °C, e - magneticky separovatelný fotokatalyzátor na bázi oxidu titaničitého a železitého se strukturou jádro-slupka (core-shell), f - nanokrystaly kobaltu v matrici oxidu křemičitého připravené metodou magnetronového naprašování, g - nanokompozit chirálních kapalných krystalů a nanočástic maghemitu.

Kapitola 3

Soubor publikací a komentáře

Následující kapitola obsahuje soubor publikací, které tvoří stěžejní základ habilitační práce, a stručné komentáře k těmto publikacím. V jednotlivých sekcích jsou vždy uvedeny plné citace prací společně s jejich odkazem na seznam publikací, který byl předložen pro potřeby habilitačního řízení, a číslem citace v seznamu použité literatury. Jak již bylo zmíněno v Úvodu, publikace jsou tématicky rozděleny do tří hlavních částí, které se dále dělí do specifických tématických okruhů.

3.1 Nanočástice a nanokompozity ternárních spinelů

Tato sekce se zabývá výsledky strukturních a magnetických studií systémů s nanokrystaly ternárních spinelů. První část je zaměřena na materiály s feritem kobaltnatým, druhá zahrnuje práce zabývající se nanokompozity s dopovaným feritem kobaltnatým, třetí část je věnována nanočásticím feritu hořečnatého a poslední část diskutuje výsledky studia nanočástic chromitu kobaltnatého.

3.1.1 Nanočástice a nanokompozity feritu kobaltnatého

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První soubor prací zabývajících se problematikou magnetických částic vznikly ve spolupráci se skupinou Dr. Nižňanského již v roce 2005, předmětem studia byly nanočástice a nanokompozity feritu kobaltnatého, které vykazovaly za nízkých teplot koercivitu až 2 T. Dále navazovaly práce zabývajících se touto tematikou, indukované zejména novými metodami přípravy monodisperzních a vysoce krystalických nanočástic feritu kobaltnatého s různým pokrytím, opět ve spolupráci se skupinou Dr. Nižňanského a od roku 2008 také se skupinou Dr. Morales (ICMM, Madrid).

Práce [82, 83] se zabývají přípravou nanokompozitů, které se skládají z nanokrystalů feritu kobaltnatého v amorní matici oxidu křemičitého. Nanokompozity byly připravovány metodou sol-gel, výsledná velikost nanokrystalů v amorfní matici byla řízena pomocí žíhání na různé teploty. S využitím transmisní elektronové mikroskopie a RTG difrakce bylo zjištěno, že velikost částic rostla z 3 nm na 15 nm při nárůstu teploty z 800 °C na 1100 °C. Vznik spinelové fáze byl potvrzen i pomocí Mössbauerovy spektroskopie, která poskytla informaci o inverzi spinelové struktury a naklonění povrchových spinů. Vzorky vykazovaly typické atributy superparamagnetického systému s poměrně slabou interakcí, proto byly výsledky analyzovány pomocí jednoduchého modelu neinteragujících částic. Na základě analýzy magnetizačních izoterm nad teplotou blokace byla určena distribuce velikosti částic, a to pomocí analýzy log-normálního rozdělení superspinů v generalizovaném škálování magnetizačních izoterm (tzv. Langevinovo škálování). V blokováném stavu byl pozorován nárůst koercivity až k enormní hodnotě 2.5 T při 10 K pro nanokompozit žíhaný na 1100 °C. Teplotní závislost koercivity bylo možné popsat pomocí Stonerova-Wohlfartova modelu, tj. koercivita rostla s odmocninou teploty až do teploty blokace. Na základě analýzy reálné a imaginární části střídavé susceptibility, měřené v rozsahu frekvencí od 10 Hz do 10 kHz, byl určen charakteristický relaxační čas superspinu a hodnota efektivní anizotropní konstanty.

Podobný systém byl připraven s využitím dvoukrokové syntézy [79]. Povrchově asistovanou koprecipitací byly nejprve syntetizovány mikrokuličky oxidu křemičitého o velikosti 11 μm , do kterých byly zabudovány nanokrystaly feritu kobaltnatého o střední velikosti 5 nm pomocí mikroemulzní metody. Výsledné nanokompozity vykazovaly superparamagnetické chování se slabými dipolárními interakcemi, nicméně zabudováním nanočástic do mikrokuliček oxidu křemičitého došlo k částečné chemické modifikaci částic vedoucí k větší distribuci magnetické velikosti částic.

Další práce [84] je zaměřena na studium magnetických vlastností nanoaglomerátů feritu kobaltnatého. Aglomeráty o velikosti 100 nm tvořené cca 5 nm částicemi byly připraveny opět pomocí mikroemulzní metody. Měření teplotní závislosti magnetizace v magnetickém poli 0.01 T (tzv. ZFC - FC křivky) ukázaly na přítomnost silných dipolárních interakcí mezi částicemi, odpovídající projevům super-spinového skla (SSG, z angličtiny super-spin-glass) nebo superferomagnetickému (SFM, z angličtiny super-fero-magnet) stavu. Výsledky analýzy relaxačního času superspinu a kritické spinové dynamiky z teplotní závislosti reálné a imaginární části střídavé susceptibility potvrdily přítomnost kolektivní relaxace ve smyslu SSG stavu.

Studium magnetických vlastností koncentrovaných systémů nanočástic feritu kobaltnatého, připravených různými metodami (koprecipitace, termální dekompozice) je prezentováno v práci [86]. Velikost částic se pohybuje v rozmezí 8 - 76 nm v závislosti na metodě přípravy. Měření magnetizace, střídavé susceptibility společně s experimenty tzv. stárnutí termoremanentní magnetizace poukazují na přítomnost silných dipolárních interakcí, v případě nanočástic pokrytých kyselinou olejovou byl potvrzen SSG stav.

Další práce věnující se problematice přípravy a studiu magnetických vlastností nanokrystalů feritu kobaltnatého popisuje novou metodu přípravy monodisperzních nanočástic, založenou na hydrotermální syntéze v soustavě kyselina olejová - voda - pentanol [70]. Výsledné nanokrystaly vykazují velice úzkou distribuci velikostí. Jejich velikost lze řídit v rozmezí 5 - 8 nm pomocí teploty reakce a poměru složek v kapalně fázi, které determinují polaritou řízenou precipitací nanokrystalů. Následná modifikace kyselinou dimerkaptosukcinovou vedla k hydrofilním nanočásticím s identickými magnetickými vlastnostmi a s hydrodynamickým průměrem 20 nm, což je činní vhodnými kandidáty pro biomedicínské aplikace.

Poslední práce v této sekci se zabývá návrhem nanokompozitů na bázi monodisperzních nanočástic feritu kobaltnatého a funkčních dielektrik [78]. Představuje zcela novou metodu přípravy nanokompozitu feritu kobaltnatého a materiálů s velkou dielektrickou konstantou (tzv. high-K systems) a prezentuje detailní charakterizaci připravených nanokompozitů

$\text{CoFe}_2\text{O}_4\text{-Al}_2\text{O}_3$, $\text{CoFe}_2\text{O}_4\text{-ZrO}_2$ a $\text{CoFe}_2\text{O}_4\text{-TiO}_2$ pomocí RTG difrakce, elektronové mikroskopie, magnetických měření a Mössbauerovy spektroskopie [78]. Nový syntetický postup je unikátní proto, že je možné jej použít pro různé systémy, kde lze připravit hydrofobní nanokrystaly a existují alkoxidy příslušných kovů, např. kompozity luminiscenčních nanočástic v matici vhodného dielektrika. V letošním roce byla metoda modifikována tak, že byly úspěšně připraveny nové nanokompozity o složení $\text{CoFe}_2\text{O}_4\text{-CeO}_2$ a $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-NCD}$ (z angl. nanocrystalline diamond).

Magnetism of sol-gel fabricated $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ nanocomposites

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Details of synthesis and characterization of sol-gel-produced CoFe_2O_4 nanoparticles embedded in the amorphous SiO_2 matrix are presented together with results of an extended magnetization study of these materials. The particle size was found to increase from 6 to 15 nm by varying the temperature of a subsequent annealing from 800 to 1100 °C. All samples exhibited superparamagnetic behavior with values of the blocking temperature T_B increasing with the particle size. At temperatures above T_B the magnetization curves follow the expected Langevin scaling of M vs H/T , which is consistent with the formation of the superparamagnetic state. For $T < T_B$, the coercivity field H_c was found to be proportional to $\sqrt{T}$ and the frequency-dependent ac susceptibility was found to obey the Néel–Arrhenius law. Both observations are compatible with a model of noninteracting randomly oriented single-domain particles. © 2005 American Institute of Physics. [DOI: 10.1063/1.1929849]

I. INTRODUCTION

Recently, the nanoscaled magnetism has attracted huge scientific interest owing to the application potential based on variety of interesting physical properties of nanoparticles.¹ The high coercivity fields revealed for magnetic nanoparticle system² make these materials interesting for applications in the field of high-density magnetic media.

Theoretical predictions concerning energetic stability of a single magnetic domain were established by Kittel in 1946,³ defining a certain critical size of a particle (typically 10^{-8} – 10^{-9} m for usual ferromagnets); in smaller particles the formation of a single ferromagnetic domain is preferred. Moreover, it was shown by Néel that at temperatures above the so-called blocking temperature T_B a stable bulk magnetization cannot be established due to thermal fluctuations acting on small particles and consequently the system exhibits the so-called superparamagnetic (SPM) behavior.⁴ At low temperatures (below T_B) the thermal fluctuations do not dominate and magnetic moments of SPM particles “freeze” in random orientation and cannot rotate freely.

The model of magnetization reversal in a single-domain particle (assuming coherent rotation of the magnetic domain moment) presented by Stoner and Wohlfarth⁵ provides sufficient explanation to the high coercivity below T_B ; when the energy of magnetocrystalline anisotropy becomes compa-

rable with the thermal activation energy, the direction of the particle magnetic moment starts to fluctuate and goes through a rapid superparamagnetic relaxation. At temperatures above T_B (supposing a system of uniform noninteracting nanoparticles) the thermal effects allow flips of magnetic moments between the easy magnetization directions by getting over the energy barriers in zero field and consequently the $H_c=0$. At temperatures ($T < T_B$) the thermal activation cannot overcome the magnetocrystalline anisotropy and the magnetic moment of each particle rotates from the field direction back to the nearest easy magnetization axis that yields a nonzero coercivity field. Since the nanoparticles and so the corresponding easy magnetization directions are randomly oriented, the total magnetization is naturally reduced with increasing temperature.

The appeal of predicted properties of nanoparticles eventuated in a boom of manufacturing and investigation of nanoparticle systems of various kinds despite of persisting difficulties of the larger-scale production, namely, the problems with size uniformity and interparticle interactions. An intelligent way on how to control both, the size of particles and their isolation, is embedding them in a magnetically inert (e.g., Si or SiO_2) matrix.^{6–8}

Generally, such nanocomposites can be obtained either by physical or chemical methods of preparation. Physical methods generally lead to a narrow particle size distribution. However, complicated fabrication procedures and/or expen-

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sive facilities are needed (e.g., ball milling⁷ or recently developed microwave synthesis⁹). On the other hand, the chemical way of synthesis is usually less expensive; the most common method is the sol-gel procedure (beside, e.g., template synthesis¹⁰).

The advantages of the sol-gel method are the better homogeneity of materials and lower temperatures of heat treatment in comparison with the classical ceramic ways.

Numerous delicate studies on elemental nanoparticles (Ni, Co, and Fe) have been performed,^{11–13} while only few reports on ferrite-based systems are available up to now. This may be due to the difficult control of particle shape and particle size distribution when preparing isolated ferrite nanoparticles.¹⁴ The cobalt ferrite composites usually exhibit pretty high values of coercivity fields H_c and saturated magnetization M_s , that makes them highly attractive for applications^{15–18} and therefore these systems are worth of further experimental effort.

In this work, we present the results of study of ac and dc magnetic properties (with respect to temperature and magnetic field) of well-defined CoFe_2O_4 nanoparticles embedded in amorphous SiO_2 matrix.

II. EXPERIMENT

A. Sample preparation

The conventional sol-gel method using Tetraethyl orthosilicate (TEOS), HNO_3 as an acid catalyst, formamide as a modifier, and methanol as a solvent was employed for silica matrix preparation. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were first dissolved in methanol. The Si/Fe molar ratio was fixed to 100/15. The gelation time was approximately 24 h at 40 °C. The samples were left 2 days for ageing followed by progressive drying at 40 °C for 3 days in flowing N_2 atmosphere. After drying, the samples were preheated first at 300 °C in vacuum for 2 h and then annealed for 4 h under atmospheric pressure at one of the following temperatures: 800, 900, 1000, and 1100 °C and labeled accordingly as S800–S1100. Longer annealing times (even in the range of days) lead neither to increase of the particle size nor to phase changes. The final products were characterized using powder x-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM).

B. Characterization and magnetic measurements

A high-resolution transmission electron microscope Topcon was used for the direct observation of the particle appearance. The particle size was determined using the SCION IMAGES software. The XRD patterns were measured at room temperature using a Siemens D5000 diffractometer.

The dc magnetization and ac susceptibility were measured in PPMS 14T and PPMS 9T devices (Quantum Design, San Diego). Samples of a typical mass ~ 100 mg were placed in a gelatine capsule and fixed by acetone-based glue to avoid orientation of particles of the sample to the field direction when being magnetized.

The zero-field-cooled (ZFC) and field-cooled (FC) curves were measured in the temperature range of 2–350 K

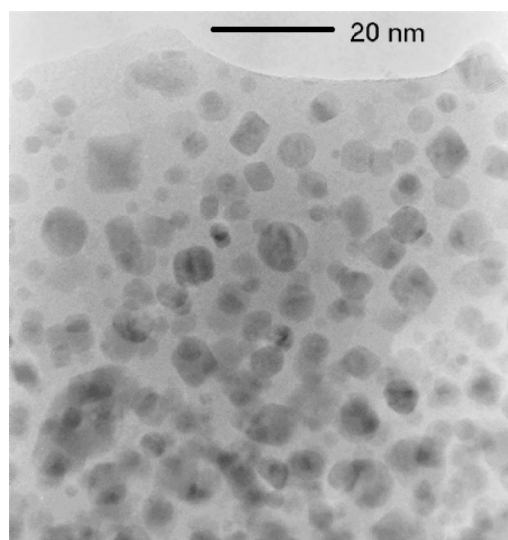


FIG. 1. HRTEM observation of the $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ nanocomposite, molar ratio 15/100, and heating at 1000 °C (S1000).

for different values of the dc magnetic field (10 mT, 50 mT, and 0.1 T). After measuring the ZFC curve (the sample was cooled to 2 K in zero magnetic field, then the magnetic field for measurement was applied and subsequently M vs T data were taken with increasing temperature), the sample was cooled down to 2 K holding the magnetic field unchanged and the M vs T data were taken again with increasing temperature. In order to determine the values of the coercivity fields and their development with temperature, the hysteresis loops were measured at selected temperatures in magnetic fields varying up to 8 T (in both polarities). The samples were first cooled down to 2 K in zero magnetic field. Then the virgin curve and the hysteresis loop were measured; the hysteresis loops at higher temperatures were further measured after heating the sample above the blocking temperature T_B and cooling in zero magnetic field to the temperature of measurement.

The temperature dependence of the ac susceptibility (with the magnetic-field amplitude of 1 mT and the frequency ranging from 100 to 10 kHz) was measured in zero dc magnetic field.

III. RESULTS AND DISCUSSION

A. XRD measurement and HRTEM observation

The $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ nanocomposites annealed at 800 °C show very well-defined grains with the mean particle size of 4 nm (Fig. 1). The particle size increases with an increase in the annealing temperature; finally, the mean particle size of the samples annealed at 1100 °C was 15 nm (in diameter).

All samples were characterized by XRD measurements (step 0.02°) and the results are shown in Fig. 2 ($\text{CoFe}_2\text{O}_4/\text{SiO}_2$ samples heated at 800 and 1000 °C). The XRD patterns of the samples heated at 800 °C indicate the presence of amorphous SiO_2 manifested by the characteristic very broad diffraction maximum at 25° (2 theta), see Fig. 2. The diffraction patterns of phases other than silica exhibit broad peaks that become sharper with the increasing tem-

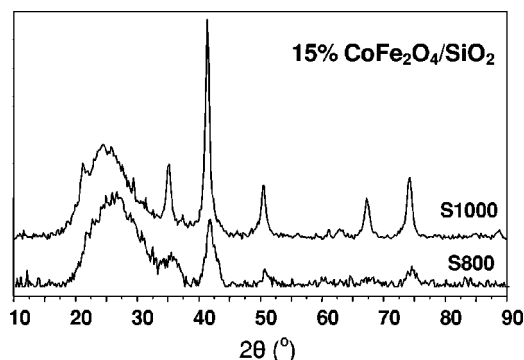


FIG. 2. Examples of powder x-ray diffraction patterns of the S1000 and S800 samples.

perature of the heat treatment. This corresponds well to crystalline particle growth. In the $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ system, the diffraction pattern of the spinel phase was observed and no other iron containing phases were detected. Direct particle size observation by means of HRTEM confirms the tendency shown by the XRD.

B. Magnetization study: Coercivity and superparamagnetism

The ZFC and FC temperature dependencies seen in Fig. 3 exhibit the main attributes of the SPM system. The ZFC curves exhibit a broad maximum at T_{max} . At sufficiently high temperatures the ZFC and FC data coincide. When decreasing temperature towards T_B the FC curve deviates from the ZFC data to higher magnetization values. The temperature of the first deviation is denoted as T_{diff} . The discrepancy between T_{max} and T_{diff} , which are supposed to be equal in the ideal case, usually signalizes a significant nanoparticle size distribution in the composite. The moments of the largest particles freeze already at T_{diff} whereas the majority fraction of nanoparticles in the sample is blocked at T_B corresponding to T_{max} . The evolution of T_B , T_{max} , and T_{diff} values across the series of the samples S800–S1100 is shown in Table I. The value of T_B increases with increasing the particle mean size (corresponding to higher annealing temperatures) as expected. The T_B values remain more or less intact in low applied magnetic fields up to ~ 10 mT whereas they become gradually reduced with further increasing the field (reaching, e.g., $T_B \sim 100$ K for S1100 in 8 T). The shift of T_B can be explained by a very slow relaxation to the nonmagnetic state.

Inspecting the low-temperature part of the FC curve, a small decrease of magnetization can be observed below ~ 50 K for the S1000 and S1100 samples. This effect could be caused either by the presence of a tiny amount of antiferromagnetic Fe phase (although no traces of Fe phases have been detected on XRD patterns) or rather due to non-negligible shape anisotropy of nonspherical nanoparticles.

The SPM behavior of these samples above T_B has been confirmed when plotting M/M_s vs $\mu_0 H/T$ (M_s is the saturated magnetization) resulting in a universal curve seen in Fig. 4. This scaling is consistent with the SPM response, although it is correct only in low fields.^{11,19} The contribution from the SPM nanoparticles to the total magnetization can be described by

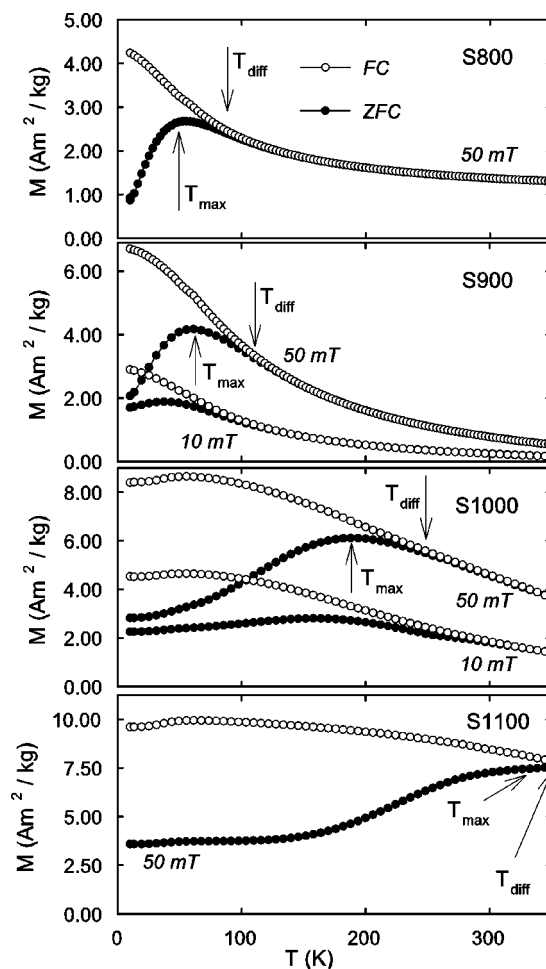


FIG. 3. Temperature dependence of ZFC-FC magnetization of the S800–S1100 samples at low fields.

$$M = M_s L(x), \quad x = \left(\frac{\mu H}{k_B T} \right), \quad (1)$$

where M_s is the saturation magnetization of N particles with magnetic moment μ and $L(x)$ is the Langevin function. This expression is valid only for a system of monodisperse non-interacting particles. However, since real systems have a non-negligible distribution of magnetic moments, the magnetization of SPM grains is better described as a weighted sum of the Langevin functions,^{11,19,20}

$$M = \int_0^\infty L(x) M_s dx, \quad x = \left(\frac{\mu H}{k_B T} \right), \quad (2)$$

where M_s is given by

TABLE I. Comparison of blocking temperatures T_B obtained from ac susceptibility (at 0 T, 1 kHz), ZFC-FC magnetization at T_{diff} , T_{max} , and (5).

Sample	ac	ZFC-FC (T_{diff})	ZFC-FC (T_{max})	(5)
S800	87	92	50	80
S900	107	116	60	105
S1000	290	305	180	275
S1100	...	350	300	295

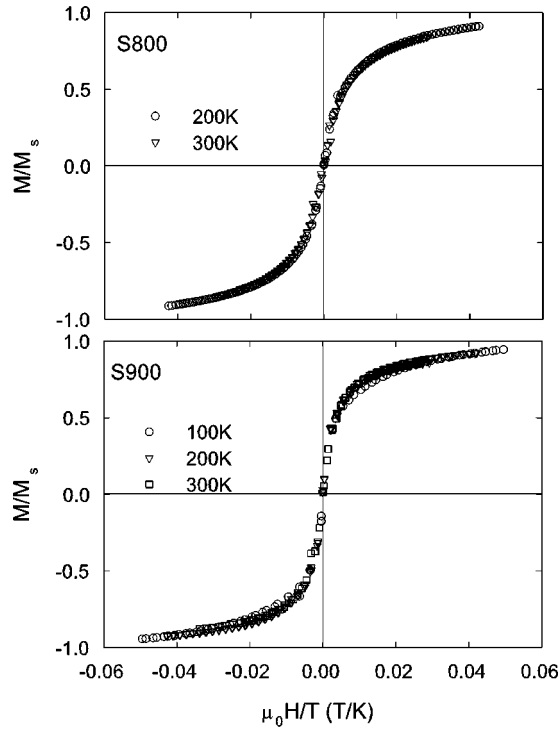


FIG. 4. M vs $\mu_0 H$ curves of the S800 and S900 samples presented in the universal Langevin scaling.

$$M_S = \int_0^\infty \frac{1}{\sqrt{2\pi}\mu\sigma} \exp\left[-\frac{\ln^2(\mu/\mu_0)}{2\sigma^2}\right] d\mu, \quad (3)$$

where σ is the log-normal distribution width and μ_0 is the median of the distribution related to the average magnetic moment μ_m by

$$\mu_m = \mu_0 \exp\left(-\frac{\sigma}{2}\right). \quad (4)$$

The parameters obtained by the fit of the weighted sum to the experimental data are summarized in Table II. The fit of the single Langevin function provided generally higher values of μ accompanied by a much worse standard deviation and therefore it is not presented. The determined values of the mean nanoparticle radius are in a reasonable agreement with the TEM results; the difference between the corresponding values is mainly due to a rather broad distribution of particle size. An example of the fit for the S1100 sample is presented in Fig. 5.

The hysteresis loops measured at 2 K presented in Fig. 6 demonstrate that the value of the coercivity field H_c (sym-

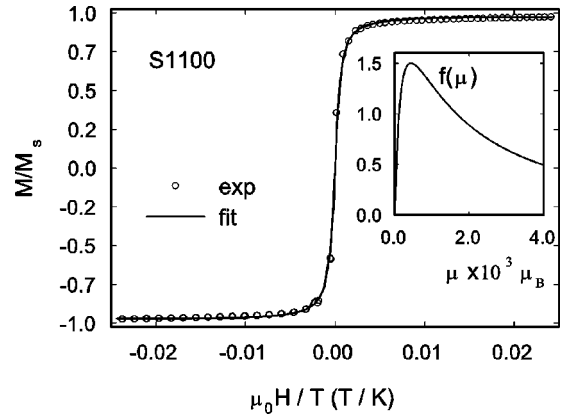


FIG. 5. Fit of the universal M/M_s vs $\mu_0 H/T$ curve for S1100 together with the fit of weighted sum of the Langevin functions as an example. The inset shows the resulting distribution for S1100.

metric for opposite polarity of the magnetic field, $H_c = -H_c$) is increasing with increasing the particle size (yielding only a slightly varying value of saturated magnetization $M_s \sim 16 \text{ A m}^2 \text{ kg}^{-1}$ at 2 K). The very slow increase of the virgin magnetization curve manifests a pinning-type magnet without reversible region, however, the observed S-like shape of the virgin curve (after ZFC) is not expected for the system of randomly distributed superparamagnets and can be ascribed to non-negligible dipolar interparticle correlations.¹⁵ Therefore, the resulting high coercivity field may be enhanced due to intrinsic anisotropy of particles together with non-negligible interparticle dipolar fields.

At low temperatures the coercivity of a system of non-interacting and randomly oriented particles is expected to follow the relation,

$$H_c(T) = H_{c0} \left[1 - \left(\frac{T}{T_B} \right)^{1/2} \right]. \quad (5)$$

The above expression considers, that the magnetization reversal process takes place coherently, a situation which can be achieved only when the interparticle correlations are neglected.¹¹ An extrapolated value of H_{c0} , see Fig. 7, together with T_B (summarized in Table I) has been derived for all samples. The T_B values are appreciably consistent with those obtained from the temperature dependencies of the dc magnetization and the ac susceptibility as shown further. Surprisingly, the H_{c0} value for the S800 and S900 samples is practically the same, which may be caused by a specific nanoparticle size distribution within a very similar interval obtained at the corresponding annealing temperatures.

TABLE II. Results of the Langevin fits with semilogarithmic distribution of μ and corresponding calculated radii of spherical nanoparticles in comparison with those obtained from (6) for T_B defined at T_{diff} and *T_B at T_{max} , respectively.

Sample	$\mu_0 \times 10^{-3}$ (μ_B)	r_0 (nm)	$\mu_m \times 10^{-4}$ (μ_B)	r_m (nm)	σ	$\langle r \rangle$ (nm)	$^*\langle r \rangle$ (nm)
S800	4.7	3.0	1.5	4.1	1.5	3.0	2.5
S900	5.7	3.1	1.9	4.4	1.5	3.3	2.6
S1000	8.1	6.2	2.9	6.4	1.5	4.5	3.8
S1100	8.7	6.8	3.2	7.0	1.6	4.7	4.5

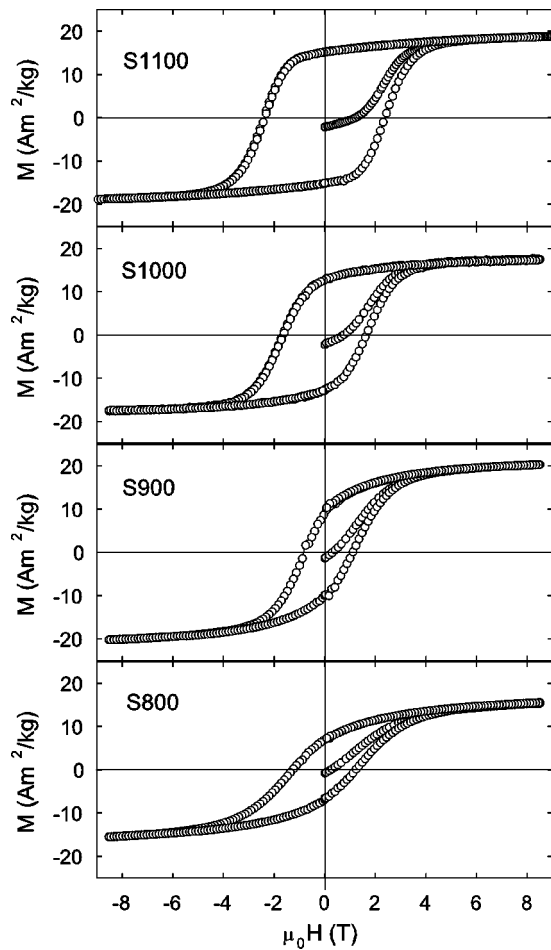


FIG. 6. Virgin curves and hysteresis loops of the S800–S1100 samples measured at 2 K.

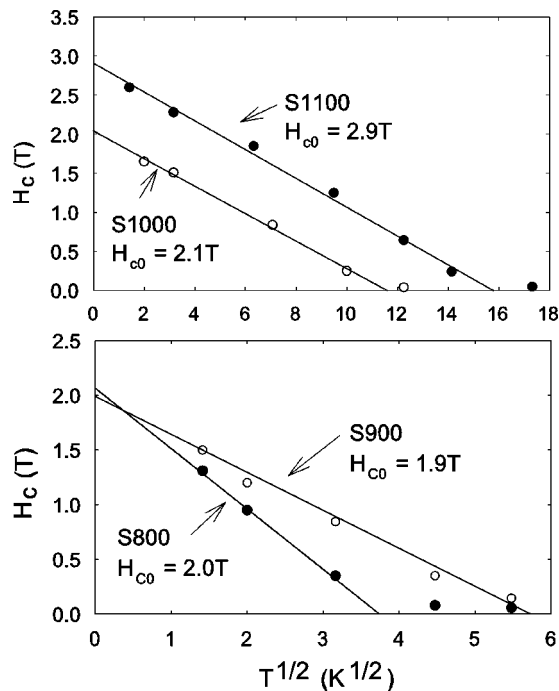


FIG. 7. Temperature dependence of coercivity fields appreciably below T_B (H_c vs. $\sqrt{T}$ representation) for all samples.

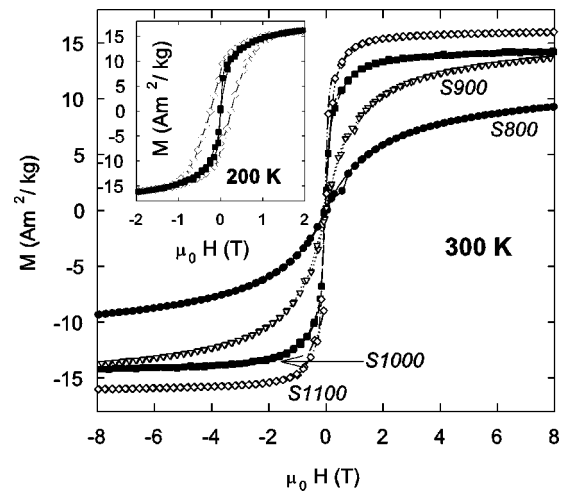


FIG. 8. Anhysteretic M vs $\mu_0 H$ curves of the S800–S1100 samples measured at 300 K reflecting increasing value of M_s ; the inset shows the curves for S1000 and S1100 at 200 K indicating small hysteresis persisting together with squeezed-like loop for the S1100 sample.

An estimation of the mean radius of nanoparticles can be obtained using the general formulas,

$$T_B = \frac{K\langle V \rangle}{25k_B}, \quad (6)$$

$$\mu = M_s^{\text{bulk}}\langle V \rangle, \quad (7)$$

where K is the first-order magnetocrystalline anisotropy of bulk CoFe_2O_4 ferrite,²¹ supposing to be temperature independent, $\langle V \rangle$ is the average particle volume, M_s^{bulk} is the saturated magnetization of bulk CoFe_2O_4 , and T_B and k_B have the usual meaning. The values of the nanoparticle radius are in a good agreement with those obtained by other methods.

The M vs $\mu_0 H$ curves measured at 300 K, which are presented in Fig. 8, exhibit no hysteresis. The saturated magnetization values at 300 K are in an excellent agreement with the results published recently by Garcia-Cerda *et al.*¹⁶ on similarly fabricated Co ferrite nanocomposites. The same curves taken at 200 K for the S1000 and S1100 are presented in the inset of Fig. 8, where the zero coercivity accompanied by the permivarlike character of the hysteresis loop is observed for the S1000 composite. Similar “narrowing” of the hysteresis loop in the low-field region has been found for the S800 and S900 samples at temperatures just below T_B as well in contrast with the expectation for randomly distributed noninteracting SPM particles. The effect is probably caused by the mean dipolar field acting on a particle, which depends on the direction and size of the magnetic moments of surrounding particles.²¹

C. Dynamic properties (ac susceptibility)

The temperature dependence of the ac susceptibility (χ' , χ'') shows characteristic maxima corresponding to the blocking temperatures T_B (Ref. 4) (the actual values of T_B are summarized in Table I), which are shifted to higher temperatures with increasing frequency, see Fig. 9. This observation corroborates the idea that the nanoparticles behave

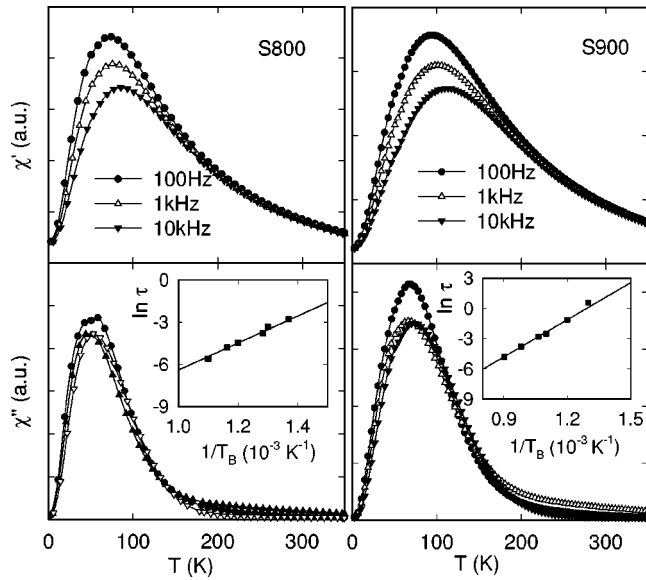


FIG. 9. Temperature dependence of ac magnetic susceptibility (both χ' and χ'') of the S800 and S900 samples. The inset shows the fit according to the Arrhenius law.

like noninteracting and single-domain species excluding any additional significant dipole-dipole or interparticle interactions.

A useful criterion for classifying the observed freezing process is the empirical parameter Φ ,²² which represents the relative shift of the blocking temperature per frequency decade,

$$\Phi = \frac{\Delta T_f}{T_f \Delta \log_{10}(f)}, \quad (8)$$

where ΔT_f is the difference between the blocking temperature measured in the $\Delta \log_{10}(f)$. For the both the S800 and S900 samples we have obtained the value of $\Phi = 0.09$, which is very close to the 0.1 value found for the SPM system. On the other hand, smaller values of Φ are usually caused by the spin-glass-like behavior of the nanoparticle surface or simply due to non-negligible interparticle interactions.^{23–25}

The linear dependence of $\ln f$ vs $1/T_B$ follows the Néel–Arrhenius law for the S800 and S900 samples, see the inset in Fig. 9,

$$\tau = \tau_0 \exp \frac{E_a}{k_B T}, \quad (9)$$

where τ is the relaxation time, E_a is the anisotropy energy barrier, and τ_0 ranges from 10^{-9} to 10^{-11} s for the SPM systems. In the absence of the external magnetic field, the energy barrier E_a is proportional to the particle volume V and can be expressed as $E_a = K_{\text{eff}} V \sin^2 \theta$, where K_{eff} is an effective magnetic anisotropy constant and θ is the angle between the easy magnetization axis of the particle and its magnetic moment direction. The resulting values of τ_0 , E_a , and K_{eff} are 1.8×10^{-8} and 1.3×10^{-8} s, 1227 and 920 K, 4×10^5 and 3×10^5 ergs/cm³ for the S800 and S900 samples, respectively. The resulting effective anisotropy is practically the same as the first-order anisotropy bulk constant [3.5×10^5 ergs/cm³

(Ref. 21)] indicating negligible surface effects and interparticle interactions.^{24,25}

IV. CONCLUSIONS

In summary, we have prepared the CoFe₂O₄ nanoparticles embedded in the SiO₂ amorphous matrix which exhibit superparamagnetic behavior with $T_B \sim 70$, ~ 100 , ~ 280 , and ~ 350 K, respectively. These values correspond to the temperatures (800, 900, 1000, and 1100 °C) of the final annealing, which controls the mean particle size increasing from 4 to 15 nm. The results of the magnetic characterization of these samples are consistent with the theoretical predictions made for the systems with randomly oriented noninteracting particles when the temperature dependence of the magnetic anisotropy is neglected. Although the TEM micrographs of our samples do not show any evidence of significant particle agglomeration, one cannot exclude that the weak dipolar interactions are inducing the evolution of the magnetization reversal toward more incoherent and heterogeneous mechanism, supporting the unusually high H_{c0} observed and the S-shape virgin magnetization curve for all samples. On the other hand, the values of the relaxation times together with the effective anisotropy constants obtained from the ac susceptibility experiments suggest that these effects are almost negligible in our nanocomposites.

ACKNOWLEDGMENTS

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Sol-Gel Fabricated $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ Nanocomposites: Synthesis and Magnetic Properties

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Well-defined CoFe_2O_4 nanoparticles embedded in an amorphous SiO_2 matrix have been synthesized by a sol-gel method, characterized and investigated by Mössbauer spectroscopy and magnetic properties measurements. The mean particle size increases from 3 to 15 nm consistently with the temperature of the subsequent annealing, which varied from 800°C to 1100°C, respectively. The composites exhibit superparamagnetic behavior with the blocking temperature T_B increasing with the mean particle size from 80 to 350 K, respectively. Sufficiently high value of $H_C \sim 2.5$ T (at 2 K) has been observed for the sample annealed at 1100°C.

Index Terms—Ferrite nanoparticles, sol-gel method, superparamagnetism.

DUE to expected applications of nanoparticles, the demand for their manufacture rises despite persistent difficulties in larger-scale production. So far, many studies of elemental nanoparticles (Ni, Co, Fe) have been published, e.g., [1] and [2], while overall reports on ferrite-based systems are still few in number. One reason is that to obtain isolated ferrite nanoparticles is often a crucial problem, due to difficult control of the particle shape and size distribution [3]. Promising candidates are cobalt ferrite composites because of high coercivity fields H_C and saturated magnetization M_s values provided [4], [5]. In this paper, we present details of fabrication, characterization, and selected magnetic characteristics of well-defined CoFe_2O_4 nanoparticles embedded in an amorphous SiO_2 matrix.

We used a conventional sol-gel method with tetraethyl-orthosilicate (TEOS), HNO_3 as an acid catalyst, formamide as a modifier, and methanol as a solvent for silica matrix preparation. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were first dissolved in methanol, and the Si/Fe molar ratio was fixed to 100/15 (gelation time —24 h at 40°C). The samples were left two days for ageing, followed by progressive drying at 40°C for three days in a flowing N_2 atmosphere. After drying, the samples were preheated at 300°C in a vacuum for 2 h, and then under atmospheric pressure at one of the following temperatures: 800°C, 900°C, 1000°C, or 1100°C, and finally labeled according to the last annealing temperature as S800–S1100, respectively.

A high-resolution transmission electron microscope, Topcon, was used for the direct observation of the particle appearance. Particle-size determination was done using the Scion Images software. The nanocomposites show well-defined grains, with the increasing mean particle size from 3 nm up to 15 nm in diam-

TABLE I
SUMMARY OF MAGNETIC CHARACTERISTICS: BLOCKING TEMPERATURES T_B [DETERMINED FROM AC SUSCEPTIBILITY, T_{diff} , T_{max} , (1)], AVERAGE MAGNETIC MOMENT PER PARTICLE μ , AVERAGE PARTICLE DIAMETER (R) OBTAINED BY THE FIT OF THE WEIGHTED SUM OF LANGEVIN FUNCTIONS (L), MEAN PARTICLE DIAMETER OBSERVED BY TEM AND FROM FWHM, EXTRAPOLATED COERCIVITY FIELD H_{C0}

Sample	T_B (K) AC	T_B (K) diff	T_B (K) T_{max}	T_B (K) eq. (1)
S800	87	92	50	80
S900	107	116	60	105
S1000	290	305	180	275
S1100	x	350	300	295
Sample	$\mu(\mu_B)$ L	R (nm) L	R (nm) TEM/FWHM	H_{C0} eq. (1)
S800	4700	1.5/2	1.5	1.9
S900	5700	2/3	2	1.8
S1000	8100	5.5/4	5.5	2.2
S1100	8700	7.5/8	7.5	2.9

eter, according to the annealing temperature for the S800–S1100 samples, respectively. See Table I.

All samples were characterized by powder X-ray diffraction (XRD) using a Siemens D500 diffractometer equipped with a cobalt anode ($\lambda(\text{CoK}\alpha) = 1.7890 \text{ \AA}$) and a quartz primary monochromator in order to identify the phase composition. The XRD patterns of the samples after final thermal treatment are shown in Fig. 1. A tendency of crystallization as a function of the heating temperature is reflected by a broad diffraction peak at around 25° (2θ). The process of crystallization as a function of the heating temperature can be followed from the full width at half maximum (FWHM) of diffraction peaks, which follows the Scherrer equation, and it also permitted us to estimate the particle size, see Table I [6]. The Mössbauer spectra measurement was done in the transmission mode with ^{57}Co diffused into a Rh matrix as the source, moving with constant acceleration. The

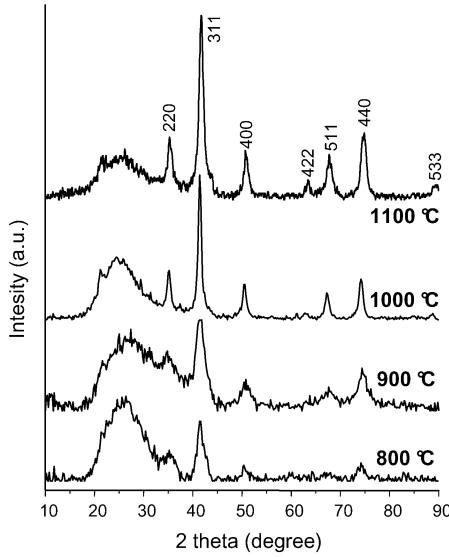


Fig. 1. XRD patterns of S800–S1100 samples.

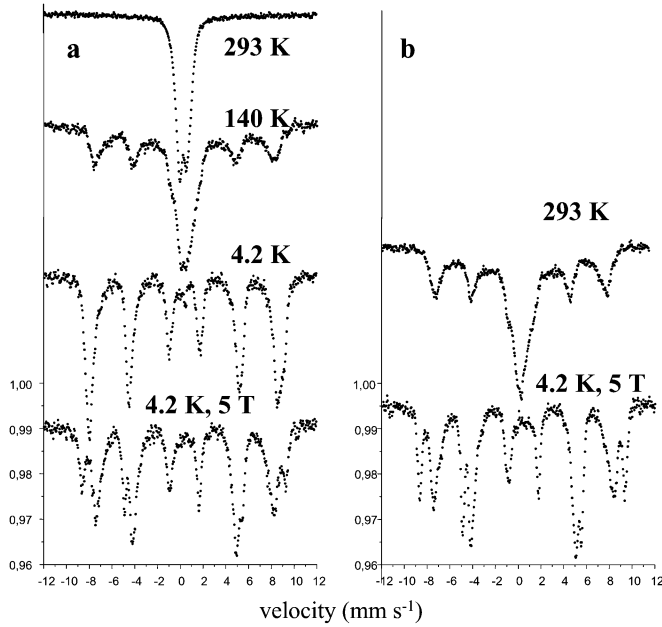


Fig. 2. Comparison of Mössbauer spectra of S900 (a) and S1000 (b) recorded at zero magnetic field and at 5 T at selected temperatures.

spectrometer was calibrated by means of a standard α -Fe foil, and the isomer shift was expressed with respect to this standard at 293 K. The spectra were recorded at several different temperatures in magnetic fields up to 5 T, applied perpendicular to the direction of the γ -ray emission and fitted with the help of the NORMOS program. The temperature development of the spectra of S900 is shown in Fig. 2(a). The sample is superparamagnetic (SPM) at room temperature (no sextet is observed), while after cooling to 140 K, partial magnetic arrangement is observed (sextet appearance). Simultaneous occurrence of both the sextet and the doublet reflects a certain size distribution of the CoFe_2O_4 particles. At 4.2 K, complete ferromagnetic ordering of the magnetic moments in Co ferrite particles is observed. Due to a very strong overlap of the subspectra, one cannot distinguish between iron positions in the spinel structure (Td-tetra-

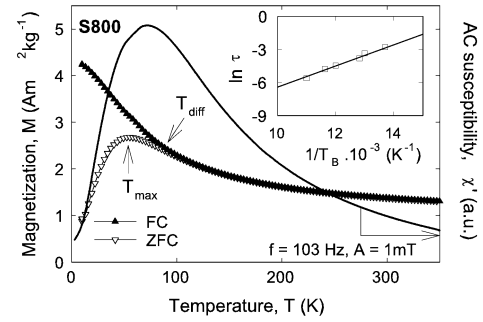


Fig. 3. Temperature dependence of ZFC-FC magnetization of S800 sample at 50 mT in comparison with that of AC susceptibility (real part, χ'). The inset shows the logarithmic dependence of the relaxation time τ against the inverse blocking temperature T_B , according to the Néel–Arrhenius law.

hedral, Oh-octahedral sites). When we take generally accepted recoilless factors for the spinel structure ($f_{Td} : f_{Oh} = 1.2$) [7] into account, we can express the real formula of our spinel as $(\text{Co}_{0.41}\text{Fe}_{0.59})[\text{Co}_{0.59}\text{Fe}_{1.41}]\text{O}_4$. Great deviation from the ideal structure can be explained by the presence of very small particles and significant influence of surface atoms. The spectra of the S1000 sample are represented in Fig. 2(b). Simultaneous occurrence of both sextet and doublet can be explained by a certain size distribution of the CoFe_2O_4 particles reflecting a partly ferromagnetic sample at 293 K. At 4.2 K in 5 T, the spectrum shows a magnetically ordered structure of cobalt ferrite (no doublet is present). Moreover, there is again a deviation from the ideal inverse spinel structure (area ratio ($S_{Td} : S_{Oh}$) differs from 1.2).

The DC magnetization (M) as a function of temperature (2–350 K) and magnetic field (0–14 T), together with the AC susceptibility (frequency range 83–8333 Hz, DC amplitude 1 mT), were measured in the PPMS 14 T and PPMS 9 T devices (Quantum Design, San Diego, CA). The temperature dependencies of the DC magnetization were measured at 50 mT; first after cooling the sample in a zero magnetic field (ZFC curve), followed by cooling the sample under an applied magnetic field (FC curve) and measuring during heating at the same field. The furcation of ZFC and FC curves at a certain temperature (denoted as T_{diff} in our case) is one of the characteristic features of an SPM system, as seen in Fig. 3 for S800. However, the coinciding broad maximum observed on the ZFC curve occurs at a slightly lower temperature (symbolized as T_{max}) than T_{diff} . Such behavior usually signals a certain particle-size distribution in the nanocomposite; while a fraction of the largest particles already freeze at T_{diff} , the majority fraction of the nanoparticles in the sample is being blocked at T_{max} , resulting in a distribution of the blocking temperatures T_B in the sample; the distinctive values (at T_{diff} and T_{max} , respectively) of the blocking temperatures T_B for all four samples are summarized in Table I. The value of T_{max} and T_{diff} monotonously increases with the increasing mean size of the particles (corresponding to the higher annealing temperatures) as expected; for the S1000 and S1100 samples, the maximum on the ZFC curve at T_{diff} becomes less pronounced than for S800 and S900, respectively. At low temperatures, the value of coercivity field H_c (symmetric for opposite polarity of magnetic field $H_c = -H_c$) is increasing with increasing size of particles

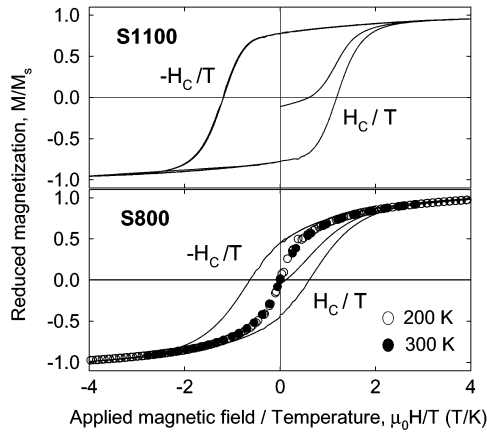


Fig. 4. Virgin magnetization curves and hysteresis loops of S800 and S1100 samples measured at 2 K (solid line), together with unhysteretic curves of S800 in SPM state.

(despite a slightly varying value of saturated magnetization from $M_s \sim 19 \text{ Am}^2\text{kg}^{-1}$ for S1100 to $M_s \sim 16 \text{ Am}^2\text{kg}^{-1}$ for S800 at 2 K), see Fig. 4. At low temperatures, coercivity of a system of noninteracting and randomly oriented particles is expected to follow the relation

$$H_C(T) = H_{C0} \left[1 - \left(\frac{T}{T_B} \right)^{1/2} \right]. \quad (1)$$

An extrapolated value of H_{C0} , together with T_B (summarized in Table I) have been derived for all samples. The T_B values are appreciably consistent with those obtained from temperature dependencies of the DC magnetization and the AC susceptibilities, as shown later. An estimation of nanoparticle mean radius was obtained using general formulas

$$T_B = \frac{K\langle V \rangle}{25k_B} \quad (2)$$

where K is the first-order magneto-crystalline anisotropy constant of bulk CoFe₂O₄ ferrite [8], supposed to be temperature-independent, $\langle V \rangle$ is the average particle volume ($\mu = M_s^{\text{bulk}}\langle V \rangle$), M_s^{bulk} is the saturated magnetization of bulk CoFe₂O₄, and T_B and k_B have the usual meaning. The values of radii of the nanoparticles are in a good agreement with those obtained by other performances.

Finally, the SPM behavior above T_B has been confirmed when plotting M/M_s versus $\mu_0 H/T$ (M_s is the saturated magnetization at the corresponding temperature), resulting in a universal curve (see Fig. 4). This scaling is consistent with the SPM response; the contribution from the SPM nanoparticles to the total magnetization can be described as a weighted sum of Langevin functions [1], [9], [10] providing a mean particle diameter, distribution width, and mean magnetic moment per particle, respectively (see Table I for results).

The temperature dependence of the AC susceptibility shows characteristic maxima corresponding to the blocking temperatures T_B [11] (derived from the maximum position at 103 Hz are summarized in Table I), which are shifted to higher temperatures with increasing frequencies. This observation corroborates the idea that nanoparticles behave like noninteracting and single-domain species, excluding any additional dipole-dipole or interparticle interactions. The linear dependence of $\ln f$ (f is the frequency of AC field 83–8333 Hz) versus $1/T_B$ follows the Néel-Arrhenius law [11] $\tau = \tau_0 \times e^{[E_a/k_B T]}$, where τ is the relaxation time, E_a is the anisotropy energy barrier, and τ_0 ranges from 10^{-9} to 10^{-11} s for SPM systems. The resulting values of τ_0 and E_a are 1.8×10^{-9} s and 1.3×10^{-8} s; 1227 K and 920 K for the S800 and S900 samples, respectively. The values of τ_0 are rather close to the ones expected for an ideal SPM system, indicating almost negligible interparticle interactions in the composite. In summary, we have prepared a series of CoFe₂O₄ nanocomposites embedded in an amorphous SiO₂ matrix. Nonhomogeneous occupation of Fe positions in the structure has been observed by the Mössbauer spectroscopy under magnetic field. Magnetic behavior of the composites follows the Néel theory of single-domain noninteracting entities exhibiting SPM behavior above T_B increasing with the temperature of the heat treatment according to the mean particle size. Below T_B , appreciably high values of coercivity develop, increasing up to H_{C0} 2.9 T for S1100.

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Preparation and characterization of SiO₂ microspheres doped with CoFe₂O₄ nanocrystals

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Main goal of the reported work was to fabricate silica microspheres doped with magnetic nanocrystals. Cobalt ferrite nanocrystals were fabricated separately via surfactant-assisted coprecipitation. The sol-gel method in microemulsion was subsequently used for encapsulating of the magnetic nanonocrystals into the silica microspheres. Final products were characterized by various techniques and magnetic measurements. The obtained silica microspheres doped with CoFe₂O₄ were of average diameter 11 μm.

Keywords: *sol-gel; microemulsion; cobalt ferrite; microspheres; nanocomposite*

1. Introduction

Fabrication of new functional materials tailored for specific applications is a challenge for chemistry and material science. Magnetic nanoparticles have been of a great interest ever since pioneer works of their simple preparation, reported for example in [1]. The sol-gel chemistry, mainly of silicate precursors has been undergoing through a renaissance since 1980 [2–4]. Combination of ever more progressive techniques leads to a variety of new materials based on magnetic or superparamagnetic (SPM) nanoparticles with functionally modified surface. The presence of a silica gel surface layer could shift the point of zero charge (p.z.c.) into acidic one, while an amino-modified silica layer could shift it in a basic range [5, 6]. A silica layer could be introduced by a number of preparation methods, two of them being widely used. The Stöber method uses ammonia catalyzed gelation of tetraalkoxysilane [7, 8], and the so-called microemulsion method is based on the formation of droplets of the emulsion,

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stabilized by surfactants, that acts as a micro-reactor for the sol-gel process [5, 9]. The advantages of the microemulsion method are, for example, independence of a catalytic mechanism (acidic or basic) of the sol-gel process, easy variation of the droplet size (by changing the amount of the water phase or changing the surfactant type), thermodynamic stability of the system, etc.

The paper concentrates on the fabrication of silica microspheres with the diameter of a few micrometers containing nanocrystals of CoFe_2O_4 . The magnetic Co-ferrite nanoparticles were prepared by coprecipitation of cobalt(II) and iron(II) dodecylsulphate solution using methylamine as the precipitant [10]. By this preparation route, many types of ferrite nanoparticles were synthesized, for example Fe_3O_4 [11], NiFe_2O_4 and MnFe_2O_4 [12]. Dodecylsulphate (an anionic surfactant) controls the shape and size of nanocrystals during the precipitation. A micellar system of water/CTAB (cetyltrimethylammonium bromide)/*n*-hexanol was used for encapsulation of the magnetic particles into silica spheres via the sol-gel microemulsion method. The proper pH (acidic solution) of droplets and temperature around 40 °C, caused gelation of the silica precursor TMOS (tetramethoxysilane). In general, microemulsion, containing droplets of an acidic cobalt ferrite ferrofluid, is a suitable system for gelation of TMOS at higher temperatures.

Nowadays, a micro-scale processing is slightly ignored due to the greater emphasis placed on the nanosized features. However, this work is an illustrative example of a bottom-up approach, where the micro-objects are formed from molecular and nanoparticle building blocks.

2. Experimental

Syntheses and materials. All chemicals were of 98% purity or higher. Nanoparticles of CoFe_2O_4 were prepared by the coprecipitation method as described earlier [10]. Cobalt(II) and iron(II) dodecylsulphate, respectively, were prepared by crystallization of 1:1 volume mixture of 0.1 M cobalt acetate (Merck) or 0.1 M iron(II) chloride (Merck) solution, with 0.1 M sodium dodecylsulphate (Merck) at 2 °C. After adding of 2 M methylamine into the mixture of $8 \cdot 10^{-3}$ M $\text{Co}(\text{DS})_2$ and $2,6 \cdot 10^{-2}$ M $\text{Fe}(\text{DS})_2$, the mixture was stirred vigorously for 2 h. Co-ferrite particles were purified by several cycles of centrifugation and decantation.

A schematic diagram of the synthetic routes of $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ microspheres is shown in Fig. 1. The non-aqueous part of the microemulsion consisted of 5 g of *n*-hexanol (Aldrich), 1.5 g of ethanol and 0.3 g of CTAB (Aldrich). Few droplets of distilled water (maximum 0.5 cm³) were added to form appropriate emulsion. Furthermore, 3.87 g of TMOS (Aldrich) were pre-hydrolyzed with 3.6 g of 0.03% HNO_3 (Lachema) for 1 h at 40 °C. 1 g of formamide (Merck) with 30 mg of ultrasonically dispersed CoFe_2O_4 particles were added, and stirred for 1 h at room temperature. 1.5 g of this mixture was slowly added into stirred nonaqueous part and evenly heated up to 60 °C. Final product was washed with acetone and ethanol, and finally dried at 100 °C.

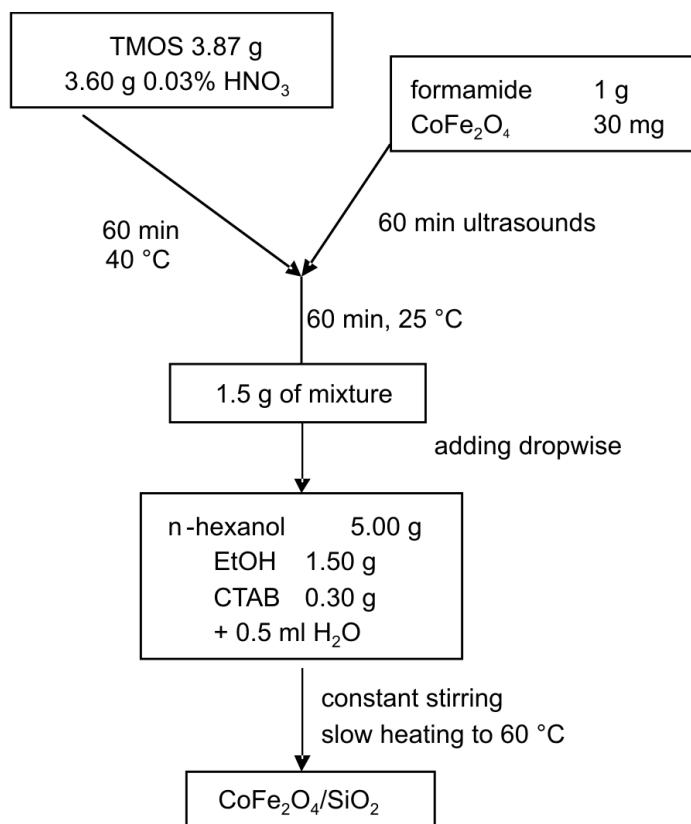


Fig. 1. The preparation scheme

Experimental techniques. Scanning electron microscopy (SEM) investigations were done on a SEM Philips XL 30 CP equipped with EDS (energy dispersive X-ray spectrometry), secondary and back-scattered electron detectors and a Robinson detector. Each powder sample was placed on the holder with an adhesive carbon slice and covered with a thin (<10 nm) Au/Pd layer. Microscale morphology was examined with a high-resolution transmission electron microscope HRTEM JEOL JEM 3010 and a conventional TEM Philips 80 kV. A copper grid coated with a perforated carbon support film was used to prepare samples for the TEM observation. The powdered sample was dispersed in ethanol and placed on the grid.

The powder X-ray diffraction (XRD) measurements were performed on the Seifert diffractometer using CuK_α radiation with a monochromator. The phase analysis was done using the PDIFF database.

Investigation of the magnetic behaviour of the final composite was performed with the PPMS 14T and PPMS 9 T devices (Quantum Design, San Diego). The temperature dependence of magnetization was recorded in the zero-field cooled (ZFC) and field-cooled (FC) regimes in an external magnetic field of 10 mT. The ac susceptibility measurements were done in strictly zero magnetic field conditions for which the amplitude of the ac field was set to 5 mT and the frequency was varied from 10 Hz to 10 kHz.

3. Results and discussion

3.1. Cobalt ferrite nanocrystals

Particles of cobalt ferrite nanocrystals had already been fully characterized earlier [10]. Briefly, the reported characteristics show the average diameter by TEM of 5 nm ($\sigma = 23\%$). Magnetization measured at 10 K is 50 emu/g and the coercive field at 10 K is 9 kOe. The TEM micrographs were made in order to confirm that the desired particle size and morphology had been achieved (Fig. 2).

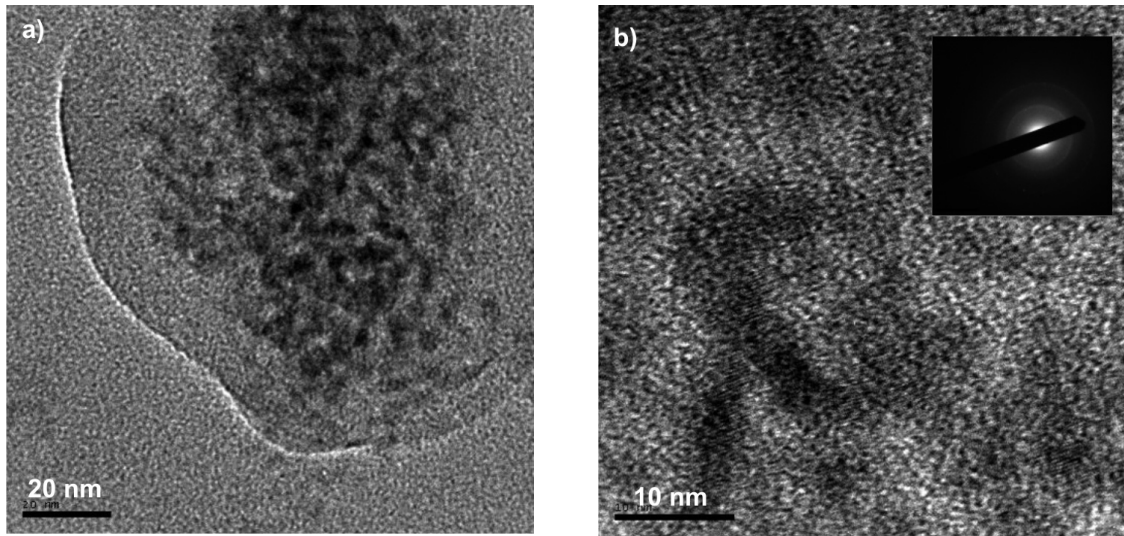


Fig. 2. TEM micrographs of CoFe_2O_4 nanocrystals: a) overview; b) details and electron diffraction pattern

3.2. $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ microspheres

The morphology of the final composite microspheres is presented in Fig. 3. The silica particles are of regular spherical shape, as required.

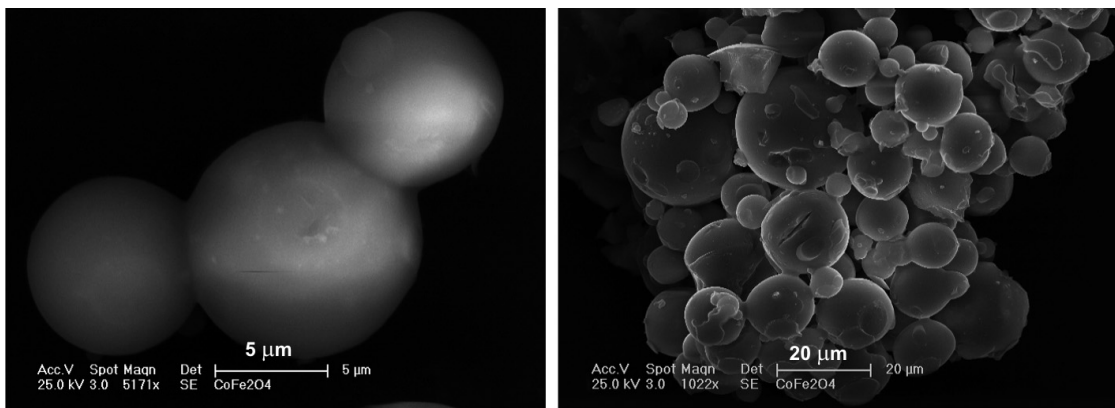


Fig. 3. SEM of the final $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ composite morphology at various magnifications

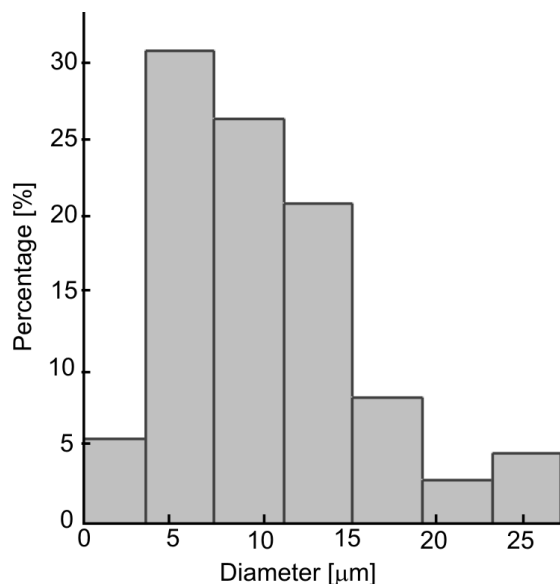


Fig. 4. Size distribution of CoFe₂O₄ doped silica spheres (calculated from SEM micrographs)

The size distribution calculated from the SEM measurements is shown in Fig. 4. The average diameter of the particles of the silica/ferrite composite was determined as $11.04 \pm 7.7 \mu\text{m}$. The size of the silica spheres is determined by the volume of the hydrophilic microdroplets of the microemulsion at ca. 60 °C, where silicon dioxide gel is formed from the pre-hydrolyzed TMOS.

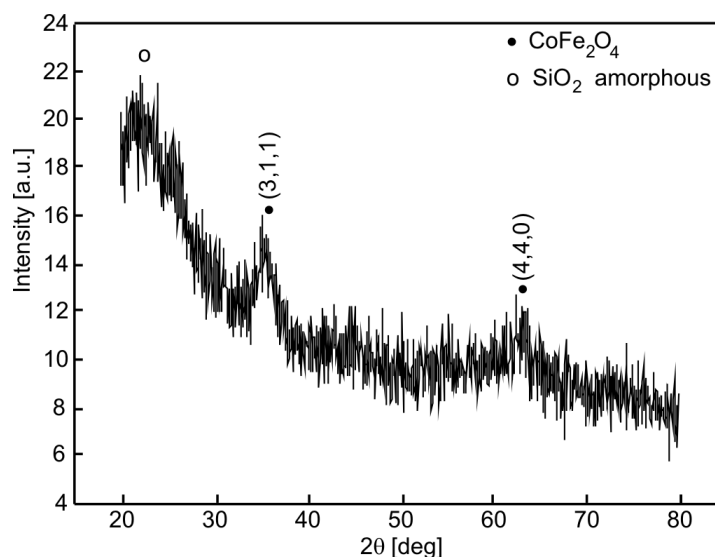


Fig. 5. Powder X-ray diffraction pattern of the final product. The two reflections above 30° are attributed to the Co ferrite nanoparticles, the broad maximum at around 25° corresponds to the contribution of the amorphous silica microspheres

The powder XRD measurements, shown in Fig. 5 proved the presence of the CoFe₂O₄ with the spinel structure, as demonstrated by the two strongest reflections in

the XRD pattern (PDF 22-1086), and amorphous silica, which contribute as a broad maximum at around 25° . The Co-ferrite related reflections are very broad and of low intensity, which points to a very small particle size.

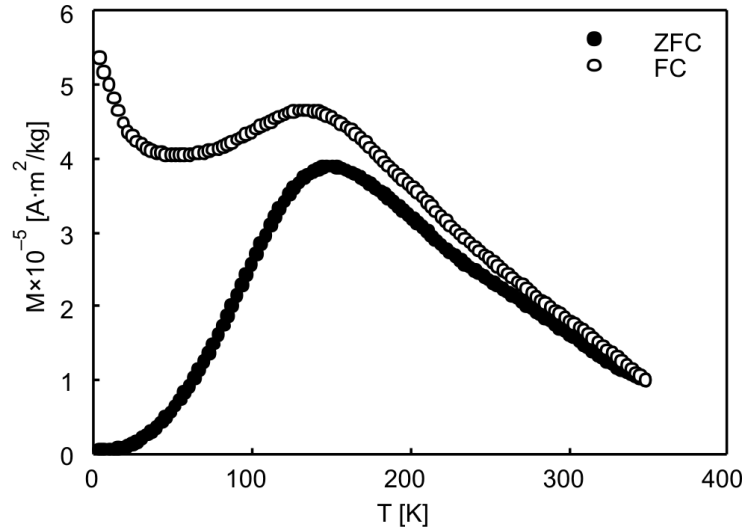


Fig. 6. Temperature dependence of the zero field cooled (ZFC) and field-cooled (FC) magnetization of SiO_2 microspheres doped with CoFe_2O_4 measured at 10 mT

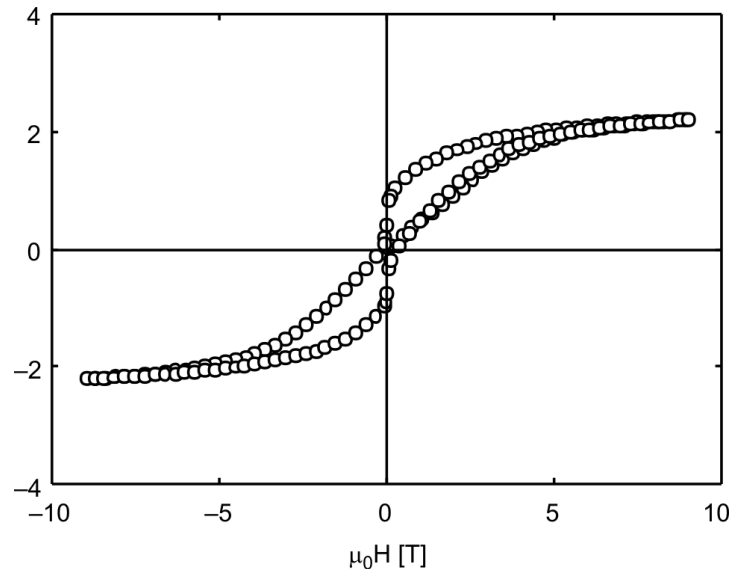


Fig. 7. Hysteresis loop of silica microspheres doped with CoFe_2O_4 recorded at 2 K

Comprehensive investigations by means of magnetization and ac susceptibility measurements were performed in the temperature range 2–350 K. The temperature dependence of the ZFC and FC magnetization is shown in Fig. 6. The ZFC curve exhibits a broad maximum at ca. 150 K, which can be attributed to the blocking temperature, T_B , of small Co-ferrite nanocrystals. The FC curve shows a similar maximum at a slightly lower temperature, and indicates an additional paramagnetic-like contribu-

tion at lower temperatures. The enhanced values on FC curve can be caused by the presence of particles below 2 nm, which do not interact with each other and follow the pure SPM trend. On the other hand, both curves correspond to slightly higher values than the proposed T_B level, which can be explained either by particle size distribution or rather by weak interparticle interactions between the majority particles of larger size, mediated by dipolar forces [13, 14].

The Co-ferrite particle diameter (R) of the majority fraction was estimated from the blocking temperature using the formula derived for a pure SPM system of non-interacting superspins: $V = 25k_B T_B / K_1$ and $R = (3V/4\pi)^{1/3}$, where V is the volume of one particle, K_1 is the first order anisotropy constant of the bulk Co-ferrite, k_B is the Boltzman constant and T_B is the blocking temperature. The estimated particle diameter was $R = (3.4 \pm 0.2)$ nm.

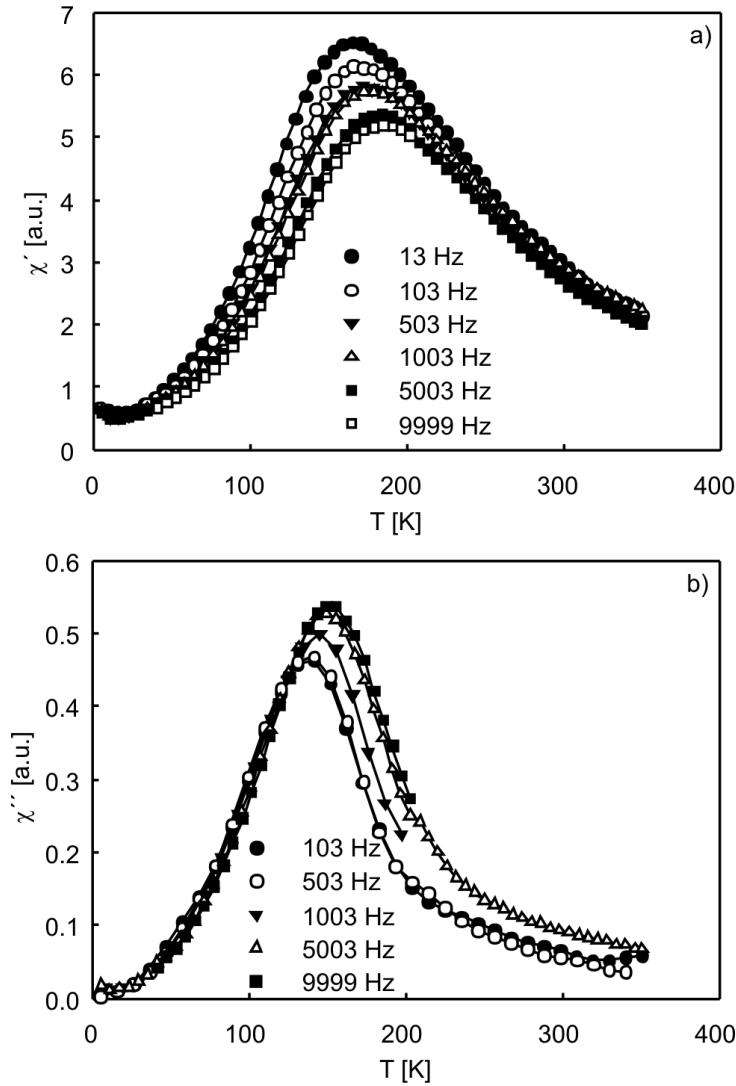


Fig. 8. Temperature dependence of the real χ' and imaginary χ'' parts of the ac susceptibility of silica microspheres doped with CoFe₂O₄

The presence of hysteresis and remanence below the TB level was investigated by taking hysteresis loop measurements at 2 K (Fig. 7). The tapering of the loop in a magnetic field close to zero can be explained by the presence of a small proportion of small particles, as already suggested in the discussion of the temperature dependence of the ZFC/FC magnetization, which does not cause any hysteresis. The saturated magnetization at 2 K reaches ca. $2 \cdot 10^{-3} \text{ A} \cdot \text{m}^2/\text{kg}$ calculated relative to the total mass of the composite).

The dynamic properties of the system were examined by taking ac susceptibility measurements, and they are shown in Fig. 8. The character of the real and imaginary part of the ac susceptibility reflects the expected SPM behaviour, demonstrated by the frequency-dependent maximum at T_B at the corresponding frequency (T_f).

A useful criterion for classifying the observed freezing process is the empirical parameter Φ , which represents the relative shift of the blocking temperature per the frequency decade: $\Phi = \Delta T_f / [T_f \Delta \log_{10}(f)]$, where ΔT_f is the difference between the blocking temperature measured in the $\Delta \log_{10} f$. We obtained the value $\Phi = 0.04$, which is slightly lower than the 0.1 value expected for a superparamagnetic (SPM) system. Smaller values of Φ are usually caused by the spin-glass-like behaviour of the nanoparticle surface, or are simply due to non-negligible interparticle interactions, which corroborate the interpretation of the magnetization measurements. The Arrhenius plot of the ac susceptibility data, namely $\ln(1/f)$ vs. $1/T_B$, revealed an almost linear dependence, however, the obtained values are unrealistic fit, probably due to the dipolar phenomena proposed above.

4. Conclusion

We reported an easy route for the preparation of silica microspheres doped with cobalt ferrite magnetic nanocrystals. The synthesis was based on the acid-catalyzed sol-gel process in microemulsion. The final product consists of microspheres with average diameter of 11 μm , and very small Co-ferrite nanocrystals, as proved by SEM, HR TEM and XRD analyses. We have further demonstrated a full magnetic characterization of the resulting powder, which revealed that the size of the Co-ferrite nanocrystals is about 3.4 nm and suggested SPM behaviour, disturbed weak interparticle interaction of dipolar origin. Embedded magnetic particles in silica microspheres show different behaviour than pure co-particles [12]. Thanks to the limited concentration of the ferrofluid inside the microemulsion, the magnetic properties seem to be weaker. The composite may be used in the case when magnetic crystals have to be protected by a chemically inert matrix (SiO_2), which can be further functionalized, and simultaneously when manipulation in the micro-scale is required.

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SSG or SFM state in CoFe_2O_4 nano-agglomerates fabricated by micro-emulsion method

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ABSTRACT

We report on magnetic properties of CoFe_2O_4 nano-agglomerates obtained by micro-emulsion technique under specific conditions. The samples form a unique morphology as observed by transmission electron microscopy and scanning electron microscopy investigations. Concerning magnetic properties, they exhibit a considerable coercivity of almost 1 T at 2 K, which continuously decreases up to the characteristic temperature, $T_g = 350$ K. The temperature dependence of the zero-field cooled (ZFC) and field cooled (FC) magnetization, respectively, is bifurcated at the T_g , and the temperature dependencies of the a.c. susceptibility exhibit a frequency-dependent maximum at $\sim T_g$. The observed behavior is discussed in terms of the super-spin-glass (SSG) and the super-ferromagnetic (SFM) regime considering the morphology of the nano-agglomerates.

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Various magnetic nanoparticles attracted much attention due to specific utilization in industrial, medical and environmental applications [1,2]. Nowadays, ferrites represent a significant group of nanoscale magnetic substances, namely due to convenient fabrication procedures yielding nanomaterials of required parameters. In our work, we present magnetic properties of Co-ferrite nanocrystals, condensed into spherical aggregates prepared by a progressive micro-emulsion method. The Co-ferrite nanoparticles were subsequently used as magnetically active cores in composites with an amorphous SiO_2 spheres in order to obtain a material where the magnetic carrier is isolated by a non-magnetic cover.

The CoFe_2O_4 nano-agglomerates were prepared by a micro-emulsion method as briefly described further. Aqueous solutions of 1.3×10^{-3} M $\text{Co}(\text{DS})_2$ (DS—dodecylsulfate), 1.3×10^{-3} M $\text{Fe}(\text{DS})_2$, and 2M methylamine, respectively, were mixed in the 1:1:1 ratio under vigorous stirring at 40 °C. The product was isolated by a subsequent precipitation from the colloid using ice-cold ethanol (50%) and centrifugation at 4500 RPM. In order to obtain the final sample, the isolate was dried at 60 °C for 12 h on air. More experimental details about the synthesis can be found in [3–6].

The sample was characterized by transmission and scanning electron microscopy (TEM, SEM), respectively, and powder X-ray diffraction (XRD).

The constitution of the sample investigated by TEM is shown in Fig. 1. The 3–5 nm Co-ferrite nanocrystals form nano-agglomerates of ~ 100 nm in diameter, as evident from the TEM images. Resolution of the TEM data prevented reliable analysis of the particle size-distribution; only the size distribution of the nano-agglomerates was performed using *ImageJ* 1.41o software. The data were fitted by a log-normal distribution yielding an average agglomerate diameter of (58 ± 25) nm ($\text{PDI} = 0.46$), which corresponds to the diameter of Co-ferrite agglomerates prepared by a very similar procedure, recently reported by Cannas et al. [6]. The morphology of the sample was also checked by SEM measurements, as presented in Fig. 2.

The XRD pattern of the Co-ferrite nanoparticles, shown in Fig. 3, revealed diffraction line broadening; the estimated particle size is about 50 nm, which point to the fact, that the coherently scattering domain roughly correspond to the size of the nano-agglomerates.

The key mechanism leading to agglomerate formation is not clear; we proposed three factors mechanisms explaining their formation. (i) van der Waals interactions acting during the evaporation of the solvent, (ii) dipolar interaction of magnetic origin, and (iii) remaining DS anion adsorbed on nanocrystals, whose amphiphilic properties help to form spherical agglomerates. The EDAX analysis confirmed presence of $\sim 1\%$ of sulfur, pointing to presence of the DS anion in the final product. A similar

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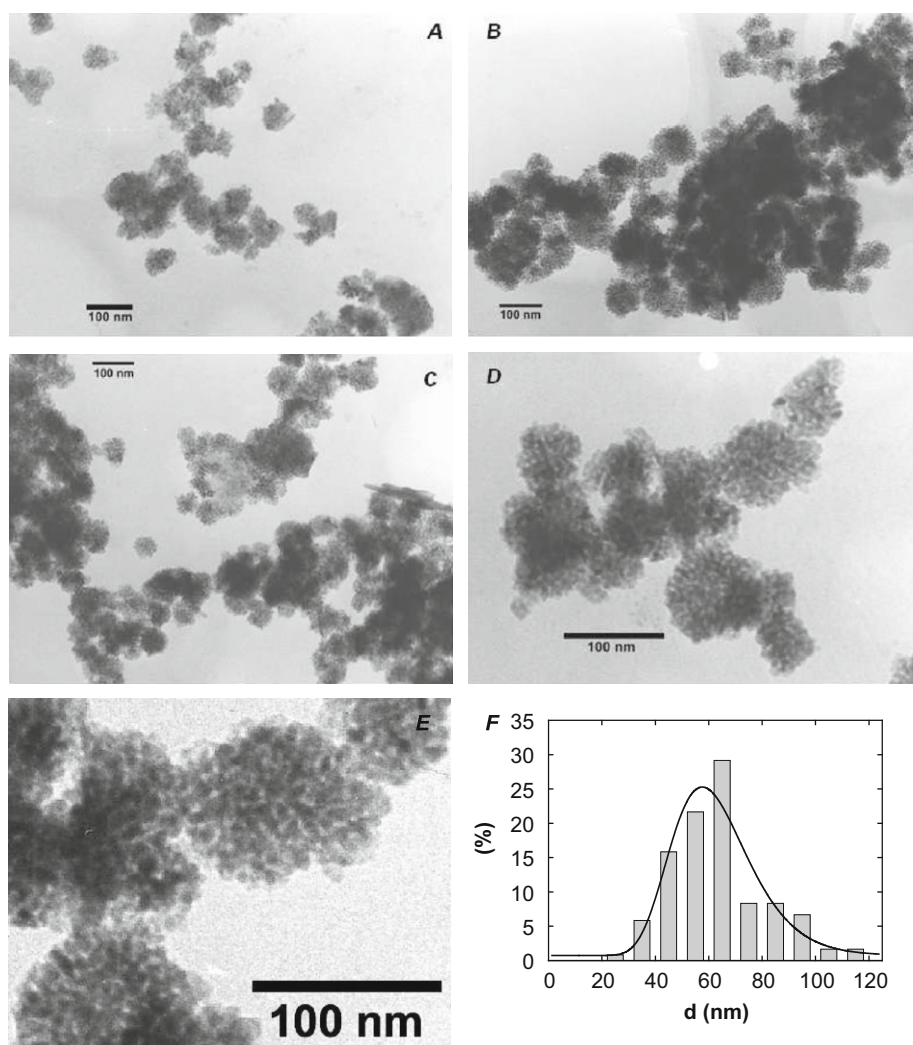


Fig. 1. Constitution of the CoFe_2O_4 sample demonstrated by the TEM images. The figures (A)–(D) represent various parts of the sample, the figure (E) shows a detail of a single agglomerate, and the figure (F) demonstrates the size distribution of the agglomerates together with the fit of a log-normal distribution.

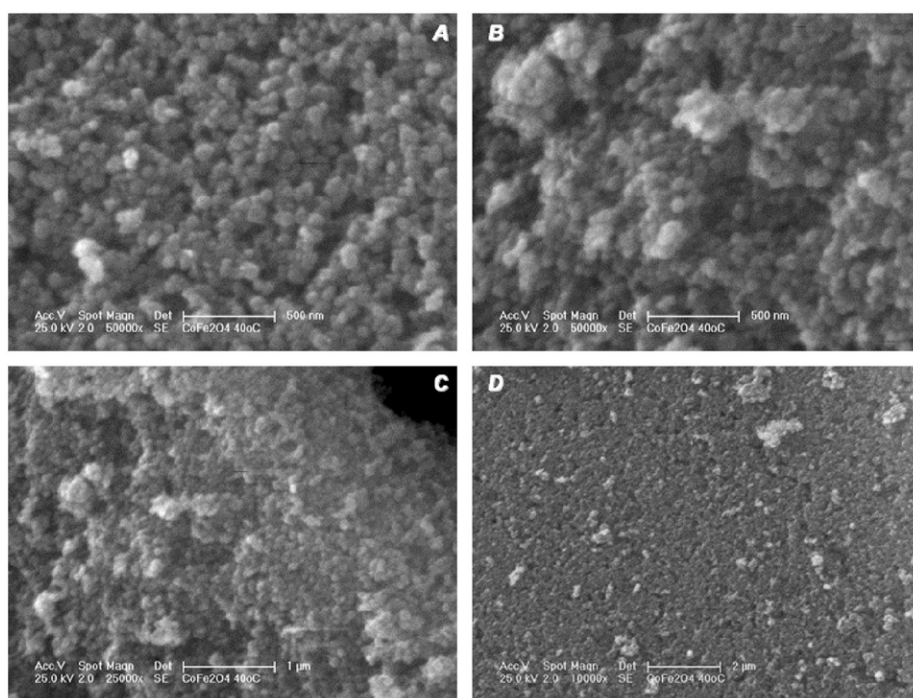


Fig. 2. Morphology of the agglomerates obtained by the SEM method. The scale corresponds to 500 nm in (A) and (B), 1 μm in (C), 2 μm in (D), respectively.

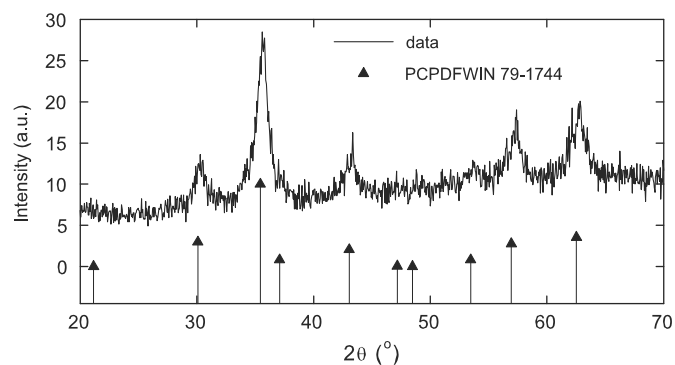


Fig. 3. Powder XRD pattern of the sample. The arrows mark Bragg position of the CoFe_2O_4 taken from the PDF database. The height of the lines corresponds to the reflection intensity presented in PDF.

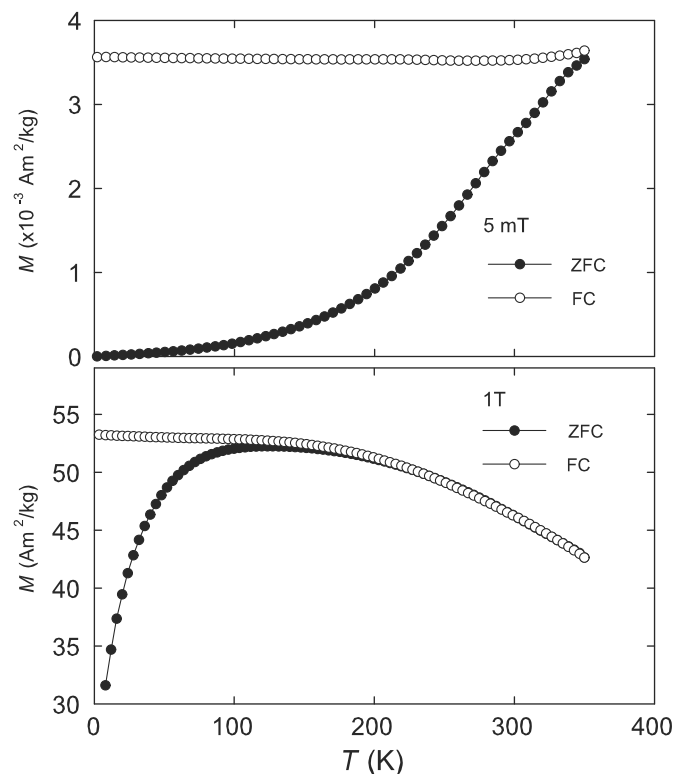


Fig. 4. Temperature dependence of the zero-field cooled (ZFC) and field-cooled (FC) magnetization measured in the external magnetic field of 5 mT and 1 T.

observation was recently presented by Held et al., who prepared maghemite nanocrystals in a presence of an amphiphilic co-peptide [7]. Therefore, the influence of DS adsorbed on the nanocrystals is probably the most important factor of the agglomerate formation.

Magnetic properties of the CoFe_2O_4 nanocrystals were investigated by detailed magnetization and frequency-dependent a.c. susceptibility measurements in the temperature range 2–350 K. The temperature dependencies of the zero-field cooled (ZFC) and field-cooled (FC) curves recorded at 5 mT and 1 T are shown in Fig. 4. The low-field ZFC and FC data furcate at 350 K (the highest temperature of the measurement), which indicate, that the value of the expected blocking (T_B) or glassy T_g temperature, respectively, is at least 350 K. The trend to saturation (or maximum formation) of the ZFC curve demonstrates, however, that the blocking or glassy temperature is not

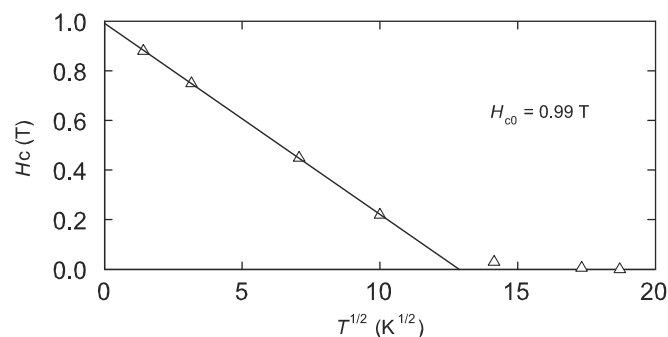
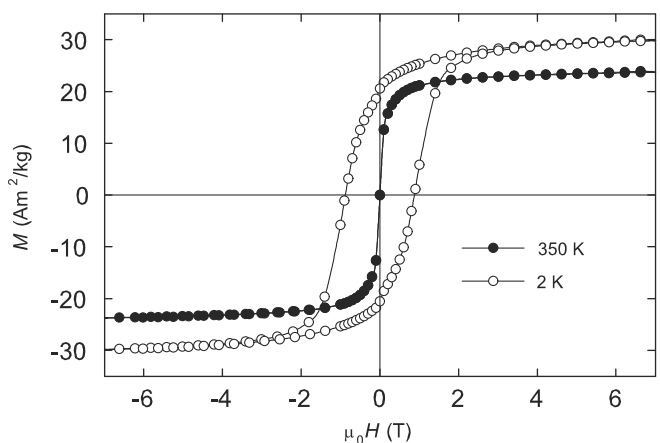


Fig. 5. Hysteresis loops recorded at 2 and 350 K. The lower plot shows the temperature dependence of the coercivity field, H_c together with the fit according to Eq. (1).

dramatically larger than the 350 K. With increasing the applied magnetic field, the furcation point shifts to 100 K as usually observed in strongly interacting SPM (superparamagnetic), SSG or SFM systems [8–10].

Magnetic properties were further inspected by measurements of hysteresis loops, as shown in Fig. 5. At 2 K, the material exhibits coercivity of almost 1 T. With increasing temperature, the coercivity decays and becomes zero at 350 K. This observation corroborates the fact, that the (T_B) or T_g is about 350 K. The temperature dependence of the coercivity is plotted in the second part of the Fig. 3. Surprisingly, at temperatures well below 350 K, the coercivity decays linearly with $T^{1/2}$ as observed in a system of non-interacting SPM particles: $H_c(T) = H_{c0}[1 - (T/T_B)^{1/2}]$, where H_{c0} is the extrapolated value of the coercivity at $T = 0$ K. From the fit to the linear part, we obtained value of H_{c0} as 0.99 T (in consistency with [6]), and the temperature, where the hypothetical coercivity contribution due to energy barrier in the purely blocked state should vanish as 166 K. The fact, that a finite value of H_c persists up to 350 K suggests, that additional interaction mechanism between the particles causes non-zero coercivity up to the T_g .

If we compare the value of the coercivity and the T_g to the data available for ~ 10 nm Co-ferrite particles embedded in a silica matrix [11], we observe, that our agglomerates show a half-coercivity at 2 K with a very similar characteristic temperature of about 350 K.

Convergence of the peak temperature, T_m on the real part of the a.c. susceptibility towards a finite value, T_g is demonstrated in Fig. 6 together with a double logarithmic plot: $(2\pi f)^{-1}$ vs. $T_m/(T_g - 1)$ (inset of Fig. 4). To explore the relaxation dynamics in the system, we made attempts to analyze the data by means of the critical dynamics: $\tau = \tau_0(T_m/T_g - 1)^{-z\nu}$, where T_g is the finite transition temperature, τ_0 is related to the relaxation time of the

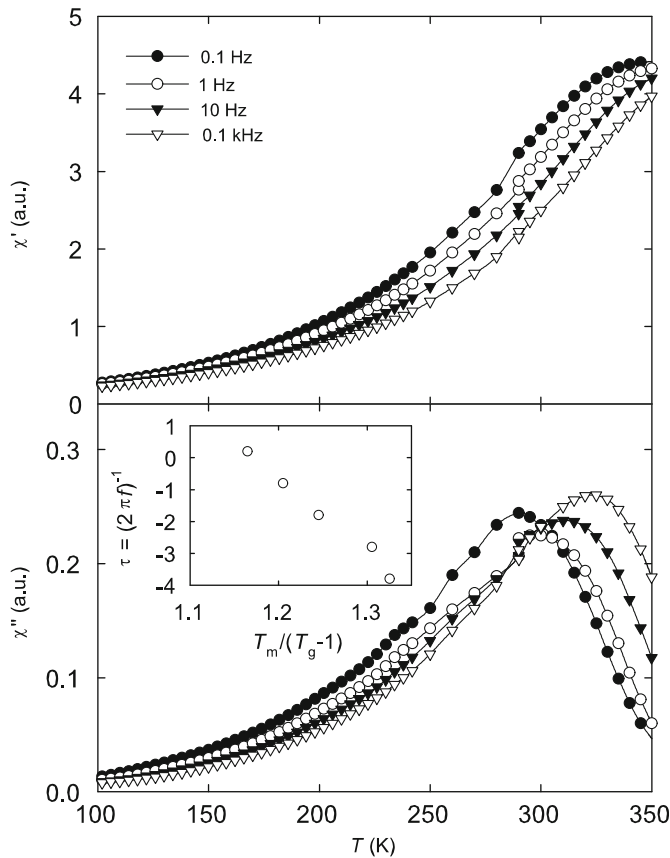


Fig. 6. Temperature dependence of the real and imaginary part of the a.c. susceptibility. The inset represents the linear behavior of the $(2\pi f)^{-1}$ vs. $T_m/(T_g-1)$ dependence with the $T_g = 250$ K.

individual particle magnetic moments, and $-zv$ is a critical exponent. In spite of sufficiently linear behavior of the $(2\pi f)^{-1}$ vs. $T_m/(T_g-1)$ dependence, the values obtained from the fit were rather unphysical. At this point, we cannot clearly distinguish, whether the dominant interaction between the superspins is of dipolar or exchange origin, respectively.

To inspect the presence of a SSG state, we performed the so-called memory effect experiment [12]; the temperature dependence of magnetization was recorded as ZFC in a low magnetic field. Subsequently, the samples were cooled to a temperature below the T_g ($T_{\text{wait}} = 50$ K in our case), and a difference between the two curves was calculated. In a SSG system, a dip is expected to appear on the differential curve at around the T_{wait} . In our case,

any anomaly of this kind was observed, which points to improbable formation of a SSG state.

Let's take into account constitution of our agglomerates. Within a single agglomerate, the particles are in the limit of close-packing and they are supposed to interact strongly. Considering recent work on SFM systems [10,13–15], an exchange interaction between the 3–5 nm particle superspins is highly probable. Because the values of the T_g does not scale well to the size of nanocrystals and/or agglomerates, we attribute the observed phenomena to manifestation of the SFM state within a single nano-agglomerate, accompanied with considerable interaction of preferably dipolar origin between the agglomerates themselves.

In conclusion, we have prepared nanocrystals of CoFe_2O_4 in a form of 60 nm large nano-agglomerates, and investigated their magnetic properties. We observed a characteristic temperature, $T_g \sim 350$ K below which the ZFC and FC curves furcate, and coercivity develops. Analysis of the relaxation dynamics did not reveal a straightforward proof of SSG phenomena in the material, which was corroborated by the lack of ZFC memory effect. We suggest, that a SFM state is established in our materials, however, its detailed mechanism with relation to the two scales of the magnetic objects in our samples need further studies.

Acknowledgments

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Relaxation phenomena in ensembles of CoFe_2O_4 nanoparticles

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ABSTRACT

Collective magnetic behavior of CoFe_2O_4 nanoparticles with diameters of 76, 16, 15 and 8 nm, respectively, prepared by different chemical methods has been investigated. Particle composition, size and structure have been characterized by inductive coupled plasma (ICP), transmission electron microscopy (TEM) and powder X-ray diffraction (PXRD). Basic magnetic properties have been determined from the temperature dependence of magnetization and magnetization isotherms measurements. The three samples exhibit characteristic of a superparamagnetic system with the presence of strong interparticle interactions. Magnetic relaxation phenomena have been examined via frequency-dependent ac susceptibility measurements and aging and memory effect experiments. For the particles coated with oleic acid, it has been demonstrated that the sample reveals all attributes of a super-spin glass (SSG) system with strong interparticle interactions.

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1. Introduction

It is well known that non-interacting single domain particles exhibit superparamagnetic properties. Susceptibility of such system follows the Curie law and its magnetization curve can be described by the Langevin function. The critical size of the single domain nanoparticle is determined by microstructural parameters of the material (atomic composition and crystallographic structure) and reaches the size of 10^{-8} – 10^{-9} m. The characteristic parameters that define SPM are the blocking temperature T_B , particle magnetization (the so-called superspin) μ and magnetocrystalline anisotropy, E_A . T_B is the blocking temperature of the superspins, when the particles anisotropy energy E_A is overcome by the energy of thermal fluctuations and particles get into the blocked state, in which the stable magnetization cannot be established. The magnetic state of nanoparticles in the blocked state (below T_B) is characterized by non-zero coercivity, H_C [1]. Pure superparamagnetism is, however, observed only in extremely diluted samples with low density, like ferrofluids or in nanoparticles diluted in an inert matrix [2–6]. In real concentrated systems, in which the particles are close to each other, the interparticle interactions are noticeable and significantly affect the macroscopic magnetic properties [2,6]. Depending on the strength of these interactions, the so-called weakly and strongly interacting systems are defined. An example of a strongly interacting system is a super-spin glass (SSG) or a super-spin-glass-like (SSG-like) arrangement [6]. It has been

demonstrated by Dormann et al. [2] that with increasing concentration of particles, the strength of the interactions is also increasing and the magnetic behavior of the nanoparticles may evolve from superparamagnetic to SSG or SSG-like [2,7].

SSG behavior is characterized by a creation of stable clusters of nanoparticles under the glassy temperature, T_g whereas in a SSG-like system, the clusters are created temporarily and the nanoparticles fluctuate between them. The relaxation in such a strongly interacting systems is described by the critical spin dynamic model; the relaxation time τ_0 of a particle is much lower than that of an ideal superparamagnet which follows Arrhenius–Néel law [8,9]. Above the T_g , the relaxation time τ obeys the relation [10] (1)

$$\tau_m = \tau_0 \left(\frac{T_m}{T_g} - 1 \right)^{zv}, \quad (1)$$

where T_m is the temperature maximum (e.g. maximum of a temperature dependence of the ac susceptibility curve), T_g is the glassy temperature and zv is the dynamic critical exponent [11]. The values usually found in the literature for the SSG systems are $zv = 5$ – 11 [5,7,8,12], the τ_0 is ranging [5] from 10^{-5} up to 10^{-11} s.

Typical experiments to determine the value of the τ are the frequency-dependent ac susceptibility measurements in small dc external magnetic fields. Because relaxation times of nanoparticles in the SSG and the SSG-like systems are of the same order, it is impossible to distinguish between them by performing only this kind of experiment. Further measurements are required to evaluate the formation of stable clusters in SSG systems via the measurements of the zero-field-cooled (ZFC) magnetization below the T_g at a finite temperature as a function of the waiting

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time: the so called ‘memory effect’. Also the aging and rejuvenation, typical for such systems, have to be examined.

The goal of the work is the investigation of the collective phenomena in CoFe_2O_4 nanoparticles with different size, prepared by two different methods, 1. by coprecipitation in aqueous media and 2. by decomposition of metal-organic precursors in organic media. These nanoparticles could be used in the same way as the popular iron oxide particles—as magnetic carriers for biological and industrial applications [13–18], but their properties are much better for those applications requiring high coercivity, H_c and saturated magnetization, M_s . Depending on the synthesis method, nanoparticles present different sizes around the multi/single domain limit and surface characteristics.

2. Experimental section

2.1. Synthesis of CoFe_2O_4 nanoparticles prepared by coprecipitation in aqueous media (CFCx samples)

The coprecipitation reactions were performed under different conditions using various metal salt precursors and concentrations. Samples were labeled as CFCx as the shortcut of the Cobalt Ferrite coprecipitation no. x.

In case of CFC1 sample, the mixture of 85 mM $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 42.5 mM $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ was dissolved in 40 ml of water containing 15 mM KNO_3 acting as a mild oxidant. The preheated solution was dropped into 400 ml of 0.5 M NaOH and heated up to 90 °C under the continuous purging of nitrogen gas to prevent the atmospheric oxidation of the Fe salt.

The CFC2 sample was synthesized using two independently prepared solutions: 2 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 5 ml of H_2O containing 0.3 ml of 37% HCl and 0.5 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in 40 ml of H_2O . Precursors were preheated to 50 °C and added into 200 ml of boiling 1 M NaOH.

The CFC3 sample was prepared following the preparation procedure of the CFC2 sample at double dilution of solutions: 2 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in 9 ml of H_2O containing 1 ml of 37% HCl and 0.5 M $\text{FeCl}_3 \cdot 9\text{H}_2\text{O}$ dissolved in 80 ml of H_2O . Precursors were preheated to 50 °C and added into 400 ml of boiling 1 M NaOH.

In the preparation of all samples, the black precipitate was washed with water for five times and magnetically separated afterwards. The liquid fraction was stored in de-ionized water and the powder was obtained by drying the sample in the nitrogen flow. To stabilize the liquid fraction of nanoparticles and prevent them from aggregating, the colloid containing particles was diluted in 100 ml of water (pH=2) and 4 g of citric acid were added. Solution was heated up to 70 °C, final product was washed with water for five times and magnetically separated.

2.2. CoFe_2O_4 nanoparticles prepared by decomposition of organometallic precursor in organic media (CFD sample)

A mixture of 4.6 g of $\text{Fe}(\text{acac})_3$, 2.35 g of $\text{Co}(\text{acac})_3$, 18.66 g of oleic acid and 22.3 g of dodecanediol were added to 200 ml of benzyl-ether. After 3 min of nitrogen gas purging, solution was heated up and then kept at 200 °C for 2 h, the N_2 flow was cut afterwards and solution was boiling at 300 °C for another 3 h. Particles were washed with ethanol, magnetically separated and liquid fraction was stored in hexane. The powder fraction was prepared by drying the sample under the flow of nitrogen gas.

2.3. Characterization of the samples

The samples were characterized by several methods, such as inductively coupled plasma (ICP), powder X-ray diffraction (PXRD)

and the transmission electron microscopy (TEM). Using the ICP method, the ratio of heavy elements presented in the sample was obtained.

The PXRD was used for determination of the material phase composition and the size of the crystallites in the collection of nanoparticles. The X-ray diffraction patterns were recorded in parafocusing Bragg–Brentano geometry (Bruker XRD diffractometer) using Cu K_α radiation at room temperature. The intensity vs. 2θ scans were taken with the step of 0.05° within 20°–140° range with the 10 s duration per point.

The diffraction patterns data have been evaluated by the advanced Rietveld fitting procedure implemented in the FullProf programme [19]; the precious values of lattice parameter and size of the crystallites have been determined. Particles were considered to be spherical, the shape anisotropy and the anisotropic strain were not involved in the fitting procedure.

TEM images of CoFe_2O_4 nanoparticles were captured using a 200 keV JEOL-2000 FXII microscope. The samples were prepared by dropping the diluted solution of nanoparticles on the carbon coated copper grid and the solvent was allowed to evaporate at room temperature. The ImageJ software was used for statistical treatment of at least 200 particles, and the data were fitted by a log-normal distribution yielding the mean particle diameter and the size distribution.

All magnetic measurements were performed using MPMS7 device (Quantum Design) up to magnetic field of 7 T in the temperature range from 2 to 400 K and with PPM9 device up to 450 K. The zero-field-cooled (ZFC) and field-cooled (FC) curves were measured in small external magnetic fields (20 and 50 mT). The temperature dependence of the ac susceptibility (with the alternating field amplitude of 3 mT) was measured in non-zero magnetic field (1–100 mT) in frequency range of 0.1–50 Hz.

2.4. Aging, rejuvenation and memory

The aging, rejuvenation and memory effects were studied using the two following protocols. At first, the so called thermoremanent (TRM) measurement protocol was followed. The FC magnetization was measured in field of 10 mT down to 10 K with the intermittent 1 h stops at 150, 80 and 20 K, respectively. At each stop, the particles relaxed for the waiting time τ_w —system has been aging. After resuming cooling, system has been rejuvenated. Consequently, the FC curve was recorded upon heating the sample up to 300 K [20]. The theoretical explanation of expected behavior for both the interacting and non-interacting systems of nanoparticles during cooling and reheating steps is following: when the external magnetic field is switched off, the magnetization decay should be observed both in SPM or weakly/strongly interacting systems [21]. During the re-heating, the temperature dependence of magnetization should clearly manifest that the system keeps the memory imprinted in the previous FC process—the ‘steps’ on the reheated FC curve should correspond with the decays of magnetization at the waiting temperatures; as was demonstrated by Sun et al. [20]. However, this memory effect is qualitatively same both for the SPM and SSG systems, as was declared by Sasaki et al. [21] and it does not itself provide information about the nature of interaction in the system.

In the genuine ZFC memory effect protocol, the classical ZFC curve has been measured in external magnetic field of 10 mT, then the sample was cooled down again with the 6 h stop at 80 K and the ZFC magnetization was measured again, the second ZFC curve was subtracted from the first one. In the ideal case of the non-interacting collection of particles, the ZFC magnetization is independent on the waiting time, τ_w ; whereas in SSG systems, the characteristic relaxation of the particle spins, which depends on

τ_w , is manifested by the cusp on the subtracted curve at the waiting temperature [21].

However, it has also been demonstrated that in the real SPM systems, the small τ_w dependence of ZFC magnetization in comparison with the TRM magnetization usually appears; whereas in SSG, the strong τ_w dependence is observed both in the TRM and ZFC magnetization [21]. Additionally in the SSG-like systems, the ZFC magnetization is independent on the τ_w in the large time scale and the mean value of the ZFC magnetization at a selected temperature is constant in the typical time scale of the measurement [22]. Thus it could be claimed that the memory effect obtained in genuine ZFC protocol is significant only for the SSG systems [21].

3. Results and discussion

3.1. Characterization

The TEM images of nanoparticles together with the particle size distribution are depicted in Fig. 1. Comparing the images of individual samples, it is obvious that the particles prepared by the coprecipitation exhibit irregularity of shapes and higher distribution of particle size whereas the particles prepared by the decomposition are more uniform both in the size and the shape.

The TEM images of the CFC1 sample demonstrate that the size of the most particles does not obey the single domain limit; the mean value of the particle diameter determined from the log-normal distribution is 76 ± 21 nm with the significant size distribution ranging from 30 to 160 nm. The samples labeled as CFC2 and CFC3 exhibit both the lower size distribution and the mean particle diameter: 16 ± 5 nm and 15 ± 2 nm for the CFC2 and CFC3 sample, respectively. The diameter of nanoparticles in the CFD sample ranges from 5 to 12 nm with the mean particle diameter 8 ± 2 nm.

The ICP method provided the ratio of heavy elements as present in the sample. Considering the samples were composed of pure CoFe_2O_4 , the Fe:Co ratio should be equal to 2:1. The resulting attendance of elements in CFC1 and CFC2 samples is 33 of Co and 66% of Fe and 32% of Co and 64% Fe for the CFC3 sample suggesting the samples contain pure CoFe_2O_4 . Also the CFD sample is stoichiometric.

The PXRD patterns of all samples reveal that all peaks positions correspond to those of the spinel structure of CoFe_2O_4 (space group $\text{Fd-}3\text{m}$). PXRD patterns of individual samples together with the refined structure are presented in Fig. 2, the lattice parameters a and particle diameters d_{XRD} are summarized in Table 1. The refined mean particle diameters are 42, 12, 13 and 5 nm for the CFC1, CFC2, CFC3 and CFD samples, respectively. Comparison of the particle diameters obtained by PXRD, d_{XRD} and TEM, d_{TEM} suggests the particles are single crystalline, except the CFC1 sample. The discrepancy in the values of d_{XRD} and d_{TEM} is following: the whole particle could be viewed as the crystalline core encapsulated in amorphous shell, which is expected artefact arising from the method of preparation. Thus the diameter of the particle obtained from the TEM is higher than that refined using PXRD, which is sensitive only to the crystalline part. The huge discrepancy in d_{TEM} and d_{XRD} in case of CFC1 sample signalizes either the poor crystallinity of particles or point at their polycrystalline structure. In both cases, this sample is not suitable for further analysis of interactions in the systems of monodomain nanoparticles and is not involved in further investigation.

3.2. Magnetization studies

The ZFC-FC curves of the CFC2, CFC3 and CFD samples (Fig. 3) exhibit the blocking feature characteristic for a SPM system. The significant maximum at all ZFC curves, labeled as T_{MAX} , does not coincide with the bifurcation point of the ZFC-FC curves, T_{DIFF} , which

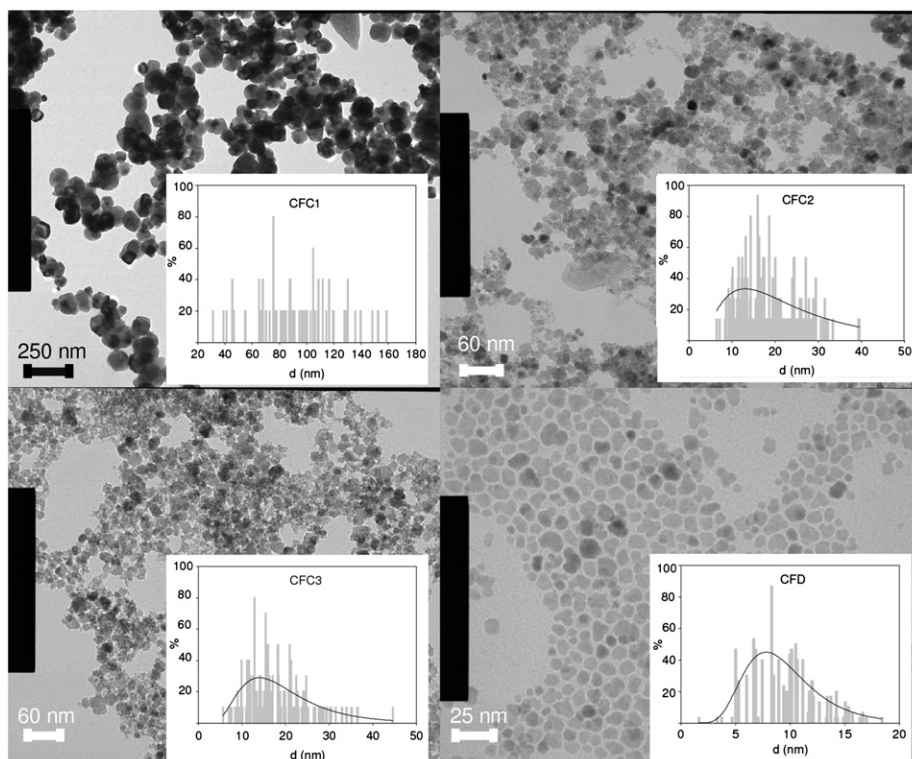


Fig. 1. TEM images together with the distribution of particle diameters.

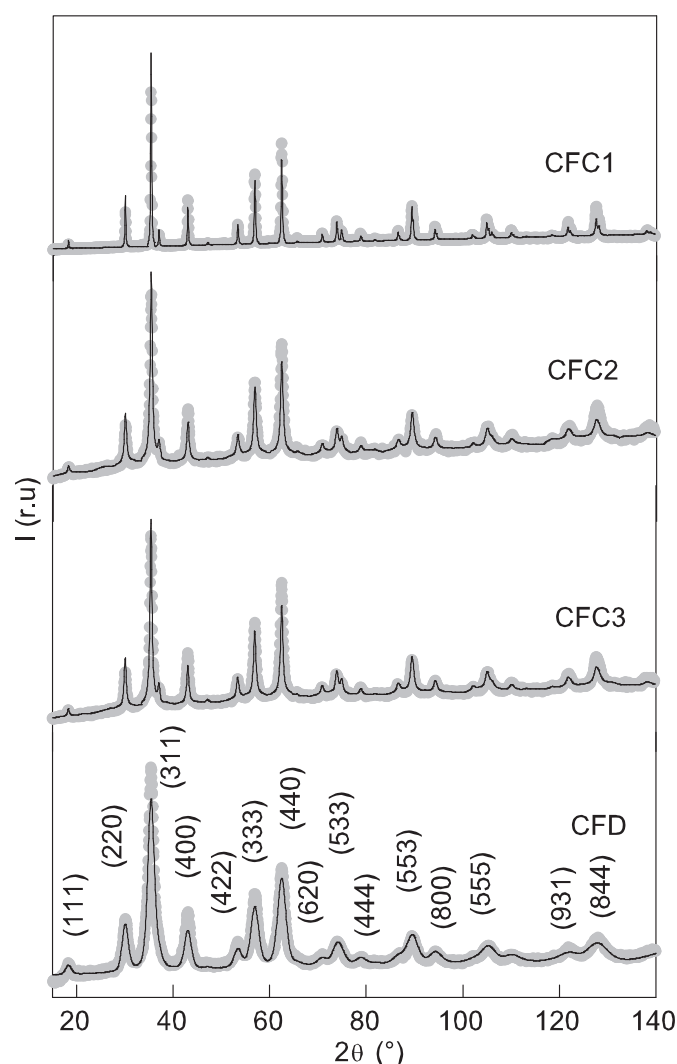


Fig. 2. XRD patterns (gray) and results of the Rietveld refinement (black line) for all samples.

Table 1

Basic properties of CoFe_2O_4 nanoparticles. d_{XRD} and d_{TEM} are the particle diameters obtained from the PXRD and TEM measurements, respectively, a is the value of lattice parameter.

Sample	Method	d_{XRD} (nm)	d_{TEM} (nm)	a (Å)
CFC1	Coprecipitation	42 ± 5	76 ± 21	8.41 (1)
CFC2	Coprecipitation	12 ± 1	16 ± 5	8.41 (3)
CFC3	Coprecipitation	13 ± 1	15 ± 2	8.41 (1)
CFD2	Decomposition	5 ± 0.4	8 ± 2	8.36 (5)

points at the particle size distribution in the samples, as is consistent with the TEM. The broad saturation at the low-temperature part of the FC curves is a consequence of the inter-particle interactions probably of dipolar origin.

As was claimed in Introduction, the strength of the inter-particle interactions determines the nature of the system. Even if the strength of the inter-particle interaction in our samples is not known exactly, the interactions are expected to be strong because of the direct contact between magnetic nanoparticles, even within the clusters of particles. If the samples are assumed to exhibit collective phenomena (such as in the SSG), the T_{MAX} and

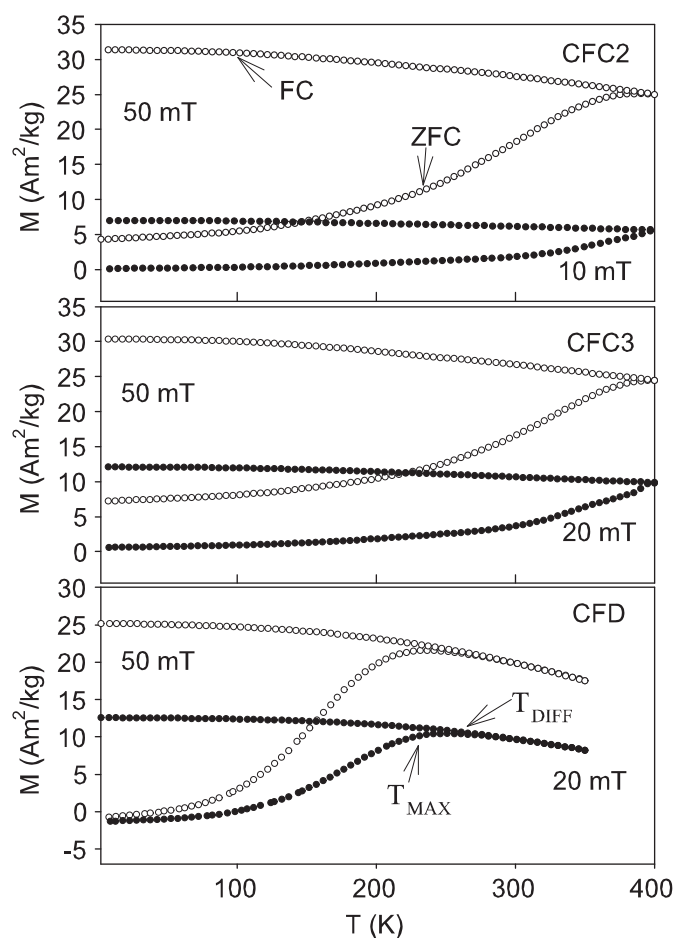


Fig. 3. The temperature dependence of the ZFC-FC magnetization of the CFC2, CFC3 and CFD samples, respectively, measured in small magnetic fields.

Table 2

Characteristic values determined from various magnetic measurements. T_{MAX} is the temperature of the maximum at ZFC curve, T_{DIFF} is the bifurcation point of ZFC-FC curves. H_c^{2K} is the coercivity value of isotherms measured at 2 K, M_s^{300K} is the saturated magnetization at 300 K.

Sample	T_{MAX} (K)	T_{DIFF} (K)	$\mu_0 H_c^{2K}$ (T)	M_s^{300K} (Am²/kg)
CFC2	390 ± 3	> 400	1.0 (2)	91 (2)
CFC3	390 ± 3	> 400	1.0 (2)	97 (2)
CFD2	390 ± 3	390 ± 5	0.8 (2)	65 (2)

T_{DIFF} should be affirmed as the freezing temperatures, T_f , of the mean fraction and fraction of largest nanoparticles, respectively. In our case, we will use the term blocking until it is clear, that we are dealing with strongly interacting systems. The T_{MAX} of our systems of nanoparticles varies from 236 to 390 K for the CFD and CFC2(3) sample, respectively. All values are summarized in Table 2.

Magnetization isotherms of CFD, CFC2(3) samples were measured at 2 K, 150 K and 300 K in the magnetic field varying up to 7 T in both polarities (Fig. 4). The hysteresis was observed for isotherms measured under the freezing temperature in each sample, as expected. The coercivity, H_c , exhibits symmetric values for both polarities of the applied field ($\mu_0 H$) of almost 1 T for samples made by coprecipitation and 0.8 T for samples made by decomposition, respectively. Also the saturated magnetization, M_s , is higher for the CFC2(3) samples than for the CFD sample; the

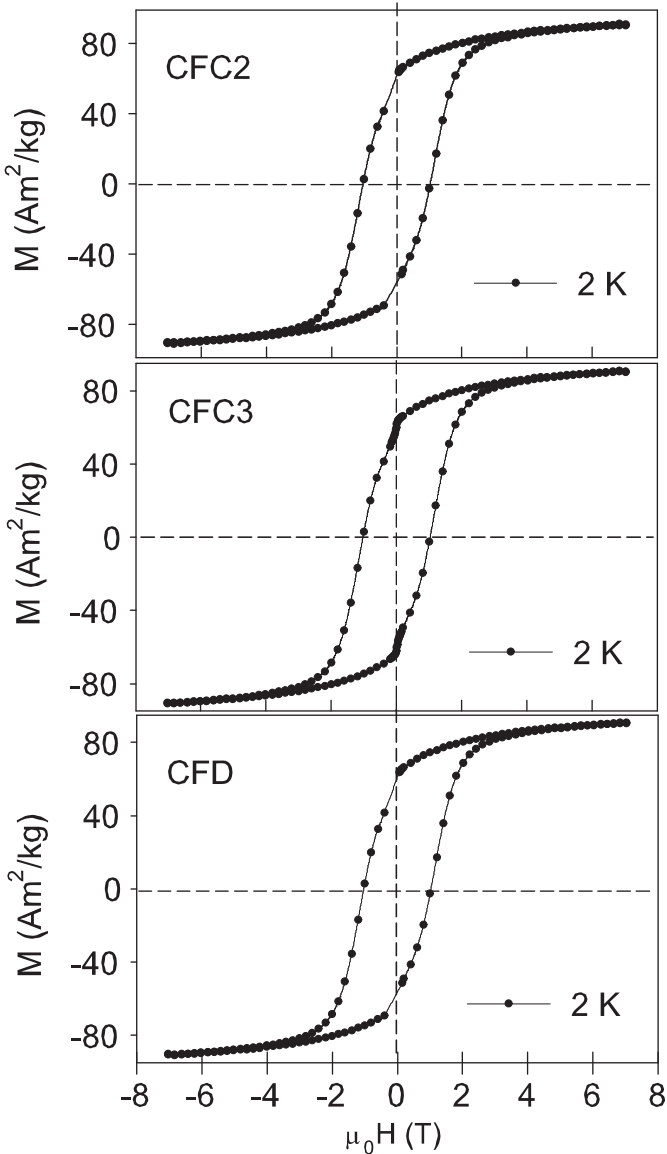


Fig. 4. Magnetization curves of the CFC2, CFC3 and CFD samples measured at 2 K.

Table 3
Results determined from the fit of the weighted sum of the Langevin functions to the un-hysteretic magnetization isotherms in Langevin scaling. The μ_0 is the median of the particle magnetic moments distribution, σ is the log-normal distribution width and the μ_m is the average magnetic moment related with the μ_0 by relation $\mu_m = \mu_0 \exp -\sigma/2$.

Sample	$\mu_0 \times 10^3 (\mu_B)$	σ	$\mu_m \times 10^3 (\mu_B)$
CFC2	8.2	2.1	2.8
CFC3	7.6	2.23	2.5
CFD2	1.4	1.29	0.7

values obtained at room temperature are summarized in Table 2. The un-hysteretic curves measured at 300 K (CFD sample) and 450 K (CFCx samples) were fitted by the weighted sum of Langevin functions with the log-normal distribution of magnetic moments [6,23] and the average magnetic moment per particle, μ_m , have been determined. The parameters obtained from the fitting procedure are summarized in Table 3, the example for the CFD sample is given in Fig. 5.

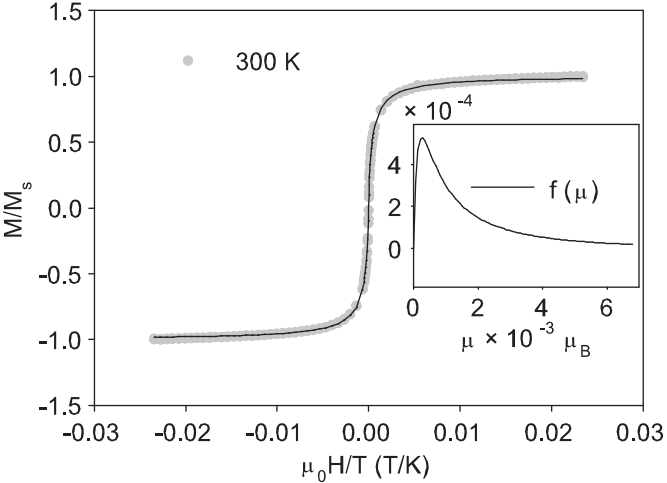


Fig. 5. Magnetization isotherm of the CFD sample in universal Langevin scaling, measured at 300 K, together with the line representing the fit of the weighted sum of the Langevin functions (black line). The inset shows resulting distribution of magnetic moments.

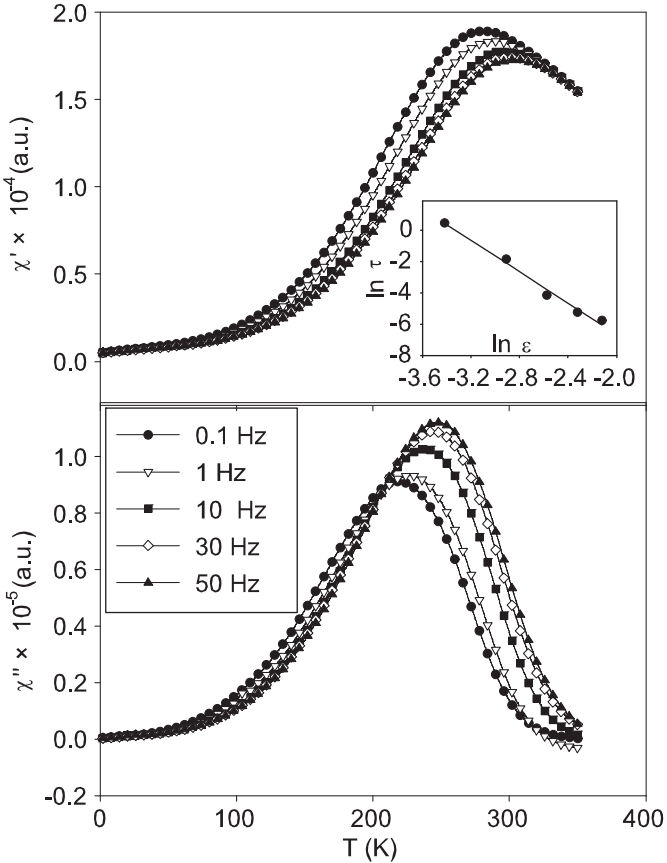


Fig. 6. χ' and χ'' vs. T for the CFD sample in field of 20 mT, $\tau = (2\pi f)^{-1}$ vs. $T_m/T_g - 1$ dependence in the inset.

3.3. Dynamic properties (ac susceptibility)

As was discussed previously, the similar character of the low-temperature part of the FC curve (Fig. 3) of samples made both by coprecipitation and decomposition suggests the presence of strong inter-particle interactions; thus the relaxation phenomena of the CFD sample has been examined via measurements of the

real (χ') and imaginary (χ'') parts of the ac susceptibility in non-zero external magnetic field (Fig. 6). The temperature dependence of χ' exhibits characteristic maximum T_m , which shifts to higher temperatures with increasing frequency, that is considered as a consequence of the super-spin relaxation of SSG nature (dipolar inter-particle interactions). In the case of strongly interacting systems, interaction could not be mediated only via dipolar but also via exchange interactions—it is the example of so-called superferromagnetic (SFM) system. It is not possible to differentiate both systems experimentally [24], but interactions in the systems of coated particles (as in case of CFD sample) should be mainly of dipolar origin [25]. The linear dependence of $\ln \tau$ vs $\ln \varepsilon$ (where ε is equal to $T_m/T_g - 1$) follows the law of critical spin dynamics (1). Resulting values derived from this equation are $T_g = 275$ K, $zv = 5$ and $\tau_0 = 5.6 \times 10^{-8}$ s; the critical exponent zv and relaxation time τ_0 are similar to those typical for the SSG (or SSG-like) systems. These parameters do not unambiguously prove the collective freezing of particle spins, thus further studies of the aging, rejuvenation and memory effects are required. 'It is not possible to examine how the system behaves dynamically in case of CFCx samples, because the anomalies at the ac susceptibility data are above the temperature limit. Despite this, the saturation at the low temperature part of the FC curve still signalizes presence of strong interaction within the system'.

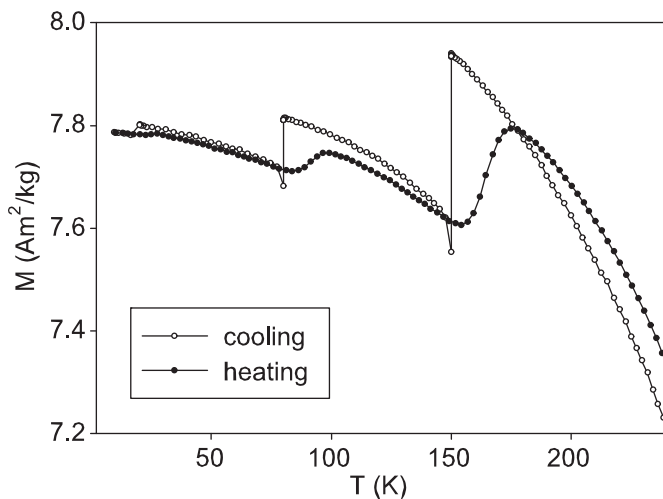


Fig. 7. The thermoremanent magnetization of the CFD sample with the further reheating curve.

3.4. Aging, rejuvenation and memory effects

To confirm collective freezing of particles typical for SSG systems, the memory effect phenomena have been inspected in case of the CFD sample. Fig. 7 demonstrates the aging and rejuvenation in thermoremanent magnetization and the memory effect in further reheating, which qualitatively corresponds to those typical both for the SPM and SSG systems, as was reported by Sasaki et al. [21]. The reason why the cooling and reheating curves do not match each other in the 'flattened' parts is that the cooling and reheating rates were different, 6 K/min and 1 K/min, respectively.

The experiment based on genuine ZFC protocol lead to the appearance of the peak at waiting temperature (80 K) far below freezing temperature, T_f , which is characteristic only for the SSG systems [6,21] (Fig. 8). This result together with the previous measurements of the ac susceptibility finally confirmed collective freezing of strongly interacting 'collection' of particles and hence the CFD sample could be classified as the super-spin glass.

4. Conclusion

We have prepared CoFe_2O_4 nanoparticles by different methods; coprecipitation in aqueous media and decomposition in organic media, to obtain different sizes and surface characteristics of particles. The phase composition, shape and size of the particles have been determined by complementary techniques such as ICP, TEM and XRD. It has been shown that the largest particles (sample CFC1) with the mean size of 76 nm (from TEM), are polycrystalline and do not obey the requirements for a SPM systems; whereas the rest of the particles appears to be single-crystals with diameters ranging from 8 to 16 nm. The temperature dependencies of magnetization exhibit a maximum characteristic for SPM systems and also signalize the presence of strong interparticle interactions (typical for the 'collection' of nanoparticles in powder form). The strength and the nature of the interparticle interactions have been examined via advanced studies of dynamic properties (ac susceptibility in non-zero magnetic field) and memory effects, respectively, for the CFD sample in which the interactions are expected to be minimum due to the oleic acid coating. The dynamic properties in CFD sample are in agreement with those typical for SSG or SSG-like systems. The memory effect observed in the genuine ZFC memory experiment finally confirmed that the strongly-interacting 'collection' of particles in the sample made by decomposition obey the super-spin glass behavior.

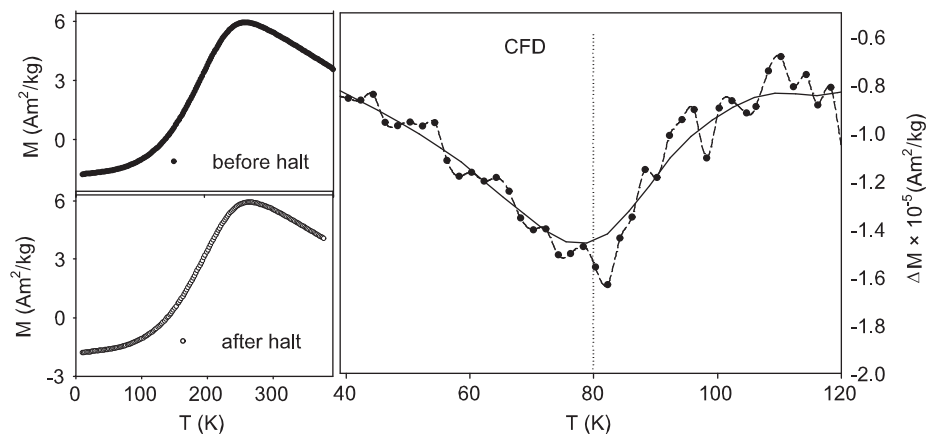


Fig. 8. Left—the ZFC curves with and without halt at the waiting temperature. Right—peak significant for ZFC magnetization memory effect of the CFD sample (dotted line). The black line represents the polynomial fit of the data.

Acknowledgments

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A study of oleic acid-based hydrothermal preparation of CoFe_2O_4 nanoparticles

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Abstract Nearly monodisperse, well crystalline, superparamagnetic CoFe_2O_4 nanoparticles with diameter of 6 nm were synthesized in oleic acid–water–pentanol system at 180 °C. Hydrothermal procedure, as an efficient and environment friendly alternative to organic decomposition methods, was investigated by variation of reaction conditions, and the particle formation mechanism was finally proposed (i.e., hydrolysis of metal oleates in organic phase, with size of the particles (5–8 nm) controlled by polarity-driven precipitation into water phase). As-prepared particles were hydrophobic due to coating by oleic acid. Further modification with dimercaptosuccinic acid led to water-dispersible particles with hydrodynamic diameter of 20 nm. Prepared particles were investigated by TEM, XRD, ICP-AES, light scattering, SQUID magnetometry, and Mössbauer spectroscopy.

keywords Cobalt ferrite · Hydrothermal synthesis · Magnetic particles · Superparamagnetism

Introduction

Magnetic nanoparticles, especially ferrites, have been attracting large attention in last years because of their wide potential application and easily tunable properties. Decreasing the size of nanocrystals below a critical dimension leads to the so-called superparamagnetic (SPM) behavior, demonstrated by collectivization of spins within a single nanoparticle (Liu et al. 2000).

As a result, the magnetic properties are characterized by sum of individual spins within a single particle, the so-called superspin. At temperatures much higher than the blocking temperature of the system (T_B), determined by the particle volume and magnetic anisotropy constant, the magnetic properties mimic those of a paramagnet, while below the T_B , hysteretic phenomena in magnetization develops and the superspins enter the so-called blocked state.

The magnetic nanoparticles are great candidates for various biomedical applications ranging from magnetic resonance imaging (Jun et al. 2005), drug delivery (Goodwin et al. 1999), cancer diagnostic and treatment (Sincai et al. 2001), to in vitro labeling and separation experiments (Tartaj et al. 2003). Larger particles could be used for information storage and new generation electronic devices (Sugimoto 1999).

However, each of the above-mentioned applications requires nanoparticles strictly in either superparamagnetic or in blocked state, respectively, in the desired temperature of utilization. Therefore, fine

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tuning of the particle size, shape, and crystallinity is essential for large-scale production of nanoparticles aimed to a specific application.

Old-fashion preparation routes, based mainly on coprecipitation (Blaskov et al. 1996), suffer from poor size distribution, aggregation, and low crystallinity of the resulting product. Some problems were solved by reverse micelle (Liu et al. 2000; Gyergyek et al. 2010), redox (Gu et al. 2008), or glycol (Hanh et al. 2003; Cao et al. 2008) approach, all leading directly to hydrophilic particles, but usually agglomerated. To increase stability of the particles in water dispersions, they are usually coated by silica layer (Philipse et al. 1994). Owing to indicated drawbacks, current development is focusing on high-temperature (250–320 °C) decomposition of metal acetylacetonates or oleates in organic solvents (Sun et al. 2004; Bao et al. 2009). This method leads to well crystalline, hydrophobic, and almost monodisperse magnetic nanoparticles with fairly controllable shape and size. To be used for biomedical applications, prepared magnetic particles need to be made hydrophilic. This can be achieved by silica coating (Cannas et al. 2010) or surface ligand exchange, e.g., by 2,3-dimercaptosuccinic acid (Jun et al. 2005; Roca et al. 2009b).

However, organic decomposition method is not environment friendly due to toxic organic solvents and by-products, which are difficult to remove from the prepared particles. Recently, hydrothermal treatment in fatty acid–water–ethanol system was proposed to lead to high-quality hydrophobic particles of various types (precious metals, dielectric, magnetic, semiconductor, luminescent) (Wang et al. 2005). Prepared particles have similar properties as those from organic decomposition methods, but do not contain any toxic organic residues. Moreover, this method is environment friendly and easier to conduct, as it doesn't need special water- and oxygen-free procedures. Despite these advantages, the precise mechanism of the hydrothermal synthesis is more difficult to investigate (due to closed system involved) and so far, a liquid-solid-solution (LSS) phase-transfer is proposed. Although this method has been further investigated for semiconductor (Ge et al. 2006) and up-converting (Hu et al. 2008; Wang and Li 2007; Zhang et al. 2009) nanoparticles, only a few reports on magnetic ferrite particles were published so far (Liang et al. 2006; Taniguchi et al. 2009; Li et al.

2010). In this study, we are trying to better understand mechanism involved in the particle formation and to develop inexpensive, efficient and environment-friendly method for preparation of high-quality cobalt ferrite nanoparticles targeted to biomedical applications. The cobalt ferrite was chosen as a prototype material with good stability against oxidation (compared to widely used magnetite Fe_3O_4), high saturation magnetization, high magnetic anisotropy, and also without biological hazard.

Experimental

Materials

Iron(III) nitrate nonahydrate (puriss. p.a.), myristic acid (purum $\geq 98.0\%$), dimethyl sulfoxide (puriss.) and meso-2,3-dimercaptosuccinic acid (DMSA, purum $\geq 97\%$) were obtained from Fluka. Oleic acid (tech. 90%), 1-pentanol (99+%), *n*-hexane (anhydrous 95%), sodium hydroxide (ACS reagent, 97+%) were obtained from Aldrich. Toluene (GR for analysis) was obtained from Merck. Cobalt(II) nitrate hexahydrate (p.a.) was obtained from Penta-Chemicals. Ethanol (96%, Ph.Eur.) was obtained from Panreac.

Hydrothermal treatment was carried out in Berghof DAB-2 with 50 mL teflon liner.

Hydrothermal synthesis of CoFe_2O_4 nanocrystals

Magnetic nanoparticles were synthesized following the published hydrothermal procedures (Wang et al. 2005; Liang et al. 2006) with smart modifications.

In a general procedure, 10 mmol (0.400 g) of NaOH was dissolved in 2 mL of water, 10 mL of ethanol and 12 mmol (3.39 g) of oleic acid was added with stirring which led to clear solution. It was transferred to autoclave tube and water solution of 2 mmol (0.808 g) of iron nitrate and 1 mmol (0.291 g) of cobalt nitrate was added with vigorous stirring and sonication. 20 mL of distilled water was added in total. Autoclave was closed and placed into preheated oven at 180 °C for 16 h. After cooling, final mixture was composed of upper organic phase, lower water phase and sediment of particles. Liquid phases were discarded. Remaining particles were washed four times by re-dispersion in 5 mL of hexane and

Table 1 Properties of CoFe₂O₄ particles prepared at different conditions: size from TEM weighted by number and volume, size, and polydispersity index from dynamic light scattering and elemental composition by ICP-AES

No.	Acid	Alcohol (mL)	Water (mL)	Temperature (°C)	TEM size (nm)		DLS size (nm)		composition: Fe/Co	
					By number	By volume	Z-average (nm)	PDI	As-prepared	+DMSA
1	Oleic	Ethanol: 10	20	180	7.4 ± 1.8	8.7 ± 2.2	9.1	0.28	2.89	2.20
2	Oleic	Pentanol: 10	20	180	5.8 ± 1.1	6.4 ± 1.2	5.3	0.12	1.96	2.17
3	Myristic	Ethanol: 10	20	180	7.2 ± 1.9	8.6 ± 2.3	8.8	0.23	2.03	2.19
4	Oleic	Ethanol: 20	10	180	6.0 ± 1.9	8.3 ± 3.0	6.9	0.21	2.14	2.31
5	Oleic	Ethanol: 10	20	200	7.1 ± 2.4	11.0 ± 4.6	9.2	0.24	2.69	2.87
6	Oleic	Pentanol: 10	20	200	6.1 ± 1.2	6.8 ± 1.4	6.2	0.20	1.94	2.09
7	Myristic	Pentanol: 10	20	200	5.7 ± 1.1	6.4 ± 1.4	5.6	0.16	1.91	2.03
8	Oleic	Toluene: 20	5	200	6.2 ± 1.2	6.9 ± 1.4	6.0	0.09	2.00	2.14
9	Oleic(3x) ^a	Ethanol: 10	20	180	6.0 ± 1.3	6.8 ± 1.5	6.6	0.20	2.38	2.59

^a Sample 9 was prepared with three fold amount of oleic acid and NaOH as described in “Hydrothermal Synthesis of CoFe₂O₄ Nanocrystals” section

precipitation by 15 mL of ethanol. Sonication was used to speed up re-dispersion and precipitation. Finally, particles were separated by a permanent magnet. After washing, they were re-dispersed into 10 mL of hexane and dispersion was centrifuged at 4500 rpm to remove larger agglomerates (if any).

Samples 2–7 (see Table 1) were prepared with change of the fatty acid (oleic/myristic), alcohol (ethanol/1-pentanol), alcohol amount (10/20 mL), and reaction temperature (180/200 °C), respectively.

Sample 8 was prepared starting by the same procedure as sample 1, but before autoclave treatment, metal oleates from reaction mixture were extracted by 20 mL of toluene, water phase was discarded, and 5 mL of distilled water was added. This toluene-water mixture was treated in autoclave at 200 °C for 16 h. After cooling, the particles were not sedimented, so ethanol was added to precipitate them.

Sample 9 was prepared as sample 1, but using 28 mmol of NaOH and 38 mmol of oleic acid, reproducing procedure of Liang et al. (2006).

Surface modification with DMSA

Surface modification was based on procedure used by Roca et al. (2009b) which was designed for magnetite nanoparticles prepared by organic decomposition.

CoFe₂O₄ particles were precipitated by addition of ethanol to 4 mL of hexane dispersion (ca. 100 mg of particles by ICP-AES, not counting oleic surface

layer). Particles were fixed by a magnet to remove solvents, and a mixture of 25 mL of toluene and a solution of 100 mg of meso-2,3-dimercaptosuccinic acid (DMSA) in 5 mL of dimethyl sulfoxide was added. Reaction mixture was sonicated for 5 min and mechanically stirred 30 h. During this time, modified particles precipitated. Solvent was discarded and particles were washed with mixture of 20 mL of ethanol and 20 mL of acetone followed by centrifugation at 9000 rpm for 5 min. Washing was repeated three times. Particles were re-dispersed in ca. 10 mL of water and 8 mg of NaOH was added. Dispersion was dialyzed in 4.5 L of deionized water for 72 h. Final pH was around 6.

Transmission electron microscopy (TEM)

The particles were observed by JEOL JEM-2000 FXII transmission electron microscope. A drop of dilute hexane dispersion was dried on a carbon-coated copper grid. Water dispersions of hydrophilic particles were diluted by ethanol and a drop was dried on the grid. All pictures were taken at 200 k magnification and size (diameter) was measured visually for at least 200 particles for each sample. Each particle was measured in two perpendicular directions and the geometric mean was taken. The sizes of the particles were arithmetically averaged either directly (weighting by number), or as an average of particle volume with subsequent cube-root

(weighting by volume). The volume average is larger due to the higher weight of bigger particles and therefore it is more appropriate in evaluation of some physical properties (blocking temperature etc).

Elemental analysis

Co and Fe content was measured by inductively coupled plasma atomic emission spectrometer (ICP-AES) PERKIN ELMER OPTIMA 2100 DV. Solutions were prepared by drying 50 μ L of hexane dispersion and dissolving it by HCl and HNO₃, and diluting to 50 mL by distilled water.

Powder X-ray diffraction (XRD)

The XRD was carried out on PANalytical X'Pert PRO using Cu K α radiation (1.5418 Å) with secondary monochromator and PIXcel position sensitive detector. The range was 10 to 80° with step 0.039°. Profiles were fitted in reciprocal space ($q = 4\pi/\lambda \cdot \sin \theta$) with gaussians by Gnuplot 4.2 software in the range 28°–69°. Crystallite size was obtained from full widths at half maximum B by Scherrer equation ($k = 0.94$):

$$d = \frac{k\lambda}{B \cos \theta} \quad (1)$$

Peak widths were constrained in groups 311–511–422–222, 440–220–531, 400.

Thermogravimetry

Thermogravimetric analysis was done on SEIKO EXSTAR 6300 (simultaneous differential thermal analysis and thermogravimetry) in the air atmosphere (100 mL/min), with heating rate 10 °C/min. Amount of the samples was 7–11 mg.

Light scattering

Hydrodynamic diameter (called "DLS size" in the following text) and ζ potential were measured on Malvern ZETASIZER NANO-ZS ZEN3600. The hexane dispersion was measured in glass cell with 1 cm optical path, and the water dispersion was measured in plastic cell (1 cm path) and plastic zeta-potential cell. The dynamic light scattering was done at focus position 4.65 cm and a proper concentration

was adjusted to obtain attenuation of 10 or 11 and photon count from 160 to 200 kcps. The hydrophilic particles were measured in 0.01 M KNO₃ without filtering, and pH was adjusted by 0.01 M KOH, 0.01 M, and 0.1 M HNO₃, respectively.

Magnetic measurements

Temperature dependences of zero-field-cooled (ZFC) and field-cooled (FC) magnetizations (at field of 5 mT) and hysteresis loops (at 10 and 300 K, maximum field of 7 T) were measured on Quantum Design MPMS7XL (SQUID magnetometer). Samples were put into a gelatine capsule and fastened by a drop of instant glue to avoid rotation of particles when being magnetized.

Mössbauer spectroscopy

Mössbauer spectroscopy of ⁵⁷Fe was done on Wissel spectrometer using transmission arrangement and scintillating detector ND-220-M (NaI:TI⁺). An α -Fe foil was used as a standard and fitting procedure was done using NORMOS program. Measurements at low temperature (4 K) under magnetic field of 6 T was done in perpendicular arrangement.

Results and discussion

Composition of the reaction mixture

Hydrothermal reaction takes place in oleic acid–oleate–water–ethanol mixture ("[Hydrothermal Synthesis of CoFe₂O₄ Nanocrystals](#)" section). Before addition of iron and cobalt nitrates, solution appears to be homogeneous and clear. After addition of the nitrates it becomes dark and turbid, and further stirring and sonication leads to formation of dark drops composed of iron and cobalt oleates and oleic acid, respectively. After prolonged stay at room temperature (or after addition of hexane or toluene) the mixture separates to a dark organic phase and a colorless water phase. Composition of the reaction mixture before the hydrothermal treatment is therefore: Fe(oleate)₃ 2 mmol, Co(oleate)₂ 1 mmol, oleic acid 2 mmol, Na(oleate) 2 mmol, NaNO₃ 8 mmol, water + ethanol 30 mL.

Size and phase composition of the particles

Influence of the reaction mixture composition was investigated by TEM size measurements, dynamic light scattering and elemental analysis; the results are summarized in Table 1. The TEM images (Fig. 1) show well-separated particles of CoFe_2O_4 covered by oleic acid. Only the sample 2 modified with DMSA (Fig. 1d) shows lower inter-particle distance, but again, particles are not agglomerated. Size distribution of the sample 2 is shown in Fig. 2. Phase purity was confirmed by XRD (Fig. 3) and crystallite size was obtained from the profile analysis (as described in “Powder X-ray diffraction” section). From the view of monodispersity, the Fe/Co ratio and the phase purity, respectively, the best particles are obtained from the reaction mixtures containing pentanol.

Influence of acid/alcohol/temperature on the particle formation

The particle size and distribution are not significantly influenced both by choice of the fatty acid and the reaction temperature. It indicates that the nucleation step is not critical in the hydrothermal method and probably takes place together with the growth of the particles.

However, the particle parameters strongly depend on the type and the amount of alcohol. Pentanol is less polar and its distribution ratio in organic phase is higher than that for ethanol. A higher amount of alcohol in organic phase then leads to smaller particles and better size distribution. After the hydrothermal treatment of reaction mixture no. 1 (containing ethanol), organic phase contains residual particles with very bad size distribution (Fig. 1b). It should be noted that there are no particles in organic phase when using pentanol. Alcohol content in organic phase thus plays crucial role in particle precipitation from organic phase during hydrothermal treatment.

Considering those facts, it can be concluded that nucleation and growth of the particles takes place continually (no temperature dependence of size) and the size of the particles is exclusively controlled by polarity of the organic phase (dependence on alcohol type and content). After reaching a certain size, particles are no more stable in organic phase, and

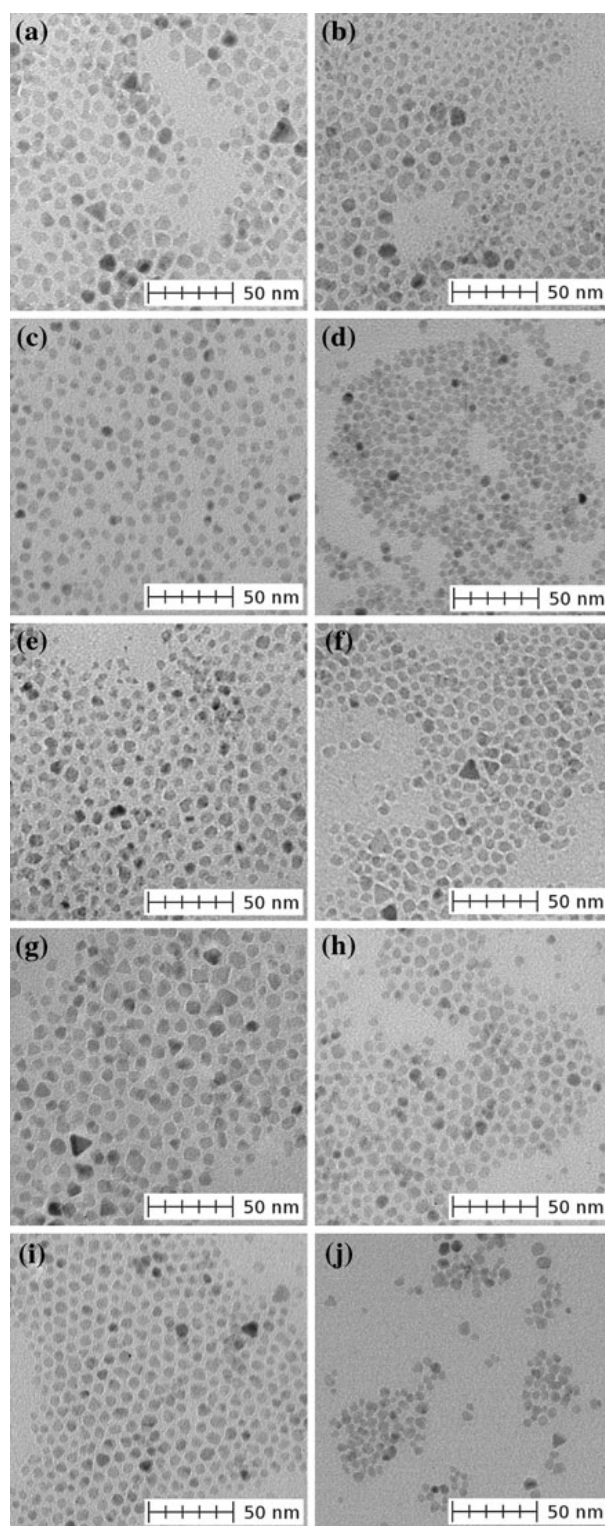


Fig. 1 TEM images of sample 1 (a), particles isolated from the oleic phase of sample 1 after hydrothermal treatment (b) (this phase was usually discarded and particles were isolated only from the sediment), sample 2 (c), sample 2 surface modified with DMSA (d), sample 3 (e), 4 (f), 5 (g), 6 (h), 8 (i), 9 (j)

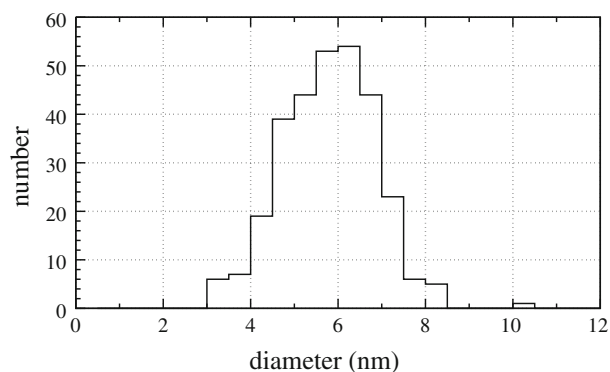


Fig. 2 Size histogram of sample 2 (300 particles included)

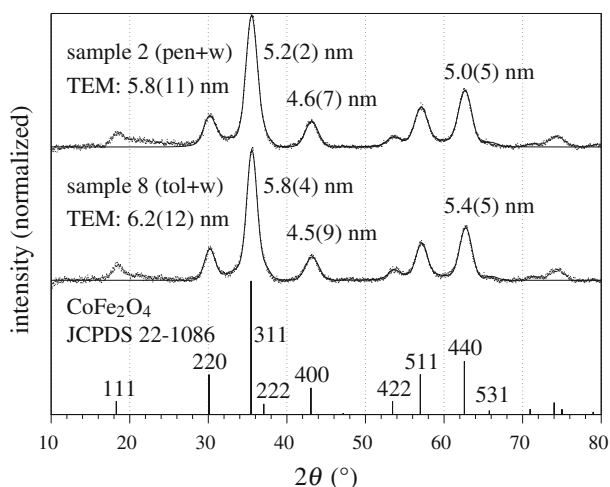


Fig. 3 X-ray diffraction of sample 2 (prepared in pentanol + water) and sample 8 (prepared in toluene + water). Crystallite size was obtained from line broadening

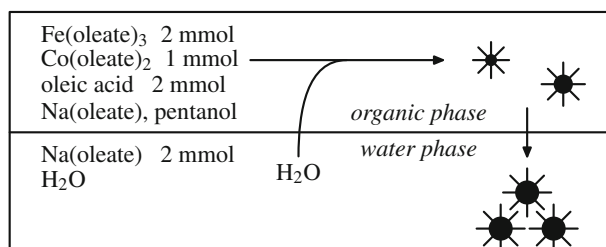


Fig. 4 Schematic depiction of hydrothermal formation of nanoparticles: metal oleates are hydrolyzed, and the formed nanoparticles precipitate into water phase after reaching the critical diameter

they precipitate into water phase, where their growth is terminated (see Fig. 4). A formation of solid phase (sodium oleate) was observed only in the reaction mixture no. 9, therefore it was not found to be crucial for nanoparticle formation as claimed in liquid-solid-

solution mechanism proposed previously (Wang et al. 2005; Liang et al. 2006; Li et al. 2010).

Formation of nanoparticles with similar properties was observed also in the system Fe,Co oleate–toluene–water under 200 °C—this method would be less environment friendly, but can be optimized for fabrication of bigger particles (e.g., by seed-mediated growth).

It is reported (Sun et al. 2004; Bao et al. 2009) that for the organic decomposition method, the control of nucleation and growth stage (by well-controlled heating rate) is critical for the narrow size distribution. Also the temperature dependence is more pronounced. Our result suggests, that mechanism involved in particle formation significantly differs in the hydrothermal and the organic decomposition methods.

Surface characterization

Infrared spectroscopy showed presence of CH_2 stretching (2922 and 2851 cm^{-1}) and bending (1409 cm^{-1}) vibrations for the hydrophobic but not for the hydrophilic particles. Stretching COO vibrations were found at 1600 – 1550 cm^{-1} for both cases. The oleic acid was therefore completely replaced by DMSA during surface modification step (“[Surface modification with DMSA](#)” section).

Surface modification led to shift of the Fe/Co ratio (Table 1) which was usually lower than 5%. This shift can be attributed to the certain amount of unreacted precursor attached to the surface (this is suggested also by the Mössbauer spectroscopy, “[Magnetic measurements](#)” section, Table 3)

Amount of organic material on the surface of the particles was investigated by thermogravimetric analysis. The hydrophobic particles are covered with oleic acid, so only 75% of their mass correspond to the cobalt ferrite core (Fig. 5 up). The remaining mass can be attributed to oleic anions strongly bound to surface, as there is no peak (at 1760 – 1700 cm^{-1}) for COOH group in the IR spectrum. About 3% could be attributed to adsorbed hexane which evaporates slowly until rapid burning of the whole organic layer occurs at around 250 °C.

Surface of the hydrophilic particles is different from the previous (as-prepared) case. The surface layer is thinner and forms only 20% of the total weight (Fig. 5 down). During the heating, decomposition and evaporation takes place gradually, until

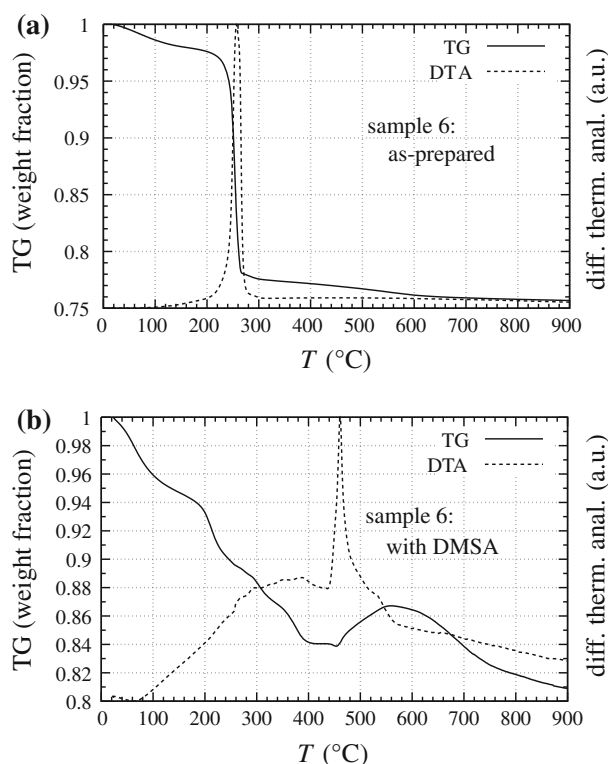


Fig. 5 Thermogravimetric analysis of the sample 6: as-prepared (capped with oleic acid, hydrophobic) and modified with dimercaptosuccinic acid (hydrophilic)

sudden burning of sulfur occurs at 460 °C connected with increase of weight (sulfates are created). However at even higher temperatures, sulfur evaporates (probably in form of SO_3 , considering similar behavior of $\text{Fe}_2(\text{SO}_4)_3$) and weight of the particles gradually decreases.

The zeta potential (Fig. 6) is negative down to pH 2.5, but for well dispersed particles of 20 nm hydrodynamic size, its value is not as negative as expected for a stable dispersion: -40 mV (Roca et al. 2009b). However, it is possible that the obtained numerical value (-15 mV) could be appropriate for particles of small size. Adding more NaOH during the preparation of hydrophilic particles leads to agglomerates, as was indicated by higher hydrodynamic radius. These agglomerates then show expected behavior of the ζ potential (< -30 mV for diameter 150 nm).

Discussion of the surface modification

One of the most usual methods of surface modification to make particles hydrophilic is coating with

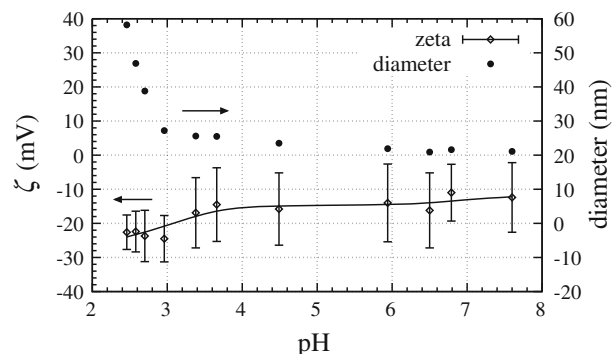


Fig. 6 Zeta potential and hydrodynamic size measurement of water-dispersed particles of CoFe_2O_4 prepared in oleic acid–pentanol–water at 180 °C (sample 2) and modified by dimercaptosuccinic acid

silica (SiO_2) created by hydrolysis of tetraethoxysilane (Philipse et al. 1994). However, thickness of the silica layer is not well controllable and particles tend to agglomerate (probably due to formation of Si–O–Si bonds between individual particles) and gradually sediment after few weeks.

Therefore, other type of modification has been developed, namely substitution of the oleic acid ligands by 2,3-dimercaptosuccinic acid (DMSA). DMSA bonds to the particle surface through the COO groups, and SH groups are available for further modifications needed in biomedical applications. This method was successfully applied to particles prepared by organic decomposition (Jun et al. 2005; Roca et al. 2009b). The modification takes place in mixture of toluene and dimethylsulfoxide, which well dissolves DMSA, and also hydrophobic particles can be well-dispersed in it. However, modified particles are not more dispersible, and sediment on the walls of a reaction vessel. After washing with ethanol and acetone, they can be re-dispersed into water, but to obtain stable and clear dispersion, it is necessary to add NaOH as was found by Roca et al. (2009b). The supposed scheme of NaOH function in stabilization of the particle dispersion is depicted in Fig. 7 (only the first step has been proposed by Roca et al. (2009b)).

However, as can be seen from the Fig. 7, adding more NaOH than necessary leads to extraction of the DMSA from the particle surface and results in irreversible agglomeration of the particles. It was observed, that only with well controlled amount of NaOH (in this case about 8 mg per 100 mg of particles, as 4 mg were not sufficient to obtain clear

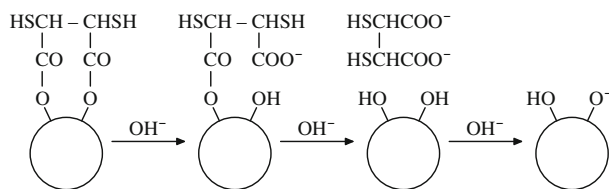


Fig. 7 Scheme of NaOH function during redispersion in water after surface modification of magnetic particles with DMSA (clear water dispersion is produced only in the second case)

dispersion), it was possible to obtain DLS size less than 100 nm, even without filtration through millipore filter.

Further increasing of the amount of NaOH leads to precipitation of the particles. Increasing amount of NaOH even more leads again to dispersible particles, but dispersion is not clear (high agglomeration occurs).

It was found that also the SH groups are important for good hydrophilicity, as particles modified by the succinic acid (by the same procedure) were dispersible only in ethanol and not in water.

Magnetic measurements

Magnetic properties of the CoFe_2O_4 particles were investigated by SQUID magnetometry and Mössbauer spectroscopy of ^{57}Fe .

The temperature dependence of the ZFC and FC magnetization confirmed, that the particles are superparamagnetic at room temperature (Fig. 8). The most important features observed on the ZFC–FC curves are: 1. broad maximum on the ZFC curve (denoted as T_{B1}), 2. furcation of the ZFC–FC curves (denoted as T_{B2}), and 3. saturation of the FC curve at low temperatures. Saturation of the FC curve suggests presence of considerable dipolar interactions between the individual particles. The nonequivalence of the T_{B1} and T_{B2} can be therefore interpreted by the interparticle interactions, rather than by particle size distribution (which appears to be very narrow from the TEM analysis). Such behavior of the ZFC–FC curves is typical for systems with collective phenomena. Moreover, in the case of hydrophilic particles with thin surface layer, where intersection of ZFC and FC curves occurs only at 400 K, the collective behavior is even enhanced due to reduced distance between individual particles and creation of magnetic clusters can be expected.

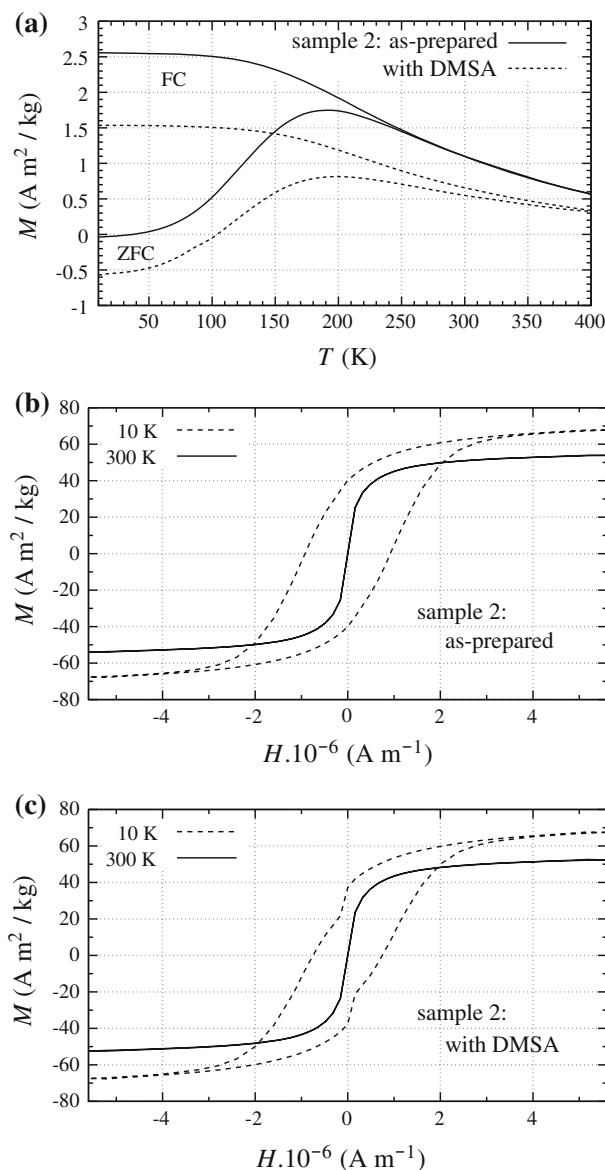


Fig. 8 ZFC–FC measurement and hysteresis loops of sample 2 (hydrophobic and hydrophilic)

The superparamagnetic behavior at 300 K was further confirmed by the measurements of magnetization isotherms, which showed zero coercivity for all measured samples at 300 K. From the fully developed hysteresis loop at 10 K, coercive field H_c , remanent magnetization M_r and magnetization at 7 T M_{7T} were obtained (Table 2). However, weight of the surface oleic acid layer (which comprised about 25%) was not subtracted, as it was not known exactly for all samples, which may explain variation of M_{7T} .

The key magnetic parameters of the nanoparticles are comparable to those obtained by thermal

Table 2 Magnetic properties of CoFe_2O_4 nanoparticles obtained from ZFC/FC measurement at 5 mT—blocking temperatures: T_{B1} (peak of ZFC), T_{B2} (intersection of ZFC

and FC), parameters of the hysteresis loop at 10 K: coercive field, remanent magnetization, and magnetization at 7 T, K_{eff} (obtained using T_{B1} value)

Sample	T_{B1} (K)	T_{B2} (K)	$\mu_0 H_c$ (T)	M_{7T} (A m ² kg ⁻¹)	K_{eff} (10 ⁶ J/m ³)
1	222	318	1.14	45.1	0.22
2	191	286	1.16	67.7	0.48
2 + DMSA	199	400	0.94	67.6	0.50
5	268	380	1.12	57.1	0.13
8	274	397	1.26	67.1	0.55

decomposition of $\text{Fe}(\text{acac})_3$ and $\text{Co}(\text{acac})_2$ at high temperatures (Torres et al. 2010). Those 5 and 7 nm particles show coercivity of 1.4 and 1.7 T (at 5 K), $M_s \sim 77$ and 73 A m²/kg (at 5 K), and $T_B \sim 174$ and 230 K, respectively. Gyergyek et al. (2010) reports $H_c = 1.9$ T, $M_s = 61$ A m²/kg (at 10 K) and $T_B \sim 240$ K for 9 nm particles prepared by thermal decomposition. Hysteresis loop at 10 K of our modified sample 2 suggests presence of two magnetic phases, probably caused by magnetic clusters created during drying. Similar deformation of the hysteresis loop was observed for FePt particles coated by silica (Lee et al. 2006) and was attributed to inter-particle interactions (the effect increased for thinner SiO_2 layer). It should be noted that dried hydrophobic particles are again re-dispersible into hexane, but this is not true for modified (hydrophilic) particles, for which drying of water dispersion is an irreversible process.

To evaluate ‘magnetic quality’ of our samples, we have considered the following: the particle size obtained from the TEM and XRD is almost comparable, which points to high crystallinity of the particles. Further, the effective anisotropy constant, K_{eff} can be assumed as a sum of the intrinsic magnetocrystalline anisotropy constant of the bulk CoFe_2O_4 ($K_1 \sim 0.2\text{--}0.4 \times 10^6$ J/m³) (Bozorth et al. 1955) and surface/disorder contribution K_s , and can be roughly estimated using the relation $K_{\text{eff}} = 25 k_B T_B / V$ (Lu et al. 2000). The values K_{eff} obtained from blocking temperatures T_{B1} and volume-weighted TEM diameters (Table 1) are included in Table 2. In spite of the fact, that the approach used is rather rough, they correspond well to the value for the bulk CoFe_2O_4 , suggesting, that the surface effects are minor.

Sample 2 was further investigated by Mössbauer spectroscopy. Clear sextets were found at 4 K and field 0 and 6 T (Fig. 9). During the fitting of the

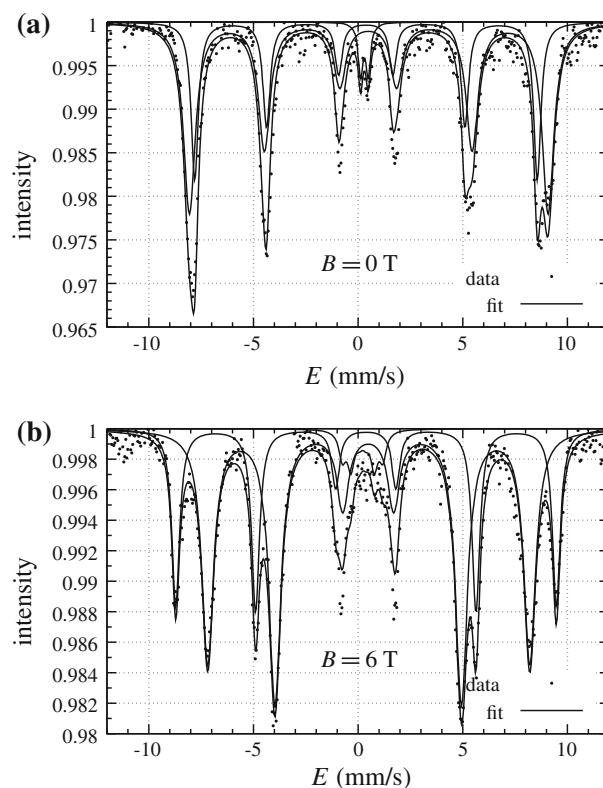


Fig. 9 Mössbauer spectrum of sample 2 at 4 K in magnetic field 0 and 6 T

sample measured at 0 T, isomer shift (δ) and quadrupole splitting (ΔE_Q) were fixed at values obtained at 6 T due to strong overlap of the multiplets. Results of fitting procedure are summarized in Table 3 and compared with literature data (Bouhas et al. 1993) on bulk CoFe_2O_4 . They show, that iron ions are nearly statistically distributed in spinel structure, i.e., $(\text{Co}_{0.33}\text{Fe}_{0.66})[\text{Co}_{0.66}\text{Fe}_{1.33}]\text{O}_4$, where () indicates A sites (tetrahedral) and [] indicates B sites (octahedral). The observed remaining iron in paramagnetic state is probably due to unreacted precursor and is apparently responsible for

Table 3 Analysis of Mössbauer spectrum of sample 2 at 4 K. Two sextets corresponding to tetrahedral (A site) and octahedral (B site) Fe^{3+} were found

	Area (%)	δ (mm/s)	ΔE_Q (mm/s)	$B_{\text{ext}} = 0$ T	$B_{\text{ext}} = 6$ T	θ
Sextet 1 (A site)	31	0.37	0.01	50.8 T	56.5 T	19°
Sextet 2 (B site)	65	0.50	0.03	53.2 T	47.8 T	27°
Paramagnetic Fe^{3+}	4	0.30	0.36	0.0 T	6.0 T	
Bulk ^a (A site)	45	0.36	0	51.2 T	56.5 T	29°
Bulk ^a (B site)	55	0.49	0	54.4 T	49.2 T	28°

Canting angles θ are from cosine rule

^a Bulk values were measured at 4.2 K and correspond to structure $(\text{Co}_{0.09}\text{Fe}_{0.91})[\text{Co}_{0.91}\text{Fe}_{1.09}]\text{O}_4$ (Bouhas et al. 1993)

Fe/Co change during surface modification (Table 1). Measurement under magnetic field showed nonzero canting angle—this is often reported to be caused by disordered surface layer (in not well crystalline particles), but it can be caused also by the particles frozen in non-easy-axis orientation (Pankhurst and Pollard 1991). In case of our particles, the later hypothesis seems to be the case, as other experiments evidence highly-ordered structure, which generally coincide with the ordered surface spin layer (Roca et al. 2009a).

At room temperature, only very weak singlet was found, with 0.5% intensity compared to sextets at 4 K. Calculation shows, that in one 6 nm particle, there are around 3000 atoms of Fe (16 Fe in $(8.39 \text{ Å})^3$ unit cell). Overall weight corresponds to 6000 atoms of Fe. Momentum carried by particle after photon absorption would be (where $E_\gamma = 14.413 \text{ keV}$)

$$\Delta E_{\text{recoil}} = \frac{p_\gamma^2}{2 \cdot 6000 \cdot m_{\text{Fe}}} = \frac{E_\gamma^2}{2 \cdot 6000 \cdot m_{\text{Fe}} c^2} = 2.3 \times 10^{-11} E_\gamma \quad (2)$$

which is far more than the width of photon energy distribution (calculated from mean life $\tau = 142 \text{ ns}$) $\Gamma = \hbar/\tau = 4.6 \times 10^{-9} \text{ eV} = 3.2 \times 10^{-13} E_\gamma$. Because the particles have flexible oleic acid molecules on their surface, which facilitate their movement, resonant absorption at room temperature is not possible.

Conclusions

Hydrothermal synthesis in oleic acid–sodium oleate–water–pentanol was successfully applied to preparation of high-quality cobalt ferrite nanoparticles with diameter $(5.8 \pm 1.1) \text{ nm}$ ($w = 0.19$) covered with

oleic anions (25% by weight) and readily dispersible in non-polar solvents. Dependence of particle properties on the variations in composition of reaction mixture was investigated and the mechanism of particle formation was proposed. Based on this mechanism, a new route using toluene under pressure was proposed. Prepared particles were characterized by TEM, elemental analysis, thermogravimetry, powder X-ray diffraction, dynamic light scattering and magnetic measurements. They are superparamagnetic at room temperature, and show excellent magnetic parameters.

The particles were further modified by dimercaptosuccinic acid. Particles were then treated with well-defined amount of NaOH, what facilitated creation of stable water dispersion with the hydrodynamic diameter of particles as low as 20 nm, and agglomeration-free down to pH 3. The magnetic properties were conserved, but indication of stronger inter-particle interaction was observed.

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Nanocomposites of monodisperse nanoparticles embedded in high-K oxide matrices – a general preparation strategy

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We present a general approach, which enables preparation of multifunctional nanocomposites of monodisperse nanoparticles embedded in oxide matrices. The two-step route has been successfully applied to nanocomposites composed of CoFe_2O_4 nanoparticles embedded in high-K oxide matrices (ZrO_2 , Al_2O_3 and TiO_2). First, hydrophobic CoFe_2O_4 nanoparticles were produced by hydrothermal synthesis and then their incorporation in the oxide matrix was completed by the sol–gel method using the corresponding alcoxides. The as-prepared samples were subjected to annealing at temperatures ranging from 200 to 700 °C, and characterized in detail by the Powder X-Ray Diffraction (PXRD), Energy Dispersive Analysis (EDX), Mössbauer Spectroscopy (MS) and magnetic measurements. The particle size does not change with the annealing temperature, while the amorphous matrices crystallize at temperatures above 400 °C. At much higher annealing temperatures, partial decomposition of the CoFe_2O_4 occurs accompanied by formation of additional phases. The magnetic measurements also confirmed presence and stability of the uniform CoFe_2O_4 nanoparticles in the matrices. Thus the proposed method allows preparation of new types of nanocomposites constituted of uniform nanoparticles of the desired type (magnetic, luminescent etc.) embedded in the favored oxide matrix.

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1. Introduction

Recently, nanocomposites of nanoparticles embedded in a functional matrix attracted considerable attention due to large application potential in various fields like biomedicine, catalysis, data storage and smart sensing.^{1–3} The functional matrix is chosen according to its required intrinsic physical, chemical and mechanical properties; however, it plays several important roles in the nanocomposites as well. It reduces contact of the embedded nanoparticles hence their interactions, enhances their stability due to minimized contact with the environment and avoids their agglomeration during thermal treatment leading to better control of their final size.

The most frequent material of the matrix used in nanocomposites is the amorphous silicon dioxide, which can be easily obtained by several variants of the sol–gel method.^{4,5} It is an excellent insulator, with low level of electronic defects, great transparency and possibility of surface functionalization by various functional groups. It can be easily etched and patterned down to a nanometer scale.⁶ By a simple modification of the sol–gel route using nitrates or chlorides as a source of the

corresponding cations, nanoparticles of transition metal oxides can be grown in the porous silica matrix by controlled annealing.⁷ The particle size is driven by the annealing temperature due to the diffusion of the ions in the matrix, so the higher the annealing temperature, the larger particle size.

However, for many applications, a well-defined and uniform particle size is essential. Therefore, additional heat treatment is a limiting factor as the variation of the particle size is limited by the concentration of the cations, their diffusion coefficients and solubility in the silica matrix. Moreover, the in-matrix grown particles have a significant size distribution. At higher temperatures, the matrix transforms to crystalline form, which typically leads to formation of high-temperature phases. Another point is that the modified sol–gel method is limited to nanoparticles of simple oxides with low solubility of the cations in the matrix, which also prevents rapid formation of higher oxide phases even at much lower temperatures.

To avoid the above mentioned difficulties, we have introduced a novel two-step procedure, which can be applied to preparation of a large spectrum of nanocomposites, where the common sol–gel derived approach fails. In the first step, hydrophobic nanoparticles are prepared by a hydrothermal method. In the second step, the nanoparticles are embedded in an oxide matrix formed by hydrolysis of the corresponding alcoxides, followed by gelation and mild drying. This procedure can be applied to many types of nanoparticles such as magnetic

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(iron oxides, spinel ferrites), quantum dots, luminescent, photoactive (TiO_2), up-conversion (Ln-doped NaYF_4), SERS active (Au , Ag) *etc.* in combination with different matrices.

In our study, we have tested the proposed method on preparation of the nanocomposites of CoFe_2O_4 nanoparticles integrated in selected oxide matrices (TiO_2 , Al_2O_3 and ZrO_2), diverse to the prevalent SiO_2 . The CoFe_2O_4 nanoparticles are well-known for their convenient magnetic properties (saturation magnetization $80 \text{ A m}^2 \text{ kg}^{-1}$, coercivity 2 T at low temperatures), also their hydrothermal preparation is mastered.^{8–10} The ZrO_2 , TiO_2 , and Al_2O_3 oxides show many attractive properties, like high dielectric constant and optical transparency, and their preparation by the sol-gel method is rather routine.¹¹

The TiO_2 is a photoactive material, that is mainly used as an antibacterial agent, a component of self-cleaning surfaces or water and air purification technologies based on the photocatalysis.^{3,12} The $\text{CoFe}_2\text{O}_4/\text{TiO}_2$ nanocomposites have been now intensively studied due to their advantage of magnetic separation from the liquid phase after the purification process.^{13,14}

The Al_2O_3 exhibits promising catalytic properties¹⁵ and has been widely studied as a candidate for surface passivation of the solar cells.¹⁶ The Al_2O_3 matrix is mostly used as a passive spacer to avoid the particle agglomeration and to control the interparticle interactions.^{17,18} ZrO_2 is known as a diluted magnetic semiconductor (DMS).^{19,20} To our best knowledge there are no reports on the $\text{CoFe}_2\text{O}_4/\text{Al}_2\text{O}_3$ and $\text{CoFe}_2\text{O}_4/\text{ZrO}_2$ nanocomposites yet. Therefore we also address the most appropriate conditions for preparation of the $\text{CoFe}_2\text{O}_4/\text{Al}_2\text{O}_3$ and $\text{CoFe}_2\text{O}_4/\text{ZrO}_2$ nanocomposites by the general two-step route.

All samples were characterized in detail by the Powder X-Ray Diffraction (PXRD) and Transmission Electron Microscopy (TEM) in order to observe the phase composition, particle size and dispersion of the nanoparticles in the matrix. The Mössbauer Spectroscopy (MS) was performed for deeper studies of the iron-containing phases in the samples. Finally, the magnetic measurements were carried out to confirm the presence of the CoFe_2O_4 particles in the composites and to determine the CoFe_2O_4 -to-oxide matrix ratio. All results were compared with those of the bare CoFe_2O_4 nanoparticles. We demonstrate that the uniform CoFe_2O_4 nanoparticles can be homogeneously embedded in the high-K oxide matrices without change of their diameter, size distribution and magnetic response.

2. Experimental details

2.1. Preparation

The two-step synthesis was used to prepare the nanocomposites of CoFe_2O_4 embedded in various oxide matrices. The hydrophobic CoFe_2O_4 nanoparticles were prepared by the hydrothermal synthesis¹⁰ and subsequently incorporated in the matrices, as is schematically shown in Fig. 1.

2.1.1. Preparation of CoFe_2O_4 nanoparticles. The 4.0 g of sodium hydroxide was dissolved in mixture of water (20 ml) and ethanol (100 ml) and then 38.10 ml of oleic acid was added to the mixture (solution 1A). The 2.91 g of cobalt(II) nitrate hexahydrate and 8.08 g of iron(III) nitrate nonahydrate were

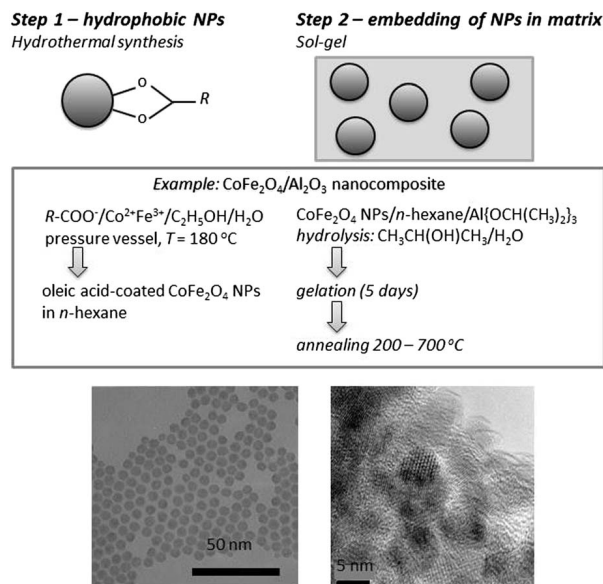


Fig. 1 (Top panel) Scheme of the general two-step route including preparation of monodisperse nanoparticles by the hydrothermal method (step 1) and their incorporation in the oxide matrix by the sol-gel route (step 2). (Bottom panel) TEM image of the CoFe_2O_4 nanoparticles prepared by hydrothermal synthesis (on the left) together with the HR-TEM image of the powder form of the Co_{free} sample.

dissolved in 180 ml of water (solution 1B). Solution 1A was stirred intensively at room temperature and added drop-wise to the solution 1B. The final mixture was stirred and sonicated at room temperature for 30 min (at 40 W transferred power). Afterwards, the mixture was heated at 180°C for 10 h under autogeneous pressure in autoclave. The clear fraction was removed and the black-brown fraction was precipitated by addition of ethanol, decanted in magnetic field and dispersed in *n*-hexane using ultrasonic bath. This purification was repeated for four times. Concentration of the cobalt ferrite in the prepared ferrofluid was determined gravimetrically and by Thermogravimetry-Differential Thermal Analysis (TG-DTA). The reference (matrix-free) sample, labeled as Co_{free} was obtained by drying the ferrofluid at 100°C .

2.1.2. Preparation of the nanocomposites – incorporation into matrices. The 0.22 mmol of cobalt ferrite nanoparticles in hexane was diluted with dry *n*-hexane to required amount (12.5 ml for Al_2O_3 , 14.9 ml for TiO_2 and 9.8 ml for ZrO_2). The 3 mmol of aluminium isopropoxide, titanium *n*-butoxide and zirconium *n*-butoxide was added to the solution, respectively and stirred thoroughly. The mixtures were then stirred intensively and 2 ml solution of isopropylalcohol in water was added in ratio of 200 : 1 (v/v), 50 : 1 (v/v) and 20 : 1 (v/v) for the Al_2O_3 , TiO_2 and ZrO_2 matrices, respectively. The final mixture was left to stay at 40°C for 5 days. All gels were finally treated thermally in vacuum within two steps. First, the gel was heated to 200°C ($0.2^\circ\text{C min}^{-1}$), keeping the gel at 200°C for 2 hours, and finally annealed at 300, 400, 500, 600, or 700°C with the step of 1°C min^{-1} keeping the product at the final temperature for 2 hours. The samples were labeled accordingly to its matrix and the annealing temperature, respectively, as M_T , where $M = \text{Al, Ti, Zr}$ and $T = 200\text{--}700^\circ\text{C}$.

2.2. Characterization methods

All samples were characterized using the PXRD at room temperature by the Bragg Brentano geometry on the Philips X'Pert PRO MPD X-ray diffraction system equipped with the X'Celerator detector using Cu-anode (CuK_{α} ; $\lambda = 1.5418 \text{ \AA}$) or Co-anode (CoK_{α} ; $\lambda = 1.7889 \text{ \AA}$). The phase composition, particle size (using the isotropic approximation) and lattice parameters of the selected samples were obtained by Rietveld refinement implemented in the FullProf software.²¹

Concentration of the nanoparticles in the ferrofluid was determined gravimetrically by Thermogravimetry-Differential Thermal Analysis (TG-DTA) using a TG-DTA device by SETARAM. The TEM and High-Resolution TEM (HR-TEM) using HRTEM JEOL JEM 3010 was performed in order to study the morphology of the prepared nanocomposites and determination of the particle size of the CoFe_2O_4 nanoparticles. The samples were also studied by the Energy Dispersive X-ray Spectroscopy (EDX) analysis using scanning electron microscope MIRA 3 LMH by Tescan with the accelerating potential of 15 kV.

The MS measurement was done in the transmission mode with ^{57}Co diffused into Rh matrix as the source moving with constant acceleration. The spectrometer (Wissel, Germany) was calibrated by standard $\alpha\text{-Fe}$ foil and the isomer shift is related to this standard at 293 K. The resulting parameters were determined in the NORMOS program.

The magnetic measurements were carried out using the SQUID magnetometer (MPMS7XL, Quantum Design). The zero field-cooled (ZFC) and field-cooled (FC) curves were recorded as follows: at first, the sample was cooled down to 10 K, then the magnetic field of 0.01 T was applied and the temperature dependence of the magnetization was measured up to 400 K (ZFC curve). Afterwards, the sample was cooled down to 10 K in the applied field and the FC curve was obtained. The magnetization isotherms (field dependence of the magnetization) were measured in the range of $\pm 7 \text{ T}$, at selected temperatures.

3. Results and discussion

3.1. Phase analysis

The PXRD was carried out to obtain the phase composition of the samples and to determine the temperature of crystallization of the matrix. The results are summarized in Table 1, together with the phase composition determined by MS. Generally, the increasing annealing temperature caused decomposition of the CoFe_2O_4 nanoparticles leading to the creation of parasitic phases and crystallization of the matrix above 500°C . The presence of the amorphous matrix at lower annealing temperature ($200\text{--}400^\circ\text{C}$) is manifested by the broad maxima at diffraction angle about 22° and increased intensity of the background. The particle diameter, d_{XRD} determined as the size of the coherently diffracting domain of the CoFe_2O_4 nanoparticle is in the range of $5.5\text{--}7.0 \text{ nm}$ and does not change significantly with the increasing annealing temperature. The overlapped reflections of the crystalline matrices and CoFe_2O_4

phase disallowed the precise determination of the particle size of the CoFe_2O_4 nanoparticles in multiphase samples.

The EDX reveals the CoFe_2O_4 /matrix weight ratio for the samples containing only CoFe_2O_4 phase and matrix. The values are summarized in Table 2 together with the theoretical ratio and the ratio calculated from the values of the saturation magnetization, M_s as is discussed further.

The TEM images were captured to obtain the morphology of the nanocomposites. The particle diameter determined by TEM, d_{TEM} is in good agreement with the d_{XRD} for all evaluated samples. The representative TEM images are shown in Fig. 4, 6 and 8, respectively. The MS was performed to confirm the presence of CoFe_2O_4 and exclude presence of the other iron phases, for the samples for that the PXRD measurements were not sufficient for the analysis due to the overlapped reflections. MS can clearly distinguish between the Fe^{2+} and Fe^{3+} ions due to the total different isomer shift as will be presented further, thus clearly indicates presence of other phases than CoFe_2O_4 .

The crystal structure determined by PXRD and MS of individual nanocomposites will be now discussed in more details followed by the results of magnetic measurements.

3.1.1. The matrix-free sample, Co_free. The diffraction pattern displays only the reflections corresponding to the spinel structure with the lattice parameter $a = 8.40 \text{ \AA}$, that is in good agreement with the CoFe_2O_4 phase (PDF4 databasis, card no. 00-022-1086). The particle size determined using the Rietveld refinement is $5.5 \pm 0.5 \text{ nm}$. The TEM image (Fig. 1) shows well-crystalline particles with $d_{\text{TEM}} \approx 6 \text{ nm}$.

The MS spectra reveals that the most of the particles are in the blocked state, as is observed by the presence of sextet with asymmetric absorption peaks corresponding to the small particle size with non-zero size distribution. Therefore, the convolution of the Gaussian distribution function and the Lorentzian profile function was used to refine the spectra. The smaller values of the hyperfine fields (46.6 T for the O_h -sites; 41.3 T for the T_d -sites) are consistent with the small particle size, $d_{\text{XRD}} = 5.5 \text{ nm}$. The isomer shift, $\delta \approx 0.33 \text{ mm s}^{-1}$ and zero quadrupole shift are attributed to the ferrite spinel structure. The doublet and the singlet correspond to the particles in superparamagnetic (SPM) regime and close to the blocking temperature, respectively. The PXRD patterns together with the MS spectra and magnetic measurements are depicted in Fig. 2.

3.1.2. $\text{CoFe}_2\text{O}_4/\text{TiO}_2$ nanocomposites. The diffraction patterns of the Ti_200, Ti_300 and Ti_400 samples depicted in Fig. 3 exhibit only reflections corresponding to the spinel structure with the lattice parameters, $a = 8.38 \text{ \AA}$, that is in good agreement with the reference sample, Co_free. The lower intensities of the CoFe_2O_4 reflections with the increasing annealing temperature are observed, suggesting the decomposition of the CoFe_2O_4 to additional phases. This observation has been further confirmed by the MS, where the doublet with high $\delta = 0.98 \text{ mm s}^{-1}$ corresponding to the Fe^{2+} ions is detected in all samples except Ti_200 (Fig. 3). The high quadrupole splitting ($\Delta E_q = 2.15 \text{ mm s}^{-1}$) can be ascribed to the Fe_2TiO_4 phase that crystallizes in the spinel structure,²² therefore can be hardly resolved in PXRD due to the overlapped reflections with the CoFe_2O_4 phase.

Table 1 The phase composition of all samples determined by PXRD and MS. The matrix is either amorphous or crystalline, where (C) and (M) denote cubic and monoclinic structure, respectively. The content of individual crystalline phases in the samples is described as follows: * 5–30%, ** 30–60%, *** >60%

Sample	Matrix PXRD	Phases PXRD	Phases MS
Al_200	Amorphous	CoFe ₂ O ₄ ***	CoFe ₂ O ₄ ***
Al_300	Amorphous	CoFe ₂ O ₄ ***	CoFe ₂ O ₄ ***
Al_400	Amorphous	CoFe ₂ O ₄ ***, AlO(OH)*	CoFe ₂ O ₄ ***
Al_500	Amorphous	CoFe ₂ O ₄ ***, CoAl ₂ O ₄ *	CoFe ₂ O ₄ ***
Al_600	Amorphous	CoFe ₂ O ₄ **, CoAl ₂ O ₄ **	CoFe ₂ O ₄ ***
Al_700	Amorphous	CoFe ₂ O ₄ *, CoAl ₂ O ₄ *, FeAl ₂ O ₄ **	CoFe ₂ O ₄ ***, FeAl ₂ O ₄ *
Ti_200	Amorphous	CoFe ₂ O ₄ ***	CoFe ₂ O ₄ ***
Ti_300	Amorphous	CoFe ₂ O ₄ ***	CoFe ₂ O ₄ ***, Fe ₂ TiO ₄ *
Ti_400	Amorphous	CoFe ₂ O ₄ ***	CoFe ₂ O ₄ /Fe ³⁺ *, Fe ₂ TiO ₄ ***
Ti_500	TiO ₂ anatase***, TiO ₂ rutile*	CoFe ₂ O ₄ *, FeTiO ₃ *	CoFe ₂ O ₄ /Fe ³⁺ *, Fe ₂ TiO ₄ ***, FeTiO ₃ *
Ti_600	TiO ₂ anatase**, TiO ₂ rutile*	CoFe ₂ O ₄ *, FeTiO ₃ *	CoFe ₂ O ₄ /Fe ³⁺ *, Fe ₂ TiO ₄ ***, FeTiO ₃ *
Zr_200	Part. ZrO ₂ (C)**	CoFe ₂ O ₄ **	CoFe ₂ O ₄ ***
Zr_300	Part. ZrO ₂ (C)**	CoFe ₂ O ₄ **	CoFe ₂ O ₄ ***
Zr_400	Part. ZrO ₂ (C)**	CoFe ₂ O ₄ *	—
Zr_500	ZrO ₂ (C)**	CoFe ₂ O ₄ **	Fe ³⁺ ions***
Zr_600	ZrO ₂ (C)**	CoFe ₂ O ₄ **	Fe ³⁺ ions***
Zr_700	ZrO ₂ (C)***, ZrO ₂ (M)*	CoFe ₂ O ₄ **	—
Co_free	N/A	CoFe ₂ O ₄ ***	CoFe ₂ O ₄ ***

Table 2 Comparison of the weight content of CoFe₂O₄ in the matrix determined by EDX analysis, W_{EDX} and magnetic measurements at 10 and 300 K, W_{M10} , W_{M300} respectively with the theoretical one, W_{T}

Sample	W_{T} (wt%)	W_{EDX} (wt%)	W_{M10} (wt%)	W_{M300} (wt%)
Al_200	25.0	30.4	20.7	20.8
Al_600	25.0	—	—	7.1
Ti_200	17.0	15.5	15.5	14.6
Ti_600	17.0	—	—	5.2
Zr_200	12.0	13.7	13.8	12.5
Zr_600	12.0	—	—	1.5

The crystalline matrix is detected for the samples annealed at 500 °C and higher temperatures, predominantly in anatase form. The asymmetry of the anatase reflections indicates presence of the rutile with tendency to increase the amount of the rutile at the expense of the anatase upon further annealing of the sample at 600 °C, which is connected with the increase of the size of the crystallites of the matrix.^{23,24} The reflection located at 38° can be attributed to the FeTiO₃ phase, as is consistent with the results obtained by MS, where another doublet appears for the Ti_500 and Ti_600 samples with $\delta = 1.1 \text{ mm s}^{-1}$, $\Delta E_{\text{q}} = 0.58 \text{ mm s}^{-1}$ corresponding to the FeTiO₃ phase.²⁵

The TEM image depicted in Fig. 4 of the Ti_200 sample shows crystalline nanoparticles (see HR-TEM image) with low size distribution dispersed in amorphous matrix. The particle size, $d_{\text{TEM}} = 6 \text{ nm}$ is in good agreement with the d_{XRD} .

3.1.3. CoFe₂O₄/Al₂O₃ nanocomposites. The diffraction patterns together with the MS spectra are depicted in Fig. 5. Clearly resolved peaks corresponding to the spinel structure are observed at low temperatures (200, 300 °C) with the lattice parameters around $a = 8.38 \text{ Å}$, which is in good agreement with the reference sample. The matrix remains amorphous through the whole series, as is consistent with A. Corrias *et al.*²⁶ who

observed the crystallization of the Al₂O₃ matrix at temperatures higher than 700 °C. Annealing of the nanocomposite at 400 °C led to the occurrence of pseudoboehmite phase AlO(OH) manifested by broad reflections at 28°, 49° and 54°.²⁷ The presence of AlO(OH) is supported by the TEM observation (see Fig. 6), where the needle-shape aggregates typical for this phase is observed for the Al_400 sample.²⁶

Increase of the annealing temperature to 500 °C has resulted into the asymmetry of the peak profiles, that can be elucidated by the presence of the parasitic CoAl₂O₄ and FeAl₂O₄ phases, that also crystallize in spinel structure with slightly different lattice parameter ($a = 8.104 \text{ Å}$ and 8.156 Å respectively, PDF4 databasis, cards no. 00-044-0160; 01-086-2320). The shift of the peaks to the higher angles for the Al_700 sample is clearly observable and points to the dominant presence of these spinel structures. The CoAl₂O₄ and FeAl₂O₄ cannot be unambiguously resolved by the PXRD, due to the nearly similar lattice parameters. However, the presence of FeAl₂O₄ has been detected by MS ($\delta = 0.99 \text{ mm s}^{-1}$, $\Delta E_{\text{q}} = 1.7 \text{ mm s}^{-1}$).²⁸ For all samples except the Al_700 sample, only the Fe³⁺ ions ($\delta = 0.35 \text{ mm s}^{-1}$) corresponding to the CoFe₂O₄ phase have been detected by the MS.

3.1.4. CoFe₂O₄/ZrO₂ nanocomposites. The samples annealed at lower temperatures (200–400 °C) exhibit diffraction peaks matching with the reflections of the spinel structure with lattice parameter $a = 8.39 \text{ Å}$, that corresponds to the CoFe₂O₄ phase. The broad peak around 30° can be attributed to the partially crystalline cubic ZrO₂ matrix (see Fig. 7). This peak gets narrower with the increasing temperatures, suggesting the continuous crystallization of the matrix. The MS exhibit similar profile as for the matrix-free sample confirming the presence of the CoFe₂O₄ nanoparticles (see Fig. 7). The crystalline particle with size around 5.5 nm can be seen in HR-TEM image in Fig. 8.

The rapid change of the diffraction pattern is observed at 500 °C, where the matrix is well crystalline, predominantly in

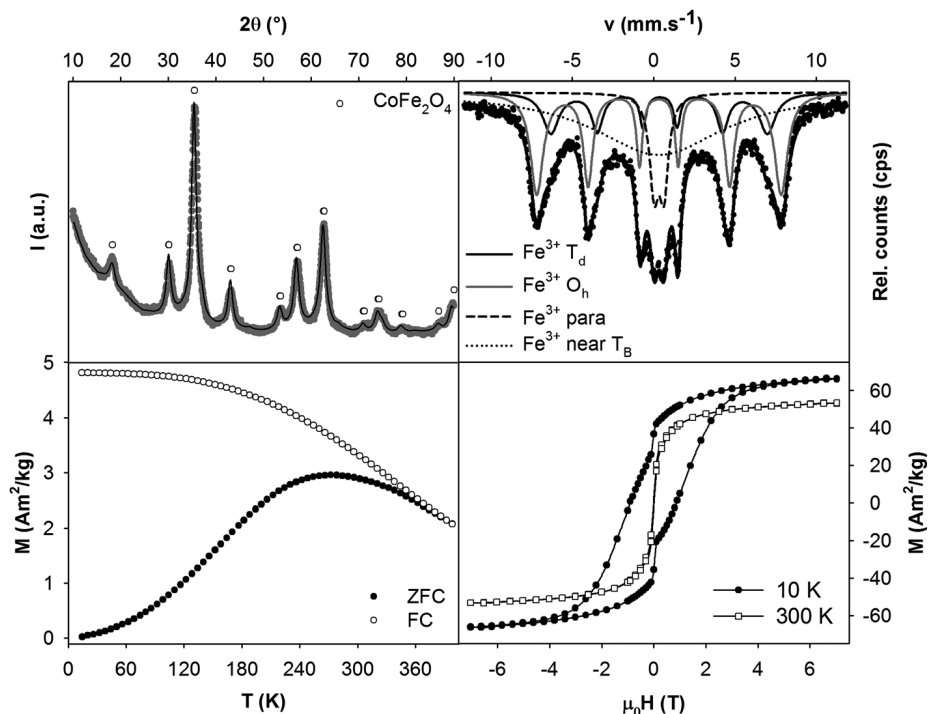


Fig. 2 (Top panel) The PXRD pattern of the Co₀ sample with the refined pattern (full black line) on the left together with the MS spectra performed at room temperature on the right. The open circles mark the Bragg reflections of the CoFe₂O₄ phase. (Bottom panel) The ZFC–FC curves at 0.01 T and the magnetization isotherms measured at selected temperatures.

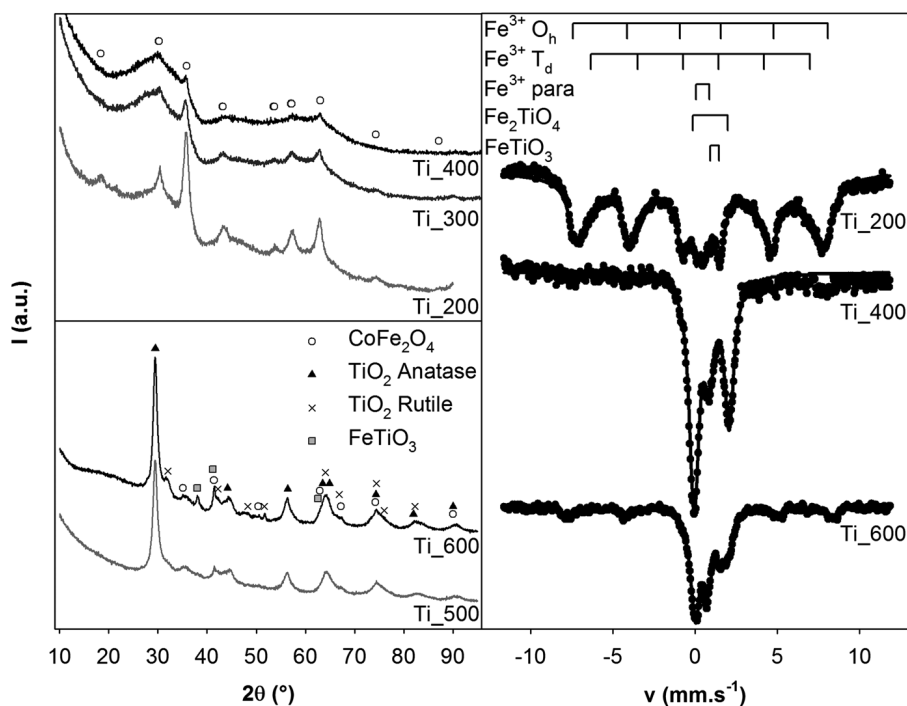


Fig. 3 The PXRD patterns of the CoFe₂O₄/TiO₂ series on the left. The MS spectra of selected samples performed at room temperature on the right.

the cubic form, partially transferring to the monoclinic form at higher temperature (700 °C). The crystalline matrix is also observed by HR-TEM (Fig. 8) for the Zr₆₀₀ sample. The

CoFe₂O₄ phase cannot be properly distinguished by the PXRD due to the overlapped reflections with the ZrO₂ phases. The MS spectra contain only the doublet with $\delta = 0.36 \text{ mm s}^{-1}$

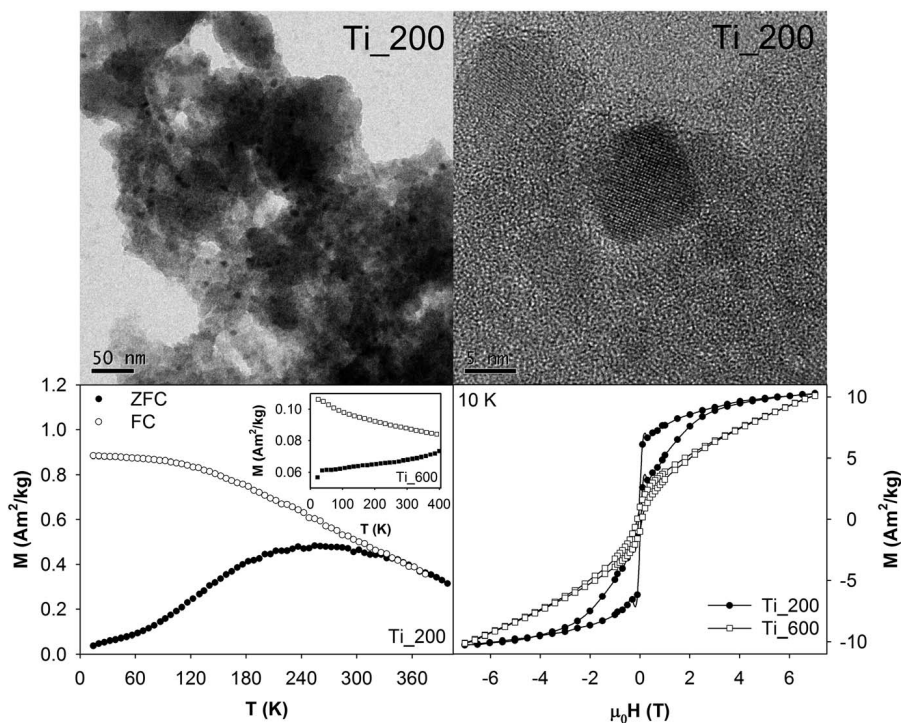


Fig. 4 (Top panel) The TEM image of the Ti_200 sample on the left with the HR-TEM image on the right. (Bottom panel) The ZFC–FC curves at 0.01 T for the Ti_200 sample and the Ti_600 sample in the inset on the left. The magnetization isotherms at 10 K for both samples on the right.

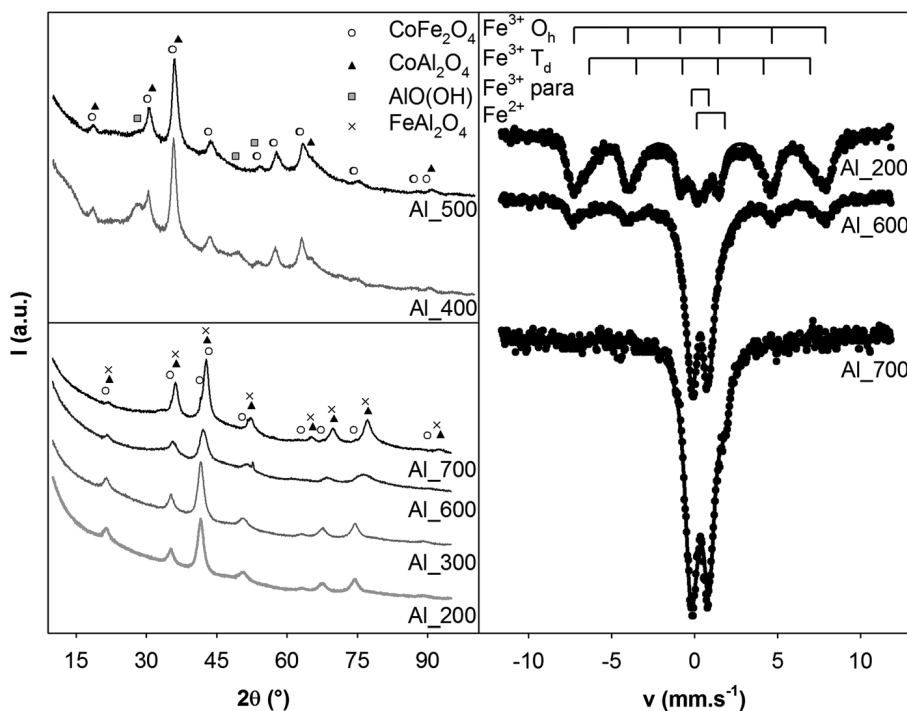


Fig. 5 The diffraction patterns of the CoFe₂O₄/Al₂O₃ series on the left. The MS spectra of the selected samples performed at room temperature on the right.

corresponding to the Fe³⁺ ions and $\Delta E_q = 1.07 \text{ mm s}^{-1}$ which is higher than for the CoFe₂O₄ phase (usually $\Delta E_q = 0.76 \text{ mm s}^{-1}$ (ref. 29)). The presence of the CoFe₂O₄ in the Zr_600 sample has

been elided by magnetic measurements, as is shown further. Therefore, the observed doublet in MS can be interpreted as the Fe³⁺ ions dispersed in crystalline matrix.

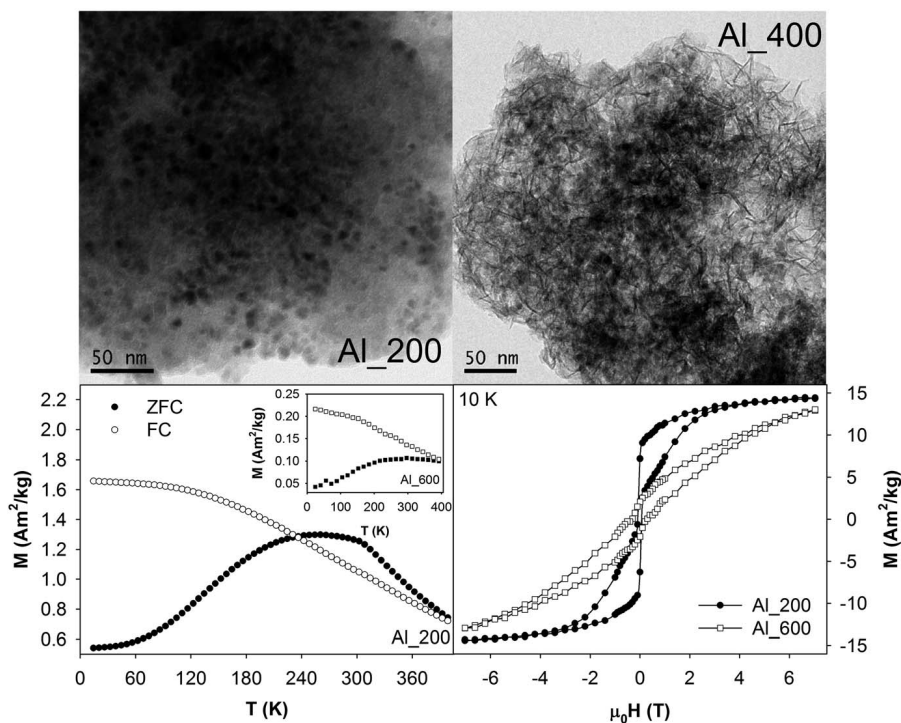


Fig. 6 (Top panel) The TEM images of the Al₂₀₀ and Al₄₀₀ samples, respectively. (Bottom panel) The ZFC–FC curves at 0.01 T for the Al₂₀₀ sample and the Al₆₀₀ sample in the inset on the left. Magnetization isotherms at 10 K for both samples on the right.

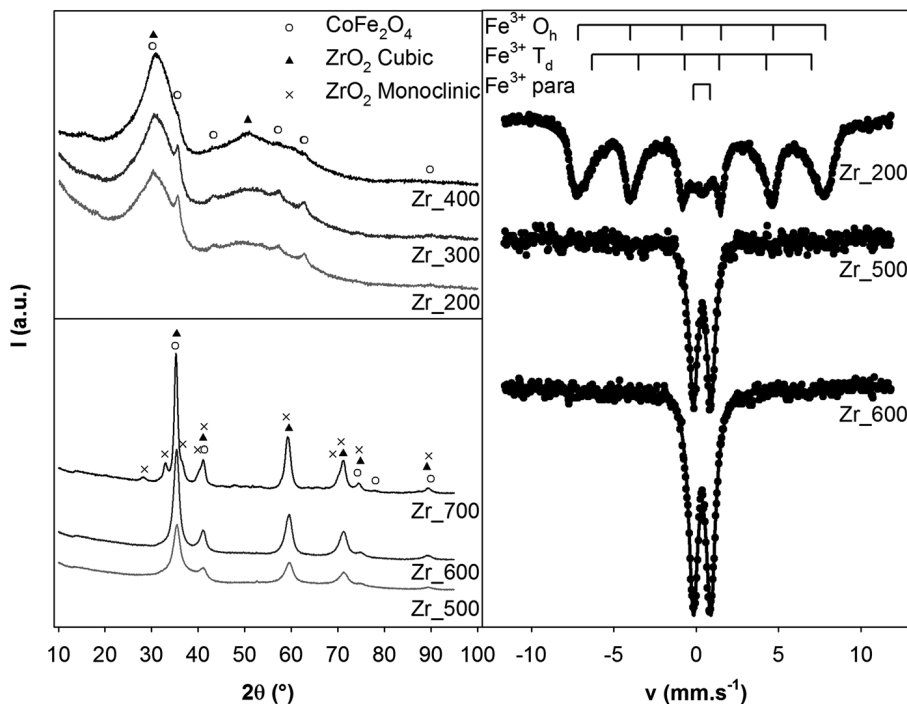


Fig. 7 The diffraction patterns of the CoFe₂O₄/ZrO₂ series on the left. The MS spectra of the selected samples performed at room temperature on the right.

3.2. Magnetic measurements

3.2.1. General remarks. The magnetic measurements were carried out in order to unambiguously confirm presence of the

CoFe₂O₄ in form of nanosized particles, through the typical high coercivity at low temperatures. The two selected samples from each series were measured, one with the amorphous

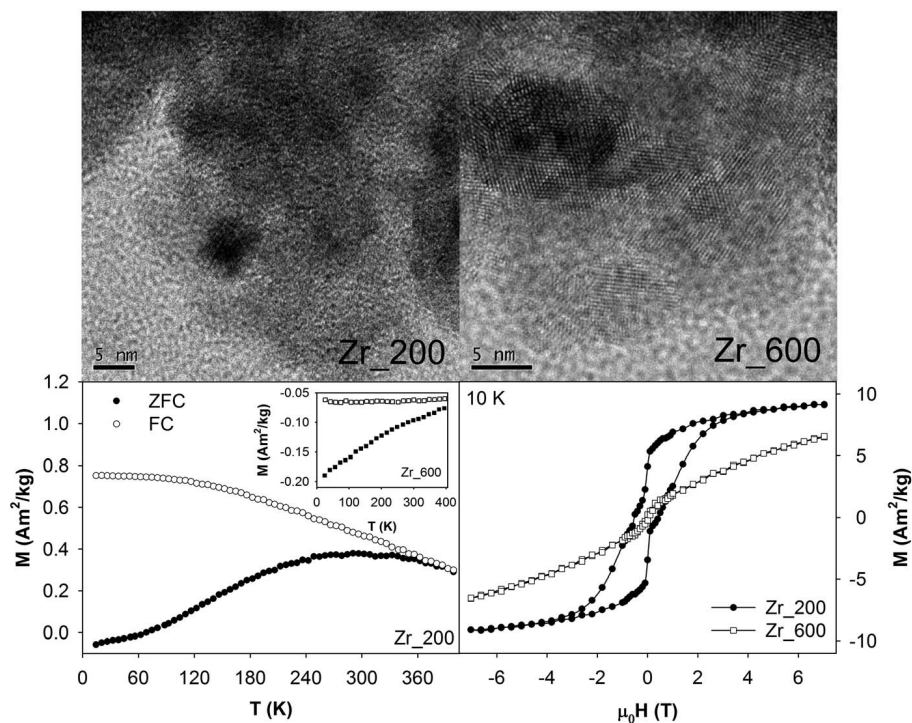


Fig. 8 (Top panel) The HR-TEM images of the Zr_200 and Zr_600 samples. (Bottom panel) The ZFC–FC curves at 0.01 T for the Zr_200 sample and the Zr_600 sample in the inset on the left. The magnetization isotherms at 10 K for both samples on the right.

matrix annealed at 200 °C, one with the crystalline matrix annealed at 600 °C. The ZFC–FC measurements were performed and character of the curves has been compared with the matrix-free sample. The necking of the magnetization isotherms that affected the determination of precise value of the coercivity, H_c^{10} is caused by the insufficient fixation of the sample. Therefore, estimation of the H_c^{10} was done by approximating the necked part by linear term. The values of saturation magnetization determined after subtraction of the paramagnetic contributions were used to determine the weight content of the CoFe_2O_4 particles in the matrices (Table 2). The resulted characteristic parameters are summarized in Table 3. The ZFC–FC curve of the Co_free sample shows the blocking temperature, T_B , around 270 K with saturation of the FC curve pointing to strong interparticle interactions.³⁰ The magnetization isotherms exhibit large H_c^{10} around 1 T typical for the CoFe_2O_4 phase (see Fig. 2 and Table 3).

Table 3 Magnetic parameters: blocking temperature, T_B ; saturation magnetization at 10 and 300 K, M_s^{10} , M_s^{300} and coercivity at 10 K, H_c^{10}

Sample	T_B (K)	M_s^{10} (A m ² kg ^{−1})	M_s^{300} (A m ² kg ^{−1})	H_c^{10} (mT)
Al_200	≈ 260	12.0	10.0	690
Al_600	≈ 295	7.0	3.4	620
Ti_200	≈ 265	9.0	7.0	720
Ti_600	>400	4.0	2.5	100
Zr_200	≈ 295	8.0	6.0	740
Zr_600	>400	1.5	0.7	50
Co_free	≈ 270	58.0	48.0	1000

3.2.2. Nanocomposites. All three samples annealed at 200 °C (Ti_200, Al_200 and Zr_200) exhibit similar ZFC–FC curves as the matrix-free sample (see Fig. 4, 6 and 8) with the nearly similar T_B pointing at the presence of the CoFe_2O_4 nanoparticles, that has been further confirmed by high coercivity at 10 K (Table 3). No coercivity is observed at 300 K, H_c^{300} suggesting the particles are in superparamagnetic regime. The weight contents of the CoFe_2O_4 in matrix calculated from M_s are in good agreement with the theoretical ones.

The ZFC–FC curves of the Zr_600 and Ti_600 samples do not match with the Co_free sample at all. The non-saturation of the FC curve of the Ti_600 sample indicates the weakening of the interparticle interactions, that can be explained by decomposition of the CoFe_2O_4 particles into smaller fragments (ions, clusters) in the matrix or by increase of the distances between the particles in the matrix or due to the phase transformation of the part of the CoFe_2O_4 particles. The mostly linear FC curve of the Zr_600 sample points at the strong interactions within the particles suggesting the formation of aggregates. The absence of the CoFe_2O_4 phase has been further confirmed by very low H_c^{10} and M_s .

On the other hand, the presence of CoFe_2O_4 has been unambiguously confirmed in the Al_600 sample by the high H_c^{10} and similar course of the ZFC–FC curve as for the Co_free sample. The unsaturation of the low temperature part of the FC curve points at the weakening of interparticle interactions that can be proved by the presence of weak magnetic phases CoAl_2O_4 and FeAl_2O_4 , detected by PXRD (see previous discussion) and also indicated by the decrease of the M_s .

4. Conclusions

We have developed a general approach, which enables preparation of nanocomposites of monodisperse nanoparticles in amorphous or crystalline oxide matrix. The proposed method was successfully applied to preparation of nanocomposites of monodisperse CoFe_2O_4 nanoparticles embedded in high-K oxide matrices – TiO_2 , Al_2O_3 and ZrO_2 , respectively. In the first step, the uniform nanoparticles were prepared by the hydrothermal synthesis and subsequently, they were incorporated into the matrices using the sol-gel method. The detailed characterization by Powder X-Ray Diffraction, electron microscopy, Mössbauer Spectroscopy and magnetic measurements confirmed presence of the CoFe_2O_4 nanoparticles without change of the particle size with the increasing annealing temperature up to the onset of crystallization of the matrices (above 400 °C). The preparation of a nanocomposite with a crystalline matrix is also possible using suitable annealing conditions. The results clearly demonstrated that nanocomposites with well-defined particles embedded in various oxide matrices can be easily obtained by the two-step preparation method. The universal principle of the route – embedding the hydrophobic nanoparticles in the matrix using the corresponding alcoxides – opens possibilities to fabricate variety of multicomponent systems, which cannot be obtained by the common methods, mainly due to absence of soluble salts, interaction of the components during synthesis or requirement of a narrow particle size distribution.

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3.1.2 Nanočástice a nanokompozity dopovaného feritu kobaltnatého

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V poslední době se do předmětu zájmu dostaly pseudoternární systémy se spinelovou strukturou založené na feritu kobaltnatém. Motivací výzkumu je optimalizace magnetických vlastností a sledování stability spinelové struktury vůči perovskitové při dopování lanthanidy, což je jedno ze zásadních témat v oblasti výzkumu katalyzátorů na bázi přechodných kovů.

Vlivu dopování lanthanem se věnují práce [85, 87]. Vzorky byly připraveny metodou sol-gel (tj. jednalo se nanokrystaly v matrici oxidu křemičitého) a mikroemulzní metodou. U vzorků získaných mikroemulzní metodou byl při dopování až do 3 molárních procent pozorován efekt zmenšení velikosti částic díky ovlivnění velikosti micel, které determinují finální velikost částice, dojde-li pouze k primární nukleaci. Magnetické vlastnosti byly dle očekávání závislé na velikosti částic, dopování lanthanem je ovlivnilo minimálně. Detailní studie pomocí Mössbauerovy spektroskopie v magnetickém poli ukázaly významný efekt sklonění povrchových spinů v dopovaných vzorcích (úhel sklonění až 40 stupňů), což bylo potvrzeno analýzou magnetizačních izoterm, které nevykazovaly saturaci až do vysokých magnetických polí.

Distribucí kationtů Co^{2+} , Ni^{2+} a Fe^{2+} ve spinelové struktuře v závislosti na stupni dopování Ni^{2+} se zabývá práce [87]. Pomocí širokého spektra metod bylo zjištěno, že kationty Ni^{2+} obsazují preferenčně tetraedrické polohy, a nárůst substituce vede dle očekávání k poklesu koercivity a saturované magnetizace. Vzhledem k velikosti nanokrystalů (nad 15 nm) bylo pozorováno, že všechny vzorky jsou za pokojové teploty v blokováném stavu.

Surface spin effects in La-doped CoFe_2O_4 nanoparticles prepared by microemulsion route

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A comparative study of pure CoFe_2O_4 nanoparticles and La-doped CoFe_2O_4 nanoparticles, prepared by microemulsion route has been performed. The samples were characterized using x-ray diffraction and transmission electron microscopy in order to obtain average particle size. The doping of small amount of La^{3+} ions (up to 3 molar %) causes significant reduction of the particle size using the identical preparation route. The samples were investigated by magnetization measurements, which revealed the coercivity values strongly dependent on particle size, but not significantly on level of La^{3+} doping. Detailed in-field Mössbauer spectroscopy studies were performed in order to determine spin canting angles and cation distribution within the spinel network. The non-negligible canting angles up to 40° in the La-doped samples were observed. The presence of the spin surface effects was also supported by magnetic measurement as the magnetization did not saturate even in considerably high magnetic fields (7 T). Moreover, significantly reduced values of the saturation magnetization were obtained. The observed features originated by the surface spin disorder in nanosized particles are explained in the frame of the core-shell model. © 2011 American Institute of Physics. [doi:10.1063/1.3642992]

I. INTRODUCTION

Magnetic nanoparticles are under intensive research within last years due to their physical properties that differ rapidly from their bulk material.^{1,2} Their unique magnetic properties are governed by their reduced size. At first, such particle reaches the so-called single-domain limit, predicted already by Kittel in 1946.³ Furthermore, in nanoparticles a non-negligible fraction of atoms lies on the surface that affects the magnetic properties of the whole particle. The surface atoms have lower coordination number and the exchange bonds are broken. If those surface effects are significant, the ideal spin structure of a nanoparticle is not valid, however, it can be well-described by the so-called core-shell model, that was firstly proposed by Coey.⁴

In the core-shell model, a nanoparticle consists of two parts: the ordered core, where all spins are aligned in direction of the easy axis, and the disordered shell, where spins are inclined at some angle to their normal direction. The distribution of this canting angle is not random but depends on the influence of the magnetic nearest neighbors of the canted spins. Therefore, the magnetization near the surface is generally lower than that inside leading to diminishing the saturation magnetization. This model could also explain the lack of the saturation of the magnetization even in high magnetic fields that was observed in small particles that exhibit significant surface effects.^{5,6}

Among the nanoparticles, spinel ferrites constitute an important class of materials. Their magnetic properties depend on magnetic interaction driven by cation occupation in the two types of the coordination polyhedra: tetrahedral and octahedral, respectively. In contrast to the bulk cobalt ferrite with inverse spinel structure, the nanosized CoFe_2O_4 (Refs. 7–10) has usually only partially inverse spinel structure, represented as $(\text{Co}_x\text{Fe}_{1-x})[\text{Co}_{1-x}\text{Fe}_{1+x}]\text{O}_4$, where x depends on temperature and method of preparation of the material.¹¹

The CoFe_2O_4 nanoparticles are mainly highly attractive due to their magnetic and dielectric properties; they exhibit large coercivity (up to 2 T at low temperatures) with moderate saturation magnetization ($80 \text{ A.m}^2.\text{kg}^{-1}$), remarkable chemical stability and mechanical hardness.^{12,13}

A promising possibility of improving the magnetic properties of CoFe_2O_4 nanoparticles is through doping by rare earth elements. It was predicted, that such a modification should affect the structure and hence the magnetic properties of the spinel, particularly enhancing the coercivity by introducing other source of the spin-orbital interaction. Only few studies of the rare-earth substituted cobalt ferrites have been presented so far, however, with contrary results.^{7,8,14,15}

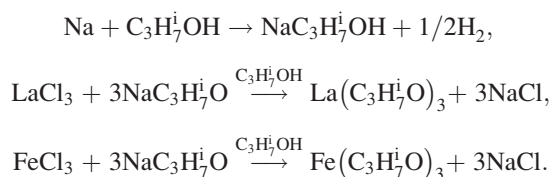
In this work, we focused on doping of the cobalt ferrite nanoparticles by La^{3+} ions with attempt to study its influence on structure (degree of inversion) and magnetic properties. Namely, the influence of the La doping on the core-shell spin structure of the nanoparticles has been investigated by in-field Mössbauer spectroscopy.

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II. EXPERIMENTAL PART

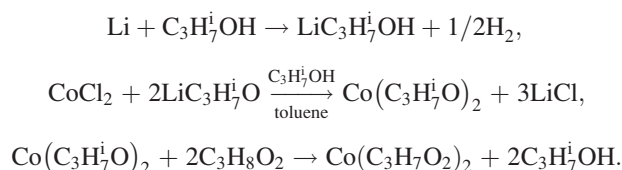
A. Preparation route

We have prepared four samples of a general chemical formula: $\text{La}_x\text{Co}_{1-x}\text{La}_y\text{Fe}_{2-y}\text{O}_4$, with $x = 0$, $y = 0$ (Co01); $x = 0.1$, $y = 0$ (La01); $x = 0.2$, $y = 0$ (La02); and $x = 0$, $y = 0.1$ (La03). The raw nanopowder was prepared through the hydrolysis of microemulsion containing alkoxides solutions by addition of water.^{16,17} The starting alkoxides solution was prepared from iron isopropoxide, lanthanum isopropoxide, and cobalt 2-methoxyethanol (although other alkoxides could also be used) in dry alcohol. Lanthanum and iron isopropoxide were obtained by reaction of sodium isopropoxide with lanthanum and iron trichloride in dry isopropanol under nitrogen atmosphere. Sodium isopropoxide was prepared from metal sodium and dry isopropanol under nitrogen by the standard procedure.¹⁸ Such a reaction must be hold under the nitrogen atmosphere, because alkoxides are very sensitive on humidity and decompose very fast on the air. The chemical processes may occur according to the following reactions:



Sodium chloride is only little soluble in isopropanol, therefore, sodium chloride could be removed from the solution. However, small amount of sodium chloride always stays in the solution even after several washes with isopropanol. Because this quantity is very small, the solution can be used as a precursor for the preparation of nanoparticles.

Because it is necessary to have a soluble form of the cobalt, the cobalt 2-methoxyethanol was prepared by following procedure: cobalt isopropoxide was obtained by reaction of lithium isopropoxide with cobalt dichloride in dry isopropanol under nitrogen atmosphere, and the final product cobalt 2-methoxyethanol was obtained by reaction of cobalt isopropoxide with 2-methoxyethanol under the same conditions as previous reactions. Lithium isopropoxide was prepared from metal lithium and dry isopropanol under nitrogen atmosphere by standard procedure.¹⁹ The chemical processes may occur according to the following reactions:



Lithium chloride can be simply removed from the solution because it is well soluble in isopropanol in contrast to the cobalt isopropoxide.

Stoichiometric mixture of alkoxide solutions was drop wise added to prepared microemulsion (*Lutensol* ON 110–10.06 wt.%, cyclohexane—1.36 wt. %, 1-octanol—5.94 wt. %, and distilled water—2.64 wt. %). After stirring for 30 minutes under nitrogen atmosphere, the alkoxides were

hydrolyzed by addition of distilled water. Precipitated raw powder was decanted by ethanol for several times, dried at room temperature and then heated up to 100 °C. Finally, the samples were heated at 400 °C for 1 h in static air atmosphere.

The list of prepared samples is summarized in Table I.

B. Sample characterization - X-ray diffraction and transmission electron microscopy

The samples were then characterized by powder x-ray diffraction (PXRD) using the Bruker diffractometer AXS GmbH using the fixed-slit geometry. The Cu-K α beam with monochromator was used. The PXRD patterns were collected in the 2Θ range: 10°–100° with a step of 0.04° for all samples. The cubic lattice parameter, a and particle size (by means of the mean size of the coherently scattering domain), d were obtained by the Rietveld refinement implemented in the Fullprof program.^{20–22} The particle appearance was observed by transmission electron microscopy (TEM) using PHILIPS EM 201 80 kV device with tungsten cathode.

C. Mössbauer spectroscopy

The Mössbauer spectra measurement was done in the transmission mode with ^{57}Co diffused into a Rh matrix as the source moving with constant acceleration. The spectrometer (Wissel, Germany) was calibrated by means of a standard α -Fe foil and the isomer shift was expressed with respect to this standard at 293 K. In order to determine degree of inversion in the spinel structure and the spin canting angle, respectively, the samples were also measured using cryostat (Janis Research) at the temperatures of 4.2 K equipped with superconducting magnet of 6 T. The magnetic field was applied perpendicular to the direction of γ -rays (Fig. 1). The fitting of the spectra was performed with the help of the NORMOS program.

In general, the spin canting angle, α requires measurement of the spectrum without and with the applied field, yielding the B_{hf} and the B_{eff} , respectively.²³ The fitting procedure in the case of spinels can be then performed as follows: At first, due to the well-resolved sextets, the in-field spectrum is fitted and the FWHM, area of peaks, A , isomer shift, δ , quadrupole splitting, Δ , and effective field, B_{eff} are obtained. Except the B_{eff} , other parameters are not affected by the external magnetic field; therefore their values can be then used for the fitting of the spectra without applied field to obtain the B_{hf} . Finally, the spin canting angle, α can be computed as follows (see Fig. 1):

$$\cos \alpha = \frac{B_{eff}^2 - B_{app}^2 - B_{hf}^2}{2B_{app}B_{hf}}. \quad (1)$$

TABLE I. Summary of the prepared samples.

Chemical composition	Label
CoFe_2O_4	Co01
$\text{La}_{0.1}\text{Co}_{0.9}\text{Fe}_2\text{O}_4$	La01
$\text{La}_{0.2}\text{Co}_{0.8}\text{Fe}_2\text{O}_4$	La02
$\text{CoLa}_{0.1}\text{Fe}_{1.9}\text{O}_4$	La03

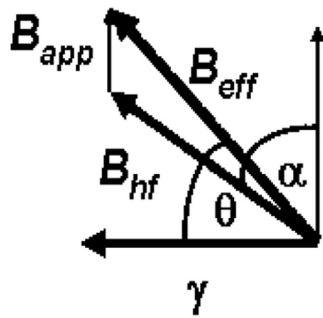


FIG. 1. Diagram of the experimental arrangement for measurements of the in-field Mössbauer spectroscopy. The spin canting angle, α is the angle between the applied field, B_{app} and the hyperfine field, B_{hf} .

It is obvious that no canting angles would correspond to values 0° or 180° . The error of fitting is about 10° .

D. Magnetic measurements

The magnetic measurements were carried out using the SQUID magnetometer (MPMS7XL, Quantum Design). The zero field-cooled (ZFC) and field-cooled (FC) curves were recorded as follows: To obtain the ZFC curve the sample was cooled down to 10 K, then the magnetic field of 0.01 T was applied, and the temperature dependence of the magnetization was measured up to 400 K. Afterwards, the sample was cooled down to 10 K in the applied field and the FC curve was obtained. The hysteresis loops were recorded up to 7 T at selected temperatures, and the maximum magnetization at 7 T, M_{7T} , remanent magnetization, M_r and coercivity, H_c , respectively, were determined for all samples.

III. RESULTS AND DISCUSSION

A. Basic characterization of the samples

The PXRD measurements confirmed formation of the spinel structure. All samples were found out to be single-phase. The La01 and La02 samples showed very similar PXRD patterns, as is displayed in Fig. 2(b) for the La03 sample. The significant broadening of the lines is observed in comparison to the Co01 suggesting smaller particles. There is no detectable trace of other impurities. The resulting lattice parameter, a and average particle size, d obtained from Rietveld refinement are presented in Table IV. The introduction of small amount of the La^{3+} ions (the La01 and La02 samples) did not give a detectable change in lattice constant, which are in good agreement with those obtained by other workers.²⁴ The La03 sample, where the La^{3+} ions were doped instead of the Fe^{3+} ions, shows significant increase of the lattice parameter, a . As was discussed by other workers the introducing of the La^{3+} ions in spinel lattice could lead to cation redistribution that affects the value of lattice parameters.⁸ Therefore, the cation distribution within spinel network in these two samples should be different as was proved by the Mössbauer spectroscopy.

TEM observations shown in the Fig. 2 confirmed the smaller particle size of the La-doped samples (La01, La02, La03) in comparison to the La-free sample (Co01). In case

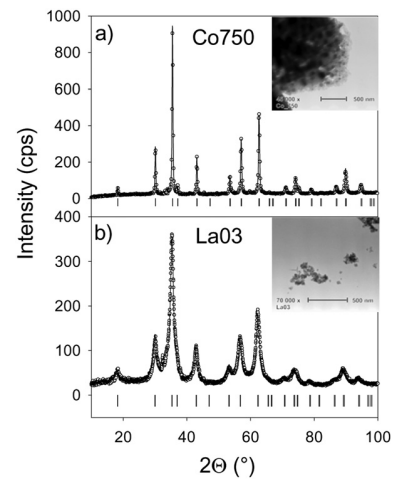


FIG. 2. PXRD patterns for the (a) Co01 and (b) La03 samples, respectively. The experimental data are depicted by the open circles, the solid line represents the fit according to the Rietveld analysis, and the vertical lines mark the corresponding Bragg positions. The insets show the TEM observation of the samples.

of the La-doped samples, the particle size exhibits considerable distribution; it ranges from 5 to 25 nm. The micrograph of the Co01 sample shows presence of small particles and also its aggregates, the typical size ranges from 20 to 50 nm in diameter.

B. Mössbauer spectroscopy

Room temperature (RT)

The Mössbauer spectrum (shown in Fig. 3(a)) of the Co01 sample consists of a sextet indicating the blocked state of the nanoparticles already at the RT.

On the other hand, the spectra of the La-doped particles (shown in Figs. 3(b)–3(d)) consist of a broad sextet with asymmetric peaks, a quadrupole doublet, and a broad singlet, respectively. In comparison to the undoped sample, the lines of the sextet are significantly broader and the obtained hyperfine fields are lower due to smaller particle size and the presence of the La^{3+} ions. As shown by the analysis of the Mössbauer spectra, the La^{3+} ions are preferably distributed within the octahedral sites due to their large ionic radii.¹⁵ The presence of the La^{3+} ions within the spinel network gives rise to variation in coordination surroundings of the octahedral and tetrahedral sites; which leads to an enhanced distribution of the hyperfine fields resulting in broadening of the spectral lines. A similar broadening of the lines upon Nd doping was observed by Zhao.²⁵ The distribution of the hyperfine fields was fitted using a single broad sextet.

The observed doublet demonstrates that part of the sample is in superparamagnetic state, and the singlet is assigned to the part of the sample that is near its blocking temperature.

The linewidth of the La02-spectrum is broader in comparison to the La01-spectrum. It can be understood as follows. Introducing twice higher amount of La^{3+} (La02) causes the higher distribution of the hyperfine fields; therefore the line broadening is more pronounced.

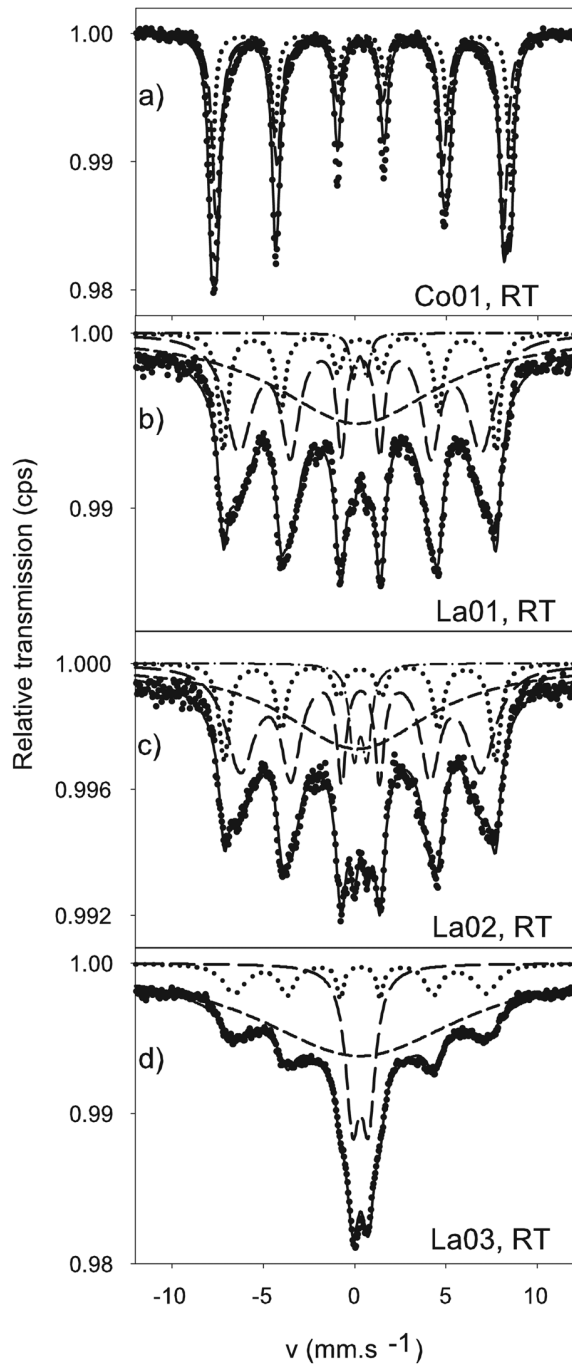


FIG. 3. The room temperature Mössbauer spectrum of the (a) Co01, (b) La01, (c) La02, (d) La03 samples. The dashed lines correspond to the sub-spectra 1, the dotted lines correspond to the sub-spectra 2, the dot-and-dash lines correspond to the sub-spectra 3 (doublet).

The La03 sample shows a different tendency, majority of the sample is in superparamagnetic state at the RT. This is consistent with magnetic measurement (shown further), where the mean blocking temperature for the La03 sample is below the room temperature.

In-field Mössbauer spectroscopy (spin canting and degree of inversion)

The in-field Mössbauer spectroscopy gives information of the spatial orientation of a magnetic sublattice with

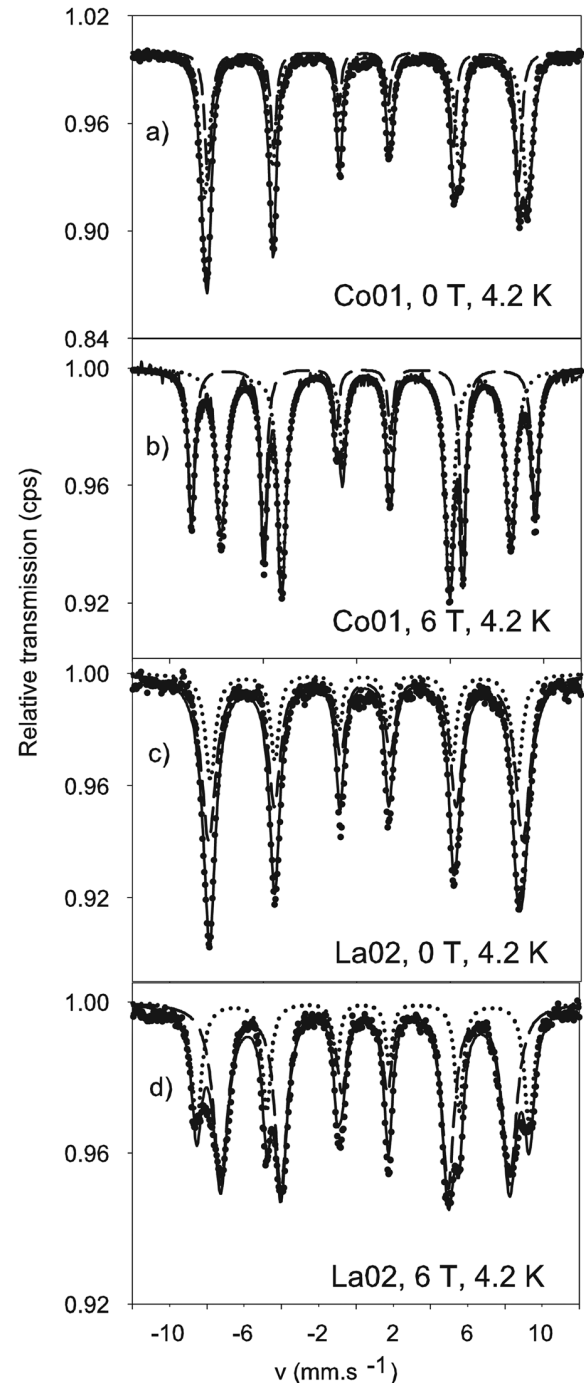


FIG. 4. Comparison of the Mössbauer spectra of the Co01 and La02 sample, respectively, measured at 4.2 K (a) in zero magnetic field and (b) with external applied field of 6 T. The dashed lines correspond to the sub-spectra 1, the dotted lines correspond to the sub-spectra 2.

respect to its net magnetization. Moreover, as the applied field splits the overlapping sextets the in-field spectra can be used for determination of the so-called degree of inversion of the spinel structure. The in-field Mössbauer spectra are shown in Figs. 4(a)–4(b) for the Co01 sample and in Figs. 4(c)–4(d) for the La02 sample, respectively.

The undoped Co01 sample shows well-resolved sextets, as the applied field adds to the magnetic hyperfine field at the tetrahedral sites and subtracts from the hyperfine field at the octahedral sites.²⁶

TABLE II. In field Mössbauer parameters.

	Isomer shift δ (mm.s ⁻¹)	Quadrupole shift 2ϵ (mm.s ⁻¹)	Eff. field B_{eff} (T)	Hyp. field B_{Hf} (T)	FWHM (mm.s ⁻¹)	Rel. area (%)	Interpr.
Co01							
Subsp. 1	0.35	0.00	57.1	51.5	0.31	36.7	Fe ³⁺ T_d
Subsp. 2	0.49	0.01	48.1	53.7	0.41	63.3	Fe ³⁺ O_h
La01							
Subsp. 1	0.38	0.00	55.8	51.2	0.37	30.6	Fe ³⁺ T_d
Subsp. 2	0.48	0.02	48.0	52.3	0.63	69.4	Fe ³⁺ O_h
La02							
Subsp. 1	0.38	0.00	55.5	50.9	0.36	31.1	Fe ³⁺ T_d
Subsp. 2	0.48	0.02	48.2	52.2	0.60	68.9	Fe ³⁺ O_h
La03							
Subsp. 1	0.37	0.00	56.2	51.3	0.37	25.6	Fe ³⁺ T_d
Subsp. 2	0.49	0.05	47.2	51.4	0.864	74.7	Fe ³⁺ O_h

In the case of the doped samples, the splitting of the sextets is not so significant that can be attributed to the broadening of the spectral lines due to the presence of the La³⁺ ions, as was discussed in the previous subsection. Therefore, the distribution of the effective and the hyperfine field, respectively, was included into the fit and the resulting distribution of the canting angles has been calculated. The small saturation (the higher intensity of the inner lines (3, 4)) effect was found out in the measurements at 4 K. This corresponds to the fact, that the Mössbauer-Lamb coefficient is considerably higher at 4 K than at room temperature. Other effects that affect this ratio are polarization effects and thickness of the sample. Evaluation of these effects is rather complicated. Because the hyperfine and effective fields are determined by the positions of the peaks and not by the intensities of the saturated lines, the saturation effects do not affect these necessary parameters for evaluation of the spin canting angles. The obtained Mössbauer spectra parameters are summarized in Table II.

The resulting spin canting angles and their distributions and degree of inversion (composition) of the samples are summarized in Table III. The α_1 , α_2 denote the canting angle of the Fe³⁺ magnetic moments in the tetrahedral (subsp. 1) and octahedral sites (subsp. 2), respectively. The degree of inversion was determined from the area of the split sextets, the rounded brackets denote the tetrahedral sites and the squared brackets denote the octahedral sites, respectively.

At a first view it is obvious that the spin canting in the La-doped sample is much higher than in the undoped CoFe₂O₄ nanocrystals. This can be caused by two reasons: At first, the La-doped samples exhibit 4–5 times smaller particle size than the undoped sample, therefore the surface

TABLE III. Spin canting angles, α_1 (tetrahedral sites), α_2 (octahedral sites), and degree of inversion of the samples.

Sample	α_1 (°)	α_2 (°)	Degree of inversion
Co01	21° ± 9	162° ± 9	(Co _{0.27} Fe _{0.73})[Co _{0.73} Fe _{1.27}]O ₄
La01	42° ± 11	136° ± 12	(Co _{0.39} Fe _{0.61})[Co _{0.51} Fe _{1.39} La _{0.1}]O ₄
La02	41° ± 13	136° ± 13	(Co _{0.38} Fe _{0.62})[Co _{0.42} Fe _{1.38} La _{0.2}]O ₄
La03	39° ± 14	138° ± 15	(Co _{0.51} Fe _{0.49})[Co _{0.49} Fe _{1.41} La _{0.1}]O ₄

effects are expected to be more significant. Moreover, introducing the La³⁺ ions in the spinel lattice could cause a spin frustration that leads to higher spin canting.

The resulting cation distribution confirmed that the structure is not completely inversed as was observed before.^{11,26} In the Co01 sample about one quarter of Co²⁺ ions occupy the tetrahedral sites. The degree of inversion is higher in the La-doped samples that is in good agreement with results published by group of Tahar.⁸ They observed that the introducing of the La³⁺ ions into the spinel lattice causes transferring of the Co²⁺ ions from the tetrahedral to the octahedral sites and opposite transferring of the Fe³⁺ ions to relax the induced lattice strain.

C. Magnetic measurements - ZFC-FC and hysteresis loops

The results from magnetic measurements well support the results of the Mössbauer spectroscopy. The measurements of the ZFC and FC magnetization revealed that the blocking temperature for the Co01 sample is well above 400 K, as there is no significant maximum of the ZFC curve and also the lack of a bifurcation point of the ZFC and the FC curve. In comparison to the Co01 sample, the La-doped samples show ZFC-FC curves typical for a superparamagnetic system with size distribution and interparticle interaction² (see Fig. 5). The La-doped samples show two broad maxima over a large temperature range indicating two significant fractions of size in the samples. The broader maxima of the ZFC curve was used to estimate to the T_B that is below 400 K. However the ZFC and FC curves do not coincide up to

TABLE IV. Summary of the particle parameters. Particle diameter from PXRD d , blocking temperature determined from the bifurcation point of the ZFC-FC (T_B), coercivity (H_c), magnetization at 7 T (M_{7T}), and remanence (M_r) at 10 K.

Sample	a (Å)	d (nm)	T_B (K)	H_c (T)	M_{7T} (A.m ² .kg ⁻¹)	M_r (A.m ² .kg ⁻¹)
Co01	8.37(7)	26	>400	0.73	85.2	60.1
La01	8.38(0)	4.2	370	0.90	60.7	31.2
La02	8.37(7)	4.9	380	1.03	53.7	26.3
La03	8.42(9)	5.7	250	0.18	62.1	23.4

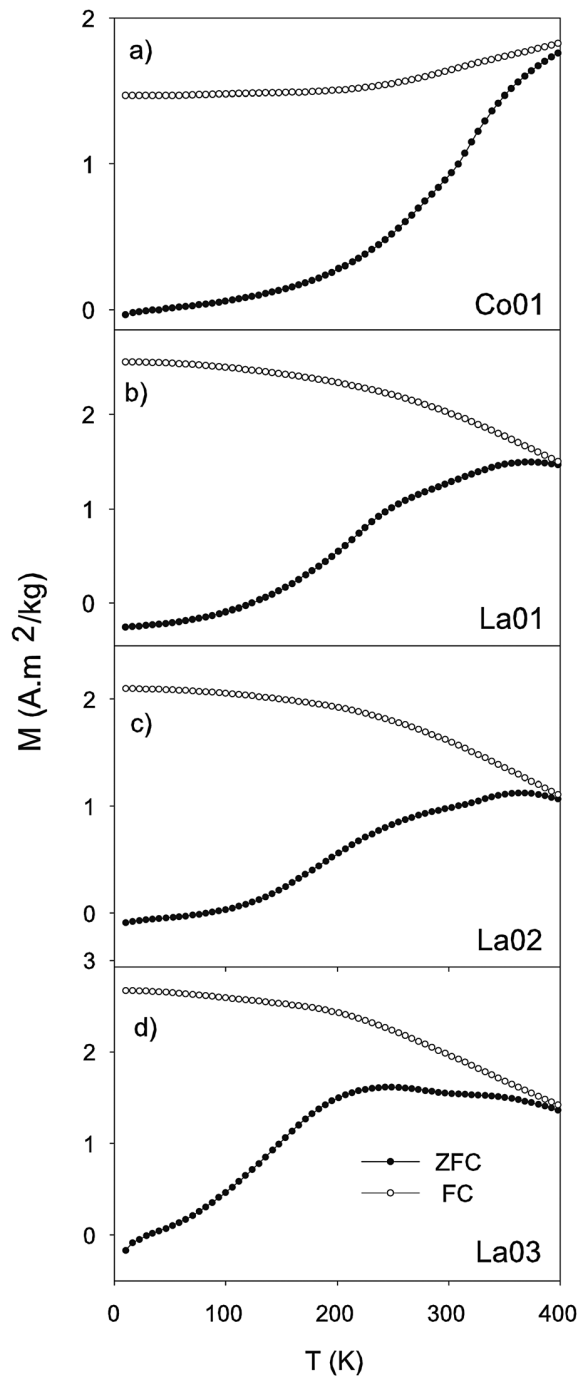


FIG. 5. Temperature dependence of ZFC-FC magnetization of the (a) Co01, (b) La01, (c) La02, and (d) La03 samples.

400 K, signaling that the irreversibility temperature, T_{irr} (the point where the ZFC curve departs from the FC curve) is above 400 K. The differences of the T_B and T_{irr} values indicate the particle size distribution and the presence of inter-particle interactions.²

The La01 and La02 samples have approximately the same particle size; therefore, the values of their blocking temperatures are comparable. With increasing amount of La^{3+} ions in CoFe_2O_4 the value of the blocking temperature remains more or less intact, taking into account the estimation error of ± 15 K. On the other hand, the T_B is signif-

cantly lower for the La03 sample where the La^{3+} ion was doped instead of Fe^{3+} ions, and the sample consists of larger particles. Also the difference of the T_B and T_{irr} is quite higher indicating larger particle size distribution. The lower blocking temperature in the La-doped samples in comparison to the undoped CoFe_2O_4 is attributed mostly to the reduced particle size.

The value of the coercivity of the Co01 sample is significantly lower than expected for the cobalt ferrite nanoparticles of comparable size.^{12,13} The significant decrease of the

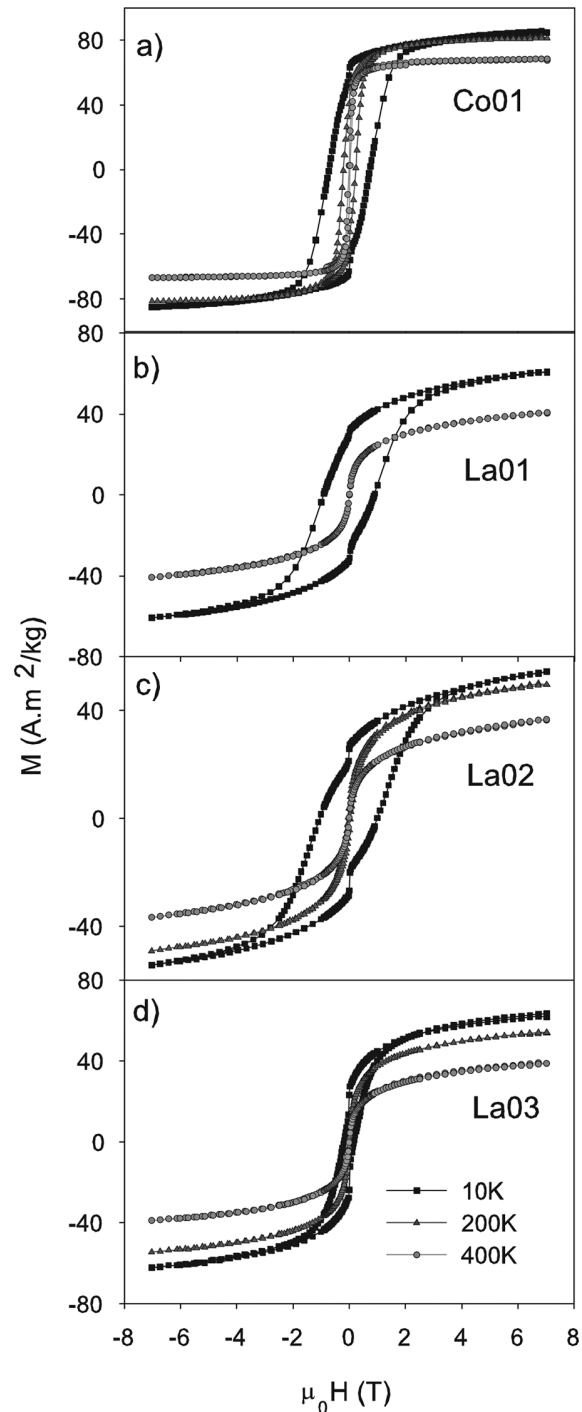


FIG. 6. Hysteresis loops of the (a) Co01, (b) La01, (c) La02, and (d) La03 samples measured at different temperatures.

coercivity in cobalt ferrite nanoparticles prepared by microemulsion method in comparison to the same-sized nanoparticles, prepared by the sol-gel method was also recently observed by other authors.²⁷ At first sight this might be surprising because the sol-gel samples encapsulated in silica matrix should exhibit lower interparticle interactions that should lead to the lower coercivity. However, the samples prepared by sol-gel method exhibit usually lower crystallinity resulting in large number of surface defects, that enhance the channels of the dipolar interactions. This all features enhance the coercivity of the sol-gel samples comparing to the samples prepared by the microemulsion route.

The smaller particle size in the La-doped samples exhibit larger coercivity at 10 K that is of the same order as those reported by Tahar in nanoparticles prepared by the polyol method.^{7,8} This enhancement can be explained by presence of the non-negligible surface effects that leads to increase of the surface anisotropy constant. The really small coercivity value of the LaO3 sample (0.18 T) in comparison to the other La-doped samples with nearly same particle size is very surprising and further experiments are needed to explain this effect.

The values of the magnetization at 7 T for the CoO1 sample reach the expected values around 80 A.m².kg⁻¹ at 10 K¹³. However, only the undoped sample (CoO1) exhibits saturation of magnetization clearly. For the La-doped samples, the magnetizations at 7 T are slightly lower and do not show saturation even in the applied field of 7 T (see Fig. 6). These results are consistent with the conclusions from Mössbauer spectroscopy as the La-doped samples exhibit non-negligible surface effects.⁴

IV. CONCLUSIONS

In summary, we have prepared the CoFe₂O₄ nanoparticles by the microemulsion route with different level of La doping instead of Co or Fe. It was observed that the La-doping affects the particle size; the doped particles are typically 5 nm in diameter, while the undoped CoFe₂O₄ nanoparticles show 26 nm even using the identical preparation procedure. The significant surface effects in the La-doped samples were confirmed by several independent measurements. First, the significant spin canting angles of the Fe³⁺ moments obtained from Mössbauer spectroscopy were observed. Second, the reduced values of magnetization at 7 T were obtained. Third, no saturation effect of the magnetization even in field of 7 T was detected. These results can be satisfactorily interpreted by the core-shell spin structure of our particles. The expected changes in magnetic properties upon La-doping were not straightforward. The particle size is much different when introducing La³⁺; therefore, the obtained magnetization data are not easily comparable. The important observation is the dramatic reduction of the coercivity upon doping of La³⁺ instead of Fe³⁺ (~0.2 T) in con-

trast to the La³⁺ doping instead of Co²⁺ (~1 T, comparable to the undoped sample).

To explain this effect, x-ray magnetic circular dichroism experiment has been scheduled to resolve element-specific contributions to the magnetic anisotropy.

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Correlation of crystal structure and magnetic properties of $\text{Co}_{(1-x)}\text{Ni}_x\text{Fe}_2\text{O}_4/\text{SiO}_2$ nanocomposites

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ABSTRACT

The $\text{Co}_{(1-x)}\text{Ni}_x\text{Fe}_2\text{O}_4/\text{SiO}_2$ ($x=0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) nanocomposites were prepared using the sol–gel method and characterized by Powder X-ray Diffraction (PXRD), Energy Dispersive X-ray Spectroscopy (EDX) and magnetic measurements. Moreover, Mössbauer spectroscopy (performed at room temperature and at 4.2 K with applied field 6 T) was performed to determine the cation distribution within the spinel network. The PXRD measurements confirmed the presence of the spinel phase in all samples. The particle diameters, obtained from the PXRD, were found out to vary between 15 and 24 nm. The lattice parameters decrease linearly with increasing content of the Ni^{2+} ions. The ZFC (zero field cooled) and FC (field cooled) measurements of the magnetization showed that the blocking temperature is well above the room temperature for all samples. Both the coercivity and the saturation magnetization decrease linearly with increasing content of the Ni^{2+} ions. The room temperature Mössbauer spectra exhibit a sextet with asymmetric lines indicating a different crystal environment for the Fe^{3+} ions, accommodated in the tetrahedral and octahedral sites. By application of the external magnetic field at 4.2 K, these overlapped sextets split up allowing determination of the ratio of the $\text{Fe}^{3+}(\text{O}_h)/\text{Fe}^{3+}(\text{T}_d)$ that exhibited slight decrease with increasing Ni content. The obtained results are discussed considering influence of the Ni doping.

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1. Introduction

The spinel ferrite oxide nanoparticles (MFe_2O_4 , where M represents a bivalent metal) have been intensively studied in recent years due to wide range of possible application, such as in magnetic recording, gas sensors, biomedicine, and catalysis [1–5]. Moreover, their magnetic properties can be tuned by variation of the M-cation and its distribution within the spinel network. The structure of the spinels can be described as the cubic close-packed arrangement of oxygen atoms, which create two different sites for the cations, the tetrahedral (A-sites) and octahedral (B-sites), respectively. Their magnetic properties are driven by the exchange interaction within (A–A, B–B) and between (A–B) these two sites, respectively. Because the ferromagnetic interactions within the same sites (A–A, B–B) are much weaker than strong antiferromagnetic interaction between the A–B sites and there are twice as many B-sites as the A-sites, the spinel ferrites usually display ferrimagnetic behavior [6].

Due to the diversity of applications, specific requirements on the magnetic properties are imposed, namely on the characteristic

parameters like the blocking temperature, coercivity and saturation magnetization. For instance, the blocking temperature above the room temperature and high coercivity are required for magnetic recording. In contrary, the low coercivity is desired in transformers and fast switchable memories.

Generally, magnetic properties of spinel nanoparticles are mostly affected by the size and shape. Even for the same size of the nanoparticles, a smooth variation of their magnetic properties can be achieved by either the substitution of various type of cations and/or their distribution within the spinel structure, e.g. by combining a hard (e.g. CoFe_2O_4) and a soft magnetic materials (e.g. NiFe_2O_4), respectively. While the CoFe_2O_4 is in potential interest due to large coercivity (up to 2 T at low temperatures) and moderate saturation magnetization ($80 \text{ A m}^2 \text{ kg}^{-1}$) [7,8], the NiFe_2O_4 is a soft magnetic material with low coercivity (tenths to hundredths of mT) and saturation magnetization ($55 \text{ A m}^2 \text{ kg}^{-1}$) [9]. Both materials are well known to have only partially inverse spinel structure, represented as $(\text{M}_y\text{Fe}_{1-y})[\text{M}_{1-y}\text{Fe}_{1+y}]\text{O}_4$, where y is the degree of inversion that depends on the temperature and the method of preparation [7]. Moreover, the nanosized spinel ferrites can be prepared in various forms; nanoparticles [10,11], nanocomposites [12] or ferrofluids [13].

In this study, we have focused on substitution of the CoFe_2O_4 nanoparticles embedded in an amorphous non-magnetic silica (SiO_2) matrix by Ni^{2+} ions with attempt to study the influence

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of the substitution on the crystal structure and the magnetic properties. Series of $\text{Co}_{(1-x)}\text{Ni}_x\text{Fe}_2\text{O}_4/\text{SiO}_2$ nanocomposites with $x=0.0, 0.2, 0.4, 0.6, 0.8, 1.0$ was prepared using a modified sol–gel method. The concentration of the nanoparticles in the matrix is kept constant through the whole series of the samples. Since we are dealing with nanoparticles embedded in the SiO_2 matrix, we address the samples as nanocomposites. Other aim of our study is to obtain the degree of inversion, y of the substituted samples that dominantly affects the magnetic properties. Usage of the in-field Mössbauer spectroscopy at low temperature enables much more precise evaluation of y than the room temperature Mössbauer spectroscopy, used by other authors [14].

2. Experimental details

2.1. Preparation route

The conventional sol–gel method using TEOS (tetraethoxysilane), HNO_3 as an acid catalyst, formamide as a modifier, and methanol as a solvent was used to prepare the $\text{Co}_{(1-x)}\text{Ni}_x\text{Fe}_2\text{O}_4/\text{SiO}_2$ nanocomposites [12,15]. The sol was prepared by mixing the stoichiometric amount of the nitrates ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in methanol. The 15 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was used to prepare all samples within the series. The started molar concentrations of 7.5 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used for the unsubstituted CoFe_2O_4 sample. With increasing $\text{Ni}^{2+}/\text{Co}^{2+}$ ratio ($x=0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) the molar concentration of the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ decreases with a step of 1.5 mmol and the molar concentration of the $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ increases with a step of 1.5 mmol. The Fe/Si ratio was kept at 1/5 for all samples within the series. The gelation time was 24 h at 40 °C and the samples were left for 48 h for ageing. Afterwards, the samples were progressively dried at 40 °C for 2 days in the flowing N_2 -atmosphere. After drying, they were pre-heated first at 300 °C under vacuum and then annealed at 900 °C under normal atmosphere for two hours.

2.2. Structure characterization

The samples were characterized by Powder X-ray Diffraction (PXRD) using the Bruker diffractometer AXS GmbH with the fixed-slit geometry. The Cu-K_α beam with monochromator was used. The PXRD patterns were collected in the 2θ range: 10–100° with a step of 0.04° for all samples. The particle diameters (mean size of the coherently diffracting domain) and lattice parameters were obtained using the Rietveld refinement implemented within the FullProf program [16,17]. The instrumental function of the diffractometer was obtained by measuring the calibration standard, LaB_6 . The samples were also studied by the Energy Dispersive X-ray Spectroscopy (EDX) analysis using scanning electron microscope MIRA by Tescan with the accelerating potential of 15 kV.

The Mössbauer spectra measurement was done in the transmission mode with ^{57}Co diffused into a Rh matrix as the source moving with constant acceleration. The spectrometer (Wissel, Germany) was calibrated by standard $\alpha\text{-Fe}$ foil and the isomer shift is related to this standard at 293 K. The samples were also measured at 4.2 K using cryostat (Janis Research) equipped with superconducting magnet of the maximum field strength of 6 T that was applied in the perpendicular direction to the direction of γ -rays. The resulting parameters were determined using the NORMOS program.

2.3. Magnetic measurement

The magnetic measurements were carried out using the SQUID magnetometer (MPMS7XL, Quantum Design). The zero field-cooled

(ZFC) and field-cooled (FC) curves were recorded as follows: at first, the sample was cooled down to 10 K, then the magnetic field of 0.01 T was applied and the temperature dependence of the magnetization was measured up to 400 K (ZFC curve). Afterwards, the sample was cooled down to 10 K in the applied field and the FC curve was obtained. The magnetization isotherms (field dependence of the magnetization) were measured in the range of ± 7 T, at different temperatures.

3. Results and discussion

3.1. Sample characterization—PXRD, EDX

The PXRD confirmed the spinel structure of all samples, no detectable amount of other phases was observed. The presence of the amorphous silica matrix is manifested by the broad peak around 25° with nearly negligible intensity with respect to the

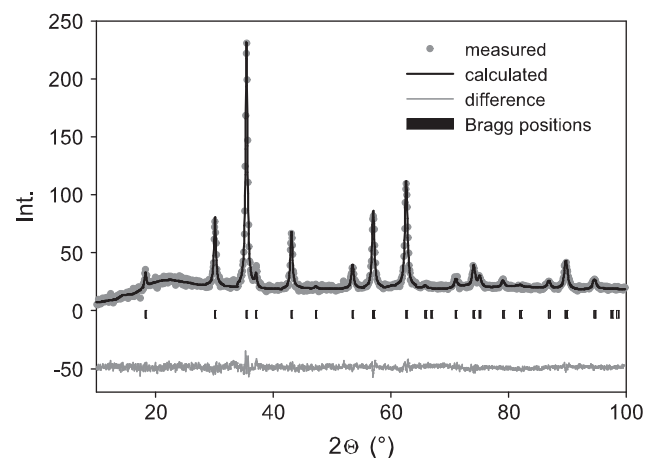


Fig. 1. The PXRD patterns for the CoFe_2O_4 sample. The experimental data are depicted by the open circles, the solid line represents the fit according to the Rietveld refinement and the vertical lines mark the corresponding Bragg positions.

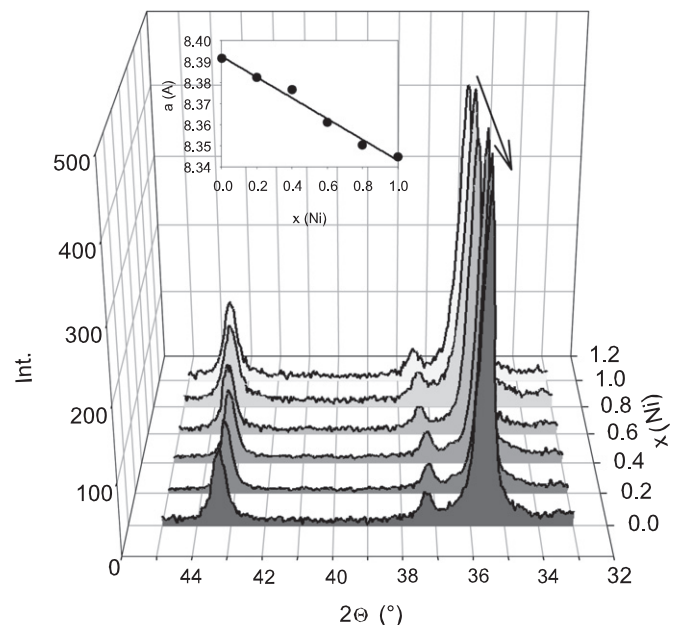


Fig. 2. The plot of the peak (PXRD) with the highest intensity for all samples. The arrow indicates the shift of the position of this peak indicating the changes of the lattice parameters. In the inset, the variation of the lattice parameter, a , with the Ni^{2+} concentration, x is shown.

intensities of the diffraction patterns. The diffraction pattern together with the fit of the CoFe_2O_4 sample is depicted in Fig. 1. The patterns of all samples exhibit a slight shift of the positions of the Bragg peaks (Fig. 2) indicating the change of the lattice parameter, a (Table 1). The lattice parameters decrease linearly with increasing concentration of Ni^{2+} ions (inset of Fig. 2) that can be well explained by the smaller ionic radius of the Ni^{2+} ions in the octahedral sites in comparison to the Co^{2+} ions ($r(\text{Co}^{2+})=0.745 \text{ \AA}$, $r(\text{Ni}^{2+})=0.690 \text{ \AA}$ [18]) which decreases the oxygen interatomic distances. This tendency was also observed by other authors [19,14].

The crystallite size is generally obtained from the broadening of the diffraction peak using the well-known Scherrer formula [20]. Such a rough evaluation of the particle size is usually not sufficient. First, the instrumental broadening should be eliminated considering the instrumental function of the diffractometer. Second, two main contributions to the physical broadening have to be resolved: the broadening due to the strain and size. These microstructural effects can be distinguished and treated using the Rietveld refinement [16,17], the procedure used in our case. The resulting particle diameters, d , are listed in Table 1. The particle size varies from 15 nm to 24 nm, randomly within the series. Based on this observation we can conclude that the particle size is driven by the mean size of the pores determined by initial

treatment of the SiO_2 matrix. Variation of the equilibrium solubility of the $\text{Co}^{2+}/\text{Fe}^{3+}$ ions in the SiO_2 matrix also influences the pore formation and hence the particle size.

The average values of the Co/Ni ratio determined from the EDX analysis are summarized in Table 1. The decreasing tendency in the Co/Ni ratio with increasing content of Ni^{2+} ions is in good agreement with the required (theoretical) ones.

3.2. Mössbauer spectroscopy

The samples with $x=0.0, 0.4, 1.0$ were characterized using the room temperature Mössbauer spectroscopy (Fig. 3, top panel). All spectra consist of sextets with asymmetric lines indicating two different coordination environments for the Fe^{3+} ions, the tetrahedral (T_d) and the octahedral (O_h) sites, respectively. In the $\text{Co}_{0.6}\text{Ni}_{0.4}\text{Fe}_2\text{O}_4$ and NiFe_2O_4 samples, the observed doublet can be attributed to the part of the sample in paramagnetic or rather superparamagnetic state. However, the in-field Mössbauer spectroscopy revealed that this doublet corresponds to the paramagnetic Fe^{3+} ions, dissolved in the SiO_2 matrix as is discussed further. The obtained values of the isomer shift ($\delta = 0.37 \text{ mm s}^{-1}$ for the O_h , 0.29 mm s^{-1} for the T_d) are consistent with the high spin state of the Fe^{3+} ions in the spinel environment and the values of the hyperfine fields ($B_{\text{hf}}(O_h) = 52 \text{ T}$, $B_{\text{hf}}(T_d) = 48.5 \text{ T}$) are typical for the CoFe_2O_4 spinel structure [21,22].

The overlapped sextets at room temperature spectra do not allow computing the degree of inversion with the appropriate accuracy; therefore the in-field Mössbauer spectroscopy with applied field of 6 T perpendicularly to the direction of γ -rays was performed. The overlapped sextet splits up by the application of the external magnetic field which is superimposed to the hyperfine field of the T_d -sites and is subtracted from the hyperfine field of the O_h -sites (Fig. 3, bottom panel). The resulting Mössbauer parameters and degrees of inversion, y are summarized in Table 2. The slight decrease in the y is observed with increasing concentration of Ni^{2+} ions, that is in good agreement with previously published results [14]. This tendency can be well

Table 1
Particle diameter (d) and lattice parameter (a) determined by the analysis of the PXRD data, together with the Co/Ni ratio obtained from the EDX analysis. (x) corresponds to the theoretical stoichiometric molar ratio of the Ni^{2+} ions.

x	d (nm)	a (Å)	Co/Ni theor.	Co/Ni exp.
0.0	21	8.391(3)	–	–
0.2	24	8.382(3)	4.0	3.4
0.4	22	8.376(7)	1.5	1.3
0.6	15	8.361(0)	0.7	0.8
0.8	15	8.350(4)	0.3	0.4
1.0	20	8.344(3)	0.0	0.0

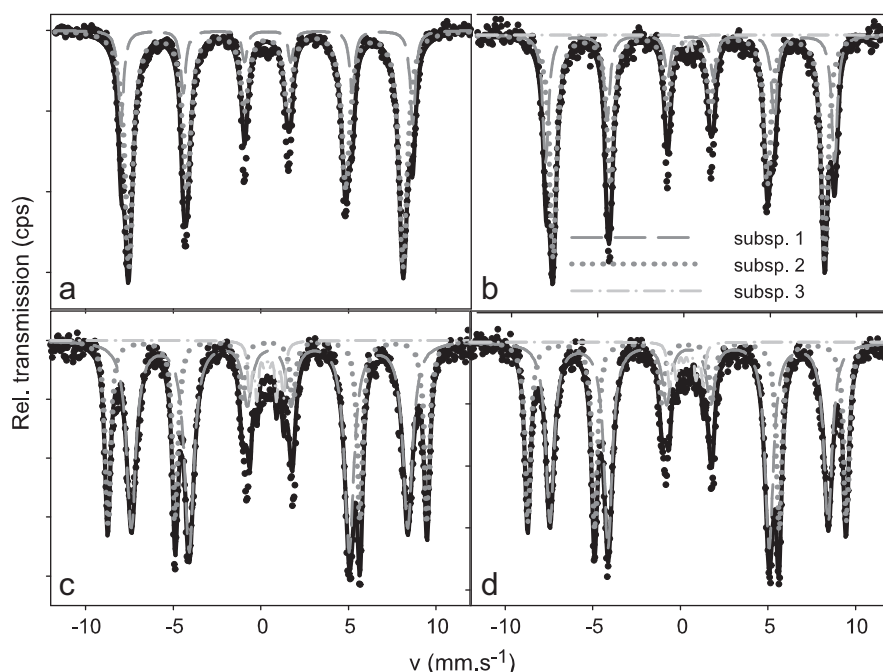


Fig. 3. The Mössbauer spectra of the (a) CoFe_2O_4 sample and (b) $\text{Co}_{0.6}\text{Ni}_{0.4}\text{Fe}_2\text{O}_4$ sample measured at room temperature, (c) CoFe_2O_4 sample and (d) $\text{Co}_{0.6}\text{Ni}_{0.4}\text{Fe}_2\text{O}_4$ sample measured at 4.2 K with external applied field perpendicular to the direction of the γ -rays. The dashed lines correspond to the octahedral sites (subsp. 1), the dotted lines to the tetrahedral sites (subsp. 2) and dash-dotted lines to the paramagnetic Fe^{3+} ions.

explained by the higher stabilization energy of the Ni^{2+} ions in the O_h -sites than of the Co^{2+} ions [23].

The sextet with $B_{\text{hf}} = 6$ T was also observed in all in-field measured spectra that confirmed the presence of the paramagnetic Fe^{3+} ions dissolved in the SiO_2 matrix as suggested by the room temperature measurement. This conclusion was also supported by the zero-field measurement at 4.2 K, where the singlet with $\delta = 0.35 \text{ mm s}^{-1}$ was detected.

3.3. Magnetic measurements

The ZFC-FC curves measured with applied field of 10 mT are shown in Fig. 4, top panel. The temperature dependencies of

Table 2

In-field Mössbauer parameters: the isomer shift, δ , quadrupole shift, 2ϵ , effective field, B_{eff} , relative area, y , and degree of inversion, y .

	δ (mm s^{-1})	2ϵ (mm s^{-1})	B_{eff} (T)	Rel. area (%)	y	Interpr.
CoFe₂O₄						
Subsp. 1	0.49	0.0	49.0	60.3	0.28	$\text{Fe}^{3+} \text{ O}_h$
Subsp. 2	0.37	0.0	56.5	33.4		$\text{Fe}^{3+} T_d$
Subsp. 3	0.34	0.0	6.0	6.3		$\text{Fe}^{3+} \text{ para}$
Co_{0.6}Ni_{0.4}Fe₂O₄						
Subsp. 1	0.49	0.0	49.3	56.8	0.19	$\text{Fe}^{3+} \text{ O}_h$
Subsp. 2	0.37	0.0	56.5	38.3		$\text{Fe}^{3+} T_d$
Subsp. 3	0.34	0.0	6.0	4.9		$\text{Fe}^{3+} \text{ para}$
NiFe₂O₄						
Subsp. 1	0.47	0.0	49.8	49.1	0.11	$\text{Fe}^{3+} \text{ O}_h$
Subsp. 2	0.36	0.0	56.2	41.7		$\text{Fe}^{3+} T_d$
Subsp. 3	0.35	0.0	6.0	9.2		$\text{Fe}^{3+} \text{ para}$

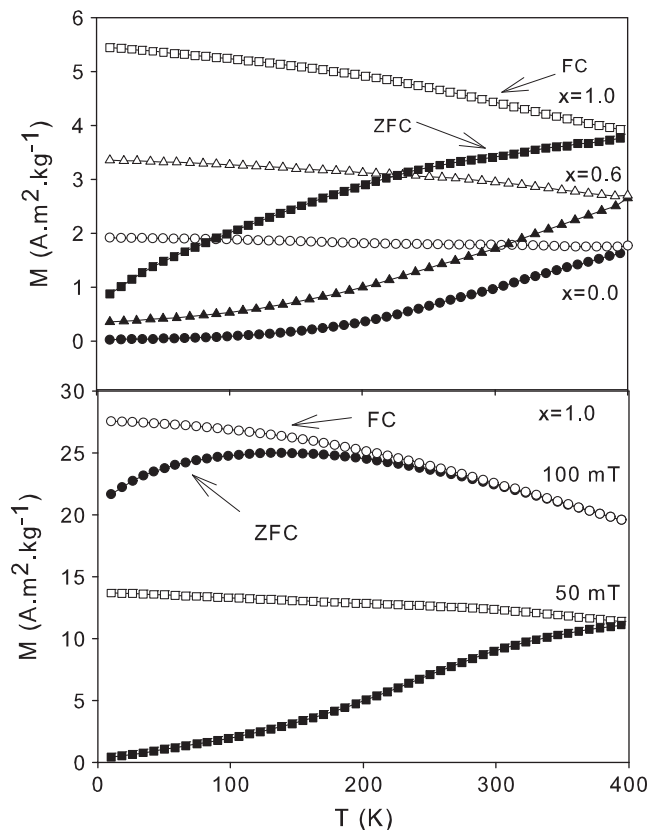


Fig. 4. Top panel: The ZFC-FC magnetization measured at 10 mT for the samples with $x=0.0, 0.6$ and 1.0 . Bottom panel: The ZFC-FC magnetization measured at 50 and 100 mT for the sample with $x=1.0$.

the ZFC-FC magnetization of all samples exhibit a very similar character; there are no significant maxima at the ZFC curve. The lack of a bifurcation point of the ZFC and FC curves indicates that the blocking temperature is well above the 400 K. The saturation of the low-temperature part of the FC curve signalizes non-negligible inter-particle interactions of the dipolar origin [24]. The ZFC-FC curves at 50 and 100 mT were measured for the sample with $x=1.0$ (Fig. 4, bottom panel). The shift of the maximum at the ZFC curve with increasing applied field confirms that the sample exhibits a superparamagnetic phenomenon with non-negligible inter-particle interactions in the blocked state [25].

The magnetization isotherms of all samples measured at 10 K and 300 K are demonstrated in Fig. 5 and the resulting parameters such as the coercivity, $\mu_0 H_c$, remanent magnetization, M_r and magnetization at 7 T, M_{7T} are summarized in Table 3. The linear term, which is superimposed on the hysteresis loop and resulted in the lack of saturation, can be explained either by the presence of the Fe^{3+} ions dissolved in the SiO_2 matrix or by the nanoparticle-matrix interface that caused surface spin canting. The obtained values for the CoFe_2O_4 and NiFe_2O_4 samples, respectively, are in good agreement with those reported previously [8,9]. The variation of these magnetic parameters with increasing Ni^{2+} concentration is depicted in the insets in Fig. 5. The high coercivity of CoFe_2O_4 is attributed to the strong spin-orbit coupling of Co^{2+} ions at the O_h -sites that generates a large anisotropy constant in comparison to the NiFe_2O_4 case [26]; therefore, the decrease in the coercivity with increasing concentration of the Ni^{2+} ions is observed. The linear decrease in the M_{7T} within the series measured both at 10 K and 300 K can be attributed to the lower magnetic moment of the Ni^{2+} ions ($\mu = 2\mu_B$) in comparison with the Co^{2+} ions ($\mu = 3\mu_B$).

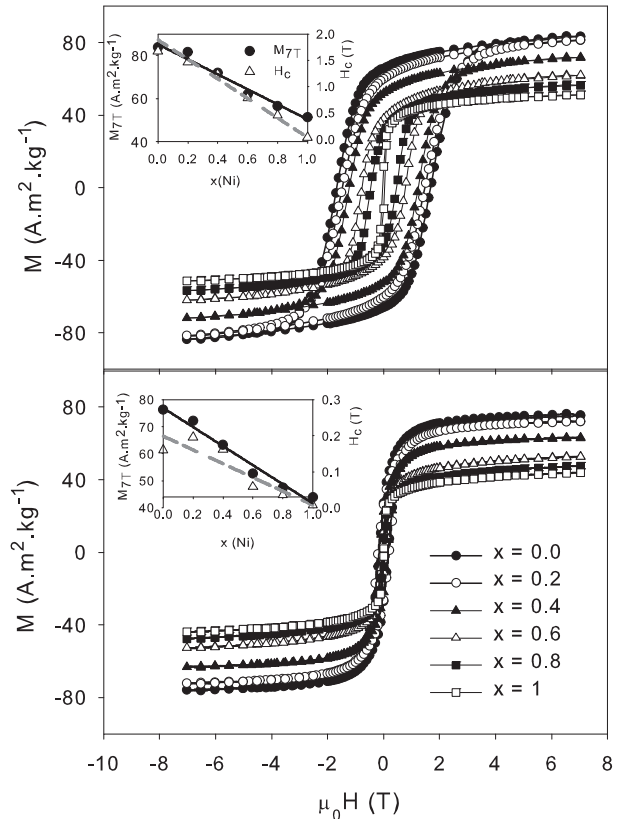


Fig. 5. Magnetization isotherms for all samples measured at 10 K (top panel) and at 300 K (bottom panel). In the insets the variation of the coercivity, H_c (dashed grey line) and the magnetization at 7 T, M_{7T} (solid line) with the Ni^{2+} concentration, x is depicted.

Table 3

The magnetic parameters measured at 10 K and 300 K: the magnetization at 7 T, M_{7T} , remanent magnetization, M_r and coercivity, $\mu_0 H_c$. The (x) corresponds to the theoretical stoichiometric molar ratio of the Ni^{2+} ions.

x	$\mu_0 H_c^{10\text{ K}}$ (T)	$M_{7T}^{10\text{ K}}$ (A m ² kg ⁻¹)	$M_r^{10\text{ K}}$ (A m ² kg ⁻¹)	$\mu_0 H_c^{300\text{ K}}$ (T)	$M_{7T}^{300\text{ K}}$ (A m ² kg ⁻¹)	$M_r^{300\text{ K}}$ (A m ² kg ⁻¹)
0.0	1.6 (7)	83.(7)	65.(8)	0.16 (0)	76.(3)	27.(2)
0.2	1.4 (7)	81.(4)	60.(3)	0.19 (5)	72.(2)	26.(4)
0.4	1.2 (3)	71.(9)	52.(8)	0.16 (1)	63.(3)	22.(1)
0.6	0.7 (8)	62.(1)	38.(1)	0.05 (8)	52.(7)	11.(3)
0.8	0.4 (6)	56.(6)	30.(4)	0.03 (6)	47.(4)	7.(9)
1.0	0.0 (3)	51.(4)	11.(6)	0.00 (8)	43.(8)	2.(2)

4. Conclusions

The modified $Co_{(1-x)}Ni_xFe_2O_4/SiO_2$ nanocomposites were prepared using the sol–gel method. The particle diameters obtained from the PXRD were found out to vary between 15 and 24 nm within the series, with no systematic trend in particle size with respect to level of the Ni substitution. The linear decrease of lattice parameters with increasing Ni^{2+} concentration, due to the smaller Ni^{2+} ionic radii was observed. The degree of inversion obtained from the in-field Mössbauer spectroscopy exhibits a slight decrease with increasing content of Ni^{2+} ions indicating higher stabilization energy of Ni^{2+} ions occupying the octahedral sites. The saturation magnetization and coercivity linearly decrease with increasing Ni^{2+} concentration due to the lower effective anisotropy constant of the whole particle and smaller magnetic moment per formula unit. We have demonstrated that a smooth tuning of the magnetic parameters can be easily realized in the $Ni_{(1-x)}Co_xFe_2O_4$ system in nanocrystalline state.

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3.1.3 Nanočástice feritu hořečnatého

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Dalším systémem se spinelovou strukturou, který byl okrajově studován, je ferit hořečnatý. Přípravou nanokrystalů feritu hořečnatého pomocí mikroemulzní metody a jejich charakterizací se zabývá práce [88]. Přítomnost pouze spinelové fáze potvrdila měření RTG difrakce a Mössbauerovy spektroskopie. Velikost nanočástic byla řízena následným žíháním v rozmezí 31 - 38 nm (určeno na základě výsledků RTG difrakce a transmisní elektronové mikroskopie). Všechny vzorky vykazovaly superparamagnetické chování za pokojové teploty.

Ve spolupráci se skupinou Dr. Naky byla publikována práce [72], která prezentuje kontinuální syntézu nanokrystalů feritu hořečnatého za tzv. superkritických podmínek a dále shrnuje výsledky strukturní charakterizace a magnetických měření.

Preparation of MgFe_2O_4 nanoparticles by microemulsion method and their characterization

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Abstract This work presents the preparation and characterization of magnesium ferrite which is one of the important magnetic oxides with spinel structure. Magnesium ferrite was prepared via microemulsion method mediated hydrolytic decomposition of mixed alkoxide solutions. This microemulsion was using for preparation magnesium ferrite for the first time. The starting solution, composed from magnesium methoxide and iron ethoxide in dry ethanol, was introduced in to the prepared microemulsion and sequentially hydrolyzed by distilled water addition (Pithan et al. in J Cryst Growth 280:191–200, 2005; Shiratori et al. in J Eur Ceram Soc 25:2075–2079, 2005; Herrig and Hempelmann in Mater Lett 27:287–292, 1996). After raw powder precipitation, the samples were decanted by ethanol and then calcined at temperatures 800, 900, 1,000 or 1,100 °C for 1 h. The resulting samples were characterized using powder X-ray diffraction, high resolution transmission electron microscopy, Mössbauer spectroscopy and magnetic measurements. X-ray diffraction and Mössbauer spectroscopy confirmed the presence of the spinel phase. The particles size was calculated from the XRD line broadening using Scherrer equation and their

size was found about 31–38 nm, with only slight dependence on the heat treatment temperature. TEM revealed the particles size of about 39 nm. Magnetic measurements showed a ferrimagnetic behavior for all samples.

Keywords Magnesium ferrite · Microemulsion · Nanoparticles · Magnetic measurements · Mössbauer spectroscopy

1 Introduction

Magnetic particles have become a subject of considerable interest in last few decades and many physical studies have been devoted of them. The ability to produce nano-sized magnetic materials opened new application for magnetic materials, such as magnetic data storage, magnetocaloric refrigeration, electronics, ferrofluid technology, magnetically targeted drugs carriers, contrast agents in magnetic resonance imaging, etc.

As is known, some magnetic properties such as saturation magnetization, remanent magnetization and coercivity depend strongly on the particle size and microstructure of the materials. Therefore, it is interesting and important to develop techniques by which the size and shape of particles can be well controlled. One of the ways to prepare the nanocomposites with the required properties represents microemulsion method. Principle of this method is hydrolysis of alkoxide solution, which is encapsulated in microdroplets of the microemulsion. Separate microdroplets act as separate “microreactors” with specific size and narrow size distribution. Final particle size is determined by the microdroplet size. Main advantage of this method is obtention of pure nanomaterial without any matrix and relatively low preparation temperatures. On the other side, main

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disadvantage of this method are synthesis under inert atmosphere and bad commercial accessibility of some alkoxides.

In this paper, we present the synthesis of MgFe_2O_4 nanoparticles and their characterization by magnetic measurements, Mössbauer spectroscopy, X-ray diffraction and high resolution transmission electron microscopy. Magnesium ferrite has spinel structure, generally denoted by the formula AB_2O_4 , where the A-ions occupy tetrahedral sites and the B-ions octahedral sites of the lattice. Magnesium ferrite has spinel structure, where magnesium and iron ions occupies in the tetrahedral A-sites and in the octahedral B-sites of the spinel. Spinel are often known that the ratio of the number of atoms in the octahedral and in the tetrahedral cavity differ from the ideal state. For this reason, it can be expected relative deviations from the theoretical sextet area ratio 1:2 (tetrahedral sites:octahedral sites).

Second purpose of this work is confirmation of the microemulsion method suitability for preparation different ferrite nanoparticles (cobalt ferrite, zinc ferrite, manganese ferrite, etc.).

2 Experimental

2.1 Sample preparation

The raw nanopowder was prepared through the hydrolysis of microemulsion containing alkoxides solution by water addition. The starting alkoxide solutions were prepared from magnesium methoxide and iron ethoxide (although other alkoxides could also be used) in dry ethanol. Starting magnesium methoxide was used commercial (Sigma–Aldrich). Starting iron ethoxide was obtained by reaction of sodium ethoxide with iron trichloride in dry ethanol under dry atmosphere. Sodium ethoxide was prepared from metal sodium and dry ethanol by standard procedure [4]. Stoichiometric mixture of alkoxide solutions was dropwise added to prepared microemulsion (Lutensol ON 110 10.06 wt%, cyclohexane 81.36 wt%, 1-octanol 5.94 wt%, and distilled water 2.64 wt%). After thorough stirring for 1/2 h under dry atmosphere, the alkoxides were hydrolyzed by distilled water addition. Precipitated raw powder was several times decanted by ethanol, dried at room temperature and then heated up 100 °C. Dry powder was divided to quarters and each of them was heated at temperature 800, 900, 1,000 or 1,100 °C respectively for 1 h in static air atmosphere.

2.2 Experimental technique

X-ray patterns were measured at room temperature on Siemens D5005 diffractometer with a Cu anode. A transmission electron microscope (TEM) was used for direct observation

of the particles. Particle size determination was carried out using Scion Images software. The Mössbauer measurement was done in the transmission mode with ^{57}Co diffused into a Cr matrix as the source moving with constant acceleration. The spectrometer was calibrated by means of a standard Fe foil and the isomer shift was expressed with respect to this standard at 300 K. Measurements were taken at 4 K with magnetic field 6 T. The fitting of the spectra was performed with help of a commercial program. The magnetization measurements were carried out in Quantum Design PPMS (Physical Property Measurement System) at 10, 100, 200, 300, and 350 K.

3 Results and discussion

3.1 X-ray diffraction measurement

X-ray diffraction measurements were carried out on all samples. A relatively long measurements time was chosen (step 0.050° 2 θ , time 45 s/step) and results are depicted in Fig. 1. The peaks position coincided with the characteristic peaks of the standard spinel phase. So, that the spinel structure was found as predominant phase in patterns for all annealing temperatures and negligible amount magnesium oxide was found in the samples but no other phases were detected. The diffraction patterns exhibit sharp peaks at all temperatures treatment which corresponds to well-crystallized solid phases. From the broadening effect of the peaks, the average particle size was determined about 31–38 nm (see Table 1).

3.2 TEM observation

The particle size observation by means of TEM confirms the tendency shown by the X-ray diffraction. The particle

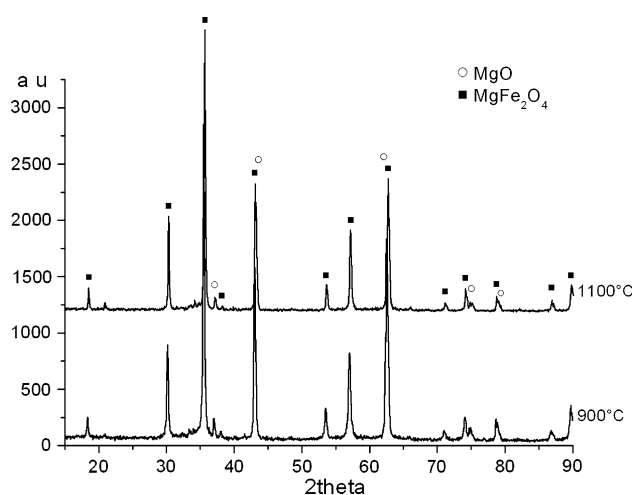


Fig. 1 X-ray diffraction patterns of MgFe_2O_4 samples heated at 900 and 1,100 °C

Table 1 Average particle size depending on the heating temperature (calculated from XRD and TEM) for MgFe_2O_4 and $\text{MgFe}_2\text{O}_4/\text{SiO}_2$

Heating temperature (°C)	800	900	1,000	1,100
Particle size MgFe_2O_4 (XRD) (nm)	31 ± 4	32 ± 3	36 ± 6	38 ± 4
Particle size $\text{MgFe}_2\text{O}_4/\text{SiO}_2$ (XRD) (nm)	–	11 ± 4	19 ± 5	25 ± 6
Particle size MgFe_2O_4 (TEM) (nm)	39 ± 4	–	–	–
Particle size $\text{MgFe}_2\text{O}_4/\text{SiO}_2$ (TEM) (nm)	4 ± 1	8 ± 3	12 ± 4	21 ± 4

size increases only slightly with increasing heating temperature. From the Fig. 2 we can see that some particles are larger than 200 nm and some particles are smaller than 16 nm. The biggest particles are so large because the particles are aggregated into one big particle. And therefore the average particles size is about 39 nm (Table 1) from TEM. Figure 2 represents TEM micrography of the MgFe_2O_4 sample annealed at 800 °C. This figure was used to calculate the mean particle size.

3.3 Magnetic measurements

The magnetization of nanocrystalline MgFe_2O_4 was determined for sample prepared at 800 °C. Measurements were done at 10, 100, 200, 300, and 350 K. From Fig. 3, it could be seen, that saturation magnetization values increase with decreasing temperature of measure, and their values are 29, 32, 38, 44, and 47 Am^2/kg at 350, 300, 200, 100, and 10 K respectively. Coercivities are zero at 350, 300, 200, and 100 K but we can see very small open hysteresis loop with a low coercivity at 10 K.

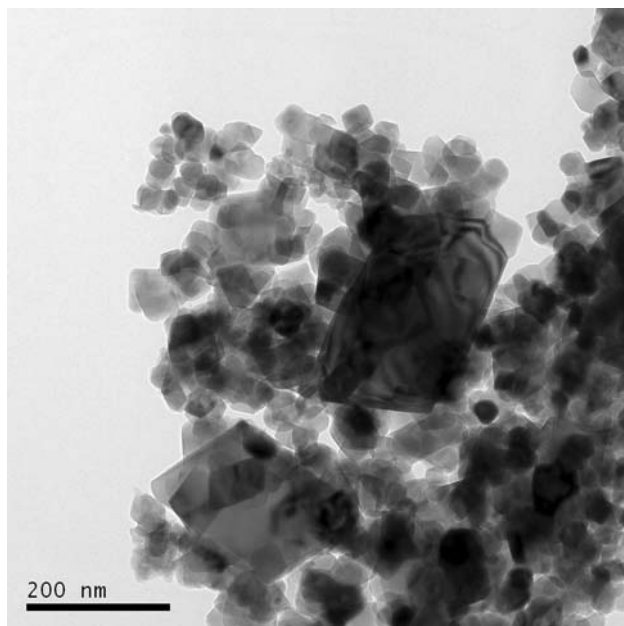
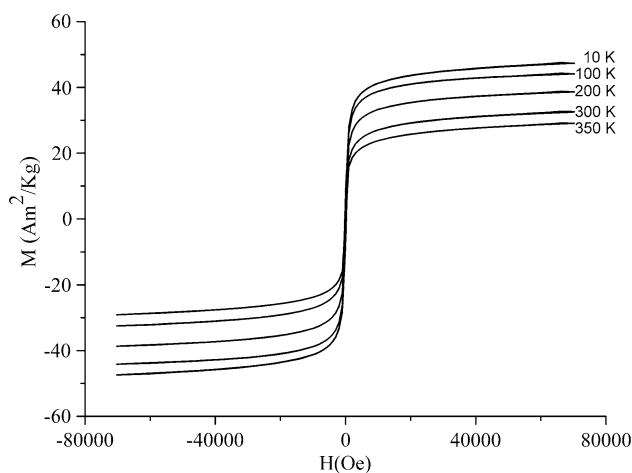
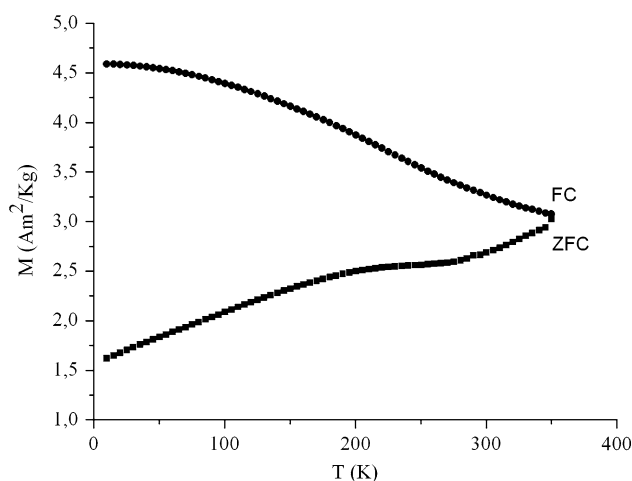
**Fig. 2** TEM of the MgFe_2O_4 sample heated at 800 °C**Fig. 3** Magnetization of the sample heated at 800 °C measured at various temperatures**Fig. 4** ZFC-FC curves of the MgFe_2O_4 sample heated at 800 °C

Figure 4 shows dependence of magnetization versus temperature. The lower curve is obtained for the sample cooled down to 10 K in zero field (ZFC), while the upper curve reflects the sample cooled down in a field of 10 mT (FC). In the maximum of the ZFC curve, which is observed at 350 K (T_B) we can see the division of ZFC and FC magnetization curves. The results of the measurements ZFC and FC reveal ferrimagnetic character nanoparticles until 350 K (T_B). Above this temperature ZFC and FC

measurements reveal superparamagnetic character. This is probably due to the time of measurement and rotation of magnetic moment. The time of the magnetic measurement is longer than the relaxation time of the magnetic moment of nanoparticles, for this reason we can see the connection of ZFC and FC magnetization curves. When we compare the results from measurement of hysteresis and ZFC and FC measurements, we can say that the nanoparticles have ferrimagnetic character. The FC magnetization slowly increases with decreasing temperature until 20 K where the saturation is found FC. Magnetic measurement showed a ferrimagnetic character of all samples.

In the following section it were compared the magnetic properties of the prepared magnesium ferrite (by microemulsion method) with magnesium ferrite in silica matrix (by sol–gel method). Magnesium ferrite has zero coercivity at 350, 300, 200, and 100 K but at 10 K it has low coercivity. Magnesium ferrite in silica matrix has zero coercivity at 100 and 300 K but the hysteresis appears in magnetization curves at 2 K with larger coercivity than in magnesium ferrite. ZFC and FC measurement, demonstrated that MgFe_2O_4 nanoparticles have blocking temperature in the range of 340–360 K, whereas $\text{MgFe}_2\text{O}_4/\text{SiO}_2$ nanocomposites have a blocking temperature about 10 K. It is clear that the samples prepared by sol–gel method and calcined at lower (800 °C) temperature are superparamagnetic and at higher (900, 1,000, 1,100 °C) temperatures have a ferrimagnetic character. While the samples prepared by microemulsion method treated at 800, 900, 1,000, and 1,100 °C have a ferrimagnetic character, which is caused by different size of particle.

3.4 Mössbauer spectroscopy

Mössbauer spectroscopy is a popular experimental technique for studying the microscopic magnetic properties of various ferrite systems. The X-ray diffraction did not give a satisfactory interpretation of our systems. For this reason, Mössbauer spectroscopy was used for the analysis.

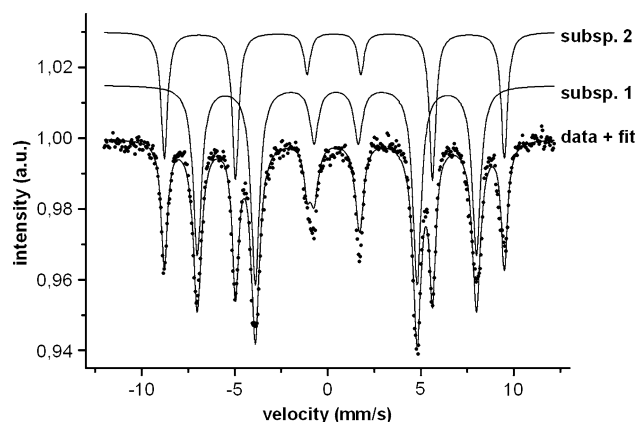


Fig. 5 Interpretation of the Mössbauer spectra of the MgFe_2O_4 nanoparticles heated at 1,100 °C

Table 2 represents the data inferred from the measurements carried out at 4 K and 6 T. Figure 5 shows the spectra of the sample annealed at 1,100 °C. All samples measurement at 4 K and 6 T show two sextets belong to nanoparticles have a ferrimagnetic character. We can write to the formula MgFe_2O_4 as $(\text{Mg}_{1-x}\text{Fe}_x)[\text{Mg}_x\text{Fe}_{2-x}]\text{O}_4$, where x is obtained from the relative substitution of the iron in tetrahedral and octahedral position. The distribution of cations in tetrahedral and octahedral positions was inferred from Mössbauer data as follows: for the sample annealed at 900 °C as $(\text{Mg}_{0.7}\text{Fe}_{0.3})[\text{Mg}_{0.3}\text{Fe}_{1.7}]\text{O}_4$, for the sample annealed at 1,000 °C as $(\text{Mg}_{0.68}\text{Fe}_{0.32})[\text{Mg}_{0.37}\text{Fe}_{1.68}]\text{O}_4$ and for the sample annealed at 1,100 °C as $(\text{Mg}_{0.64}\text{Fe}_{0.36})[\text{Mg}_{0.36}\text{Fe}_{1.64}]\text{O}_4$. Differences in the distribution of cations are influenced by the temperature processing, these distribution of cations in tetrahedral and octahedral position affects the properties of the material but amount of cations remains the same. The amount of iron in tetrahedral position grow at the expense of the octahedral position with increasing temperature processing. The Mössbauer spectroscopy confirmed the presence of an ordered phase MgFe_2O_4 at 4 K and 6 T, where MgFe_2O_4 has a partial inversion of the spinel structure.

Table 2 Interpretation of the Mössbauer spectra of the MgFe_2O_4 nanoparticles heated at 900, 1,000, and 1,100 °C

Site	Heating temperature (°C)	Isomer shift δ (mm/s)	Quadrupole splitting ΔE_Q (mm/s)	Hyperfine field BHF (T)	Relative area (%)
Fe^{3+} octahedral	900	0.4723 ± 0.0033	0.0346 ± 0.0057	46.9835 ± 0.0251	69.6 ± 0.814
Fe^{3+} tetrahedral		0.3489 ± 0.0035	0.0237 ± 0.0082	56.4300 ± 0.0345	30.4 ± 0.583
Fe^{3+} octahedral	1,000	0.4681 ± 0.0042	0.0343 ± 0.0107	46.8205 ± 0.0486	67.6 ± 1.492
Fe^{3+} tetrahedral		0.3571 ± 0.0081	0.0160 ± 0.0159	56.4730 ± 0.0659	32.4 ± 1.529
Fe^{3+} octahedral	1,100	0.4712 ± 0.0022	0.0372 ± 0.0043	46.6182 ± 0.0171	63.6 ± 0.705
Fe^{3+} tetrahedral		0.3436 ± 0.0020	0.0189 ± 0.0049	56.7854 ± 0.0199	36.4 ± 0.574

4 Conclusion

The metallic alkoxides in alcoholic solutions were used as ferrite precursors. The microemulsions used for next preparation consisted of cyclohexane, distilled water, 1-octanol and Lutensol ON 110.

The Mössbauer spectra and X-ray diffraction patterns confirmed the presence of MgFe_2O_4 . The particle size of MgFe_2O_4 nanoparticles was calculated using Scherrer's equation to 31–38 nm for samples heated from 800 to 1,100 °C. TEM showed the nanoparticles with the size about 39 nm. True the use of microemulsion method, it is possible to produce nanoparticles with narrow size distribution. Heat treatment temperature has only slight influence on the particle size in comparison with the influence of the microemulsion composition. The saturation magnetization values increase with decreasing temperature. ZFC-FC measurements, demonstrated that nanoparticles blocking temperature of the 800 °C sample was about 350 K. Hysteresis measurements and ZFC, FC curves of the MgFe_2O_4 nanoparticles revealed ferrimagnetic character at temperatures up to 350 K. The structural formula of MgFe_2O_4 is usually written as $(\text{Mg}_{1-x}\text{Fe}_x)[\text{Mg}_x\text{Fe}_{2-x}]\text{O}_4$, where round and square brackets denote sites of tetrahedral (A) and octahedral [B] coordination respectively, and where x represents the degree of inversion. The degree of inversion, calculated from the subspectral area values. So that the formula can be written as $(\text{Mg}_{0.7}\text{Fe}_{0.3})[\text{Mg}_{0.3}\text{Fe}_{1.7}]\text{O}_4$ for the sample annealed at 900 °C, for the sample annealed at 1,000 °C as $(\text{Mg}_{0.68}\text{Fe}_{0.32})[\text{Mg}_{0.37}\text{Fe}_{1.68}]\text{O}_4$ and for the sample annealed at 1,100 °C as $(\text{Mg}_{0.64}\text{Fe}_{0.36})[\text{Mg}_{0.36}\text{Fe}_{1.64}]\text{O}_4$. Magnesium

ferrite prepared via microemulsion method has a partial inversion of the spinel structure and therefore magnesium ferrite exhibit a ferrimagnetic behavior at low temperature.

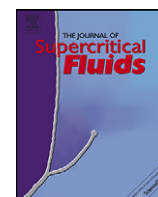
The results show that nanocomposites prepared by sol-gel method contain smaller particles than nanoparticles prepared by microemulsion method. However the nanoparticles prepared by microemulsion method are pure MgFe_2O_4 spinel phase unlike the sol-gel method.

The main result of this work, is innovative and successful utilization of microemulsion method for preparation ferrites. The results show that MgFe_2O_4 nanoparticles can be synthesized by this microemulsion method.

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Continuous synthesis of fine MgFe_2O_4 nanoparticles by supercritical hydrothermal reaction

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ABSTRACT

We produced magnesium ferrite (MgFe_2O_4) nanoparticles by hydrothermal synthesis in supercritical water. Suspensions containing varying ratios of $\text{Mg}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ at room temperature were pressurized to 30 MPa, fed into a tubular reactor by high-pressure pump, and rapidly heated to reaction temperature by mixing with supercritical water. The MgFe_2O_4 phase forms at 460 °C. The Mg/Fe molar ratio was varied from 0.5 to 1.5 with the goal of obtaining single-phase MgFe_2O_4 . At the stoichiometric ratio for MgFe_2O_4 , Mg/Fe = 0.5, the product contains both MgFe_2O_4 and $\alpha\text{-Fe}_2\text{O}_3$. At Mg/Fe = 1.0 and 1.5, the product is the desired single-phase MgFe_2O_4 . The synthesized MgFe_2O_4 nanoparticles, with particle size of about 20 nm, exhibit superparamagnetic behavior.

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1. Introduction

Magnetic particles, whose properties depend on their size, have been studied for applications such as catalysis, energy storage, high-density data storage, and ferrofluids [1]. Magnetic particles of nanometer-range size are useful in biotechnology applications such as magnetic separation, magnetic resonance imaging, and magnetic hyperthermia treatment [2]. Magnetic hyperthermia treatment involves the breakdown of cancer cells at 42–45 °C. Magnetic particles generate heat in the presence of a magnetic field; the degree of magnetic heating depends on particle size and magnetic properties [3]. Among candidate particles for use in magnetic hyperthermia treatment, magnetite and maghemite have been best studied to date because of their magnetic properties and biological compatibility [4,5], and MgFe_2O_4 particles of micrometer-range size are reported to exhibit greater magnetic heating than do other ferrites [6]. Recently, magnetic hyperthermia treatment has been investigated for use in conjunction with a drug delivery system (DDS) so as to enable heating of only cancer tissue. A requirement for use with a DDS is that particle size must be in the range 10–100 nm for accumulation in cancer tissue [7]. Therefore, syn-

thesis of MgFe_2O_4 nanoparticles of precisely controlled size is of great interest.

MgFe_2O_4 nanoparticles can be synthesized by milling, but particles thus produced lack uniform size and morphology [8,9]. Zhang and co-workers [10] synthesized the nanoparticles by the reverse micelle method and Willey et al. [11,12] by sol–gel supercritical drying, but in both cases, the synthesis at lower temperature may result in the inclusion of impurities that are not favorable for human body. Joy and co-workers [13] synthesized the nanoparticles by microwave hydrothermal treatment, but the product lacked sufficient crystallinity.

We have developed a hydrothermal synthesis method for forming advanced metal-oxide particles in supercritical water [14], and other researchers have also prepared fine metal-oxide particles by this method [15–18]. Some important advantages of supercritical hydrothermal synthesis of particles are as follows: (i) nanoparticle formation; (ii) single-crystal formation with a high level of crystallinity; (iii) capability to control particle size and morphology to some extent with pressure and temperature; and (iv) capability to create a homogeneous reducing or oxidizing atmosphere by introduction of gases or additional compounds (O_2 , H_2). We report herein the synthesis of fine MgFe_2O_4 nanoparticles in supercritical water using a flow-type apparatus, and the evaluation of their magnetic properties.

2. Material and methods

Iron (III) nitrate solution ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Kojundo Chemical Laboratory Co., Ltd., 99.9% purity) was prepared at fixed

Abbreviations: DDS, drug delivery system; FC, field-cooling; SQUID, superconducting quantum interface device; TEM, transmission electron microscopy; VSM, vibrating sample magnetometer; XRD, X-ray diffraction; ZFC, zero-field-cooling.

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concentrations of 0.01 or 0.005 M. Magnesium nitrate solution ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Kojundo Chemical Laboratory Co., Ltd., 99.0% purity) was also prepared at concentrations so as to vary the Mg/Fe molar ratio from 0.5 to 1.5. The metal nitrate solutions were mixed with equivalent amount of potassium hydroxide solution (KOH, Wako Pure Chemical Industries, Ltd.), and $\text{Fe}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ precipitates were formed. The resulting precipitates were separated by centrifugation and washed with distilled water two times. Finally, $\text{Fe}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ mixed suspensions were prepared by dilution with distilled water.

The flow-type apparatus used in this study has been described in detail elsewhere [14]. Metal oxides suspension was pressurized at 30 MPa and fed into a reactor by high-pressure pump (flow rate 1 mL/min). Distilled water was also pressurized and fed through another line by another high-pressure pump (flow rate 10 mL/min), and then heated by electric furnace to a pre-determined temperature. The suspension was mixed with the supercritical water at a junction in the reactor, which rapidly heated the mixture up to the reaction temperature. After mixing, the reactants went through a tube whose temperature was kept at the reaction temperature. The length, diameter, and volume of the tube at this isothermal zone were 50 cm, 0.18 cm, and 0.77 cm^3 , respectively. Residence time at the isothermal zone of 400 and 460°C was 2.4 and 0.9 s, respectively. At the exit of the reactor, the fluid was rapidly cooled by an external water jacket. The reaction temperature was varied from 400 to 460°C by controlling the temperature of distilled water and the Mg/Fe molar ratio was varied from 0.5 to 1.5 with the goal of obtaining single-phase MgFe_2O_4 . Synthesized nanoparticles were collected by in-line filtration, washed with distilled water and HNO_3 solution to remove $\text{Mg}(\text{OH})_2$, and then dried in an oven at 60°C .

Particle structure was determined by X-ray diffractometer (XRD; Rigaku RINT 2000 system with a $\text{Cu-K}\alpha_1$ beam). Particle morphology was observed by transmission electron microscopy (TEM; JEOL, Ltd., JEM-1200EX). Composition ratio of Mg:Fe in the products was measured by inductively coupled plasma (ICP; PerkinElmer Co., Ltd., Optima 3300) analysis. Magnetic properties were measured by vibrating sample magnetometer (VSM; Tamakawa Co., Ltd., TM-VSM1230-HHHS) and superconducting quantum interface device magnetometer (Quantum Design, MPMS).

3. Results and discussion

First, we investigated the effect of temperature on the formation of MgFe_2O_4 . Fig. 1 shows XRD patterns of the products synthesized with Mg/Fe = 0.5 at 400 and 460°C . At 400°C , the product is mostly MgFe_2O_4 phase (designated ●); $\alpha\text{-Fe}_2\text{O}_3$ (designated ■)

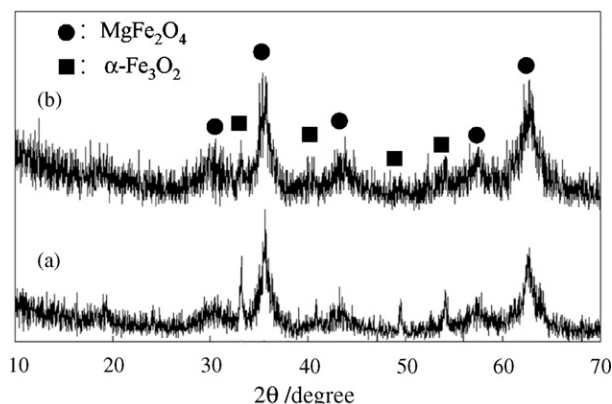


Fig. 1. XRD profiles of particles synthesized at Mg/Fe = 0.5, 30 MPa, and various temperatures: (a) 400°C ; (b) 460°C .

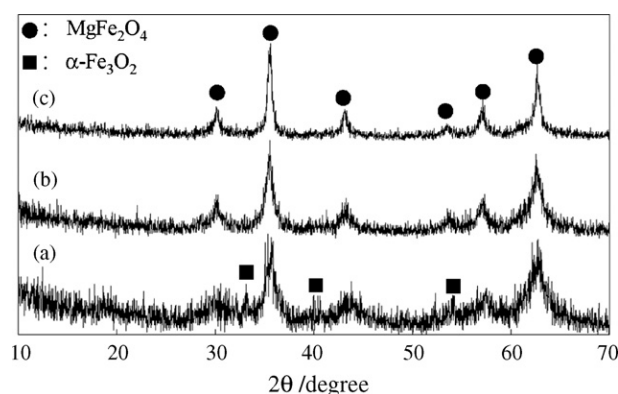


Fig. 2. XRD profiles of particles synthesized at 460°C , 30 MPa, and various Mg/Fe molar ratios: (a) Mg/Fe = 0.5; (b) Mg/Fe = 1.0; (c) Mg/Fe = 1.5.

phase also forms but as an impurity. At 460°C , the amount of $\alpha\text{-Fe}_2\text{O}_3$ product decreases. In general, metal oxide is formed through dissolution and recrystallization processes of hydroxide precursors in aqueous solution. In this study, MgFe_2O_4 was formed through dissolution–recrystallization of $\text{Fe}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ at elevated temperature. In order to confirm the solubility of $\text{Mg}(\text{OH})_2$ at elevated temperature, we have investigated the effect of temperature on the formation of MgO using batch type reactor. A $\text{Mg}(\text{OH})_2$ suspension was loaded into a batch reactor and heated by electric furnace. The reaction temperature was changed from 400 to 600°C and the pressure was fixed to 30 MPa. XRD measurements showed that MgO phase was formed only at 600°C . The result means that the solubility of $\text{Mg}(\text{OH})_2$ becomes higher with increasing temperature. It indicates that dissolution of $\text{Mg}(\text{OH})_2$ at higher temperature leads to form MgFe_2O_4 . Furthermore, formation of $\alpha\text{-Fe}_2\text{O}_3$ is inhibited due to rapid increase in temperature. Even at the higher temperature, single-phase MgFe_2O_4 product does not form at Mg/Fe = 0.5, possibly because the $\text{Fe}(\text{OH})_3$ precursor is unable to react with $\text{Mg}(\text{OH})_2$ and forms $\alpha\text{-Fe}_2\text{O}_3$ as an impurity.

Second, we investigated the effect of the Mg/Fe molar ratio to improve the phase purity. Fig. 2 shows XRD patterns of the products for Mg/Fe = 0.5, 1.0, and 1.5. For Mg/Fe = 0.5, the product contains $\alpha\text{-Fe}_2\text{O}_3$ (designated ■). For Mg/Fe = 1.0 and 1.5, MgFe_2O_4 (designated ●) forms in a single phase. Furthermore, ICP measurement of the particles synthesized with Mg/Fe = 1.0 was conducted. The result shows that the composition ratio of Mg:Fe is 1.0:2.3. The conversion ratio from $\text{Mg}(\text{OH})_2$ to MgO reaches the ratio for forming only MgFe_2O_4 . Such a nonstoichiometric synthesis of barium hexaferrite using a flow-type apparatus was also reported by Hakuta et al. [19]. Fig. 3 shows a TEM image of the synthesized MgFe_2O_4 nanoparticles. The average size of the particles is calculated as 16.5 nm with a standard deviation of 3 nm (17.8%) by counting 100 particles taken from TEM images. Generally speaking, separation of nucleation and growth periods is a key to forming monodispersed particles. In a flow-type apparatus, a large degree of supersaturation is obtained easily and renucleation is inhibited during reaction because the reaction solution is heated rapidly; therefore, the particle size is smaller than for particles synthesized by batch reactor [20].

Finally, we investigated magnetization of the synthesized MgFe_2O_4 nanoparticles. After a sample is cooled from room temperature to 2.0 K under a magnetic field (field-cooling, FC) at 200 Oe, susceptibility decreases monotonically with increasing temperature (Fig. 4a). In contrast, after a sample is cooled similarly but without external magnetic field (zero-field-cooling, ZFC), magnetization increases and reaches a maximum at the so-called blocking temperature; in this case, $T = 94 \text{ K}$ (Fig. 4b). Magnetization after ZFC coincides with that after FC above $T \sim 100 \text{ K}$. These irreversible behaviors are characteristic of superparamagnetism [21]. Magne-

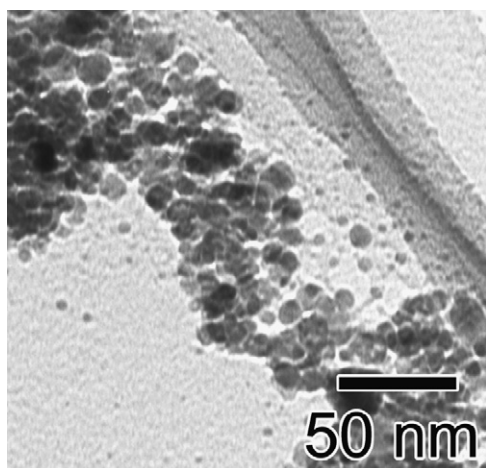


Fig. 3. TEM image of MgFe_2O_4 nanoparticles synthesized at 460°C , 30 MPa, $\text{Mg/Fe} = 1.0$.

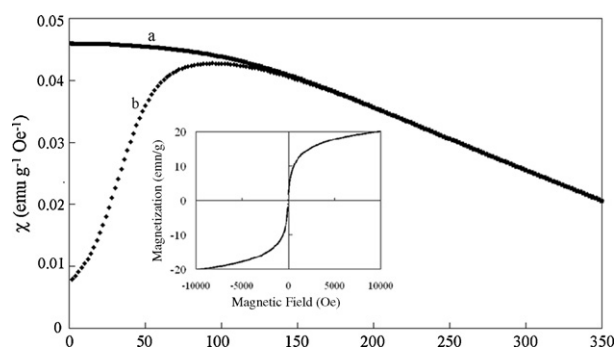


Fig. 4. Plot of magnetic susceptibility vs temperature and magnetization curve (inset) for MgFe_2O_4 nanoparticles synthesized at 500°C , 30 MPa, $\text{Mg/Fe} = 1.0$.

to crystalline anisotropy E_A decreases with decreasing particle size because E_A is proportional to KV , where K is the magnetocrystalline anisotropy constant and V is the nanoparticle size. For thermal activation energy $k_B T$, where k_B is the Boltzmann constant, at $E_A < k_B T$, the magnetic moment of the particle fluctuates randomly, showing paramagnetic character; at $E_A > k_B T$, the magnetic moment of an individual ferromagnetic particle aligns along the axis of easy magnetization. For ZFC, magnetic moments are randomly oriented, and consequently the total magnetic moment of the powder sample becomes zero; for FC, field-induced moments are quenched. The magnetization curve at 298 K indicates that the coercivity force is less than 10 Oe (Fig. 4 inset).

4. Conclusions

We succeeded in synthesizing single-phase MgFe_2O_4 nanoparticles by supercritical hydrothermal synthesis in a flow-type

apparatus. At 460°C , 30 MPa, and $\text{Mg/Fe} = 1.0$ and 1.5, we obtained single-phase MgFe_2O_4 nanoparticles. For successful synthesis of the single phase, high reaction temperature and nonstoichiometric conditions are important. The obtained nanoparticles are about 20 nm in size and exhibit superparamagnetic behavior.

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3.1.4 Nanokrystaly chromitu kobaltnatého

- D. Zakutna, A. Repko, I. Matulkova, D. Niznansky, A. Ardu, C. Cannas, A. Mantlikova, and J. Vejpravova, J. Nanopart. Res. (2014), 16, 2251. [C1-108] [71]

Vlivem velikosti nanokrystalů na magnetické uspořádání v multiferoickém chromitu kobaltnatém, CoCr_2O_4 se zabývá práce [71]. Je popsán postup přípravy nanočástic pokrytých kyselinou olejovou pomocí modifikované hydrotermální metody s následným žíháním, bylo dosaženo velikosti částic v rozmezí 4,4 - 11,5 nm v závislosti na teplotě žíhání (300 - 450 °C). Charakterizace pomocí elektronové mikroskopie, RTG difrakce a vibrační spektroskopie potvrdila jednofázové složení vzorku a úzkou distribuci velikosti částic. Magnetizace a střídavá susceptibilita nanočástic ukázaly na významný vliv poklesu velikosti částic na magnetické uspořádání, zejména vzrůstající podíl spinového neuspořádání. V případě částic o velikosti 4,4 nm došlo k téměř úplnému potlačení ferrimagnetického uspořádání a vzniku skelného spinového stavu. Možnou interpretací je dosažení srovnatelné velikosti částice a koherentní délky spirální komponenty v magnetické struktuře (3,1 nm). Tato studie iniciovala rozvoj preparativních postupů pro přípravu monodisperzních nanočástic dalších multiferoických chromitů s cílem objasnit korelaci mezi kritickou velikostí částic a magnetickým uspořádáním a následně potvrdit či vyvrátit podmínku spirálního magnetického uspořádání pro spontánní polarizaci v multiferoických systémech spinového typu.

Hydrothermal synthesis, characterization, and magnetic properties of cobalt chromite nanoparticles

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Abstract The CoCr_2O_4 nanoparticles were prepared by hydrothermal treatment of chromium and cobalt oleates in a mixture of solvents (water and ethanol or pentanol) at various temperatures. The samples were further annealed at the temperatures from 300 to 500 °C. The obtained nanoparticles were characterized using powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), high-resolution TEM, scanning electron microscopy, thermogravimetric analysis, Raman and infrared spectroscopy, and magnetic measurements. The particle size, ranging from 4.4 to 11.5 nm, was determined from the TEM and PXRD methods. The tendency of particles to form the aggregates with the increasing annealing

temperature has been observed. The magnetic measurements revealed that the typical features of the CoCr_2O_4 long-range magnetic order are suppressed in the nanoparticles.

Keywords Cobalt chromite · Hydrothermal method · Nanoparticles · Size effect · Multiferroic materials

Introduction

Up to date, the studies of magnetic nanomaterials were focused mostly on spinel ferrites due to their straightforward application potential in biomedicine, data storage, electronics, etc. However, there are only few works concerning isostructural chromite as nanoparticles (NPs) or thin films. The MCr_2O_4 (where M is metal) compounds form a normal spinel structure, where the M^{2+} and Cr^{3+} are located in the tetrahedral (T_d) and octahedral (O_h) sites, respectively. They are known as multiferroic materials with complex magnetic phase diagrams and magnetic structure, where the ferroelectric order occurs in spite of nonzero spontaneous magnetization in the conical spin configuration (Lyons et al. 1962; Hastings and Corliss 1962; Menyuk et al. 1964; Shirane et al. 1964; Tomiyasu et al. 2004; Chang et al. 2009; Kim et al. 2009).

Among the spinel chromites, the CoCr_2O_4 is the first example of a multiferroic compound with both the spontaneous magnetization and polarization of spin

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origin (Yamasaki et al. 2006), where the strong clamping between the ferromagnetic and ferroelectric domains, leading to the magnetic reversal of the ferroelectric polarization, has been observed. Concerning the magnetic order, the compound undergoes a ferromagnetic transition at $T_C = 93$ K, and with the further lowering of temperature, the additional transition to the conical spin state occurs at 26 K. The so-called lock-in transition, $T_{\text{lock-in}}$, takes place around 15 K with minimal change of the propagation vector (Funahashi et al. 1987; Chang et al. 2009). Considering the size effects in chromites, a comprehensive work reports on MnCr_2O_4 NPs prepared by high-energy ball milling, which points to unusual Bloch exponent value 3.35, which decreases and approaches a typical value of 1.5, as expected for a common ferromagnet, with decreasing particle size (Bhowmik 2006). Recently, several works also report on the CoCr_2O_4 NPs obtained using various methods.

One of the first preparations of cobalt chromite NPs was carried out by Dutta et al. (2009). They reported the synthesis of nanocrystalline CoCr_2O_4 by a fast sonochemical route, which was based on acoustic cavitations in a liquid. The final particle size was about 30–40 nm, and the magnetic properties were only slightly influenced in comparison to the bulk material. Rath and Mohanty (2010; Rath et al. 2011) prepared the CoCr_2O_4 NPs of a mean size about 8 nm using a simple coprecipitation method and observed an unusual transition from paramagnetic to superparamagnetic (SPM) state. Edrissi and Keshavarz (2012) improved the preparation method using organic precursors: Cr^{3+} and Co^{2+} chelates of 2-mercaptopyridin *N*-oxide for the preparation of the cobalt chromite NPs. Durrani et al. (2012) prepared the cobalt chromite NPs by hydrothermal synthesis at higher values of pH (>10), and this procedure led to rather large particles (>100 nm).

So far, no work on preparation and physical properties of monodisperse cobalt chromite NPs with size below 20 nm has been reported, and, therefore, a study of magnetic and ferroelectric properties down to very low scales has not been possible yet. In order to reach the critical size range, we focused on preparation of the CoCr_2O_4 NPs using hydrothermal method, successfully applied in the case of CoFe_2O_4 NPs (Repko et al. 2011). In this paper, we report on a modified hydrothermal preparation yielding the CoCr_2O_4 NPs with size ranging from 4.4 to 11.5 nm, which is comparable to the

characteristic size of the coherence of the spiral magnetic structure. The samples were characterized using different methods such as powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and Raman and infrared spectroscopy (FTIR). Basic characterization of the magnetic properties was also performed, and the results are discussed in the context of decreasing particle size.

Experimental

Sample preparation

The samples were prepared using the hydrothermal method. Following amounts of reactants were used for the preparation: 10 mmol (400 mg) of sodium hydroxide, 12 mmol (3.39 g) of oleic acid, and metal chlorides ($\text{Cr}^{3+}:\text{Co}^{2+} = 2:1$). The preparation was carried out in the mixture of 15 ml of alcohol (ethanol/1-pentanol) and 20 ml of water. First, the sodium hydroxide was dissolved in a small amount of water, and then ethanol was added. This solution was mixed together with oleic acid to avoid the formation of soap (clear solution was formed instead). Then, the water solution of metal salts which served as a precursor was added, and the reaction mixture became sticky. Afterward, the solution was sonicated for 5 min. Two phases were formed: water and organic phase (Fig. 1), and the following reactions took part:

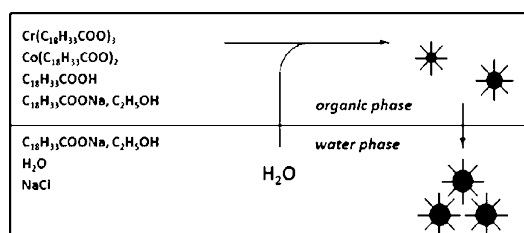
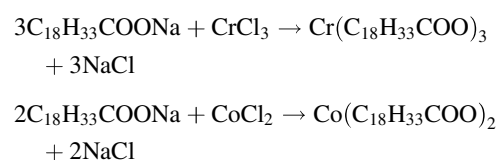


Fig. 1 The process of formation of the CoCr_2O_4 NPs. The metal salts are hydrolyzed and precipitated into the water phase after reaching a critical diameter

Table 1 The preparation conditions for the NPs prepared by the hydrothermal procedure

Sample	Reaction composition				Reaction conditions		Annealing temperature (°C)
	Ratio Cr:Co (mmol)	Alcohol (ml)	Water (ml)	Oleic acid (ml)	Reaction temperature (°C)	Reaction time (h)	
DZ 300	2:1	Ethanol: 10	10	3.82	200	16	300
DZ 350	2:1	Ethanol: 20	20	3.82	200	16	350
DZ 400	2:1	1-Pentanol: 5	10	3.82	200	10	400
DZ 450	2:1	Ethanol: 10	15	6.37	200	16	450

This reaction mixture was put into a Teflon liner (volume 50 ml), enclosed in the autoclave, and placed into oven for 10–16 h at the reaction temperature of 200 °C. After cooling down the autoclave, the following phases were obtained: upper oleic phase, which contained a small amount of NPs, aqueous phase, and sedimented NPs. Liquid phase was discarded, and remaining NPs were dispersed in 15 ml of hexane. Then, the nondispersed NPs (aggregates) were separated using centrifugation, and hexane dispersion was used for the following preparation. Then, the NPs were precipitated from dispersion using 10 ml of ethanol and were separated by means of centrifugation (4,500 rpm for 5 min). This procedure (dissolving in hexane and precipitation using ethanol) was repeated for three times. The samples possessing amorphous phase were heat treated in the furnace at the final annealing temperatures. The preparation conditions for all samples are summarized in Table 1.

Characterization methods

Powder X-ray diffraction was performed using the PANalyticalX'Pert PRO diffractometer with Cu K α radiation ($\lambda = 1.541874$ Å) equipped by secondary monochromator and PIXcel detector. All samples were measured in the 2θ range of 15–80° with the step of 0.02°. The particle diameter obtained from PXRD measurements was determined using two approaches: using the Scherrer's equation, $d_{\text{Scherrer}} = k \cdot \lambda / (\beta \cdot \cos \theta)$ and by the Rietveld analysis, d_{Rietveld} implemented within the FullProf software (Rodríguez-Carvajal 2000). In both approaches, the instrumental broadening was considered.

Transmission electron microscopy was carried out using the JEOL 200CX device operating at 200 kV using two different modes: bright field (BF) and dark field (DF). The mean particle diameter, d_{TEM} , was

statistically determined from at least 100 particles for each sample using the log-normal distribution function.

High-resolution TEM images were captured with the JEM 2010 UHR device equipped with the Gatan imaging filter (GIF) and the 794 slow scan CCD. The samples for the TEM and HRTEM analysis were prepared by drying the dispersion of NPs on the coated copper grid.

Scanning electron microscopy images were obtained using the Tescan Mira I LMH device with the energy-dispersed X-ray detector (EDX) Bruker AXS. The powders were deposited on carbon film.

Thermogravimetric analysis was carried out using the STA 449 F1 Jupiter device. The samples were heated up to 600 °C (heating rate 10 °C/min) in argon atmosphere.

Raman spectra were measured using the Thermo Scientific DXR Raman Microscope with the Olympus microscope (objective 50 $\times$) in the spectral range of 50–1900 cm $^{-1}$ with the resolution of 3 cm $^{-1}$. He–Ne laser or diode lasers (532 and 780 nm) were used for the measurement. The spectrometer was calibrated by calibration software using multiple neon emission lines and multiple polystyrene Raman bands and standardized by white light.

Raman and infrared spectroscopy spectra were obtained using the Thermo Scientific Nicolet 6700 FTIR spectrometer (resolution 2 cm $^{-1}$, DTGS detector, KBr beam splitter, Happ-Ganzelapodization, KBr windows, and zero filling 2) in region 400–4000 cm $^{-1}$ with Nujol technique.

The zero-field-cooled (ZFC) and field-cooled (FC) magnetizations (applied field of 10 mT) and magnetization isotherms at selected temperatures were measured on the Quantum Design MPMS7XL device (SQUID). The temperature dependencies of the a.c. susceptibility were recorded in zero external magnetic

field at frequencies: 0.1, 1, 10, 10^2 , and 10^3 Hz with the amplitude of the a.c. magnetic field of 0.3 mT. The prepared samples were put into the capsule and fixed with the piece of polystyrene.

Results and discussion

Powder X-ray diffraction

Powder X-ray diffraction was used for determination of the phase composition, particles size, and lattice parameters of prepared samples. The measured diffraction patterns together with the refined profiles of the samples are shown in Fig. 2. All samples exhibit the characteristic diffractions corresponding to a cubic spinel phase with the space group $Fd\bar{3}m$ (card No. JCPDF 22-1084). The small amount of NaCl has been detected in the DZ 350 and DZ 400 samples, probably due to nonsufficient washing procedure after the reaction, which has no negative impact on the physical properties of the spinel phase. Moreover, the DZ 350 sample contains also a small amount of Cr_2O_3 .

The lattice parameter, a and NP diameters, d are summarized in Table 2. It has been observed that both the a and d increase with increasing annealing temperature. The a values of our samples are slightly lower than the tabulated ones ($a = 8.3299$ Å, card No. JCPDF 22-1084). These effects can be explained by

defects present in crystal lattice (dislocation and vacancies) and by numerous dangling bonds on a NP surface, as is typical for small-sized NPs. The increase of a and d with the increasing annealing temperatures indicates the decrease of the structural disorder or cation redistribution within the spinel network (Sickafus et al. 1999). The particle diameters obtained from PXRD, d_{Scherrer} and d_{Rietveld} are almost identical for all samples.

Transmission electron microscopy

The BF mode images reveal spherical shape of the NPs. The DF mode provides additional information about crystallinity of the prepared NPs. The Figs. 3 and 4 show the TEM images of the samples together with the corresponding size distributions. It can be seen that the NPs are overlapping and have tendency to form aggregates with the increasing annealing temperature. Thus, the determination of d_{TEM} values for all samples serves only as a rough estimate of NP diameter and ranges from 6.7 to 11.5 nm for individual samples, respectively. Determined values correlate well with the d_{Rietveld} and d_{Scherrer} values in the range of the error (Table 2), which points at high crystallinity of the individual NPs.¹ The diffraction patterns of selected area measurements (SAED) were used for an additional determination of the phase composition of prepared samples (Fig. 5) and confirmed the presence of crystalline spinel cobalt chromite.

High-resolution TEM

In addition, the DZ 300 sample was characterized using HRTEM, a typical image of the well-crystalline NPs and the corresponding SAED measurement are shown in Fig. 6. The results from SAED are also summarized in Table 3. The depicted value of the interplanar distances of 2.5 Å corresponds well with the (311) plane of the cobalt chromite spinel structure.

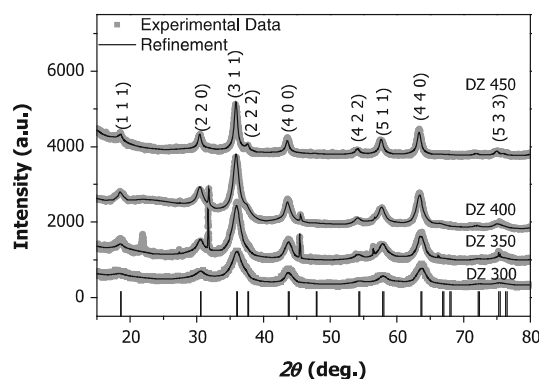
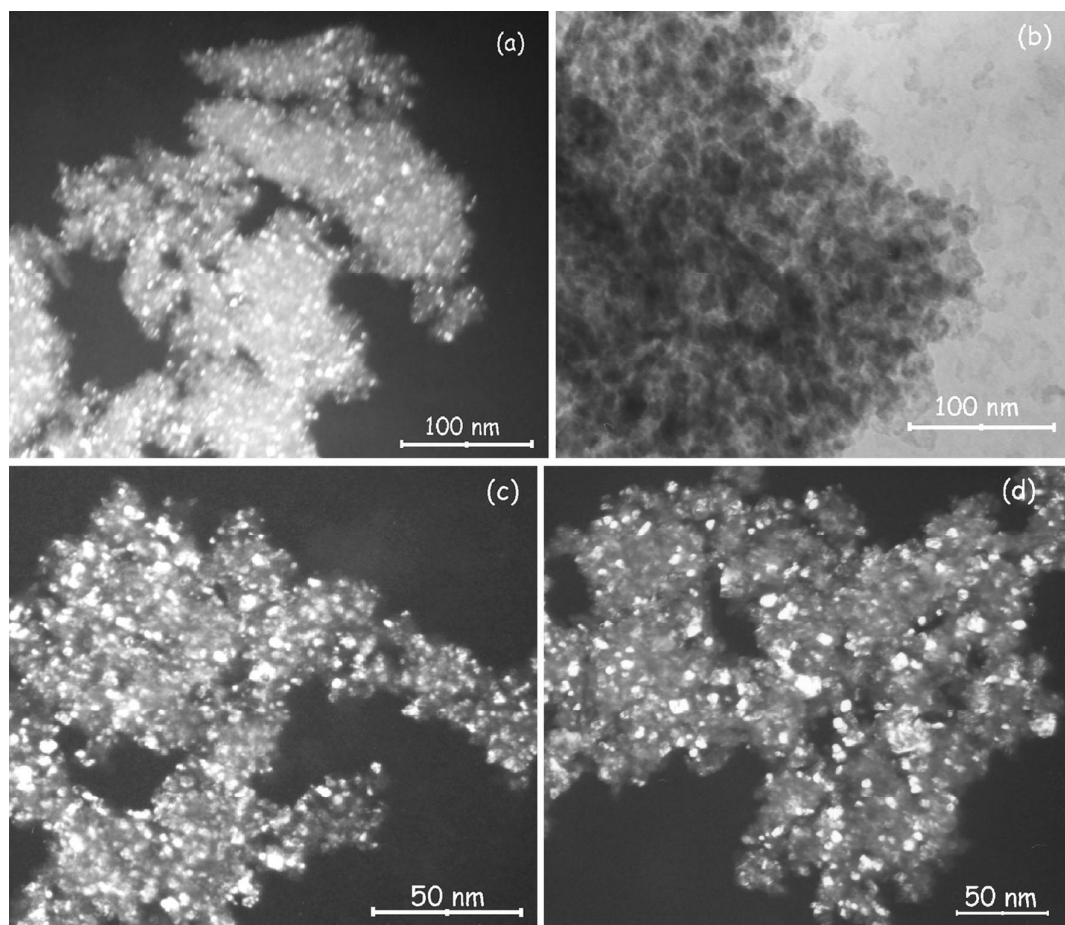


Fig. 2 Experimental data of the PXRD measurements together with the fit using the Rietveld method. The vertical lines correspond to the positions of Bragg maxima of the CoCr_2O_4 phase (card No. JCPDF 22-1084). The DZ 300 and DZ 450 samples are pure spinel phase. The DZ 400 sample also contains parasitic NaCl phase, and the DZ 350 sample exhibits presence of the NaCl and Cr_2O_3 phases

¹ Since the PXRD reflects the coherently diffracting volume of the particle and TEM size corresponds to the dimensions of the two-dimensional projection of the entire polycrystal in its specific orientation, the size obtained from PXRD should be almost identical to the TEM size in the case of the well-crystalline NP of approximately spherical shape.

Table 2 Particle size determined from the TEM and PXRD. In the column PXRD, there are two values obtained by the simple estimation (Scherrer's equation), d_{Scherrer} and using theRietveld refinement, d_{Rietveld} . The d_{TEM} represents the values of median size of the particles revealed by the fit of the log-normal distribution. The a represents the lattice parameter

Sample	Annealing Temperature (°C)	PXRD		TEM	a (Å)
		d_{Scherrer} (nm)	d_{Rietveld} (nm)	d_{TEM} (nm)	
DZ 300	300	4.9 ± 1.4	4.4 ± 0.5	6.7 ± 0.3	8.271(4)
DZ 350	350	5.4 ± 1.3	5.1 ± 0.5	5.9 ± 0.1	8.282(2)
DZ 400	400	6.9 ± 3.2	6.2 ± 0.5	6.4 ± 0.2	8.301(3)
DZ 450	450	11.8 ± 1.4	11.5 ± 0.1	11.5 ± 0.5	8.306(2)

**Fig. 3** TEM images of the samples: **a** DZ 300 (DF mode), **b** DZ 350 (BF mode), **c** DZ 400 (DF mode), and **d** DZ 450 (DF mode)

EDX and TG analysis

The EDX analysis from SEM microscopy was used for the elemental analysis of the samples. The main

elemental components of the sample are Co, Cr, and O. The EDX analysis confirms that the atomic ratio between Co:Cr $\cong$ 1:2 (Co at. 18.19 %; Cr at. 36.79 %), as has been expected.

Fig. 4 Histograms obtained from the BF mode of the TEM images. Size distribution was fitted using the log-normal distribution function with its maxima belonging to the median diameter of the particles, d_{TEM}

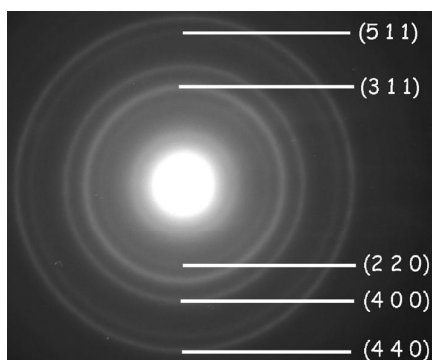
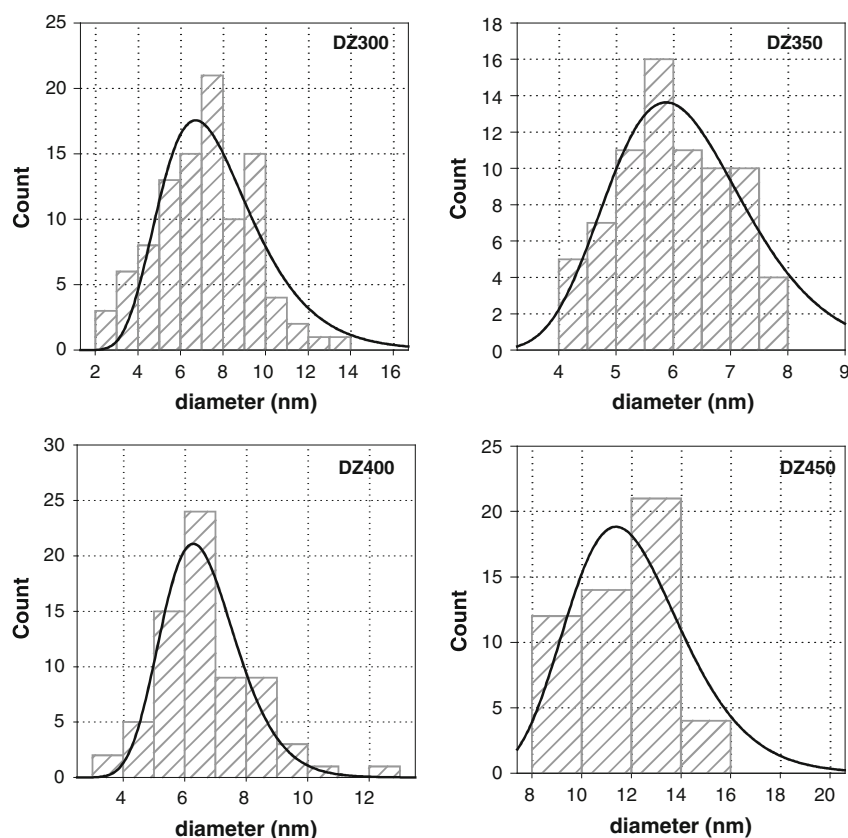


Fig. 5 The SAED image of the DZ 300 sample. The solid lines mark the corresponding reflections of the spinel structure

Finally, the TG analysis was carried out to evaluate the organic and water content in the prepared samples. The results from the TG analysis of all prepared samples are shown in Fig. 7. The TG curves of the as-prepared samples show minimal weight losses up to

500 °C due to evaporation of absorbed water. The weight losses observed above 400 °C are attributed to organic remnants in the samples. The values of the amount of the organic content in the samples, determined from the total weight losses, are summarized in Table 4.

Vibrational spectroscopy

The CoCr_2O_4 belongs to the normal cubic II-III spinels with the space group $Fd\bar{3}m$ (O_h^7). The atoms of CoCr_2O_4 occupy the 8a (T_d), 16d (O_h), and 32e (oxygen) Wyckoff sites. These sites contribute to the $F_{2g} + F_{1u}$, $A_{2u} + E_u + F_{2u} + 2F_{1u}$, and $A_{1g} + E_g + 2F_{2g} + F_{1g} + A_{2u} + E_u + F_{2u} + 2F_{1u}$ modes of theoretical vibrational representation. From these modes, the A_{1g} , F_{2g} (triply degenerate), and E_g (doubly degenerate) are active in Raman spectra while four F_{1u} (triply degenerate) are IR active and one remaining F_{1u} is acoustic mode, and, therefore, cannot be

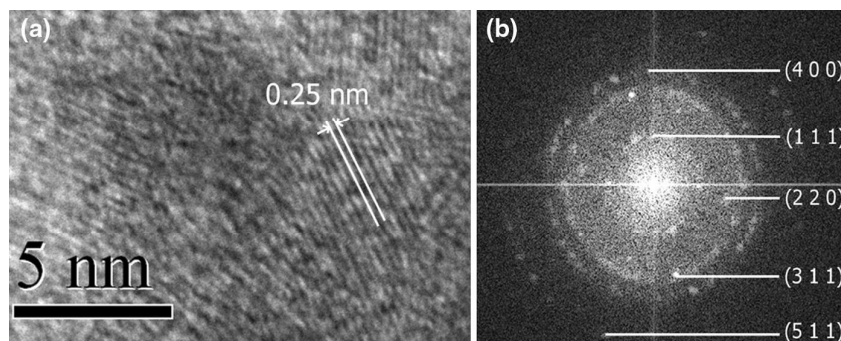


Fig. 6 The HRTEM (a) and SAED b images of the DZ 300 sample

Table 3 Assignments of the SAED image of the DZ 300 sample. The d_{hkl_exp} corresponds to the experimental values, and d_{hkl_st} corresponds to the standard values (card No. JCPDF 22-1084) of the interplanar distance values

hkl	(1 1 1)	(2 2 0)	(3 1 1)	(4 0 0)	(5 1 1)
d_{hkl_exp} (Å)	4.852	2.930	2.503	2.122	1.609
d_{hkl_st} (Å)	4.840	2.947	2.512	2.084	1.603

Table 4 Results from TG analysis of the samples

Sample	Weight loss (mass %)	Organic content (mass %)
DZ 300	5.96	2.04
DZ 350	4.30	1.74
DZ 400	3.09	1.00
DZ 450	3.00	0.98

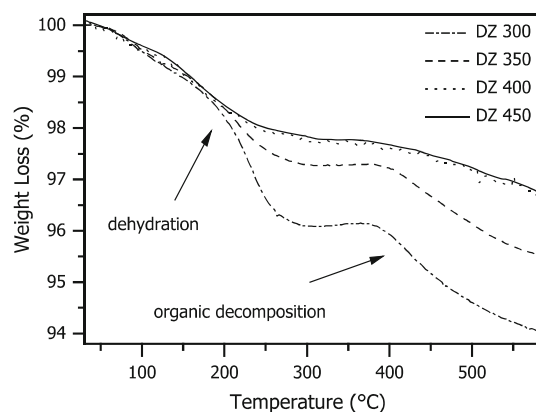


Fig. 7 TG analysis of the samples

observed in the IR spectra. The rest of modes are both Raman (F_{1g}) and IR ($2A_{2u}$, $2E_u$, and $2F_{2u}$) inactive modes. It was concluded from the theoretical prediction of the selection rules that Raman spectra of the pure cubic spinel consist of five fundamental bands ($A_{1g} + E_g + 3F_{2g}$). These narrow bands are located at 686, 604, 515, 452, and 196 cm^{-1} for the bulk CoCr_2O_4 as was presented by Maczka et al. 2013. The narrow bands were also observed in nanosized

(20–25 nm) CoCr_2O_4 in SiO_2 matrix, but they were slightly shifted to 684 cm^{-1} (A_{1g}), 603 cm^{-1} ($F_{2g}(1)$), 514 cm^{-1} ($F_{2g}(2)$), 449 cm^{-1} (E_g), and 195 cm^{-1} ($F_{2g}(3)$); for the spectra see Fig. 8. The four F_{1u} bands active in the IR spectra were found at 630, 530, 380, and 190 cm^{-1} in the bulk sample (Preudhomme and Tarte 1971a, b) and at 627 cm^{-1} ($F_{1u}(1)$), 532 cm^{-1} ($F_{1u}(2)$), 373 cm^{-1} ($F_{1u}(3)$), and 197 cm^{-1} ($F_{1u}(4)$) in nanosized $\text{CoCr}_2\text{O}_4/\text{SiO}_2$.

The Raman spectra of all samples contain five theoretically expected bands, but they are broader than those observed for bulk material (depicted in Fig. 9). Additional narrow (sharp) band located at 496 cm^{-1} was observed in Raman spectra of the DZ 300 and DZ 350 samples. The position of the bands (predicted by theory) for mentioned samples and their interpretation are summarized in Table 5. The higher number of bands in the Raman spectra than was theoretically predicted can be explained using several ways. The presence of impurity phase can produce the additional Raman active band, however, all samples were found out to be nearly single phase, only the DZ 350 sample contained a small amount of Cr_2O_3 , below the detection limit of Raman spectroscopy (band positions of Cr_2O_3 are 616, 554, 529, 352, and 295 cm^{-1}). The

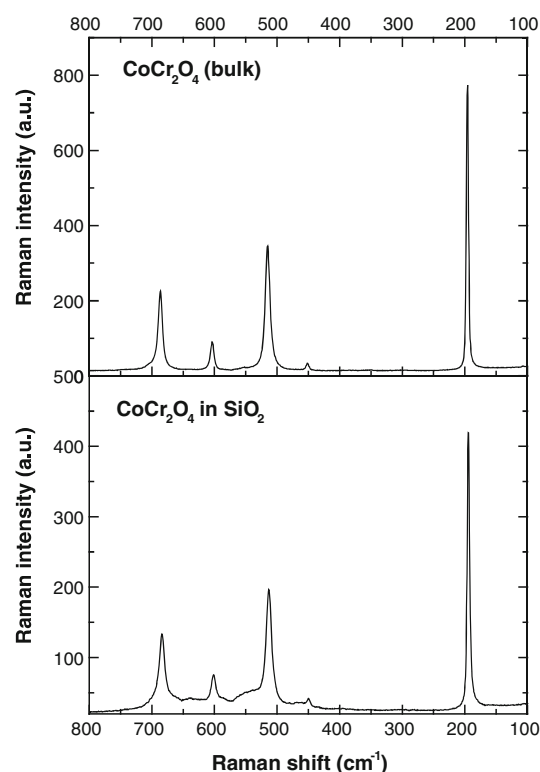


Fig. 8 Raman spectra of the bulk (top panel) and NPs in the SiO₂ matrix (bottom panel) of the cobalt chromite NPs

one additional Raman band in the spectra cannot be also elucidated by the potential lowering of the cubic O_h symmetry to tetragonal D_{4h} symmetry caused by the Jahn–Teller effect. The observed lowering of symmetry to the tetragonal one is connected mainly with the bands of $F_{1u}(1)$ and $F_{1u}(2)$ in IR spectrum and $F_{2g}(2)$ and $F_{2g}(3)$ in Raman spectrum, as has been observed in the copper chromite (Khassin et al. 2009). However, this splitting is not observed in our spectra. The most probable origin of presence of one additional band in Raman spectra in the DZ 300 and DZ 350 samples can be the order–disorder effect (Da Rocha and Thibaudau 2003; De Sousa Meneses et al. 2006; Laguna-Bercero et al. 2007; Maczka et al. 2013). The normal II–III, fully inverted, and partially inverted spinel structure belong to the same space group, and the same selection rules for vibrational spectra are applied. The fully (ideal) inverted spinel contains half of M^{III} ions in the T_d -sites and remaining half of M^{III} ions and all M^{II} ions in the O_h -sites. The described cation redistribution can lead to the shift of the Raman

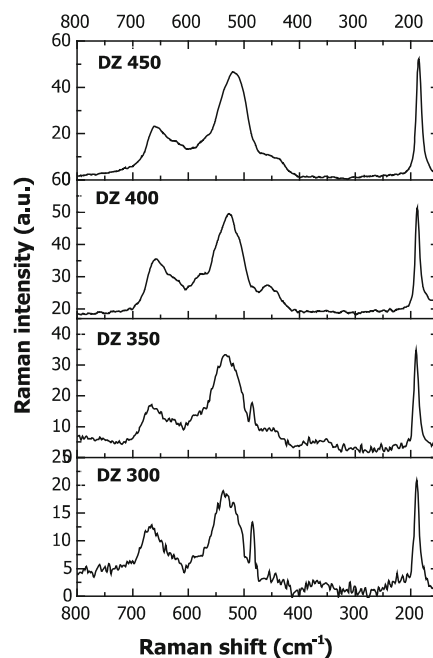


Fig. 9 Raman spectra of the CoCr₂O₄ samples

bands. The band assigned to the E_g symmetry is located at 484 cm^{-1} in spectra of the DZ 300 and DZ 350 samples, while it is shifted to 458 and 454 cm^{-1} in the spectra of the DZ 400 and DZ 450 samples, respectively. Both values of position of E_g symmetry bands predicted by theoretical calculation are located at 485 cm^{-1} (Kushwaha and Kushwaha 2007) and 454 cm^{-1} (Kushwaha 2009). The additional Raman active band at 496 cm^{-1} can be attributed to the some degree of cation redistribution within the spinel network (Maczka et al. 2013). The change of intensity of additional Raman band can be influenced by the change of particle size. The decreasing particle size can lead to higher inverse spinel configuration in comparison with the bulk CoCr₂O₄ that crystallizes predominantly in the normal spinel structure (Maczka et al. 2013).

The MID infrared spectrum with two broad more or less asymmetric bands with the centers approximately at 620 and 520 cm^{-1} (Fig. 10), which are attributed to the ν_1 and ν_2 vibrations, was obtained (for the detailed assignment see Table 6). The broadness and asymmetry of these bands essentially depend on the nature of M^{III} cation and preparation conditions and do not depend on the nature and mass of the M^{II} cation

Table 5 Interpretation of the CoCr_2O_4 Raman spectra

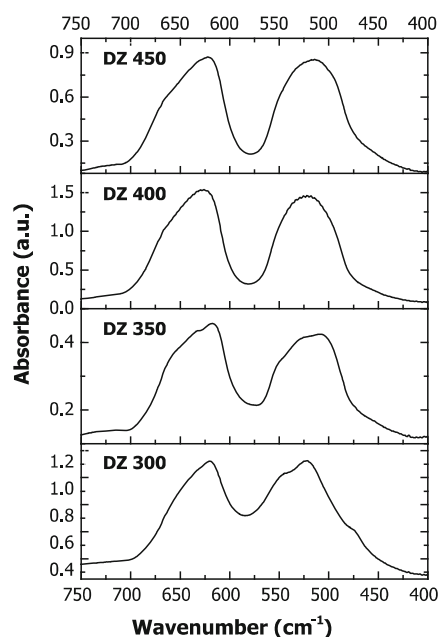
Raman shift (cm^{-1})					
DZ 300	DZ 350	DZ 400	DZ 450	Assignment	Symmetry
190	190	190	186	δ (O–Co–O)	$F_{2g}(3)$
484	484	458	454	$\nu_s(\text{Cr} - \text{O}), \nu_s(\text{Co} - \text{O})$	E_g
534	534	523	519	$\nu(\text{Cr} - \text{O})$	$F_{2g}(2)$
631	631	628	622	$\nu_s(\text{Cr} - \text{O})$	$F_{2g}(1)$
669	665	660	658	$\nu_s(\text{Cr} - \text{O})$	A_{1g}

(Preudhomme and Tarte 1971a, b, Sickafus et al. 1999). The bands can be assigned to the lattice of condensed octahedra. The ν_3 vibration seems to be related to the complex vibration involving the participation of both types of cations (T_d and O_h). The last ν_4 vibration clearly depends on the mass of the M^{II} cation and can be assigned to the vibration involving a displacement of the T_d cation. Some studies of isomorphic replacement of T_d and O_h cations were presented by Preudhomme and Tarte 1971a, b, Hosterman et al. 2013. It can be summarized that ν_1 and ν_2 vibrations are never split, ν_3 is split and shifted in the case of O_h cation replacement and only shifted in the case of T_d cation replacement, and ν_4 is split and shifted in the case of T_d cation replacement and no significant changes were observed in the case of O_h cation replacement. The very fine structure of these bands (ν_1 and ν_2) is not so sharp in the IR spectra of our samples, which is probably due to the nanosized dimension. The nanosized dimension of the samples leads to the broadness of the bands of the ν_3 and ν_4 vibrations in the FAR IR region. Therefore, it is not possible to make conclusions about the presence of partial T_d cation replacement observed in the IR spectra and it is not possible to confirm the effect observed in the Raman spectra of the DZ 300 and DZ 350 samples.

Magnetic properties

Magnetic behavior of the sample series was investigated by means of ZFC and FC magnetization recorded in moderate external magnetic field, magnetization isotherms at selected temperatures, and frequency-dependent a.c. magnetic susceptibility.

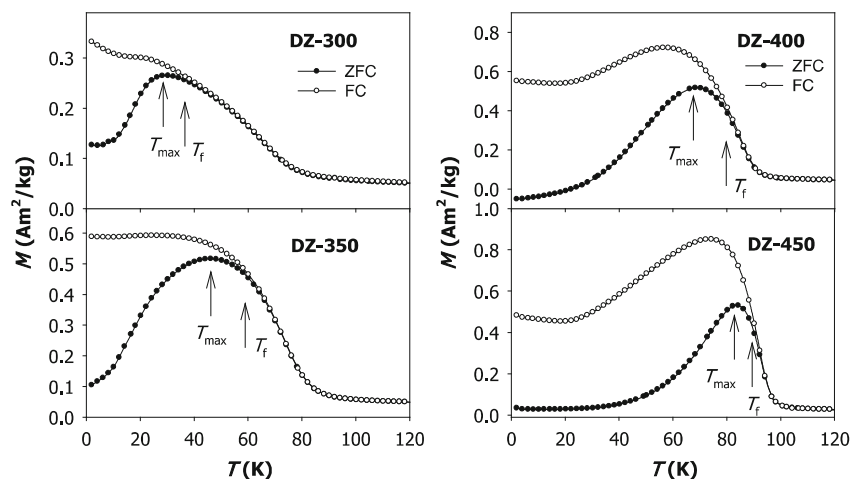
The temperature dependencies of the ZFC–FC magnetization are shown in Fig. 11. A furcation of the ZFC and FC curves (denoted as T_f) followed by a

**Fig. 10** The Infrared spectra of the CoCr_2O_4 samples using the laser with the wavelength of 532 nm**Table 6** Interpretation of the CoCr_2O_4 IR spectra

Wavenumber (cm^{-1})					
DZ 300	DZ 350	DZ 400	DZ 450	Assignment	Symmetry
522	527	522	514	$\nu(\text{Cr} - \text{O})$	$F_{1u}(2)$
620	618	626	622	$\nu_{as}(\text{Cr} - \text{O})$	$F_{1u}(1)$

maximum on the ZFC curve on cooling (T_{max}) can be observed in all samples; both the T_f and T_{max} shift to lower temperatures with decreasing particle size as depicted in Fig. 12. Figure 13 shows the temperature dependencies of the inverse ZFC and FC

Fig. 11 Temperature dependencies of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization, M of the DZ 300, DZ 350, DZ 400, and DZ 450 samples (measured at external magnetic field, $\mu_0 H = 0.01$ T). The arrows mark the position of the ZFC–FC furcation (T_f) and the maximum on the ZFC ($T_{\max}$)



magnetization that follow a typical functional form: $\chi^{-1} = T/C + 1/\chi_0 - \sigma/(T - \theta_p)$, consisting of a Curie–Weiss ferromagnetic term and a Curie paramagnetic term. Such behavior has been already reported for NPs of MnCr_2O_4 and other ferrimagnetic spinels (Bhowmik 2006). The determination of the constants C and σ from this equation is problematic, because they are coupled in the paramagnetic regime; however, an estimation of the so-called asymptotic Curie temperature, θ_p^a , can be obtained by extrapolation of the $1/M$ data in the vicinity of the T_f , as shown in Fig. 13. The closer to the bulk ordering temperature, T_c , the better developed long-range ferrimagnetic order; in other words, the increasing magnetic disorder in NPs is manifested by the large difference between the θ_p^a and T_c . According to the core–shell model of ferrimagnetic NPs (Kodama et al. 1996), the disorder is usually associated with the increasing contribution of shell surface spins while the long-range ferrimagnetic order is related to core spins. In our samples, the θ_p^a shifts to significantly lower values with decreasing particle size, as shown in Fig. 12, suggesting substantial of spin disorder.

The first order derivatives of the ZFC and FC curves are presented in Fig. 14. The minimum for the ZFC becomes broad and less pronounced for NPs with decreasing size, which is related to the above-mentioned disorder effects in NP samples. This is implied by the fact that the sample is magnetically more ordered in the FC state than the ZFC state. The first-order derivative does not show additional sharp extremes, indicating that the noncollinear spin

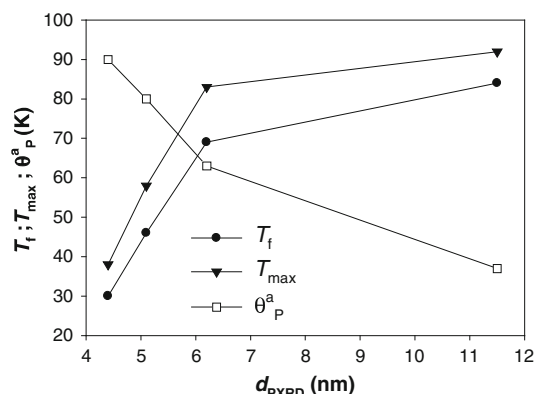


Fig. 12 The dependence of the furcation temperature, T_f ; temperature of the ZFC maxima, $T_{\max}$; and the Curie temperature, θ_p^a , on the particle diameter determined using PXRD, d_{PXRD}

configuration below the T_s and $T_{\text{lock-in}}$ lacks or weakens in the NPs. The difference between the ZFC and FC magnetizations, shown in Fig. 14, corroborates the gradual increase of the spin disorder with decreasing particle size. Except the T_f -related anomaly and a single inflex point at about 30–60 K present in all samples, the DZ 450 sample shows a shallow minimum around 20 K suggesting presence of the bulk-like order-to-order magnetic phase transitions. Shift of the ZFC minimum of NP samples to higher temperature indicates the increase of the ordering temperature with the increasing particle size, which is a trend opposite to that observed for the MnCr_2O_4 NPs (Bhowmik 2006), but corresponds to

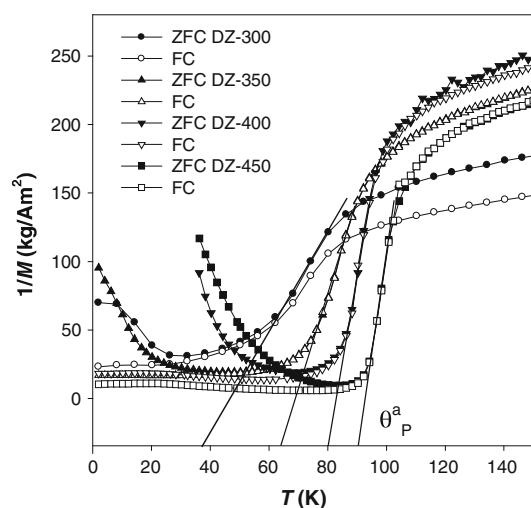


Fig. 13 Temperature dependencies of the inverse zero-field-cooled (ZFC) and field-cooled (FC) magnetization together with the asymptote of the paramagnetic Curie temperature, θ_P^a

the evolution of the spin disorder with the particle size. As reported previously (Dutta et al. 2009; Rath et al. 2011), the particles with size about 40 nm exhibit magnetic properties very similar to the bulk CoCr_2O_4 compound with the ordering temperature of about 85 K represented by a dominant maximum on the ZFC magnetization. Additional magnetic phase transitions related to the T_s and also $T_{\text{lock-in}}$ temperatures can be observed either on the a.c. susceptibility (Dutta et al. 2009) or specific heat (Rath et al. 2011). Nevertheless, the considerable size distribution of the NPs reported in (Dutta et al. 2009, Rath et al. 2011) causes minor variations in the T_s and $T_{\text{lock-in}}$ resulting in less-pronounced anomalies in contrast to sharp peaks observed on single crystals or polycrystalline samples of CoCr_2O_4 . On the other hand, the particles in our study exhibit a relatively narrow size distribution and the size converges to the typical correlation length of the spiral component in the ground state of the magnetic structure [~ 3.1 nm (Tomiya et al. 2004)]. Hence, a significant suppression of the long-range magnetic order, at least at the ground state magnetic phase, is expected.

The typical magnetization isotherms of the samples with the border particle sizes (DZ 300 and DZ 450) are shown in Figs. 15 and 16. The magnetization curves carried out above the T_f show linear dependence on the applied field without hysteresis as is generally

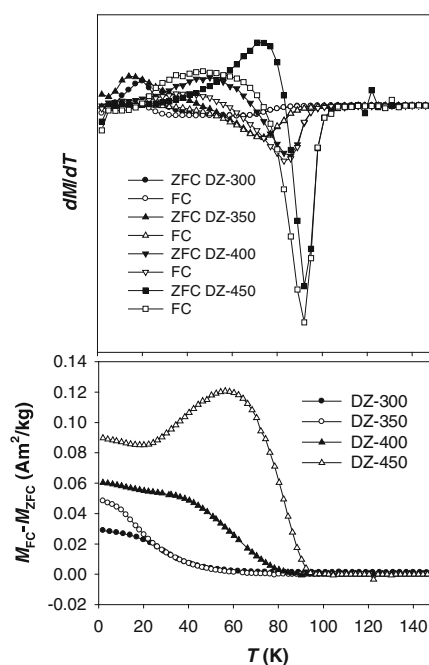


Fig. 14 Temperature dependencies of the first derivative of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization (top panel) and difference of the ZFC and FC magnetizations (bottom panel) (measured at external magnetic field, $\mu_0 H = 0.01$ T)

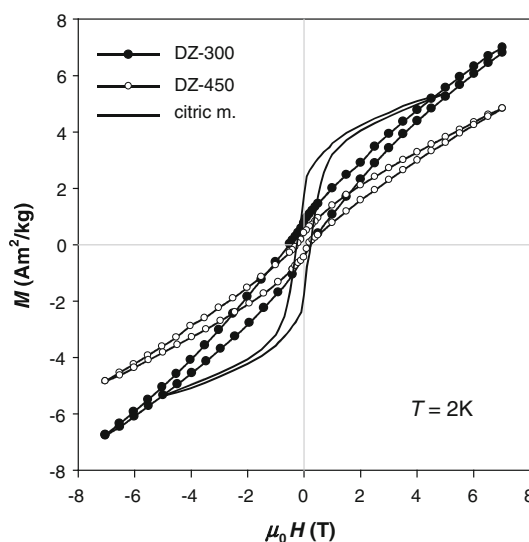


Fig. 15 Typical magnetization isotherms ($T = 2$ K) of the samples annealed at the lowest (DZ 300) and the highest (DZ 450) temperature in comparison to the bulk sample prepared using the citric method (citric m.)

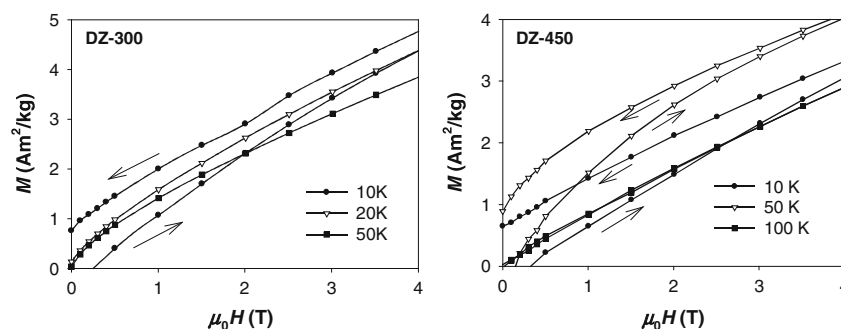


Fig. 16 Details of the magnetization isotherms of the DZ 300 and DZ 450 samples. For the DZ 300 sample, the curves are measured at selected temperatures below the T_f . For the DZ 450 sample, the curves are recorded at the temperatures corresponding to the

ground state (10 K), ferrimagnetic (50 K), and paramagnetic (100 K) phase in the bulk CoCr_2O_4 . The arrows indicate branches of the curves with hysteresis corresponding to the increasing/decreasing applied magnetic field

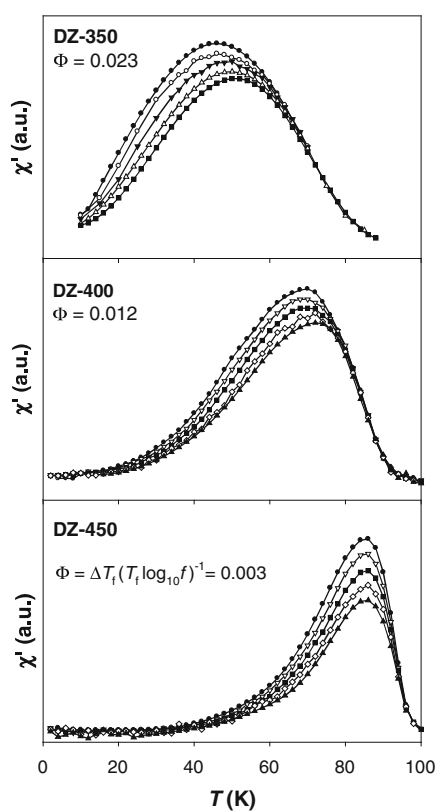


Fig. 17 Temperature dependence of the real part of the a.c. magnetic susceptibility, χ' recorded in the frequencies: 0.1, 1, 10, 10^2 , and 10^3 Hz; the maxima exhibit a moderate shift to higher temperatures with the increasing frequency

characteristic for paramagnetic phases. Those measured at 2 K show moderate hysteresis of ~ 0.2 T, which is about two orders larger than that reported for a single crystal (Tomiyasu et al. 2004), but comparable to the coercivity, H_c , of the polycrystalline sample (shown for comparison in Fig. 15). The enhancement of the H_c can be usually observed in nonstoichiometric samples or in samples containing a small amount of antiferromagnetic phases like CoO or Cr_2O_3 (not detectable by PXRD) in contact with the NPs, which can be involved in the exchange-bias phenomena (EB). Inspecting carefully both the positive and negative values of the H_c after FC (not shown), a clear shift of the hysteresis loop to the negative fields occurs, which supports the role of the EB in the H_c enhancement. The values of the EB field [defined as: $H_{\text{EB}} = (H_c^+ - H_c^-)/2$] are 0.140, 0.055, and 0.025 T for the DZ 450, DZ 300, and reference samples, respectively. Nevertheless, the magnetization does not saturate even in the field of 7 T suggesting that the fraction of the ordered sample is rather low and thus the EB is a matter of a minor sample volume. The overall lack of saturation can be attributed either to the surface spin disorder (Kodama et al. 1997), or it can be rather explained by the formation of the glassy-like state. With increasing temperature to the T_f , the magnetization isotherms of the DZ 300 sample show monotonous decrease of both the H_c and remanence, while those of the DZ 450 sample exhibit a sudden increase of the remanence at about 50 K suggesting

transition to a different magnetic phase as observed in the bulk sample.

The temperature dependencies of the real part of the a.c. susceptibility of the DZ 350, DZ 400, and DZ 450 samples are shown in Fig. 17. The curves show a single maxima for each frequency (f), which shift to higher temperatures with increasing f , as expected. In order to classify the nature of the relaxation processes in the samples, a simple estimation of the relative shift of the maximum temperature per frequency decade was performed (Goya et al. 2003). The corresponding parameter, Φ , is defined as $\Delta T^*(T^*\log_{10}f)^{-1}$, where T^* is the temperature of the susceptibility maximum at given frequency, f . The Φ values decrease with the increasing particle size as 0.023, 0.012, and 0.003 for the DZ 350, DZ 400, and DZ 450 samples, respectively. Typically, the Φ values about 0.02–0.05 suggest formation of concentrated spin-glass (SG) or cluster-glass (CG) states, usually in the surface layer (shell) of the NPs (Dormann et al. 1997; Li et al. 2003); the Φ values in order of 0.001 are either characteristic for canonical SG or ferromagnetic CG compounds (Nishioka et al. 2000) or suggest formation of rather well-ordered magnetic phase. Considering the previously discussed results of the magnetization measurements, the a.c. susceptibility study corroborates the proposed increase of the spin disorder in NPs with decreasing particle size, leading to suppression of the long-range ferrimagnetic order.

Conclusions

The hydrothermal method in oleic acid–sodium oleate–water–ethanol was successfully used for the preparation of well-crystalline cobalt chromite NPs with the size ranging from 4.4 to 11.5 nm, yielding the as-prepared NPs capped by the oleic acid. The mechanism of the NP formation in the oleic acid–sodium oleate–water system was also proposed. The water and organic content was determined using the TGA; the as-prepared particles contain about 2 % of the organic phase. It was found that the particles size increases with the increasing annealing temperature, as expected, and the size distribution, determined from the TEM analysis, is relatively narrow. The Raman and FTIR spectroscopy studies confirmed presence of inverse spinel structure; however, additional bands related to disorder were also observed.

Finally, magnetic properties of the samples were investigated and related to the particle size. Typical features of glassy-like state become more pronounced with the decreasing particle size, as it is evidenced by the temperature and in-field dependence of magnetization and frequency-dependent a.c. susceptibility. The shift of the ZFC–FC furcation point (T_f) and the maxima on the ZFC curve ($T_{\max}$) toward lower temperatures with the decreasing particle size are attributed to continuous increase of the spin disorder. While the ferrimagnetic order still dominates in the largest particles, it almost collapses in the sample with the least particle size close to the coherence length of the spin wave in the ground state magnetic structure. As the magneto-electric coupling in the bulk CoCr_2O_4 is believed to be conditioned by formation of the spiral magnetic phase, a study of dielectric properties with respect to the particle size is of high demand to clear up the scenario of multiferroicity in the CoCr_2O_4 and related compounds.

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3.2 Nanomateriály s oxidy železa

V této sekci jsou shrnuty práce zabývající se nanočásticemi a nanokompozity různých fází oxidů železa. První část se zaměřuje na nanokompozity s oxidem železitým a druhá část se věnuje pracem zaměřeným na izolované částice magnetitu a maghemitu.

3.2.1 Nanokompozity na bázi oxidu železitého

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V této části jsou zahrnuty publikace zabývající se přípravou různých nanokompozitů s nanokrystaly oxidu železitého. Připravené materiály jsou detailně analyzovány pomocí Mössbauerovy spektroskopie, elektronové mikroskopie, RTG difrakce a dále jsou určeny jejich magnetické vlastnosti pomocí již dříve zmíněných metod (měření teplotní závislosti magnetizace a střídavé susceptibility a magnetizačních křivek).

První práce [89] se zabývá statickými a dynamickými magnetickými vlastnostmi nanokompozitů tvořených patentovanou látkou FF6.2 (absorbér elektromagnetického záření, obsahuje nanokrystalický oxid železitý) a kuličkami amorfního oxidu křemičitého. Nanokompozity byly připraveny pomocí modifikované Stöberovy metody ve skupině prof. Maruszewského (Politechnika Wroclawska) a charakterizovány výše uvedenými metodami. V nanokompozitech byla potvrzena přítomnost 5 nm nanočástic maghemitu s teplotou blokace a efektivní

anizotropní konstantou vzrůstající pro nanokompozity s vyšší koncentrací nanočástic, což je v souladu se zesilujícími dipolárními interakcemi v koncentrovanějších kompozitech.

Práce [90] se věnuje přípravě a magnetickým vlastnostem nanokompozitu ϵ oxidu železitého v matrici amorfního oxidu křemičitého. Je popsána zcela nová metoda využívající molekulárního prekursoru, který obsahuje ionty železité i stavební jednotky matrice SiO_2 . Pomocí této syntézy je možné připravit nanokompozit s více než dvojnásobnou koncentrací Fe_2O_3 oproti standardní metodě sol-gel. Práce dále popisuje charakteristické magnetické vlastnosti této metastabilní fáze oxidu železitého. Další práce [91] využívá standardní metody sol-gel pro přípravu vícesložkového nanokompozitu $\text{Fe}_2\text{O}_3\text{-CeO}_2\text{-SiO}_2$. Cílem je optimalizovat způsob přípravy tak, aby byl dosažen maximální výtěžek fáze $\epsilon\text{-Fe}_2\text{O}_3$.

Další dvě práce popisují přípravu a studium strukturních a magnetických vlastností magneticky separovatelného katalyzátoru na bázi $\gamma\text{-Fe}_2\text{O}_3$ a TiO_2 [77]. Je popsána ekologicky šetrná dvojkroková syntéza, která spočívá v přípravě nanokrystalů maghemitu a jejich následnému pokrytí TiO_2 pomocí heterogenní precipitace TiOSO_4 močovinou. Detailní charakterizace pomocí experimentálních metod zmíněných v úvodu této sekce je doplněno o studium fotokatalytických vlastností nanokompozitu žíhaného při různých teplotách od 200 do 400 °C. Měření in situ a ex situ práškové difrakce na synchrotronu ANKA, Karlsruhe umožnilo určení fázového složení, velikosti a tvaru částic a ověření struktury jádro-slupka pomocí Debyeovy rovnice, výsledky jsou součástí práce [92].

Poslední práce v této sekci se zabývá přípravou nanokompozitu chirálních kapalných krystalů a superparamagnetických nanočástic $\gamma\text{-Fe}_2\text{O}_3$ [93], jejíž motivací je intenzivní výzkum systémů s tzv. multiferoickou odezvou. Jedná se o materiály, které vykazují více než jedno feroické uspořádání, nejčastěji (anti)feromagnetické a ferolektrické, ideálně s tzv. magneto-elektrickou vazbou. Často se jedná o podvojně oxidy přechodných kovů, nicméně roste zájem o přípravu hybridních kompozitů spojením dvou a více materiálů, kdy jeden je nositelem feroelektrických a druhý vhodných magnetických vlastností. Práce popisuje postup přípravy a studium dielektrických a magnetických vlastností tohoto unikátního kompozitu v závislosti na teplotě a vnějším magnetickém poli. Byl nalezen optimální podíl magnetické komponenty - 5.6 %, kdy je zachováno unikátní elektrické uspořádání původních kapalných krystalů (chirální smektická fáze). Velikost magnetických nanočástic (4 nm) byla zvolena tak, aby odpovídala co nejlépe velikosti jednotlivých molekul kapalných krystalů (cca 1 nm), a proto generovala co nejmenší podíl poruch v uspořádaném stavu. Magnetické vlastnosti kompozitu odpovídaly de facto chování samotných nanočástic, pouze se snižující se koncentrací nanočástic v kompozitu docházelo ke snižování teploty blokace z důvodu oslabení dipolárních

mezičásticových interakcí. Interakce superspinu a polarizace se dosud nepodařilo prokázat.

Magnetism of FF6.2/SiO₂ nanocomposites as observed by static and dynamic probes

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Abstract

We report on magnetic behavior of the electromagnetic compatibility (EMC) compound FF6.2 and composites prepared by the modified Stöber method using FF6.2 as the magnetic ion-containing (Fe²⁺/Fe³⁺) precursor. The composites were characterized by the X-ray diffraction analysis (XRD) and morphology of the magnetic powders was investigated by a scanning electron microscope (SEM) and a high resolution transmission electron microscope (HR TEM). Magnetic properties of the materials were studied by measurements of the magnetization, AC susceptibility and Mössbauer spectra.

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Keywords: Sol–gel method; Magnetic nanoparticle; Superparamagnetism

1. Introduction

Recently, new class of materials with huge application potential, the so-called electromagnetic compatibility (EMC) compounds, was discovered by Kolodziej et al. [1]. The magnetic ion containing media are capable of absorbing electromagnetic energy and have been utilized as highly effective EM-field shielding. Our work was motivated by current boom of nanoparticles investigation due to unusual phenomena arising from finite size and surface effects (like superparamagnetism, high-field irreversibility, poor saturation, extra anisotropy contributions or shifted loops after cooling in a magnetic field) [2]. We used the EMC precursor to prepare a new nanocomposite system of promising physical properties.

2. Experimental and results

The nanocomposite powders have been prepared by the Stöber method [3]. The FF6.2 comprises Fe²⁺/Fe³⁺ ions

in a special organic polymer; its exact composition is protected by the UK patent [1]. The FF6.2 constituent was suspended in hexanol before adding to the sol; to keep a clear notation the samples were labeled according to the initial amount of FF6.2 suspension in ml: S100–S700. Detailed synthesis procedure is presented in Ref. [4].

The scanning electron microscope (SEM) and high resolution transmission electron microscope (HR TEM) images illustrated the highly crystalline nature of the nanoparticles (grain diameter of 5 nm) embedded in regular amorphous silica spheres (500 nm in diameter). The XRD patterns showed the spinel structure of the magnetite (Fe₃O₄) with very broad lines as expected for the nanosized particles. However, the pattern of magnetite is almost identical with that of maghemite and at this point we cannot exclude, that composites comprise γ-Fe₂O₃. Except the broad peak arising from the amorphous matrix, no additional phase was observed.

The Mössbauer spectra (MS) were collected at 4K and 300 K. Measurements were done in the transmission mode with the ⁵⁷Co in a Cr matrix as the source, standard-Fe foil at 293 K was used as the for the isomer shift (IS) expression. The fitting of the spectra was performed with

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the NORMOS program. The room temperature MS can be decomposed into one singlet and two sextets. The broad singlet ($IS = 0.31$ mm/s) represents a collapsed sextet corresponding to the Fe in the particles, which are in the SP state (fraction with the blocking temperature T_B below 300 K). The broad sextet ($IS = 0.39$ mm/s, quadrupole splitting $QS = -0.01$ mm/s, hyperfine field $B_{hf} = 28.4$ T) corresponds to Fe in the particles, with the T_B very close to 300 K. The second sextet ($IS = 0.32$ mm/s, $QS = 0.00$ mm/s, $B_{hf} = 42.7$ T) corresponds to the maghemite ($\gamma\text{-Fe}_2\text{O}_3$) due to $IS = 0.32$ mm/s, which is the characteristic value of Fe^{3+} . The MS recorded at 4 K can be fitted using two sextets and a doublet. The sextets ($IS = 0.47$ mm/s, $QS = 0.02$ mm/s, $B_{hf} = 53.0$ T; $IS = 0.43$ mm/s, $QS = -0.04$ mm/s, $B_{hf} = 51.1$ T) correspond to Fe in the tetrahedral and the octahedral coordination of the spinel structure, respectively. The doublet occurs due to a small amount of the superpara-magnetic phase ($IS = 0.27$ mm/s and $QS = 0.41$ mm/s).

Magnetization (M) and AC susceptibility data were recorded on commercial apparatus PPMS 9 T (quantum design) in the temperature ranges 2–350 K and magnetic field up to 9 T. The zero-field cooled (ZFC) and field-cooled (FC) $M(T)$ curves show typical features of a SP system by means of furcating below T_B in contrast to the FF6.2 data (Fig. 1a). The T_B values range between 75 up to 85 K, however show no regular dependence on the initial FF6.2 concentration. The estimation of T_B is very rough

when considering the effect of particle size distribution and magnetic field magnitude on the furcation point. We propose that the T_B value observed by this technique would correspond to the blocking process at 30 mT of the particle fraction with the largest size in the whole sample.

The conclusion on SP behavior of the studied composites is corroborated by the AC susceptibility data (Fig. 1c). Both, the real and imaginary response, exhibit a broad maximum, which is systematically shifted to higher temperatures with increasing AC field frequency. The data were further analyzed with respect to the Arrhenius law [5] yielding the values of the characteristic relaxation time, τ_0 and the energy barrier, E_a . The values of E_a slightly increase with increasing the FF6.2 content, the τ_0 values follow no monotonous trend reaching $\sim 10^{-9}$ s within the whole series consistently with expectations for a system of non-interacting SP particles. The AC response of the FF6.2 itself differs from the above-mentioned observations (Fig. 1d).

While the properties of the composites above T_B do not vary notably with changing the FF6.2 concentration, the parameters characterizing the blocked state are influenced obviously, for the comprehensive summary, please see Table 1. The hysteresis loops recorded at 2 K show that the saturated magnetization value, $M_{s,2K}$ increases consistently with the increasing FF6.2 content up to 6.4×10^{-3} A m²/kg in the S700 sample. In consistency, the remnant magnetization values at 2 K, $M_{R,2K}$ follow the analog trend ranging from 0.5×10^{-3} A m²/kg in S100 to 6.5×10^{-3} A m²/kg in

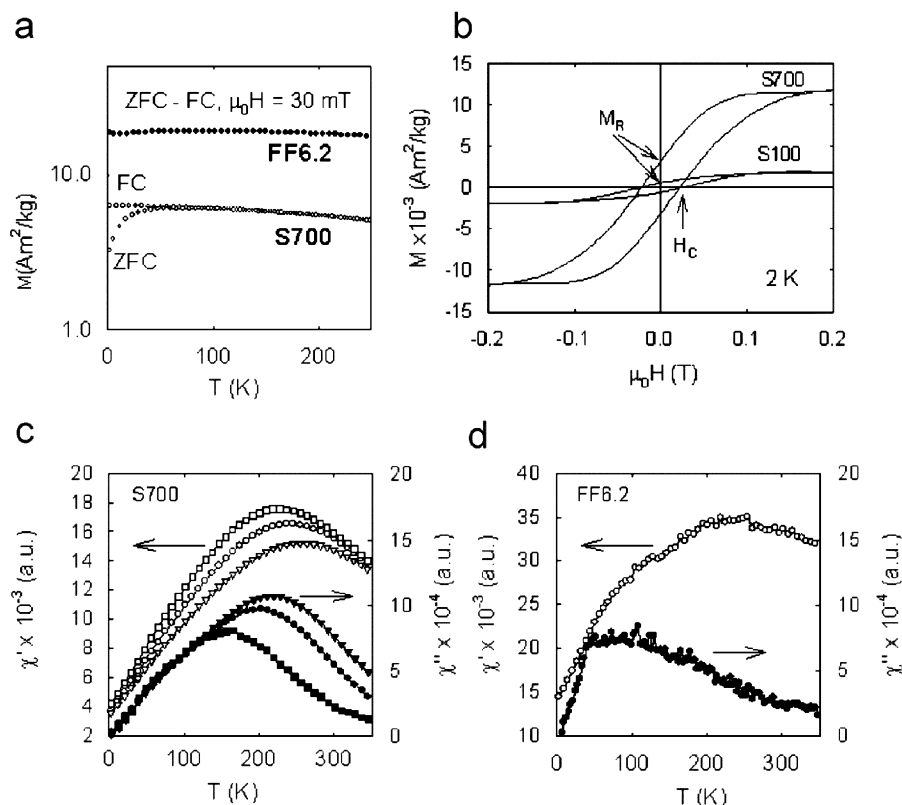


Fig. 1. Comparison of composites and FF6.2 properties: (a) ZFC–FC curves (log scale in M). (b) magnetization curves at 2 K. c, d–AC susceptibility: (c) frequencies 13, 10^3 , 10^4 Hz, (d) 103 Hz.

Table 1

Saturated magnetization, $M_{s, 2K}$ at 2 K; remnant magnetization, $M_{R, 2K}$ at 2 K, T_B estimated from the AC susceptibility, $T_{B,ac}$ and ZFC–FC magnetization, $T_{B,ZFC-FC}$ dependencies; results of the Arrhenius law fit, τ_0 , E_a/k_B

Sample	$M_{s, 2K}$ (A m ² /kg)	$M_{R, 2K}$ (A m ² /kg)	$T_{B, AC}$ (K)	$T_{B, ZFC-FC}$ (K)	τ_0 (10 ^{−9} × s)	E_a/k_B
S100	2×10^{-3}	0.5×10^{-3}	138	70	6.7	1836
S200	5×10^{-3}	1.5×10^{-3}	131	80	2.9	1878
S300	6×10^{-3}	2.5×10^{-3}	130	85	1.7	1338
S500	8×10^{-3}	4×10^{-3}	174	70	1.6	1581
S600	11×10^{-3}	5×10^{-3}	177	75	6.0	2249
S700	15×10^{-3}	6.5×10^{-3}	183	80	3.6	2875

S700, respectively. The hysteresis observed in the blocked-state characterized by the coercivity force, H_c is negligible (~ 0.025 T) and does not vary within the whole series (Fig. 1b). The FF6.2. compound does not exhibit any remnant magnetization and hysteresis.

3. Conclusions

Nanocomposite powders containing uniform iron oxide nanoparticles (~ 5 nm) dispersed in silica matrix were investigated together with the initial magnetic dopant FF6.2. Mössbauer spectra revealed superparamagnetism at room temperature (very broad peaks) while the 4 K measurement showed majority of magnetically ordered spinel structure. Magnetization and AC susceptibility investigations supported SP behavior above the blocking temperature (~ 80 K). T_B is more or less independent on the concentration of the magnetic agent FF6.2 as expected due to uniform size of FF6.2 particles accommodated in the SiO₂ spheres. The saturated magnetization value increases consistently with the increasing FF6.2 content; the remnant

magnetization values at 2 K follow the analogues trend. The hysteresis observed in the blocked state is almost negligible. In contrast, the original FF6.2 do not exhibit SP response and show no remnant magnetization. Detailed investigations of dielectric properties are in progress.

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Novel sol-gel method for preparation of high concentration ε -Fe₂O₃/SiO₂ nanocomposite

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Abstract ε -Fe₂O₃/SiO₂ nanocomposite was prepared by novel solgel method using single precursor for both nanoparticles and matrix. This method allows to prepare the samples free of α -Fe₂O₃ with 40% of Fe₂O₃ in SiO₂. Nanoparticles of 12 nm diameter were obtained by annealing at 1,000 °C. The samples were characterized by powder X-ray diffraction and transmission electron microscopy. Mössbauer spectroscopy identified ε -Fe₂O₃ as the only magnetically ordered phase at room temperature. Magnetic measurements revealed progressive necking of hysteresis loops measured at 300 and 2 K. In both cases the intrinsic coercivity reaches only 0.25 T. Measurements up to 14 T shows monotonous decreasing trend of saturated magnetization with increasing temperature.

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1 Introduction

Iron (III) oxide forms two well-known polymorphs—the maghemite (γ -Fe₂O₃), which is in fact a metastable phase, and is transformed into the hematite (α -Fe₂O₃) at higher temperatures. At certain conditions, the elusive ε -Fe₂O₃ can be obtained as an intermediate between these two phases.

Recently, the ε -Fe₂O₃ phase attracted much attention due to its enormous room-temperature coercivity of about 2 T [1–3], and coupling of magnetic and dielectric properties, the so-called magneto-electric response [4]. Its physical properties with large application potential stimulated numerous investigations, however, majority of the samples with the 2 T-coercivity reported at the room temperature contained significant fraction of the α -Fe₂O₃ phase, as observed by powder diffraction experiments and Mössbauer spectroscopy.

Preparation of the single-phase ε -Fe₂O₃ is without question a crucial step limiting investigation of its intrinsic physical properties.

The first preparation of this phase was reported by Forestier and Guiot-Guillain in 1934 [5]. Consequently, many different methods were developed in order to avoid formation of spurious iron(III) oxide phases. Schrader and Büttner [6] obtained ε -Fe₂O₃ mixed with hematite and maghemite, by vaporizing iron in an electric discharge under oxygen flux. Walter-Lévy and Quémeneur [7] obtained it mixed with hematite by heating a basic sulfate salt. Trautmann and Forestier [8] reported the preparation of pure ε -Fe₂O₃ by boiling an aqueous mixture of potassium ferricyanide, sodium hypochlorite and potassium hydroxide. The

same procedure was used by Dézsi and Coey in 1973 [9]. In 1994 Nižňanský et al. [10] showed that thermal stability of metastable iron oxides can be enhanced by encapsulating of nanoparticles in silica matrix. Formation of ε -Fe₂O₃ in this nanocomposite is assured by spatial limitation of nanoparticles' growth. Fe₂O₃/SiO₂ system was also studied Chanéac et al. [11], and Viart [12]. They obtained ε -Fe₂O₃ in mixture with hematite. Hutlová [13] prepared mixture of ε - and α -Fe₂O₃ by decomposition of Y₃Fe₅O₁₂/SiO₂ nanocomposite. Most recently Jin et al. [14], used reverse micelle method for preparation of ε -Fe₂O₃/SiO₂ nanocomposite and Kelm and Mader [15] prepared ε -Fe₂O₃ by internal oxidation of Pd-Fe alloy and by thermal decomposition of mineral nontronite. Zbořil et al. [16] prepared ε -Fe₂O₃ mixed with α -Fe₂O₃ from γ -Fe₂O₃ nanoparticles without a supporting matrix.

In this work, we report a new approach to the preparation of magnetic nanocomposites for simple system Fe₂O₃/SiO₂. In contrast to above-mentioned preparation methods dealing with this system, we use a single precursor in which both functional groups for silica matrix and iron oxide are present. The molecule serves as a brick for building of the nanocomposite. The method assures better homogeneity of sample and no spurious hematite is formed. It is also expected that this preparation way can be extended to a large set of doped systems in order to enhance the magnetic and magneto-electric properties.

2 Experimental

The samples were reproducibly prepared by the sol-gel method. Synthesis starts with the preparation of ethylenediaminetetraacetic acid (EDTA) dianhydride (**2**) from EDTA (**1**). Ligand molecule (**3**) is synthesized by reaction of EDTA dianhydride with (3-aminopropyl)trimethoxysilane (Fig. 1). In order to determine the purity of synthesized molecules, ¹H

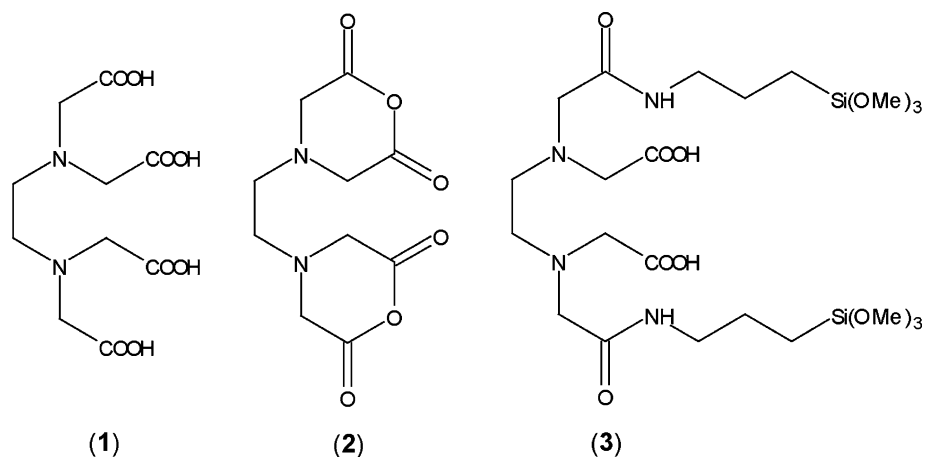
(399.95 MHz) and ¹³C (100.57 MHz) NMR spectra (23 °C) were recorded using Varian Unity INOVA 400 in following solvent with the indicated internal standards (relative to Me₄Si): DMSO-d₆, residual CD₃SOCD₂H (δ 2.50) and CD₃SOCD₃ (δ 39.47) for ¹H and ¹³C NMR, respectively.

Ethylenediaminetetraacetic acid dianhydride (**2**) was prepared according to a modified literature procedure [17]. About 20.0 g (68 mmol) of ethylenediaminetetraacetic acid was suspended in 34 mL of pyridine (purified and dried by distillation with metal sodium). To the stirred suspension at 65 °C was added 31 mL (313 mmol) of acetanhydride. After 2 days the product was collected by filtration, washed 4 $\times$ 50 mL of acetanhydride and 1 $\times$ 50 mL of diethyl-ether, protecting the collected solid from the atmosphere and dried at room temperature under vacuum to yield 15.0 g (86%) of white powder: mp 188–190 °C (dec.); ¹H NMR (DMSO-d₆) δ (ppm): 2.67 (s, 4H, N-(CH₂)₂-N), 3.70 (s, 8H, OOC-CH₂-N), ¹³C {¹H} NMR (DMSO-d₆) δ (ppm): 165.8 (s, -COO), 52.3 (s, OOC-CH₂-N), 51.2 (N-(CH₂)₂-N).

Ligand molecule (**3**). 1.5 g (5.9 mmol) of (**2**) was suspended in 12 mL of dry dimethylformamide (DMF). To the stirred suspension at 70 °C was added 2.1 g (11.7 mmol) of 3-aminopropyltrimethoxysilane dropwise over 5 min. After the addition of the amine the solid phase disappeared and the reaction mixture became homogenous. After 30 min the reaction mixture was cooled to room temperature and 80 mL of acetone was added. White precipitate was collected by filtration and washed by 10 mL of acetone, protecting the collected solid from the atmosphere and dried at room temperature under vacuum to yield 3.4 g (94%) of white powder: ¹³C {¹H} NMR (DMSO-d₆) δ (ppm): 177.1 and 173.3 (both s, C(O)X); 60.2 a 59.6 (both s, CH₂-C(O)X), 53.0 (s, N-(CH₂)₂-N), 48.8 (s, OCH₃), 42.7 (s, C(O)NH-CH₂), 25.1 (s, CH₂-CH₂-CH₂), 6.4 (s, Si-CH₂). Splitting from ²⁹Si was not observed.

Afterwards, the complexation of Fe(III) ions by (**3**) takes place. The Si-OCH₃ bonds of this complex are subsequently

Fig. 1 EDTA (**1**), EDTA dianhydride (**2**) and ligand molecule (**3**)



hydrolyzed and then condensation takes place. For complexation a solution of 3.6 g of (**3**) (5.9 mmol) in 12 mL of DMF was cooled in water/ice bath to 0 °C to prevent uncontrolled hydrolysis and condensation of $-\text{Si}(\text{OCH}_3)$ groups. Then 2.3 g (5.9 mmol) of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 5 mL of methanol was added dropwise over 5 min. The reaction mixture was stirred for 15 min at this temperature and then let warm to room temperature. Then the viscosity increased and solid phase was formed after approximately 1 h after addition of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Wet xerogel was left for ageing at 40 °C for 2 days and then the reaction vessel was opened and the liquid phase was evaporated which took several days. Then the xerogel was progressively heated up to 300 °C in vacuum and finally annealed at 1,000 °C for 1 h in air. The final molar ratio between Fe_2O_3 and SiO_2 was 1:4.

EDX analysis was performed on Philips XL 30 CP operating at 25 kV, sample was studied in native form. The electron microscopy was performed on final nanocomposites deposited on a polymer film supported in a holed copper disk by use of a JEOL JEM 3010 microscope operating at 300 kV accelerating voltage. The size distribution was estimated from a statistical count of the particles from several frames taken on different parts of the samples.

Powder X-ray diffraction patterns of final nanocomposites were recorded at room temperature using the Bragg-Brentano geometry on a Philips X-pert using Cu-anode with secondary monochromator.

Mössbauer spectra measurement were carried out in order to determine iron oxides phase composition of final nanocomposites. The Mössbauer spectra measurement was carried out in the transmission mode with ^{57}Co diffused into an Rh matrix as a source moving with constant acceleration. The spectrometer (Wissel) was calibrated by means of a standard $\alpha\text{-Fe}$ foil, and the isomer shift was expressed with respect to this standard at 293 K. The fitting of the spectra was performed with the help of the NORMOS program.

Measurements of the magnetic properties of the final nanocomposites as functions of temperature and magnetic field, respectively, were done using a commercial PPMS and MPMS device from Quantum Design. The zero-field cooled and field-cooled curves, and the frequency-dependent a.c. susceptibility were recorded in the temperature range 2–350 K. Hysteresis loops were measured at selected temperatures up to magnetic fields of 14 T.

3 Results and discussion

3.1 EDX, powder XRD and TEM

In order to evaluate the composition of our samples we performed an EDX analysis on two different areas of the

ground sample. The results of EDX confirmed, that the real composition corresponds to the calculated content of the respective elements (calculated: O 65 at.%; Si 23 at.%; Fe 12 at.%; found: O: 65 at.%; Si: 24 at.%, Fe: 11 at.%).

Figure 2 shows diffraction pattern of final nanocomposite annealed for 1 h at 1,000 °C. Except a hump centered around 22° due to amorphous silica, only $\epsilon\text{-Fe}_2\text{O}_3$ phase is evident from XRD measurement. There is no diffraction peak, which could be unambiguously attributed to $\alpha\text{-}$ or $\gamma\text{-Fe}_2\text{O}_3$. Starting from the unit cell parameters of $\epsilon\text{-Fe}_2\text{O}_3$ [15], we successfully performed a pattern matching using FULLPROF software. The fitted unit-cell parameters within Pna2₁ space group ($R_p = 14.1$ and $R_{wp} = 14.2$) are given in Table 1. Obtained lattice constants are similar to those reported in the literature [15, 18].

Diffraction patterns of samples annealed at 900 °C and lower temperature showed broad diffraction peaks which indicates small iron oxide nanoparticles. Peaks can be assigned to either $\gamma\text{-}$ or $\epsilon\text{-Fe}_2\text{O}_3$.

The size and shape of the $\epsilon\text{-Fe}_2\text{O}_3$ particles were determined by TEM (Fig. 3). Shape of particles varies from globular without any developed crystal faces to rod-like shape. Nanoparticles are homogeneously dispersed all over the SiO_2 matrix. Mean size of particle diameter was estimated to be 12 nm (Fig. 4).

3.2 Mössbauer spectroscopy

In our particular case Mössbauer spectroscopy has better detection limits of the iron oxide phases than powder XRD. It works especially for bigger $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles [18, 19] due to lower blocking temperature T_B . The crystal structure of $\epsilon\text{-Fe}_2\text{O}_3$ has four different Fe sites. Three of them have octahedral coordination of oxygen atoms and one has tetrahedral one. Thus, the Mössbauer spectrum measured on $\epsilon\text{-Fe}_2\text{O}_3$ has four contributions from four different Fe sites. The values of hyperfine field (B_{hf}) and

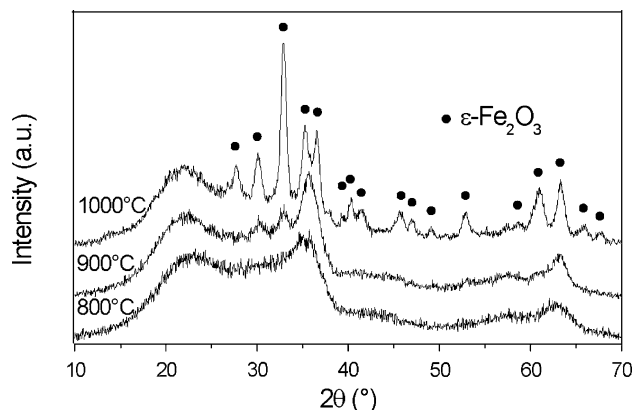
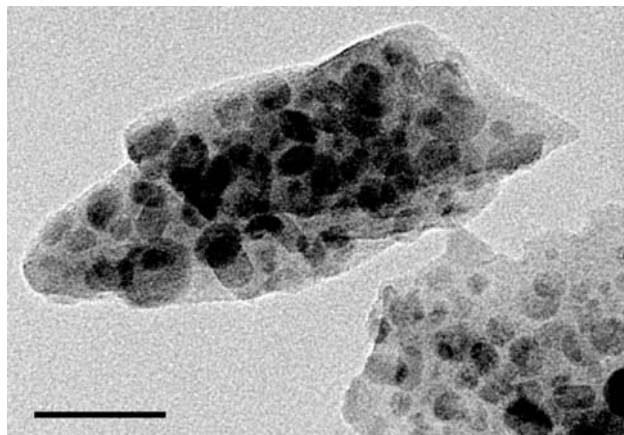
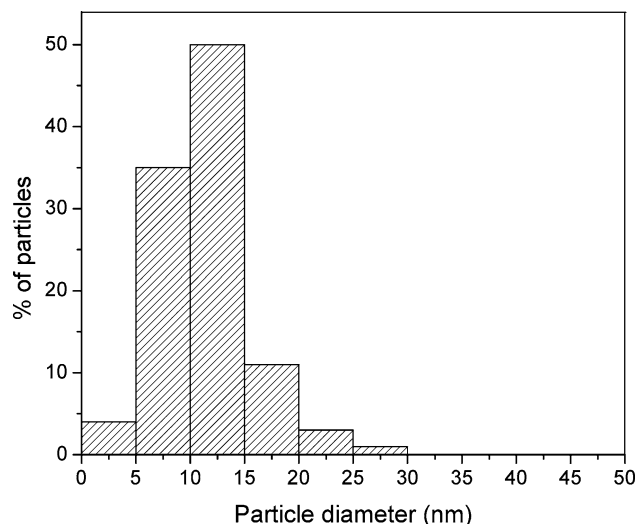


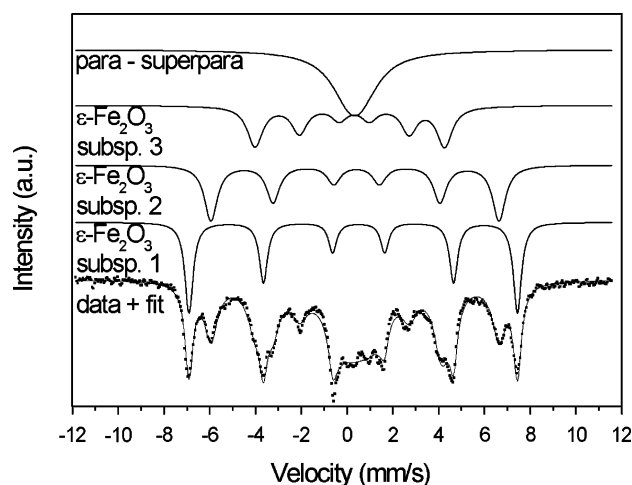
Fig. 2 Diffraction patterns of $\epsilon\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanocomposites annealed for 1 h at 800, 900 and 1,000 °C

Table 1 Lattice constants of ϵ -Fe₂O₃

	<i>a</i> (pm)	<i>b</i> (pm)	<i>c</i> (pm)
ϵ -Fe ₂ O ₃	511.1(2)	877.5(2)	948.6(3)
ϵ -Fe ₂ O ₃ [15]	507.15(2)	873.59(4)	941.78(4)
ϵ -Fe ₂ O ₃ [18]	509.5(1)	878.9(2)	943.7(3)

**Fig. 3** TEM image of sample annealed at 1,000 °C for 1 h. Length of the bar corresponds to 50 nm**Fig. 4** Particle size distribution of sample annealed at 1,000 °C for 1 h

chemical shift of two of these sites are so close to each other that they are fitted by one sextet (labeled as subsp. 1— $B_{\text{hf}} = 45$ T). Third octahedral Fe site labeled as subsp. two shows $B_{\text{hf}} = 39$ T. Fourth Fe-site has tetrahedral coordination (labeled as subsp. 3— $B_{\text{hf}} = 26$ T). Each measured spectrum was fitted by these three independent sextets corresponding to magnetically ordered phase and one doublet corresponding to magnetically non-ordered phase which can be either nanoparticles of iron oxide in the

**Fig. 5** Mössbauer spectrum of sample annealed at 1,000 °C for 1 h

superparamagnetic state or isolated iron cations. Sample annealed at 1,000 °C consists of three well defined sextets corresponding to ϵ -Fe₂O₃ and one doublet (Fig. 5; Table 2). Other sextet corresponding to α - or γ -Fe₂O₃ were not observed. On the basis of these measurements we can exclude detectable amount of α -Fe₂O₃ in the sample. Presence of γ -Fe₂O₃ cannot be excluded due to doublet of magnetically non-ordered iron (20% of spectral area). There was no evidence of ferrous ions even at lower annealing temperatures.

3.3 Basic magnetic characteristics

Selected results of magnetic characterization of the obtained composites are presented in order to demonstrate its physical properties in comparison to the ϵ -Fe₂O₃-based materials reported by other authors [1, 2].

The most outstanding is the poles-apart character of the hysteresis curves with a pronounced necking, as demonstrated in Fig. 6.

The room-temperature value of the saturated magnetization, M_s reaches 10 Am²/kg, which is twice larger than the value reported by Kurmoo et al. [1], but counts only 2/3 of the 15 Am²/kg obtained at 7 T-field presented by Jin

Table 2 Fitted Mössbauer parameters

	<i>A</i> (%)	<i>IS</i> (mm/s)	<i>QS</i> (mm/s)	<i>B</i> _{hf} (T)	<i>Γ</i> (mm/s)
Subspectrum 1	30	0.38(1)	−0.24(1)	44.5(1)	0.57(1)
Subspectrum 2	27	0.38(1)	−0.05(1)	38.9(1)	0.57(1)
Subspectrum 3	23	0.20(1)	−0.15(1)	25.6(1)	0.57(1)
Para-superpara	20	0.36(1)	0.97(1)		1.89(1)

A stands for relative area, *IS* for isomer shift, *QS* for quadrupole splitting, *B*_{hf} for hyperfine field and *Γ* for line width

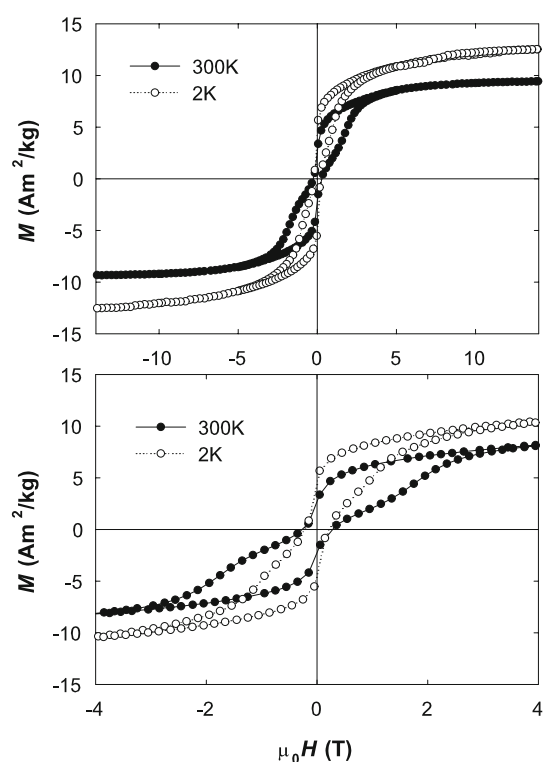


Fig. 6 Hysteresis loops measured at 2 and 300 K, respectively. The upper panel demonstrates the full curves up to 14 T-field, the lower panel depicts the detail of the coercivity

et al. [2]. The intrinsic coercivity value, $H_c = 0.25$ T is much suppressed in contrast to the 2 T-value published previously [1, 2].

The 2 K-loop shows the M_s value of almost $13 \text{ Am}^2/\text{kg}$ with intact coercivity. Both values are very similar to those presented by Kurmoo et al. [2].

The observed necking of the hysteresis loops in our sample is attributed to the fact, that the sample is composed of a fraction of the well-formed $\epsilon\text{-Fe}_2\text{O}_3$ particles and a fraction of $\gamma\text{-Fe}_2\text{O}_3$ or very small superparamagnetic (SPM) $\epsilon\text{-Fe}_2\text{O}_3$ particles entering a blocked state below ~ 50 K. Considering the work of Ohkoshi et al. [20], the $\epsilon\text{-Fe}_2\text{O}_3$ phase forms only in a restricted interval of particle diameter, d : $-6v(\sigma^\epsilon - \sigma^\gamma)/(\mu^\epsilon - \mu^\gamma) < d < -6v(\sigma^\alpha - \sigma^\epsilon)/(\mu^\alpha - \mu^\epsilon)$, where σ is the surface energy and μ is the chemical potential of the γ , ϵ and α phase, respectively, and v is the molar volume. If the iron oxide particles do not develop homogeneously in the whole sample volume during the annealing procedure, formation of a minority amount of $\gamma\text{-Fe}_2\text{O}_3$ particles with a diameter below 3 nm is highly probable. However, it is a question if all particles of the $\gamma\text{-Fe}_2\text{O}_3$ phase are small enough so we cannot see magnetically ordered $\gamma\text{-Fe}_2\text{O}_3$ ($B_{\text{hf}} \sim 49$ T) by Mössbauer spectroscopy. On the other hand, the maghemite nanoparticles of 3–5 nm size are SPM at room temperature and enter the blocking regime typically

below 50–100 K [21], so the low-coercivity phase in our samples is the most probably $\gamma\text{-Fe}_2\text{O}_3$ with grain size below ~ 4 nm.

The above-presented scenario is supported by the character of the temperature dependence of the zero field-cooled (ZFC) and field-cooled (FC) magnetization and a.c. susceptibility, presented in Fig. 7. The ZFC and FC curves exhibit a symmetric anomaly at 100 K in agreement with other reports [2]. In contrast, a broad shoulder appears on the ZFC curve below 50 K, which turns to a monotonously increasing tail on the FC curve. In context of other results, this contribution is originated by SPM response of SPM (maghemite) particles in our sample.

The real and imaginary part of the a.c. susceptibility, respectively, exhibits a sharp anomaly at ~ 100 K and an additional shoulder of SPM origin below 50 K. To support the interpretation regarding the anomalies, we present a detailed measurement of the frequency-dependent a.c. susceptibility in Fig. 8. The 100 K-peak shows an anomalous trend with respect to the applied frequency (f) as previously reported by Kurmoo et al. [2]; the peak shifts to lower temperatures with increasing f -value. The SPM

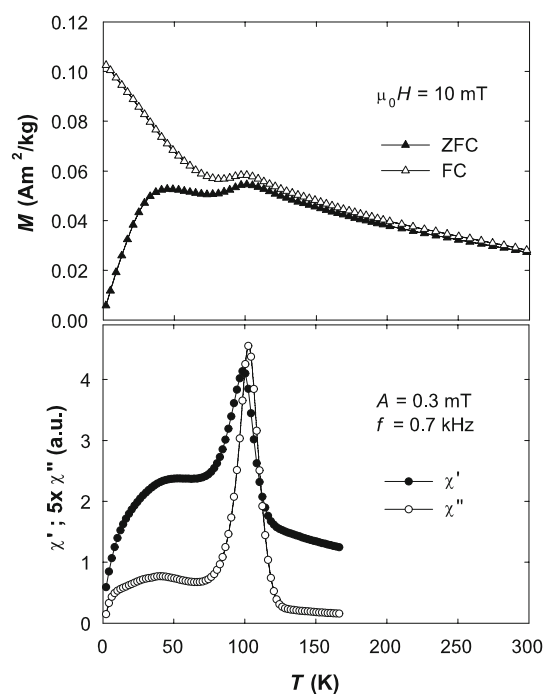


Fig. 7 Temperature dependence of the zero-field cooled (ZFC) and field-cooled (FC) magnetization recorded at 10 mT (upper). The broad anomaly at around 50 K is attributed to the contribution of the SPM particles in the composite. Temperature dependence of the real (χ') and imaginary (χ'') parts of the a.c. susceptibility recorded in zero magnetic field (lower). The single sharp peak, present on both curves, is attributed to the transition from the magnetically hard to the magnetically soft regime, and coincide with the anomaly on the ZFC–FC curves. The broad anomaly due to SPM contribution reflects the ZFC magnetization data

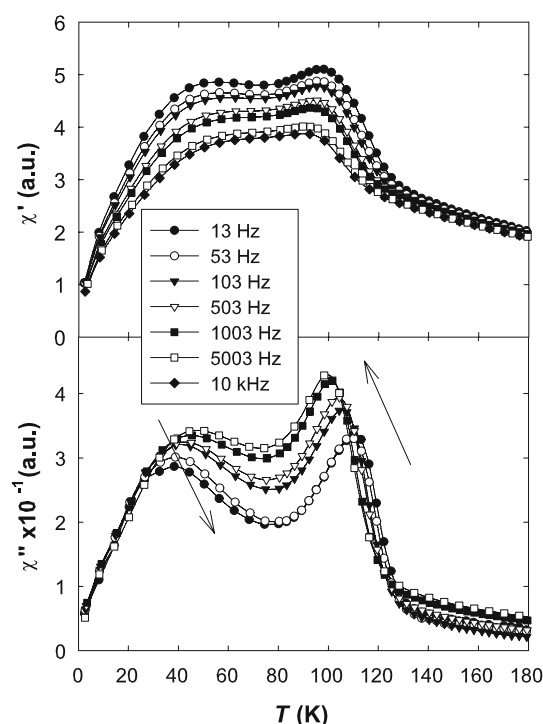


Fig. 8 Temperature dependence of the real (χ' , upper) and imaginary (χ'' , lower) parts of the a.c. susceptibility recorded in zero magnetic field at various frequencies of the a.c. magnetic field with amplitude of 0.3 mT. The arrows on the lower graph denote the shift of the anomalies with increasing frequency

response is well evidenced from the standard behavior of the broad maximum at lower temperatures (the anomaly shifts to higher temperatures with increasing frequency in consistency with the Neel-Arrhenius theory for SPM relaxation).

In spite of reduced coercivity value observed, the anomalous spin dynamics demonstrated by the a.c. susceptibility measurements proofs presence of the ε - Fe_2O_3 phase in our sample.

4 Conclusion

In summary, we report a novel method for preparation of high concentration ε - $\text{Fe}_2\text{O}_3/\text{SiO}_2$ nanocomposites free of α - Fe_2O_3 . This elegant method is based on a freestanding molecule, which is common precursor for both nanoparticles and matrix and serves as a “brick” from which the entire nanocomposite is built. Sample annealed at 1,000 °C for 1 h exhibits coercive field of 0.25 T, which is probably caused by fraction of γ - Fe_2O_3 nanoparticles in the superparamagnetic state. Further advantage of our preparation method is that metal ions are completely surrounded by organic shell, which camouflages their own properties and

prevents, in case of more than one metallic constituent, agglomeration of ions of the same element. Another advantage results from incorporation of the matrix and the nanoparticle precursor into a single molecule preventing inhomogeneities in distribution of the components in xerogel caused by different properties of the organic and the inorganic entities.

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Stabilization of the high coercivity ϵ -Fe₂O₃ phase in the CeO₂–Fe₂O₃/SiO₂ nanocomposites

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ABSTRACT

We have investigated the processes leading to the formation of the Fe₂O₃ and CeO₂ nanoparticles in the SiO₂ matrix in order to stabilize the ϵ -Fe₂O₃ as the major phase. The samples with two different concentrations of the Fe were prepared by sol-gel method, subsequently annealed at different temperatures up to 1100 °C, and characterized by the Mössbauer spectroscopy, Transmission Electron Microscopy (TEM), Powder X-ray Diffraction (PXRD), Energy Dispersive X-ray analysis (EDX) and magnetic measurements. The evolution of the different Fe₂O₃ phases under various conditions of preparation was investigated, starting with the preferential appearance of the γ -Fe₂O₃ phase for the sample with low Fe concentration and low annealing temperature and stabilization of the major ϵ -Fe₂O₃ phase for high Fe concentration and high annealing temperature, coexisting with the most stable α -Fe₂O₃ phase. A continuous increase of the particle size of the CeO₂ nanocrystals with increasing annealing temperature was also observed.

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1. Introduction

In the last years, CeO₂-containing materials have received a lot of attention due to their diversity of applications in catalysis [1–3] (component of commercial catalysts used for the reduction of CO, hydrocarbons and NO_x emissions from gasoline engines [4]), solid oxide fuel cells [5] and in spintronic devices [6–8]. The CeO₂ is an insulating material with high dielectric constant, unique UV absorption ability and high reactivity [9]; it crystallizes in the fluorite structure with the cerium atoms in the cubic closed packed arrangement and the oxygen atoms occupying the tetrahedral sites [10]. The lattice parameter is similar to that of Si, which brings the required compatibility necessary for potential application in the spintronics [8].

Introduction of other metal ions into the ceria cubic fluorite structure or creation of the CeO₂-based mixed oxides leads to the additional enhancement of their physical properties. For instance, the usage of the pure CeO₂ in the oxygen storage capacity (OSC) media is highly discouraged due to the poor thermal stability and rapid sintering at high temperatures, which generally decreases the OSC [11,12]. Substitution of the Ce⁴⁺ ion with the Fe³⁺ ion in

cerium oxides leads to increase of the thermal stability and the OSC of ceria and also reduces the costs of the OSC [11,13]. Also the Fe₂O₃–CeO₂ composites have much higher catalytic activity in CO oxidation than the individual pure CeO₂ and Fe₂O₃ [14]. Another example of modification of the physical properties is the appearance or the reinforcement of the room temperature ferromagnetism in the CeO₂ doped with transition metal ions [15–17].

Fe₂O₃ is abundant in four polymorphs: γ -Fe₂O₃ (maghemite), ϵ -Fe₂O₃, β -Fe₂O₃ and α -Fe₂O₃ (hematite) [18–21]. The α -Fe₂O₃ and γ -Fe₂O₃ are the most naturally abundant iron oxides that exist both in bulk and nano-sized forms; whereas the β -Fe₂O₃ and ϵ -Fe₂O₃ were obtained in the laboratory only in the form of nanosized objects. The maghemite and hematite have been well-studied and extensively applied in industry as the magnetic (γ -Fe₂O₃ [22] and α -Fe₂O₃ [23]) or catalytic (α -Fe₂O₃) [24] materials. Maghemite (γ -Fe₂O₃) has a defect spinel structure with space group *Fd*-3*m* and reveals ferromagnetic ordering with a Curie temperature, *T*_c close to 928 K [20,21]. This phase is stable only at temperatures below 720 K and transforms into the thermodynamically most stable phase—hematite α -Fe₂O₃ [21], which crystallizes in a rhombohedral–hexagonal prototype corundum structure with space group *R*-3*c*. The pure bulk hematite exhibits a weak ferromagnetism with slightly canted spins with the *T*_c at 950 K, which transforms into the antiferromagnetic state below the Morin temperature, *T*_M ≈ 250 K [25,26]. In case of the

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nanoparticles, the T_M is either decreased or totally suppressed [27]. Another two phases, β -Fe₂O₃ and ϵ -Fe₂O₃ are rare with scarce natural abundance, thermally unstable and it is very difficult to prepare them as single phases [28]. The β -Fe₂O₃ phase has a bixbyite cubic structure with the space group $la\bar{3}$ and displays antiferromagnetic ordering with the Néel temperature, T_N approximately 119 K. At sufficiently high temperatures (≈ 770 K), it also transforms to hematite [29].

The last polymorph ϵ -Fe₂O₃ represents an intermediate phase during the thermal conversion from nano-sized γ -Fe₂O₃ to α -Fe₂O₃ accompanied with increase of the particle size [28,30]. Also the adjacent branch of transformation between the epsilon and beta phase with increase of the particle size has been observed [30]. The ϵ -Fe₂O₃ is highly interesting and important due to its large room-temperature coercivity (up to 2 T) [31] and presence of a coupling of its magnetic and dielectric properties with a potential usage in many applications such as magnetic recording, high-speed wireless communication and electric/magnetic field-tunable devices [32]. The crystal structure of the epsilon phase is described as an orthorhombic non-centro-symmetric structure with Fe atoms occupying four different crystallographic sites—one tetrahedral and three different octahedral sites [28,33], belonging to the space group $Pha2_1$. It exhibits a ferrimagnetic ordering with T_c near to 495 K and also typical magnetic phase transition appearing between ≈ 100 and 150 K, which is connected with dramatic decrease of the coercivity [28,34].

As was mentioned previously, the binary oxide composite systems containing the iron oxide (especially hematite) and cerium oxide, find applications in catalysts, because of their higher catalytic performance in comparison to the pure α -Fe₂O₃ and CeO₂ [14,35]. Creation of the nanocomposite system comprising the CeO₂ and the ϵ -Fe₂O₃ could, due to the high coercivity of the ϵ -Fe₂O₃, extend possible applications of such material due to enhancement of its magnetic response. However, the preparation of the ϵ -Fe₂O₃ phase is rather difficult because of its high thermal instabilities. The well-known strategy of the ϵ -Fe₂O₃ stabilization is the growth of the Fe₂O₃ nanocrystals in an amorphous silica matrix under a specific heat treatment regime [34,36], however, there are no reports on the preparation of the ϵ -Fe₂O₃ phase using this approach when introducing other oxide material, like the CeO₂ in our case. In our work, we have focused on the stabilization of the metastable ϵ -Fe₂O₃ phase in the CeO₂-Fe₂O₃/SiO₂ nanocomposites. Our aim is to study the influence of the preparation conditions (such as the concentration of ions in the matrix and annealing temperature) on the phase composition of the Fe₂O₃ in CeO₂-Fe₂O₃/SiO₂ nanocomposites and to determine the best conditions leading to the formation of the ϵ -Fe₂O₃ phase with high room temperature coercivity in the CeO₂-Fe₂O₃/SiO₂ nanocomposites.

2. Experimental

The sol-gel method using tetraethoxysilane (TEOS), HNO₃ as an acid catalyst, formamide as a drying control chemical agent, and methanol as a solvent was used for the preparation of nanocomposite CeO₂-Fe₂O₃/SiO₂ [37,38]. Fe(NO₃)₃·9H₂O and Ce(NO₃)₃·6H₂O were first dissolved in methanol. The Ce/Fe/Si molar ratios were fixed to 1/1/20 and 1/2/9. The gelation time was approximately of 24 h at 40 °C. The samples (dimensions of 3 mm × 10 mm × 20 mm) were left one day for ageing. Then, they were progressively dried at 40 °C for three days in flowing dry N₂-atmosphere. After drying, they were preheated first at 300 °C in a vacuum for 2 h and then at various temperatures (950, 1050 and 1100 °C) under atmospheric conditions. The details of the annealing regime, which was used for optimization of formation of the ϵ -Fe₂O₃ [36] are summarized in Table 1. Final samples were

Table 1

Course of annealing (annealing regime) of the samples to the final temperature, T_F with the partial steps: r , heating rate with °C/min; d , dwell time in h; T , waiting temperature in °C.

T_F (°C)	r	T	d	r	T	d	r	T	d	r	T	d
950	1	900	1	1	950	2	–	–	–	–	–	–
1050	1	900	1	1	950	1	1	1000	1	1	1050	2
1100	1	900	1	1	950	1	1	1000	1	1	1100	2

represented by semi-transparent pieces of the size of about 1 mm × 3 mm × 7 mm and for needed characterization they were powdered in agate mortar.

The samples were labeled accordingly to the Ce/Fe/Si ratio and final annealing temperature as the low concentration series, L consisting of the L950–L1100 samples, keeping the ratios of Ce/Fe/Si=1/1/20 and samples with the high concentration of Fe ions, H series composed of the H950–H1100 samples, with the elemental ratio Ce/Fe/Si=1/2/9.

The samples have been characterized by several methods to gain comprehensive amount of data enabling analysis of the phase composition of obtained composites.

The Powder X-ray Diffraction (PXRD) was used for the determination of the phase composition and calculation of the apparent particle size, d_{XRD} using the Rietveld refinement method implemented within the FullProf program [39]. Further evaluation of the PXRD patterns with respect to the Fe₂O₃ phases was impossible because of the prevalent contribution of the CeO₂ phase. The diffraction patterns were measured at room temperature using Bruker diffractometer AXS GmbH with the CuK α radiation. The data were collected in the 2θ range of 10–80° with the step of 0.04°.

The Scanning Electron Microscope (SEM) Tescan Mira I LMH with Energy Dispersive X-ray analysis (EDX) Bruker AXS was used for the verification of the Ce/Fe/Si ratio in the samples. The Transmission Electron Microscope (TEM) JEOL 100C operating at 100 kV was used for the direct observation of the particle appearance in selected samples. The mean value of the particle size, d_{TEM} was analyzed using the ImageJ software including more than 100 particles in each TEM image.

The Mössbauer spectroscopy was employed as the only valuable experiment to resolve individual iron phase(s) in the samples. The measurement was done in the transmission mode with ⁵⁷Co diffused into a Rh matrix as the source moving with constant acceleration. The spectrometer (Wissel, Germany) was calibrated by standard α -Fe foil and the isomer shift is related to this standard at 293 K. The resulting parameters were determined using the NORMOS program.

Magnetic measurements that served mainly as the complementary method to the Mössbauer spectroscopy as the confirmation of the suggested phase composition, were performed using MPMS 7XL (SQUID) device (Quantum Design, San Diego) up to the magnetic field of 7 T in temperature range 2–400 K. The zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves were measured in the dc magnetic field equal to 0.01 T. The values of the coercivity field, H_c and their temperature dependencies were determined from the magnetization isotherms, measured at selected temperatures in magnetic fields varying up to 7 T in both polarities.

3. Results and discussion

3.1. Determination of the iron phases in the samples

The TEM performed at the L950 and L1100 samples confirmed the presence of nanoparticles homogeneously dispersed in the

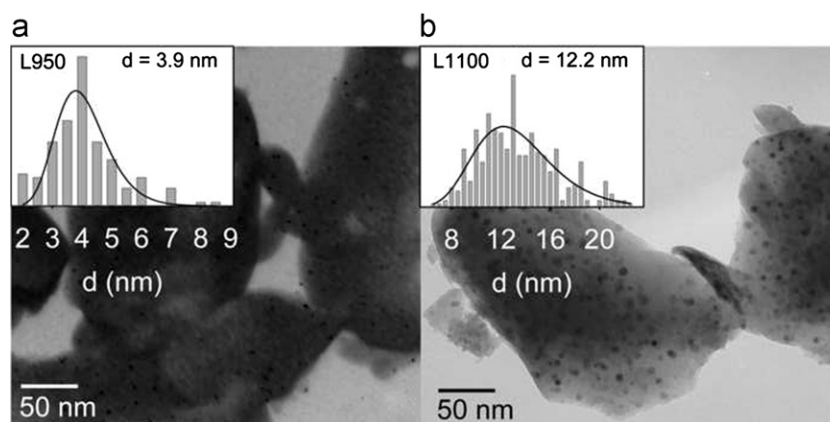


Fig. 1. TEM images of the L950 (a) and L1100 (b) samples together with the distributions of the particle diameters in the insets.

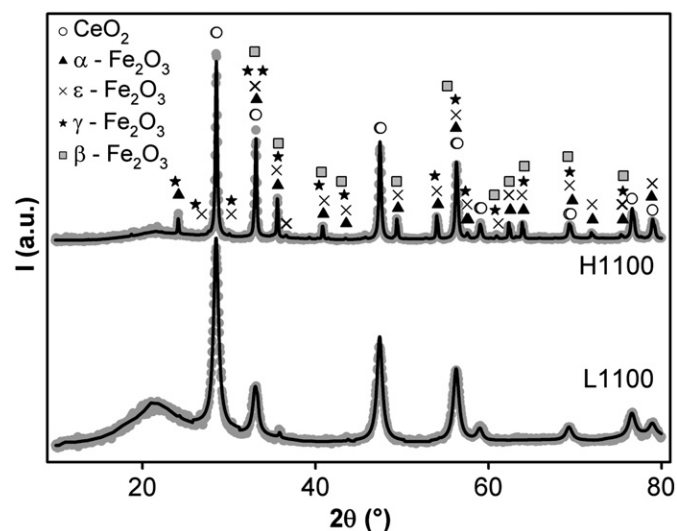


Fig. 2. PXRD patterns (grey) of the L1100 and H1100 samples with the result of the Rietveld refinement (black). Bragg positions corresponding to the CeO_2 and all four polymorphs of Fe_2O_3 are depicted by different symbols.

amorphous silica matrix. Also the expected increase of the particle size with increasing annealing temperature (Fig. 1) has been observed.

The PXRD of all samples verified the presence of the CeO_2 nanoparticles (NPs) and the amorphous SiO_2 matrix manifested by the characteristic broad peak at $2\theta = 25^\circ$ (Fig. 2). The evaluated sizes of the CeO_2 NPs, d_{CeO_2} , are in agreement with the TEM results (d_{TEM} for the L950 and L1100 samples are 3.9 and 12.2 nm, respectively), pointing at the increase of the particle size with the annealing temperature (Table 2). The clear evidence of the presence of the Fe_2O_3 phase(s) has been observed on the H series of samples. Because of the overlap of the Bragg peak position for all the iron oxide phases, it was not possible to strictly attribute the diffraction peaks only to a single phase, but any coincidence of the presence of the γ , α , β , and ϵ phases could not be neither confirmed nor omitted by this measurement. The presence of the some iron oxide phase in the L series is manifested only by a single peak at $2\theta = 35.5^\circ$, thus any evolution of the data is impossible (Fig. 2).

To specify the presence of the particular Fe_2O_3 phases in the samples, the room temperature Mössbauer spectroscopy has been used. The measured spectra for the L1050 and H1050 samples are depicted in Fig. 3 and the resulting fitted parameters are listed in Table 3. In the case of the L950 sample, the analysis of the

Table 2

The ratios of the elements in the samples, obtained from the EDX, the Ce/Fe and Si/Ce ratios, the average size and lattice parameters of the CeO_2 nanoparticles, d_{CeO_2} and a_{CeO_2} , together with the temperature of the $M(T)$ maxima for the superparamagnetic, $T_{\text{max}}^{\text{SP}}$ and $\epsilon\text{-Fe}_2\text{O}_3$, $T_{\text{max}}^{\epsilon\text{-Fe}_2\text{O}_3}$ phases.

Sample	Ce/Fe	Si/Ce	d_{CeO_2} (nm)	a_{CeO_2} (Å)	$T_{\text{max}}^{\text{SP}}$ (K)	$T_{\text{max}}^{\epsilon\text{-Fe}_2\text{O}_3}$ (K)
L950	1.3	19.3	3.8	5.414	14	–
L1050	1.2	18.5	6.6	5.420	42	97
L1100	1.2	18.3	9.4	5.424	56	100
H950	0.4	9.3	14.0	5.418	–	140
H1050	0.4	8.5	21.0	5.419	–	145
H1100	0.5	9.7	30.0	5.418	–	145

Mössbauer spectra was only qualitative because of the low relative mass of the iron oxide in the sample. Generally, the method provided the results suggesting the presence of the $\epsilon\text{-Fe}_2\text{O}_3$ phase in most of the samples and pointed at the existence of an additional iron oxide phases both in the L and H series. The detail process of the fitting procedure of the epsilon phase was following. The Mössbauer spectra of the $\epsilon\text{-Fe}_2\text{O}_3$ consist of the four subspectra belonging to the four different crystallographic sites, three octahedral and one tetrahedral. Because the two octahedral sites display nearly the same Mössbauer parameters ($B_{\text{hf}} = 44.5$ T [33]), they were fitted using only one sextet (assigned to $O_{\text{h}1}$). Due to the equal occupancy of different crystallographic sites, the intensity ratios were fixed to 2:1:1, assuming the same recoilless factor. The parameters of the $\epsilon\text{-Fe}_2\text{O}_3$ phase detected in all samples are in good agreement with those published by other authors [28,30]. In case of the whole H series, the stable $\alpha\text{-Fe}_2\text{O}_3$ phase has been detected (typical parameters $B_{\text{hf}} = 51.6$ T and $2\epsilon = -0.2$ mm s^{-1}) besides the $\epsilon\text{-Fe}_2\text{O}_3$, with the dominating attendance with increasing annealing temperatures. The presence of the $\epsilon\text{-Fe}_2\text{O}_3$ phase has been therefore confirmed for the L1050 and L1100 samples and has been strictly elided for the L950 sample where only the $\gamma\text{-Fe}_2\text{O}_3$ phase has been detected. In both the L1050 and L1100 samples the presence of doublet has been identified as the $\beta\text{-Fe}_2\text{O}_3$ phase and additional sextet in the L1100 sample has been assigned to the $\alpha\text{-Fe}_2\text{O}_3$ phase.

The temperature dependencies of the magnetization for the L and H series are depicted in Fig. 4(a) and (b), respectively. The magnetic properties of the samples with different concentrations of Fe, annealed at different temperatures reflect well the phase composition determined by the Mössbauer spectroscopy. The L series exhibit a typical superparamagnetic (SPM) behavior with the mean blocking temperature, T_B increasing from 14 K for the L950 sample up to the 56 K for the L1100 sample. This increase proves the increase of the mean particle size with

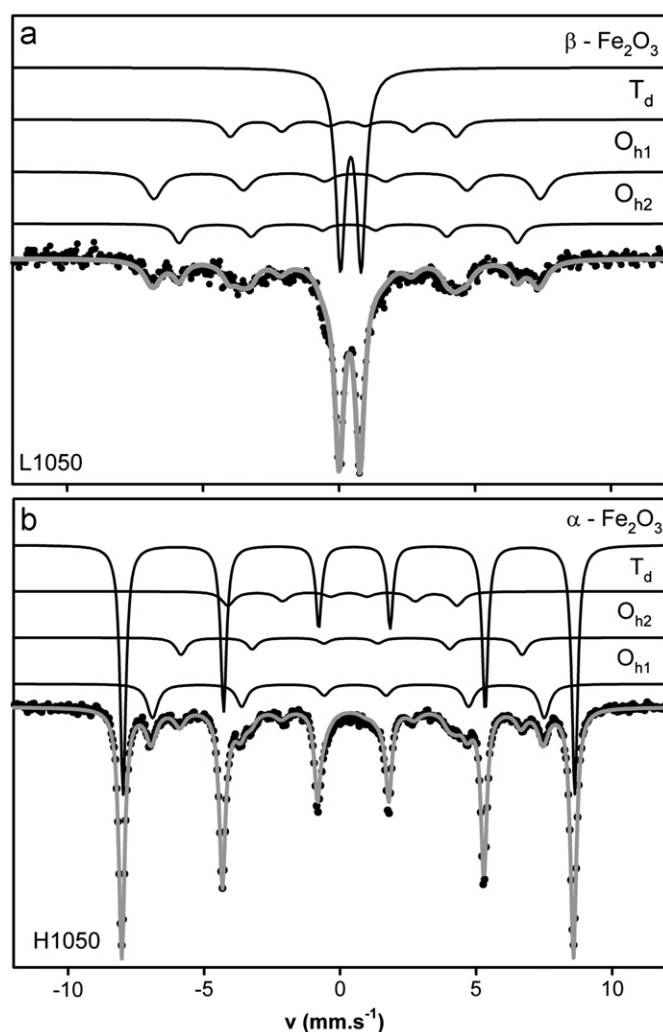


Fig. 3. Mössbauer spectra of the L1050 (a) and H1050 (b) samples. Subspectra represent individual iron oxide phases.

increasing annealing temperature, as was suggested also for the CeO₂ NPs by TEM and PXRD measurements. The L950 sample exhibits pure (SPM) behavior, which confirms the presence of only the γ -Fe₂O₃ phase and absence of the ϵ -Fe₂O₃, in consistency with the Mössbauer spectroscopy.

The temperature dependencies of both the L1050 and L1100 samples embody magnetic transition at around 100 K that is a typical feature of the ϵ -Fe₂O₃ [28,30,34,40,41] phase and the apparent traces of transition at $\approx$ 50 K point at the presence of β -Fe₂O₃. Despite the occurrence of the ϵ -Fe₂O₃ phase at higher temperatures and presence of the γ -Fe₂O₃ phase at low temperature in the L series, the formation of the different iron oxide phases is more uniform in case of the H series. A clear evidence of the magnetic transition between 100 and 150 K attributed to the ϵ -Fe₂O₃ phase with negligible sign of SPM behavior dominates.

Further examination of the magnetization isotherms was also in agreement with the determined phase composition of the samples. The dominant content of the ϵ -Fe₂O₃ phase in the H series samples has been manifested by the large room temperature coercivity, H_c , which increases with the increasing annealing temperature; from 0.85 T for the H950 sample, 1.5 T for the H1050 sample up to 2 T for the H1100 sample, respectively. The value of the H_c mostly corresponding with the previous studies of the ϵ -Fe₂O₃ [28,31,39] has been observed for the H1100 sample. The continuous decrease of the H_c for the L950 sample

Table 3

Room temperature Mössbauer parameters. The isomer shift δ , quadrupolar shift, 2ϵ or quadrupole splitting, ΔE_q , hyperfine field, B_{hf} , full width at half maxima, FWHM and the interpretation of the spectra. The $\text{Fe}^{3+}\text{O}_{h1}$, $\text{Fe}^{3+}\text{O}_{h2}$, Fe^{3+}T_d belong to the ϵ -Fe₂O₃ phase.

Sample	Sub.	δ (mm/s)	$\Delta E_q/2\epsilon$ (mm/s)	B_{hf} (T)	FWHM (mm/s)	R. area (%)	Interp.
L1050	1	0.38	0.76	N/A	0.41	49.8	β -Fe ₂ O ₃
	2	0.39	-0.29	44.1	0.75		$\text{Fe}^{3+}\text{O}_{h1}$
	3	0.35	-0.03	38.6	0.53	50.2	$\text{Fe}^{3+}\text{O}_{h2}$
	4	0.18	-0.15	25.8	0.60		Fe^{3+}T_d
L1100	1	0.38	0.74	N/A	0.36	47.4	β -Fe ₂ O ₃
	2	0.37	-0.19	51.6	0.36	18.5	α -Fe ₂ O ₃
	3	0.41	-0.25	44.0	0.42		$\text{Fe}^{3+}\text{O}_{h1}$
	4	0.37	0.00	38.7	0.40	34.1	$\text{Fe}^{3+}\text{O}_{h2}$
	5	0.17	-0.19	25.9	0.38		Fe^{3+}T_d
H950	1	0.37	-0.21	51.2	0.29	59.2	α -Fe ₂ O ₃
	2	0.38	-0.26	44.6	0.59		$\text{Fe}^{3+}\text{O}_{h1}$
	3	0.36	-0.02	38.8	0.53	40.8	$\text{Fe}^{3+}\text{O}_{h2}$
	4	0.19	-0.13	26.2	0.55		Fe^{3+}T_d
H1050	1	0.37	-0.20	51.6	0.26	67.1	α -Fe ₂ O ₃
	2	0.38	-0.25	44.7	0.46		$\text{Fe}^{3+}\text{O}_{h1}$
	3	0.36	0.02	38.9	0.47	32.9	$\text{Fe}^{3+}\text{O}_{h2}$
	4	0.15	-0.23	26.1	0.56		Fe^{3+}T_d
H1100	1	0.38	-0.21	51.6	0.26	70.5	α -Fe ₂ O ₃
	2	0.36	-0.22	44.9	0.37		$\text{Fe}^{3+}\text{O}_{h1}$
	3	0.36	0.04	39.0	0.42	29.5	$\text{Fe}^{3+}\text{O}_{h2}$
	4	0.14	-0.23	26.2	0.35		Fe^{3+}T_d

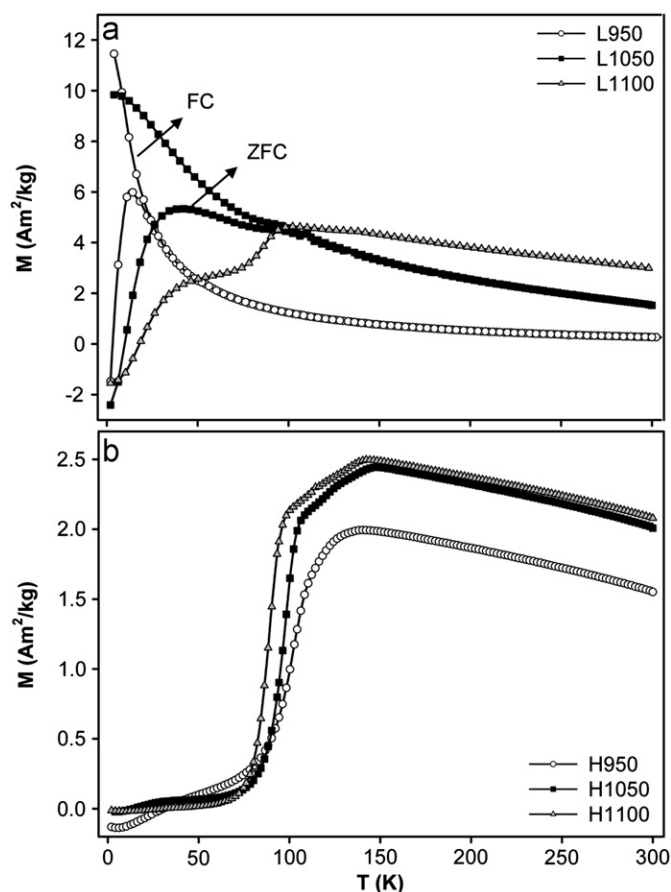


Fig. 4. Temperature dependencies of ZFC and FC magnetization of the L (a) and H (b) samples measured at 10 mT.

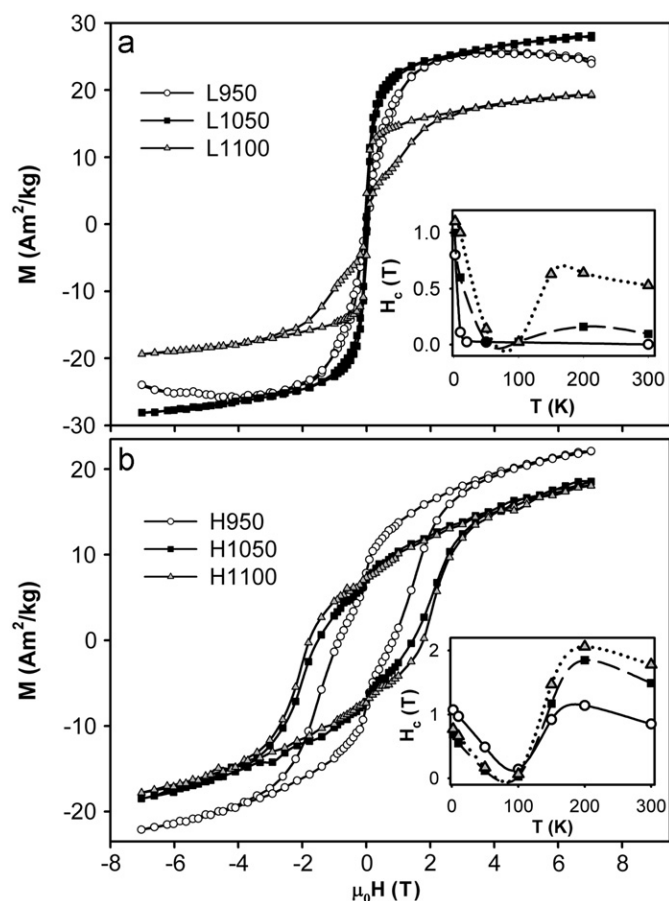


Fig. 5. Magnetization isotherms of the L (a) and H (b) samples measured at 300 K with the temperature dependencies of the coercivity, H_c in the insets.

from its maximum value at low temperatures (below T_B) to the almost zero value at room temperature confirms the majority of the SPM (γ -Fe₂O₃) phase in the sample (Fig. 5). The temperature dependence of the H_c for the L1050 sample already exhibits a little increase above 150 K, which is the consequence of the presence of the ϵ -Fe₂O₃ phase in the sample, as was suggested by the Mössbauer spectroscopy. The room temperature magnetization isotherm of the L1100 sample shows large “necking”, which results to strongly reduced value of the H_c that would be expected for pure ϵ -Fe₂O₃, which is again the effect of the presence of the additional, superparamagnetic iron oxide allomorph in this sample [36].

3.2. Scenario of the stabilization of the iron oxide phases in the samples

The observed results suggest the possible scenario of the evolution of the ϵ -Fe₂O₃ phase, based on the increase of the particles size, that seems to be one of the leading factors implicating the formation of the individual iron oxide phases. The typical evolution of the particular iron oxide phase with increasing size, already reported in literature starts with the γ -Fe₂O₃ phase with subsequent transformation to the allomorphs ϵ and β and final transformation to the stable α , hematite phase ($\gamma \rightarrow \epsilon \rightarrow (\beta) \rightarrow \alpha$) [28,30,39].

As was presented in the previous paragraphs, the Mössbauer spectroscopy together with the analysis of the magnetic measurements demonstrated that the evolution of the iron oxide phase in the low concentration L series of samples begins with the γ -Fe₂O₃ for the lowest annealing temperature, 950 °C with further

transformation of nanoparticles in the β -Fe₂O₃ and ϵ -Fe₂O₃ phases in case of the L1050 sample and subsequent creation of the α -Fe₂O₃ phase at the expense of the ϵ -Fe₂O₃ phase for the L1100 sample. The creation of the ϵ -Fe₂O₃ phase is connected with the increasing particle size due to the increasing annealing temperature, as was suggested by the comparison of the crystallite size of CeO₂ NPs observed by TEM and PXRD up to the maximum size limit, where the more stable α -Fe₂O₃ phase preferably arises.

In case of the H series, the size of the nanoparticles increases with respect to the L series due to the higher concentration of iron, allowing the creation of the ϵ -Fe₂O₃ phase even at lower annealing temperatures. The size limit of the NPs has been also exceeded to enable simultaneous formation of the most stable, α -Fe₂O₃ phase. The coexistence of the α -Fe₂O₃ and ϵ -Fe₂O₃ phases could not be verified only by examining the magnetic properties, where only the ϵ -Fe₂O₃ phase is detectable, but the Mössbauer data clearly acknowledged the presence of this phase, with slightly increasing attendance according to the increasing annealing temperature.

The optimal conditions for the formation of the ϵ -Fe₂O₃ phase with the minimization of the presence of other Fe₂O₃ phases are the high concentration of Fe in composite (Ce/Fe/Si ratio equal to 1/2/9) and high final annealing temperature, equal to the 1100 °C in our case, in order to keep the particle size at the values allowing both the formation of the metastable ϵ -Fe₂O₃ and preventing domination of the stable α -Fe₂O₃ phase.

4. Conclusion

In summary, we have focused on the stabilization of the ϵ -Fe₂O₃ phase in the Fe₂O₃-CeO₂/SiO₂ nanocomposites varying the conditions of preparation as follows: (1) the concentration of the iron in the composites was adjusted in the Ce/Fe/Si ratio equal to 1/1/20 and 1/2/9, respectively, and (2) the different final annealing temperature from 950 °C to 1100 °C was applied. The evolution of the Fe₂O₃ phases followed the phase transformation sequence $\gamma \rightarrow \epsilon \rightarrow (\beta) \rightarrow \alpha$ with increasing size of the nanoparticles, which is the limiting factor for the formation of the individual iron oxide phases.

The Mössbauer spectroscopy has been the key method in the phase determination; the Transmission Electron Microscopy and the Powder X-ray Diffraction have been used as the complementary methods for the specification of the size of the CeO₂ nanoparticles, confirming the increase of the particle size with increasing annealing temperature. The measurements of magnetic properties served as the final confirmation of the phase composition of the samples and were in the perfect agreement with the Mössbauer spectroscopy data.

In case of the L series (with the lower concentration of the Fe ions), the superparamagnetic, γ -Fe₂O₃ phase has been detected as a single iron oxide phase in the L950 sample, containing the smallest particles. Increase of the annealing temperature manifested by the increasing particle size led to the transformation to the ϵ -Fe₂O₃ phase and creation of the β -Fe₂O₃ phase in the L1050 and L1100 samples with traces of the α -Fe₂O₃ phase in the L1100 sample.

The higher concentration of the Fe ions in the H series resulted into further increase of the particle size, which resulted in elimination of the superparamagnetic phase and significant increase of the amount of the ϵ -Fe₂O₃ in the samples. The highest value of the room temperature coercivity, H_c has been observed for the H1100 sample. Therefore, the most optimal conditions for the stabilization of the ϵ -Fe₂O₃ phase by the sol-gel method are the high concentration of the Fe ions (Ce/Fe/Si ratio equal to the

1/2/9 in our case) and high annealing temperature (equal to the 1100 °C).

Acknowledgments

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Magnetically separable photocatalytic composite $\gamma\text{-Fe}_2\text{O}_3\text{@TiO}_2$ synthesized by heterogeneous precipitation

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ABSTRACT

Synthesis of magnetically separable photocatalytic active composite $\gamma\text{-Fe}_2\text{O}_3\text{@TiO}_2$ is the main objective of this work. In the first step, maghemite nanoparticles were prepared by a precipitation method and consequently covered by the citric acid in order to adjust the zeta-potential of the particle surface. The magnetic carrier was enfolded by TiO_2 via heterogeneous precipitation of TiOSO_4 using urea as a precipitation agent. The procedure was designed to minimize the production costs in order to be easily transferred into the industry scale conserving the high quality of the photoactive product. Nontoxic element oxides were used because of the ecological acceptance. Various methods were employed to characterize and study the intermediate (magnetic nanoparticles) and final materials (TiO_2 -maghemite composite), respectively. Moreover, the influence of the subsequent annealing on the structure, phase composition and properties of the products is discussed.

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1. Introduction

Titanium dioxide is nowadays a well-known and commercially used photocatalyst. The possibilities of application of this material are being investigated since early 1970s of the 20th century after a pioneering work by Fujishima [1]. A partial technological complication in the promising application of the TiO_2 for aqueous solution cleaning is a residual powder dispersion in water after the photocatalytic decomposition of an organic impurity. The problem can be solved by the use of a functionalized titania composites; for example, resistant surface layers adsorbed on the apparatus walls, hollow spheres with titania surface layers that can float on the water, and magnetic carrier – titania composites [2].

The magnetic nano(micro)crystals are promising carriers that can simply load the active compound. For example, the maghemite-silica core-shell nanoparticles with a surface modified by amino-groups are usable for biomedical species grafting [3], other functional systems are magnetic oxide/gold/silica composites and magnetic oxide/silica/photoluminescent composites [4].

The motivation of our work is to employ the magnetic particles for caring the active photocatalyst. Recently, several authors

focused on this topic; most of them used the well-known sol-gel process with various precursors, mainly $\text{Ti}(\text{OC}_3\text{H}_7)_4$ (titanium isopropoxide) and $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (titanium n-butoxide), for deposition of TiO_2 on the surface of the magnetic core. For example, Fu et al. reported the synthesis of $\text{BaFe}_{12}\text{O}_{19}/\text{TiO}_2$ via sol-gel process with PEI (polyethyleneimine) as the zeta-potential modifier of the magnetic nanoparticles [5,6]. Other zeta-potential modifier was a thin layer of SiO_2 gel (p.z.c. = 2.5) published by Lee et al. in the system $\text{BaFe}_{12}\text{O}_{19}/\text{SiO}_2/\text{TiO}_2$, where the silica layer was deposited by the conventional Stöber method and the TiO_2 layer was deposited using the acid-catalyzed sol-gel process [7]. This idea is also used in the preparation of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ composite reported by Watson et al. [8]. A different procedure is based on reactions in the microemulsion system, for example a $\text{NiFe}_2\text{O}_4/\text{TiO}_2$ powder was prepared in a mixture of isooctane (oleic phase), AOT (dioctylsulfocinate sodium salt – surfactant) and a metal salt solution as the oxide precursors, and TiCl_4 as the TiO_2 precursor [9,10].

The goal of our approach is to avoid the sol-gel process in the synthesis due to the high price of the initial alkoxides. Other advantage is the lack of expensive polymers for the zeta-potential adjustment. We also discarded a possibility of preparation in microemulsion due to the high amount of nonaqueous solvents, reagents and low efficiency.

In our work, a simple ferric oxide, $\gamma\text{-Fe}_2\text{O}_3$ was used as the magnetic material for its low price, simplicity and non-toxicity. After the surface modification by citric acid, the magnetic carrier was cov-

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ered by a photocatalyst layer using a homogeneous hydrolysis of a metallic salt solution by urea [11].

2. Experimental

2.1. Synthesis and materials

10.01 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Fluka) and 8.08 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Fluka) were dissolved in 50 ml of water that was previously bubbled by nitrogen gas in order to eliminate oxygen gas dissolved in water, and to fix the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in 1:1.8. The iron salts solution was slowly added to a deoxygenated 400 ml solution of NH_4OH (Fluka) and was homogenized using a magnetic stirrer. When the iron salts solution was added, the reaction was kept under magnetic stirring and nitrogen atmosphere for 5 h. After that, pH of the dispersion was adjusted to 2 and 4 g of sodium citrate (Sigma) were added and heated until 80°C . The temperature was kept for 30 min while the dispersion was being stirred. Several cycles of centrifugation at $5650 \times g$ were done to purificate the sample from impurities, and one cycle of centrifugation at $2500 \times g$ was done in order to eliminate large aggregates.

1.02 g of the as-prepared magnetic nanocrystals was dispersed in 1 l of distilled water that contained 4 ml of pure H_2SO_4 and 1.22 g of TiOSO_4 (both by Fluka). After dissolution of TiOSO_4 , 30 g of urea (Fluka) was added. Under vigorous stirring, the temperature of the mixture was adjusted to 90°C and the reaction was kept until the pH reached 6–7. Final precipitate was washed several times and dried at 100°C . Sample was also annealed at 400 and 600°C for 30 min (with the heating rate of $2.5^\circ\text{C}/\text{min}$).

2.2. Experimental methods

2.2.1. X-ray powder diffraction

The X-ray measurement was performed at ANKA synchrotron, FZK in the Bragg $\tilde{\text{A}}$ –Brentano geometry using the wavelength of $1.00789 \text{ \AA}$. The primary beam was mono-chromatized by a $2 \times (111)\text{Si}$ monochromator and the diffracted radiation was measured by a point detector equipped with analyzer. The phase analysis was performed using the PDIFF database, and the XRD data were further analyzed using the FullProf software [12].

2.2.2. Electron microscopy

Scanning electron microscopy investigations were done on SEM Philips XL 30 CP equipped with EDS (energy dispersive X-ray spectrometry), secondary and back-scattered electron detectors and Robinson detector. Powder sample was gripped on the holder with adhesive carbon slice and covered by thin ($<10 \text{ nm}$) Au/Pd layer.

Microscale morphology was examined by high-resolution transmission electron microscope HRTEM JEOL JEM 3010 and conventional TEM Philips 80 kV. Copper grid coated with a holey carbon support film was used to prepare samples for the TEM observation. A powdered sample was dispersed in ethanol and dropped on the grid. Electron diffraction was analyzed by process diffraction software [13].

2.2.3. Zeta-potential measurements

The surface charge was measured by Zeta-Sizer NanoZS (Malvern) based on electrophoretic mobility of the nanoparticles in aqueous media at different pHs. Each measurement was performed in an aqueous solution with a constant ionic strength (in 0.01 M KNO_3), pH was adjusted by adding drops of KOH or HNO_3 solution.

2.2.4. Mössbauer spectroscopy

Mössbauer spectra were done on a Wissel apparatus in the transmission mode with ^{57}Co diffused into a Cr matrix as the source

moving with constant acceleration. The spectrometer was calibrated by means of a standard $\alpha\text{-Fe}$ foil and the isomer shift was expressed with respect to this standard at 300 K .

2.2.5. Photocatalytic activity

Photoactivity measurements were performed on a home-made photoreactor [14]. A degradation of 4-chlorophenol in an aqueous dispersion of the photocatalyst under UV irradiation was monitored.

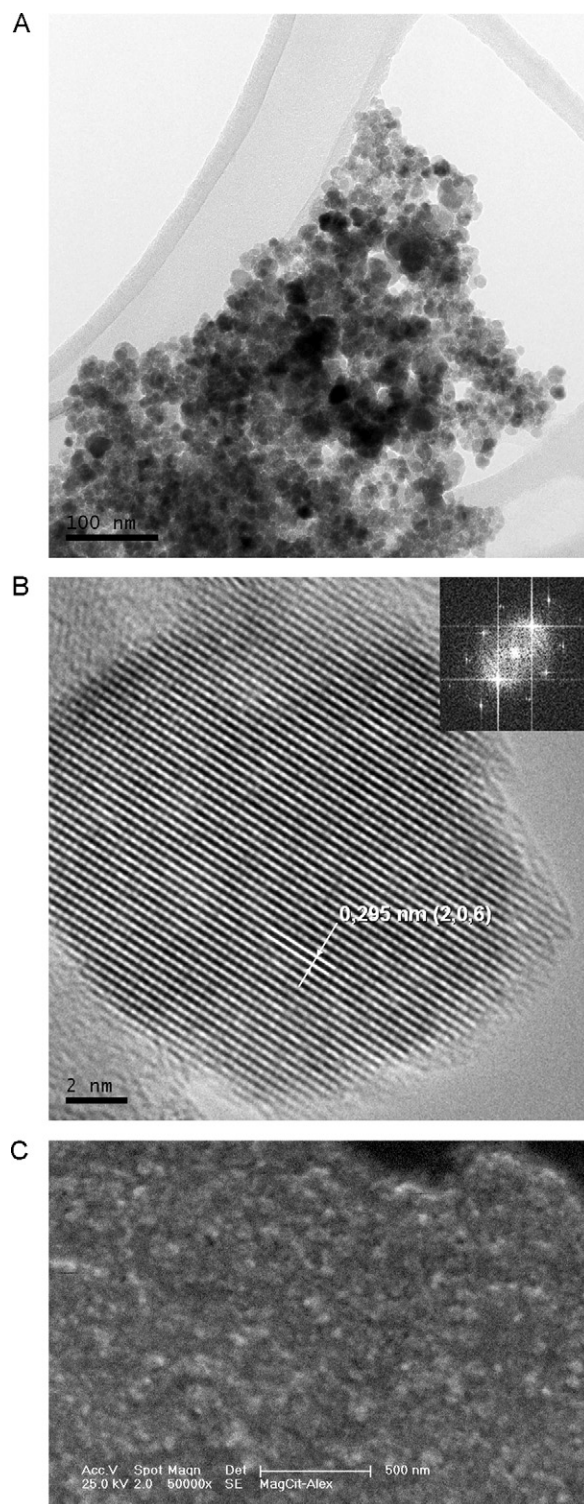


Fig. 1. Transmission electron microscopy of magnetic nanoparticles $\gamma\text{-Fe}_2\text{O}_3$ with modified surface.

At desired time, 1 mL of suspension was taken up and analyzed by HPLC. The detailed description of the experimental conditions was published earlier by Lukáč et al. [15].

2.2.6. Specific surface area

Surface areas of the samples were determined from nitrogen adsorption–desorption isotherms at liquid nitrogen temperature using a Coulter SA3100 instrument with the outgas 15 min at 120 °C. The Brunauer–Emmett–Teller (BET) method was used for surface area calculation, and the pore size distribution (pore diameter and pore volume of the samples) was determined by the Barrett–Joyner–Halenda (BJH) method [16].

3. Results

3.1. Magnetic nanoparticles

The results of the electron microscopy study of the citric acid coated magnetic carrier particles are shown in Fig. 1. Nanocrystals are of a round shape with diameter around 10 nm (Fig. 1A). Fig. 1B presents a detail of the nanoparticle structure with depicted maghemite crystal lattice planes (2,0,6) with the corresponding interlayer spacing of 0.295 nm. A rough view on the material's morphology is demonstrated by the SEM micrograph in Fig. 1C. The particles are of homogenous size distribution and well separated.

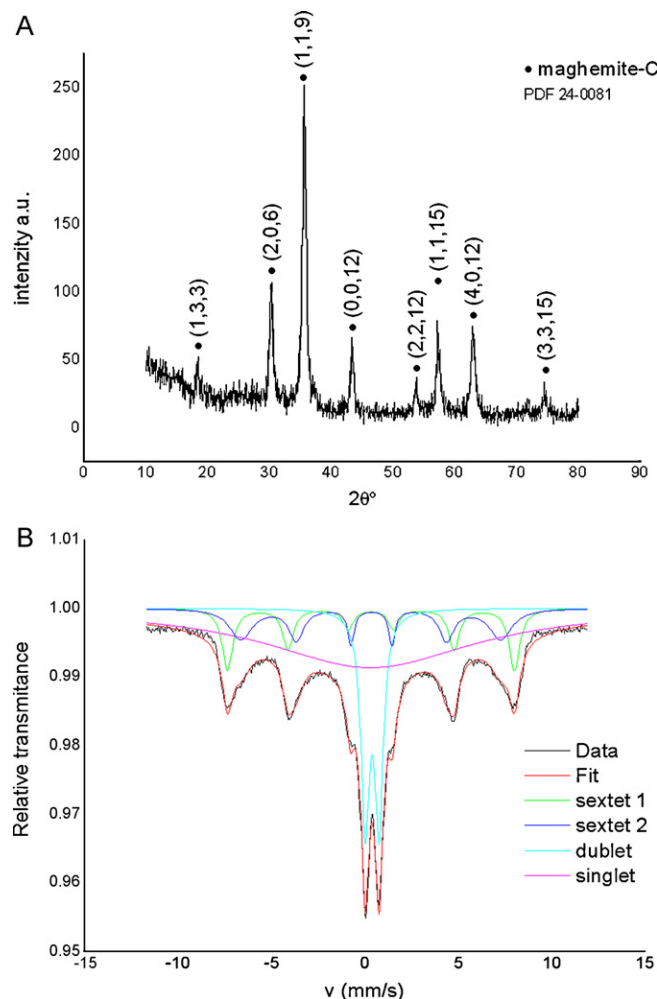


Fig. 2. (A) Powder diffraction pattern of maghemite particles; (B) Mössbauer spectra of maghemite particles.

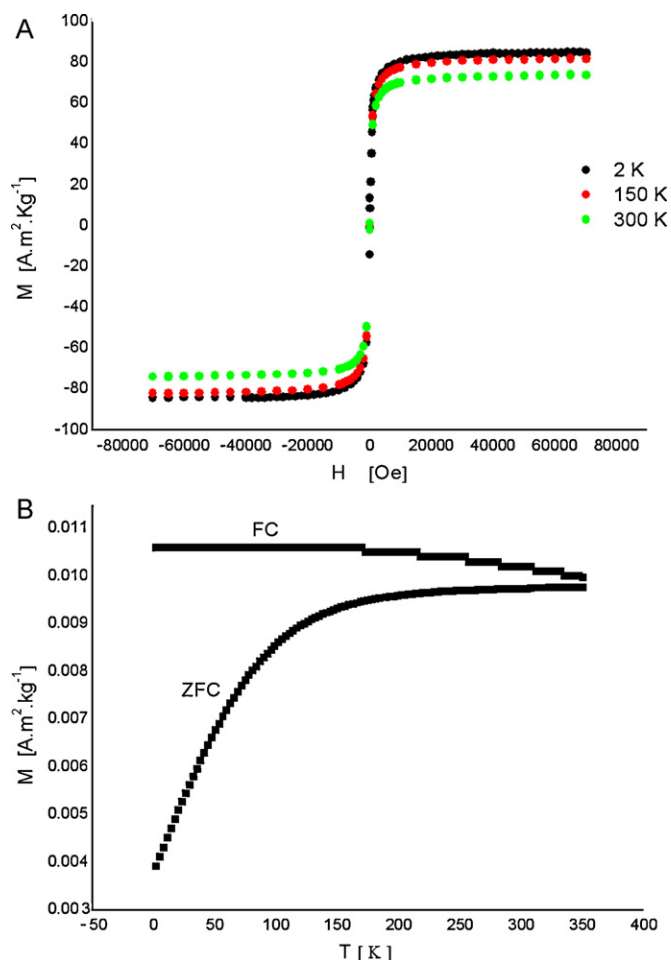


Fig. 3. (A) Hysteresis loops of $\gamma\text{-Fe}_2\text{O}_3$ particles at 2, 150 and 300 K; (B) magnetization dependence on temperature, without external magnetic field (ZFC) and with external magnetic field (FC).

Surface area of the magnetic particles calculated by BJH-desorption method is $121.9\text{ m}^2/\text{g}$.

The phase and crystal structure of the magnetic material was determined by X-ray powder diffraction (Fig. 2A). The pure maghemite phase was identified (PDF 24-0081).

Because of partial overlap of the magnetite and the maghemite XRD powder patterns, a series of Mössbauer measurements were performed (shown in Fig. 2B). Analysis of the Mössbauer spectra at room temperature is reported in Table 1. The sextets nos. 1 and 2 correspond to the maghemite phase, the doublet corresponds to a superparamagnetic phase and the singlet was considered to be the background contribution. The unsymmetrical shape of the peaks is typical for maghemite structure containing vacancies. The results clearly demonstrate, that the particles prepared by the same precipitation way as magnetite are unstable in aqueous solution and fully oxidized in maghemite.

A smart way to prove the presence of citric acid on the surface of nanocrystals is the zeta-potential pH titration of the coated and uncoated particles, respectively, as shown in Fig. 4. The point of zero charge (p.z.c.) of the uncoated particles is around pH=6. It means, that under pH=6, the particle surface is positively charged and over pH=6, it is opposite. In the case of coated particles, the p.z.c. is shifted into more acidic conditions around pH 2. Thus, the coated particles are negatively charged in almost whole range of pH, which is crucial for the precipitation of TiO_2 . The p.z.c. of freshly precipitated titanium dioxide is 6 [17], and around pH 3 when it starts to precipitate, it has positively charged surface. There-

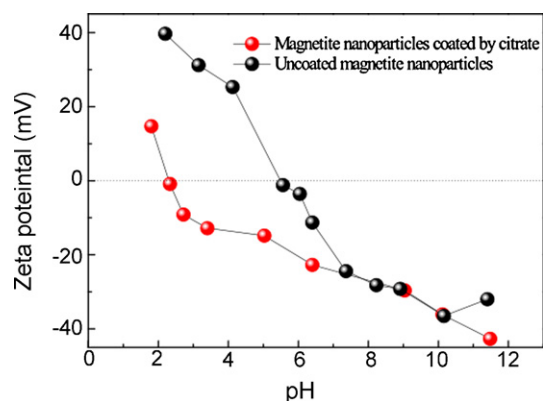


Fig. 4. Zeta-potential measurements of coated and uncoated magnetic particles at various pH values.

fore, the fresh positively charged TiO_2 particles are dragged onto the negatively charged maghemite surface. This mechanism successfully leads to the formation of the core-shell $\gamma\text{-Fe}_2\text{O}_3@ \text{TiO}_2$ composite.

Fig. 3 shows a bunch of magnetic studies of the surface-modified maghemite nanocrystals. The hysteresis loop measured at different temperatures is shown in Fig. 3A. A rather small coercive field (H_C) was observed, as expected for the 10 nm large maghemite nanocrystals. A partial reduction of the H_C value can be ascribed to a superposition of a contribution of a hysteresis-loss superpara-

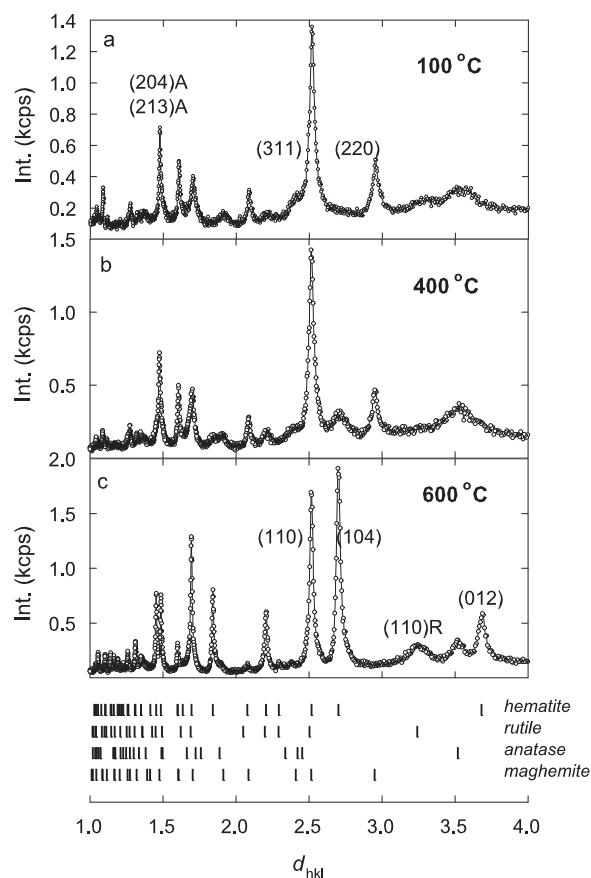


Fig. 5. Diffraction patterns of the three composite samples. The Bragg positions of the hematite, rutile, anatase and maghemite, respectively, are depicted in the bottom diagram. Significant Bragg's reflections of the dominating TiO_2 and Fe_2O_3 phases are depicted in the MagCit100 and MagCit 600 diffractograms (A: anatase, R: rutile).

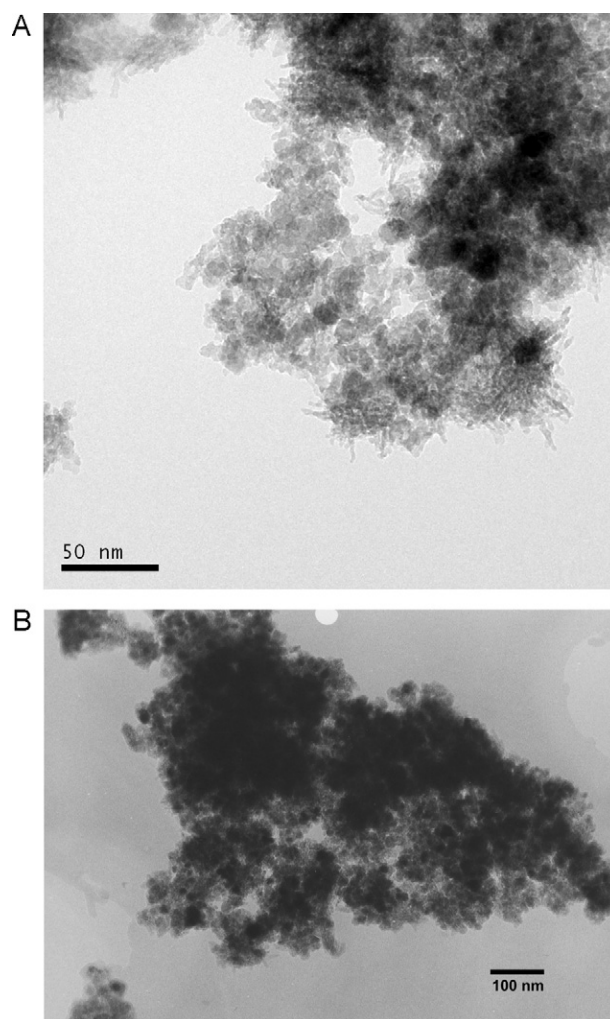


Fig. 6. Morphology of $\gamma\text{-Fe}_2\text{O}_3@ \text{TiO}_2$ 100 °C composite. (A) and (B) Transmission electron microscopy; (C) scanning electron microscopy.

magnetic fraction however, a large H_C value is not a crucial factor for the ideational application.

Fig. 3B represents a temperature dependence of magnetization recorded in a field of 5 mT under zero field cooled and field cooled regime. The results are typical for a nanoparticle system with a relatively broad particle size distribution, which is in conformity with the simplicity of preparation method.

3.2. $\gamma\text{-Fe}_2\text{O}_3@ \text{TiO}_2$ composite

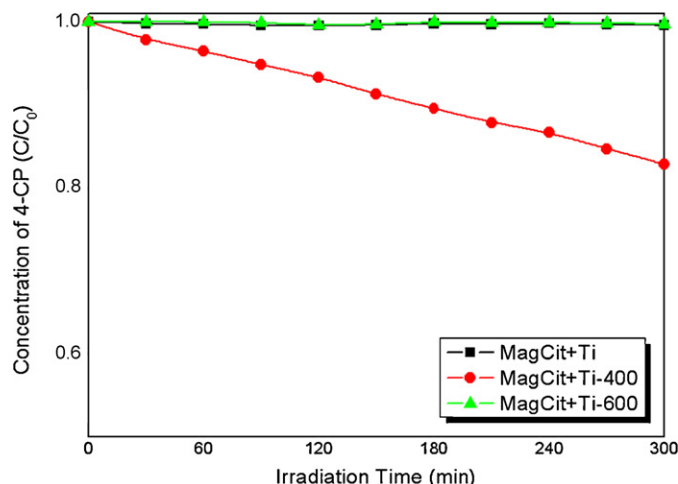
The final phase composition of the composite material comprises the anatase (PDF 73-1763) and maghemite (PDF 24-0081), respectively, and remains intact when annealing the product from 100 to 400 °C. The higher annealing temperature results in better crystallinity and increase of the particle diameter as can be followed from the XRD patterns (Fig. 5A). The sample heated at 600 °C; however, completely transferred into hematite (PDF 24-0072) and rutile (PDF 78-1508).

The composite morphology (sample dried at 100 °C) is shown in Fig. 6. The HRTEM micrograph (Fig. 6A) shows a needle-like TiO_2 particles, which surrounds the darker maghemite crystals. A better contrast between the titanium dioxide (lighter gray) and iron oxide (darker gray) phase was achieved by a low voltage high contrast TEM (Fig. 6B). The SEM picture (Fig. 6C) shows a good homogeneity and fineness of the composite powder.

Table 1

Interpretation of the Mössbauer spectra of the magnetic nanoparticles.

	Isomer shift δ [mm/s]	Quadrupole splitting σ [mm/s]	Hyperfine field B_{Hf} [T]	Relative content [%]
Sextet 1	0.32	−0.004	47.75	12.2
Sextet 2	0.33	−0.033	43.27	12.9
Doublet	0.38	0.745	–	16.5
Singlet	0.28	–	–	58.4

**Fig. 7.** Photocatalytic activity of $\gamma\text{-Fe}_2\text{O}_3\text{@TiO}_2$ 100 °C–600 °C samples measured by 4-chlorophenol decomposition.

Surface area of the dried sample is $121.0\text{ m}^2/\text{g}$. This fact is definitely favorable for high catalytic activity. The time dependence of the relative concentration of 4-chlorophenol (4-CP) for the samples dried at 100 °C and heated to 400 and 600 °C, respectively, is depicted in Fig. 7. The first sample $\gamma\text{-Fe}_2\text{O}_3\text{@TiO}_2$ 100 °C has an insignificant photocatalytic activity due to the low crystallinity and therefore not a well developed electronic structure. The sample $\gamma\text{-Fe}_2\text{O}_3\text{@TiO}_2$ 400 °C is of the highest photoactivity. The well-crystallized anatase particles can effectively decompose the organic compound in the solution. Simple first order kinetics fit was applied to this data and resulted in the $(9.5 \pm 0.3) \times 10^{-6} \text{ min}^{-1}$ rate constant. As expected due to the induced phase transformation, the sample $\gamma\text{-Fe}_2\text{O}_3\text{@TiO}_2$ 600 °C consisted of hematite and rutile which have lost all the photocatalytic activity.

4. Discussion

All the results showed that a simple precipitation of titanyl sulphate could be sufficient method for the preparation of TiO_2 layers on magnetic nanocrystals with desired morphology. The heat treatment increases the photoactivity until the point of the crystallographic transformation of both materials (magnetic oxide and titanium oxide), which seems to take place at similar temperature.

Properties of the carrier crystals before phase transformation are efficient enough to master the possible magnetic applications.

5. Conclusions

This communication describes a new synthesis of a magnetically separable photocatalyst for the decomposition of organic impurities. The chemical processes of the magnetic/photocatalytic composite synthesis are based on metallic salt solution precipitation. The desired surface charge is achieved by the surface modification with citric acid and exact pH. The as described conditions lead to the specific electrostatic attracting of the maghemite and titania nanocrystals yielding the desired core-shell composite structure. The good crystallinity of the TiO_2 photocatalyst is a crucial step for the effective catalytic activity. The presented synthesis routes are cheap and ecological, and offer smooth possibility of industrial production of this type of composite materials.

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Study of the phase composition of Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanoparticles using X-ray diffraction and Debye formula

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Phase changes in Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanoparticles were studied by X-ray diffraction. Because of a very small size of the particles, standard methods of data analysis based on the physical broadening of lines and instrumental function fail and calculations based on the Debye formula were used instead. The measured data from both types of particles were analyzed assuming a

core-shell model of the phase composition of the particles and the dependence of the particle size and phase composition on the annealing temperature was determined. In both types of nanoparticles a phase transition was observed and the amount of a new phase increases with the annealing temperature.

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1 Introduction Understanding the structure of Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanoparticles is necessary for studying their properties. Fe_2O_3 nanoparticles are interesting because of the metastable $\epsilon\text{-Fe}_2\text{O}_3$ phase of iron tri-oxide. It is an intermediate product of the $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) to $\alpha\text{-Fe}_2\text{O}_3$ (hematite) solid-state transformation, and can be isolated only in a form of nanoscaled objects [1–6]. The phase attracted much attention due to its enormous room-temperature coercivity of about 2 T [2–4], and a low-temperature collapse of magneto-crystalline anisotropy due to strong suppression of the spin-orbital interaction [7]. The main goal of our research was to optimize a high-yield preparation procedure of the $\epsilon\text{-Fe}_2\text{O}_3$ by the investigation of the ex-situ prepared samples in order to determine influence of the particle size on the Fe_2O_3 phase composition.

The other type of samples consists of nanoparticles of Fe_2O_3 and photoactive TiO_2 . Photocatalysis is a smart way to clean facilities, living environments, and even reduce

the spread of infections such as SARS in hospitals [8, 9]. Concerning treatment of liquids (e.g. in sewerage plants), the most critical aspect is an unproblematic separation of a photo-catalyst from the liquid phase. Therefore, we have recently designed a system constituted of a photoactive medium (TiO_2) adsorbed on magnetic particles (Fe_2O_3), which can be easily removed from liquids or gases by applied magnetic field. The key factor influencing the catalytic and magnetic properties of such two-component system is the phase composition, crystallinity, and particle size, respectively. In this work, we focus on the above-listed characteristics of the $\text{Fe}_2\text{O}_3/\text{TiO}_2$ composite annealed at several temperatures.

2 Experimental In this paper we report on structure of two types of nanoparticles. The first type, namely $\text{Fe}_2\text{O}_3/\text{SiO}_2$ nanocomposites was prepared for ex-situ measurements by a novel sol-gel method using a single

precursor for both nanoparticles and silica matrix [6]. The gel precursor was subsequently treated by a specific annealing procedure, stopped at a final temperature: 900 °C, 950 °C, 1000 °C, respectively. For all samples, the heating temperature increased from room temperature at the speed 1°C/min up to 900 °C and stayed at this temperature for 4 hours. The samples with the annealing temperatures 950 °C and 1000 °C were then heated with the same speed with the 4-hour waiting each 50 °C up to their final heating temperature. The particles created at the lowest temperature are expected to be in the form of maghemite and with increasing final temperature the phase of Fe₂O₃ particles should transform to ε-phase and finally to hematite. The ex-situ X-ray diffraction measurement has been carried out at ANKA synchrotron in Karlsruhe with incidence angle 5° and the wavelength of 0.95007 Å. The primary beam was monochromatized by a 2x111Si monochromator, the diffracted radiation was measured by a point detector equipped with a narrow entrance slit and a filter suppressing the Fe-fluorescence.

The preparation procedure of the second type of nanoparticles (Fe₂O₃/TiO₂) consists of three steps. Briefly, the maghemite nanocrystals were obtained by a conventional co-precipitation method using Fe²⁺/Fe³⁺ nitrates as a source of the Fe ions. The iron nitrates solution was slowly added to a deoxygenated solution of NH₄OH in order to form a precipitate of the spinel phase. Then, the pH of the reaction mixture was adjusted to 2, and sodium citrate was added in order to modify Zeta potential of the maghemite nanocrystals. The modified magnetic nanocrystals were finally dispersed in a water solution of TiOSO₄, which was hydrolyzed by urea yielding the TiO₂ phase. The final product was washed several times and dried at 100 °C. The samples were then annealed at 200 °C, 450 °C, 550 °C, 650 °C and 770 °C for 30 minutes.

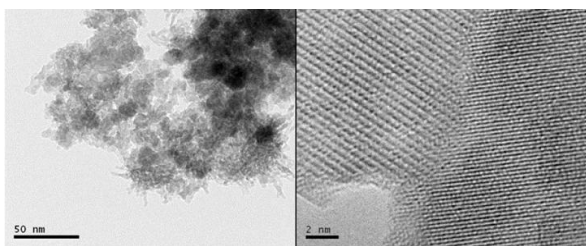


Figure 1 HR TEM image of the dried-only γ-Fe₂O₃ (maghemite)-TiO₂ (anatase) nanocomposite. The dark spots of about 20 nm correspond to the maghemite phase, while the anatase (light gray needles) forms a foamy structure encapsulating the maghemite spheres. The right panel demonstrates a detail of the juncture of both phases.

The samples were characterized by X-ray diffraction and high-resolution transmission electron microscopy (HR TEM). The dried-only sample contained maghemite (γ-Fe₂O₃) and anatase (TiO₂) phases, which fully transform into hematite (α-Fe₂O₃) and rutile (TiO₂), under annealing

at 770 °C, respectively. Annealing above 800 °C (not shown here) resulted in formation of the ternary pseudo-brookite Fe₂TiO₅. The HR TEM images of the dried-only sample are shown in Fig. 1. The maghemite nanocrystals appeared as a dark spots of about 20 nm in diameter. The anatase phase grows spokewise from the maghemite core; forming a foamy, needle like structure. The X-ray measurement was performed again at ANKA synchrotron in the Bragg – Brentano geometry using the wavelength of 1.00789 Å. The primary beam was monochromatized by a 2x111Si monochromator and the diffracted radiation was measured by a point detector equipped with analyzer.

3 Data analysis The experimental data were analyzed by a standard approach using the Debye formula formula for the diffracted intensity [10]

$$I(Q) = \sum_{i,j} f_i f_j^* \cdot \frac{\sin(Qr_{ij})}{Qr_{ij}}, \quad (1)$$

where $Q = 2K \sin(\theta)$ is the length of the scattering vector, $K = 2\pi/\lambda$ is the wave vector of the incidence beam, $f_j(Q)$ is the scattering factor of atom j , r_{ij} is the distance of atoms i and j , and the double summation runs over all atoms in the particle. The only technical limit of using of this equation is the number of terms in the double sum. For instance, a particle of Fe₂O₃ of the diameter of 13 nm contains about 10⁵ atoms, which means that there are 10¹⁰ interatomic distances that have to be taken into account for every Q . In order to speed up the calculation, we have calculated a distribution function of atomic pair distances, from which a histogram of all interatomic distances was created. An example of such a histogram is shown in Figure 2 corresponding to a spherical particle with the radius of 40 Å, the histogram has been constructed using the step width of 0.01 Å.

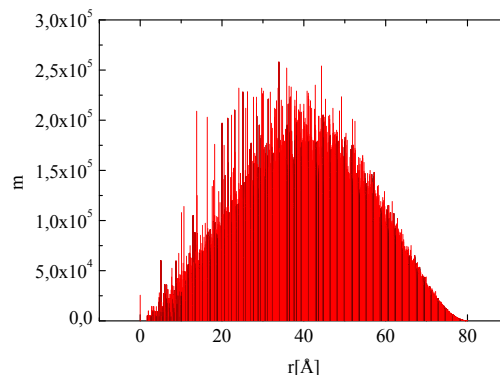


Figure 2 Calculated histogram of interatomic distances in a spherical ε-Fe₂O₃ particle of radius of 40 Å. The histogram step is 0.01 Å.

Using this distribution function, we rewrite Eq. (1) in the form enabling us to calculate the intensity diffracted from much larger particles, namely

$$I(Q) = \sum_i m_i |f|^2 \frac{\sin(Qr_i)}{Qr_i}, \quad (2)$$

where m_i is the multiplicity factor for the i -th interval of distances. The expression in Eq. (2) is valid only for one type of atoms in the particle, for a particle with various atom types an analogous formula can be found

$$I(Q) = \sum_{\alpha\beta} f^{(\alpha)} f^{(\beta)*} \sum_i m_i^{(\alpha\beta)} \frac{\sin(Qr_i^{(\alpha\beta)})}{Qr_i^{(\alpha\beta)}}, \quad (3)$$

where the sum over α and β runs over pairs of atom types (Fe-Fe, O-O and Fe-O, in our case), $r_i^{(\alpha\beta)}$ is the i -th inter-

atomic distance of the atom pair α - β ; this distance appears $m_i^{(\alpha\beta)}$ times in the distance distribution function.

3.1 Fe₂O₃ particles The samples from the series described above were analyzed by the Debye-formula approach using the core-shell model, in which the particle core and the near-surface shell contain γ -Fe₂O₃ and ε -Fe₂O₃ phases, respectively. Increasing the annealing temperature, the core/shell interface of the two phases moves from the surface to the center of the particle, and the relative volume of ε -Fe₂O₃ increases. The data from the Figure 3 (samples annealed at 900 °C, 950 °C and 1000 °C) were fitted by hand and the results are summarized in Table 1; the errors were estimated from this fit too. The background was approximated ad-hoc by a polynomial of the third power. The broad peak around 13° is caused by the amorphous SiO₂ matrix and for our fitting is not important. From the fit we determined the outer mean diameter of the

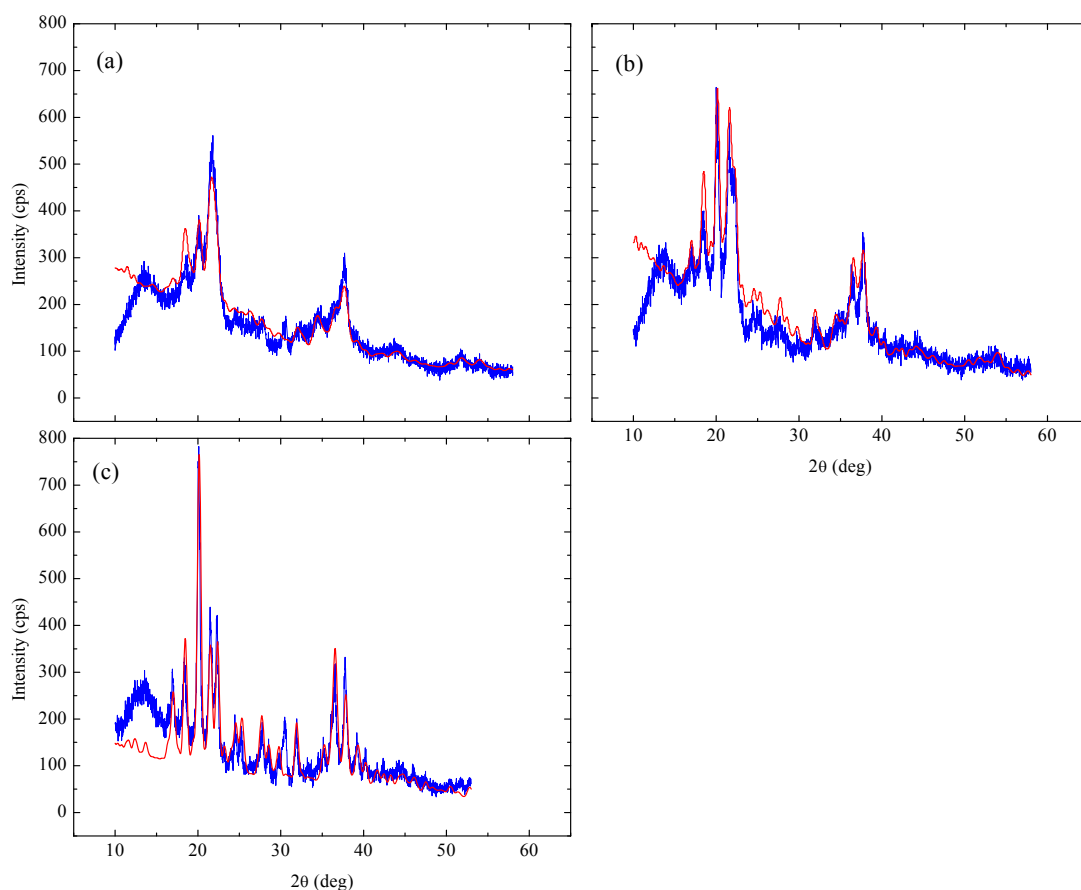


Figure 3 Measured and simulated data for all the Fe₂O₃ samples. The thick blue line represents the measured data, the thin red one is the simulation. The graphs (a) – (c) correspond to the final annealing temperatures 900 °C, 950 °C, and 1000 °C respectively.

nanoparticles and the relative volume of the maghemite and $\epsilon\text{-Fe}_2\text{O}_3$ phases. The fits describe the measured data well and the parameters of the core-shell model were obtained.

3.2 $\text{Fe}_2\text{O}_3/\text{TiO}_2$ particles These samples consist of Fe_2O_3 particles surrounded by TiO_2 particles as was seen in

Fig. 1. For the simulation of the diffraction curves we considered a mixture of Fe_2O_3 and TiO_2 spherical core-shell nanoparticles; with the structure of $\epsilon\text{-Fe}_2\text{O}_3$ (shell)/ $\gamma\text{-Fe}_2\text{O}_3$ (core) and rutile (shell)/anatase (core), respectively. We again expect that both types of the phase boundaries move from the surface of the particle towards its centre with in-

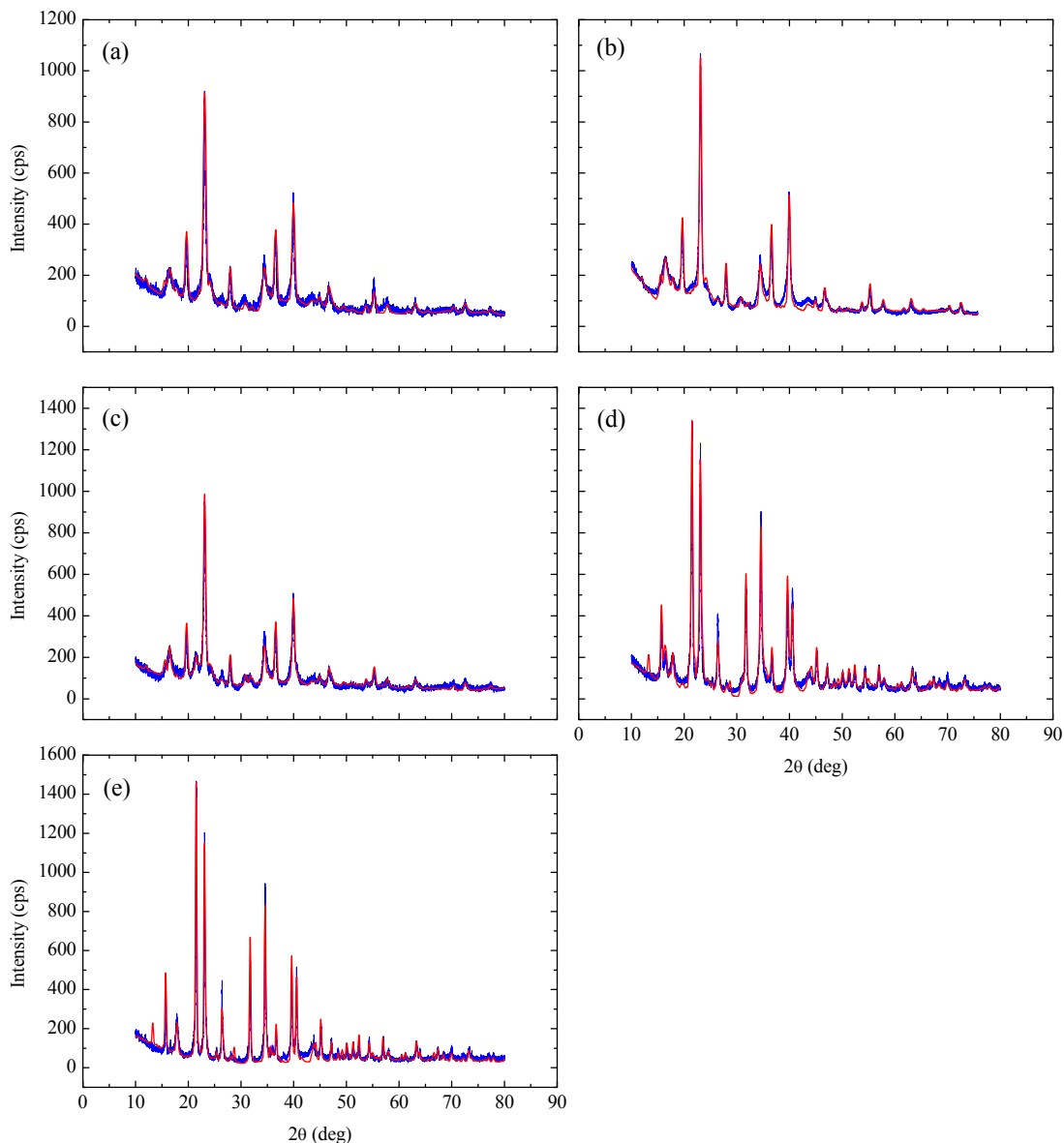


Figure 4 Measured and simulated data for all the $\text{Fe}_2\text{O}_3/\text{TiO}_2$ samples. The blue line represents the measured data, the red one is the simulation. The graphs (a) – (e) correspond to the annealing temperatures 200 °C, 450 °C, 550 °C, 650 °C, and 770 °C respectively.

creasing annealing temperature. The measured and fitted diffraction curves are shown in Fig. 4. The blue lines represent the measured points, the red lines are fitted simulations. The background was approximated by a 4-th power polynomial function.

Table 1 Results obtained from the measured data fitting for Fe_2O_3 samples. The errors of the rate of both phases are roughly estimated. The error of the total radius is not mentioned; the value of the total diameter means the lower estimate of the real diameter.

Annealing temperature (°C)	Total diameter (Å)	$\gamma\text{-Fe}_2\text{O}_3$ maghemite (%)	$\varepsilon\text{-Fe}_2\text{O}_3$ (%)
900	80	34 ± 6	66 ± 6
950	100	26 ± 4	74 ± 4
1000	116	0 ± 8	100 ± 8

From the simulations we obtained the mean external diameters of Fe_2O_3 and TiO_2 nanoparticles, and the relative volumes of individual phases in the core-shell particles; the values are summarized in Table 2. The errors were estimated from the small changes of the fitting parameters; however the relative numbers of Fe_2O_3 and TiO_2 particles of course correlate with the relative volumes of individual phases in the particle.

From the data in Table 2 it is obvious that the size of the Fe_2O_3 particles increases with increasing annealing temperature, while the size of the TiO_2 particles is almost temperature independent. The total relative volume of each type of nanoparticles is within the errors the same for all annealing temperatures. The relative volume of the hematite phase in Fe_2O_3 particles increased from 0% at 200 °C to 100% at 770 °C, while the relative volume of rutile in TiO_2 particles was around 50% for annealing temperatures up to 650 °C and then suddenly jumped to 100% at 770 °C.

4 Discussion As we showed in the previous sections, the calculated fit describes well the measured data. However, the question of the uniqueness of the model is not fully answered. For instance, we assumed that the new phase is being created at the surface of the particle; i.e., that the shell is represented by the “new” phase while the

“old” one is in the core. In order to assess the uniqueness of our model, we have to consider the case of core-shell nanoparticles with reversed phase structure, as well as a mixture of single-phase nanoparticles containing different phases.

The influence of a reversal of the phases in core-shell nanoparticles follows from Fig. 5, where we have plotted the diffraction curve of Fe_2O_3 nanoparticles (annealing temperature 900 °C) fitted by two structure models with reversed phases. Slight differences can be observed, but they are not evidential. When assuming the ε -phase being the shell, the ratio of the ε -phase in the particle is $(65 \pm 5)\%$. If we assume the maghemite phase as the shell, the ratio of ε -phase in the particle is $(60 \pm 5)\%$. This means that in this case we cannot distinguish between both cases.

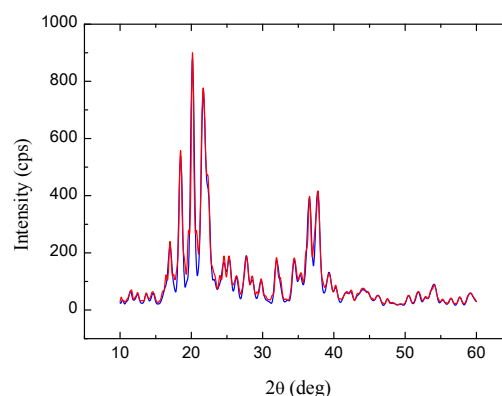


Figure 5 Analysis of the sample annealed up to 950 °C. The difference of the diffraction pattern between the core-shell structure model (maghemite in the core, radius 70 Å, red line) and the mixture of one-phase particles (radius 50 Å, blue line) mixed in the same ratio that corresponds to the ratio in the core-shell model.

In Fig. 6 we compare two fits of sample Fe_2O_3 annealed up to 950 °C, using a core-shell model and a model of a mixture of single-phase nanoparticles. One can see that the difference between both cases is rather small and it is impos-

Table 2 The obtained parameters of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanoparticles.

temperature (°C)	200	450	550	650	770
diameter of Fe_2O_3 particles (Å)	100 ± 20	100 ± 20	100 ± 20	100 ± 20	140 ± 20
relative volume of Fe_2O_3 particles (%)	75 ± 5	75 ± 5	82 ± 5	77 ± 5	83 ± 5
maghemite content (%)	100 ± 5	84 ± 5	66 ± 5	9 ± 5	0 ± 5
hematite content (%)	0 ± 5	16 ± 5	34 ± 5	91 ± 5	100 ± 5
diameter of TiO_2 particles (Å)	100 ± 20	100 ± 20	100 ± 20	100 ± 20	100 ± 20
relative volume of TiO_2 particles (%)	25 ± 5	25 ± 5	18 ± 5	23 ± 5	17 ± 5
anatase content (%)	54 ± 10	50 ± 7	66 ± 7	40 ± 7	0 ± 5
rutile content (%)	46 ± 10	50 ± 7	34 ± 7	60 ± 7	100 ± 5

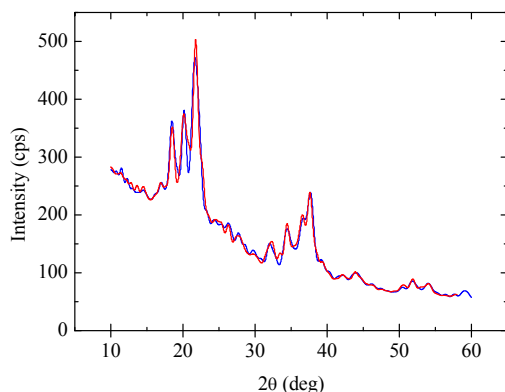


Figure 6 Analysis of the sample annealed up to 900 °C. The difference of the diffraction pattern when exchanging the ϵ -phase from the shell (red line) to the core (blue line). The total radius of the particle is 40 Å.

sible to distinguish between them. Both calculations have been made using the same ratio of present phases. Since the peak corresponding to certain phase is created only by the atoms in the particle belonging to this phase, the total size of the whole particle has to be larger for the core-shell model than for the model consisting of single phase particles. This can be seen from the Figure 6, where the widths of diffraction peaks for both models are approximately the same and for the calculation using mixture model, particles were about 30 % smaller than particles used for the core-shell model calculation. It could be possible to determine the size of the particles using other methods (TEM) and decide which model this size corresponds to. From [6] it follows that the average radius of the particles annealed up to 1000 °C is 60 Å, what is just in between both model cases (mixture model, core-shell model; Figure 6 so it is not clear for now.

5 Conclusion We investigated phase transitions in two types of nanoparticles. Fe_2O_3 nanoparticles were annealed up to three different temperatures and the phase

change from maghemite to $\epsilon\text{-Fe}_2\text{O}_3$ was observed. This change was simulated assuming a core-shell model of these two phases. From the simulations of measured data we calculated the total diameter of the particles and the relative content of both phases. The $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanoparticles were annealed at five different temperatures. The measured data were simulated assuming that the sample consists of the mixture of separate spherical core-shell nanoparticles of Fe_2O_3 and TiO_2 . We obtained the total size of the particles, the relative number of Fe_2O_3 and TiO_2 particles and the content of particular phases in each particle. In both types of particles, the relative amount of the new phase created during the phase transition increased with annealing temperature.

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PAPER

Nanocomposite of superparamagnetic maghemite nanoparticles and ferroelectric liquid crystal†

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In this study we present a novel type of hybrid nanocomposite prepared by mixing maghemite nanoparticles and a chiral liquid crystalline compound. The hybrid system exhibits ferroelectric as well as superparamagnetic properties. The impact of nanoparticles and the effect of an applied magnetic field on the ferroelectric liquid crystalline properties were established. The ferroelectric properties are conserved up to a concentration of 5.6% of maghemite. The magnetic behavior of the composites is typical for a system of superparamagnetic nanoparticles with inter-particle dipolar interactions and surface spin disorder.

1. Introduction

Liquid crystals (LCs) are a fascinating state of matter due to their self-assembling properties.¹ The presence of orientational and positional order and fluidity at the same time, is inherent to liquid crystalline systems. LCs have a great technological potential due to their electro-optical properties and are widespread in electronic displays, switches, computing, control and measuring devices *etc.* Omnipresent in nature, they can serve as a model system for biological membranes.

The development of the fabrication of particles with nanometric dimensions leads to enormous expectations. Nevertheless, the physical properties of nanoparticles can significantly differ from those of the bulk materials. Magnetic iron oxide nanoparticles, in the magnetite or maghemite phase, have been the subject of numerous studies due to their physical properties, leading to a wide range of applications in biomedicine, spintronics, catalysis and as constituents for biosensors.² As a consequence of their nanometer size, the particles exhibit superparamagnetic (SPM) behavior, associated with the formation of a single-domain state. The magnetic properties of the nanoparticles (NPs) mimic the paramagnetic behavior with a collective response of the individual spins within a particle, which can be attributed to a single giant spin (superspin). The superspin undergoes a SPM relaxation, characterized by the fluctuations of the

superspin vector among the directions of easy magnetization.³ This state occurs when the thermal energy, $k_B T$, overcomes the energetic barrier E_A of the nanoparticles (proportional to the particle volume, V), which is related to the magnetocrystalline anisotropy, defined for non-interacting nanoparticles by Stoner and Wohlfarth.⁴ An advantageous fact is that NPs in the SPM regime usually require a lower magnetic field to interact with the magnetization (superspin), in comparison with larger ferromagnetic species. In spite of the fact that the magnetic response of the iron oxide NPs is determined by their shape and size, real effects like interactions between the magnetic NPs,⁵ finite-size effects⁶ and the surface effect⁷ significantly modify their properties. The most obvious effect is the reduction of the saturation magnetization due to surface spin canting. The deviation from the ideal SPM response originates in a varying size distribution, crystallinity and the aggregation of individual NPs, which are imprinted by the preparation procedure. Recently, the suppression of the spurious spin canting effect has been observed in monodisperse highly-crystalline iron oxide NPs coated with oleic acid,⁸ which enables maximization of the saturation magnetization for a given particle size.

More attention is now paid to novel approaches for organizing NPs and different strategies are used for this purpose. Liquid crystalline materials appear as perfect candidates for such new systems as they combine order and mobility on the molecular level in a unique manner. The capability of LCs to orient small particles has been known for many years.⁹ The formation of particle aggregates and topological defects have been studied in nematic and cholesteric LCs.¹⁰ However, the interaction between particles and LC molecules strongly depends on the particular combination of both materials, on the LC molecular structure and elastic properties and on the type, size and shape of the colloidal particle. NPs can be solvated in LCs or liquid

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crystalline polymers with the aim of exploiting their self-assembling property and potentially to obtain advantageous electrical, optical or magnetic properties.¹¹ Due to the orientational and positional order in the LC host, one can expect unusual properties, in comparison with conventional colloidal systems. The dispersion of ferromagnetic particles into LCs is done with the aim of enhancing their optical, electrical and magnetic properties.

The preparation of such a hybrid composite can be a way to obtain well organized NPs. A challenge for future studies is to create hierarchically structured composites with a distinct function, to yield a mechanically integrated, multifunctional material, responsive to both electric and magnetic fields. Ordered assemblies are promising in a wide range of applications, for example in high-density media, microelectronics and charge transport devices. Recent work reported the study of a system of iron oxide NPs, prepared by co-precipitation and subsequent dispersion in a lipid-based lyotropic LC, which exhibited orientational order, tunable by the external magnetic field and a photothermal effect.¹²

This work is concentrated on rod-like molecules that create thermotropic LCs, in which liquid crystalline phases occur, on lowering temperature from the isotropic phase. Besides the nematic phase, which is well-known and widespread in display technology, smectic phases can also appear. In the smectic A phase (SmA), molecules are organized in layers with their molecular axis parallel to the layer normal. If molecules are tilted with respect to the layer normal, the smectic C phase (SmC) is observed. If the molecules are chiral, liquid crystals exhibit ferroelectricity in the tilted SmC* phase. Ferroelectric materials possess a spontaneous polarization that is stable and can be switched by an applied electric field. The ferroelectric properties of the SmC* phase are established by the electric switching and dielectric and optical methods. Chiral smectics are complex systems, certain features of which also manifest in their dielectric behavior.¹³ Dielectric spectroscopy enables us to characterize the soft mode (the fluctuation of the tilt angle), which contributes to permittivity in the vicinity of the SmA–SmC* phase transition. In the SmC* phase, the phase fluctuations (Goldstone mode) are also present and contribute to the permittivity. The dielectric strength of the Goldstone mode is much larger than that of the soft mode in the whole SmC* phase, except in the vicinity of T_c . If the electric bias field is applied parallel to the smectic layers, the helical structure is unwound and thus the Goldstone mode is suppressed.

We present a new type of hybrid system, consisting of a liquid crystalline compound and magnetic $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles coated by oleic acid (MNPs). We integrated the magnetic iron oxide nanoparticles into the LC compound (*S*)-1-(hexyloxy)-1-oxopropan-2-yl 4-(4-(4-(nonyloxy)benzoyloxy)benzoyloxy)benzoate, denoted as 9HL. The studied LC compound exhibits the ferroelectric SmC* phase. The size of the nanoparticles (4 nm) was adjusted, to be close to the length of the LC molecules, to reduce the interference in the LC order. As the efficiency of the possible magneto-electric

coupling requires the largest possible value of the superspin for the given MNP size, MNPs with a narrow size distribution were used. We focused on the ferroelectric and magnetic properties of the new hybrid composites. Our objective was to provide a new way to realize the magneto-electric coupling, which is described as the influence of the magnetic (electric) field on the polarization (magnetization) of a material.

2. Results and discussion

2.1. Liquid crystalline compound

The studied thermotropic liquid crystalline host is the lactic acid derivative 9HL, with a molecular core consisting of three phenyl rings, connected by ester linkage groups.¹⁴ The compound 9HL exhibits the isotropic (Iso)–SmA–SmC*–crystal phase sequence on cooling with the transition temperatures $T_A = 401$ K (Iso–SmA), $T_C = 347$ K (SmA–SmC*), $T_{Cr} = 308$ K (crystallization). As is characteristic for the SmC* phase, there is a helicoidally periodic arrangement with the characteristic pitch length of $2.1\ \mu\text{m}$.^{14a} Various hybrid composites were prepared from 9HL and MNPs with a defined weight concentration of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles (see the Experimental section).

2.2. Mesomorphic properties and textures

The observation of textures is a primary tool for the characterization of the mesomorphic properties of liquid crystalline composites, and differential scanning calorimetry (DSC) complements it. A phase diagram (Fig. 1) shows that the temperature range of the ferroelectric SmC* phase is gradually suppressed with increased MNP concentration and disappears at about 5.6 w/w% of $\gamma\text{-Fe}_2\text{O}_3$ (20 w/w% of MNP). On the contrary, the Iso–SmA phase transition temperature is not influenced by the presence of magnetic nanoparticles to such a large extent. The coexistence of the isotropic and SmA phases is observed for mixtures with increasing MNPs concentration.

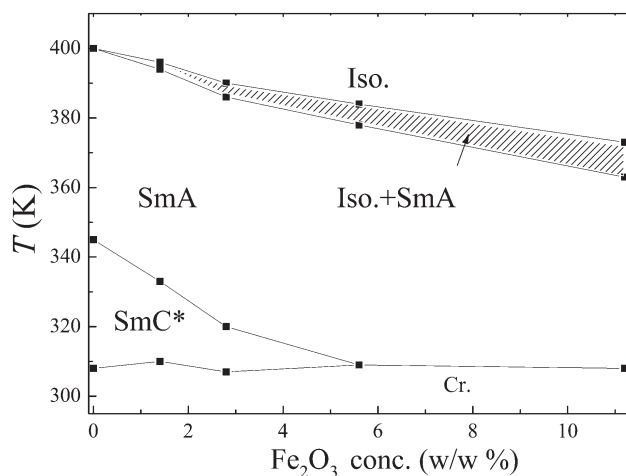


Fig. 1 Phase diagram for studied hybrid systems of LC compound 9HL and magnetic nanoparticles (MNPs). The hatched area shows the isotropic–SmA coexistence region.

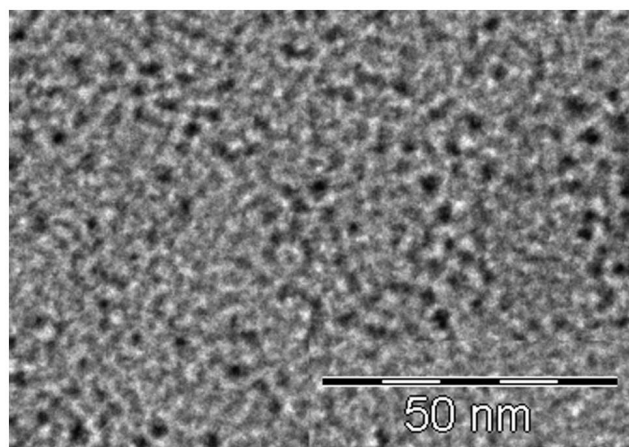


Fig. 2 TEM image of composite 1.4% Fe_2O_3 in 9HL taken at room temperature.

A transition electron microscope (TEM) photograph is presented for 1.4% of Fe_2O_3 in 9HL in Fig. 2. The photograph was taken at room temperature on a sample prepared just after the evaporation of hexane from a solution of 9HL and MNPs without heating to the liquid crystalline phase. One can see that magnetic nanoparticles with homogeneous shape and size are uniformly dispersed.

The textures observed on samples in commercial glass $6\ \mu\text{m}$ thick cells have been studied by polarizing microscopy. For lower MNP concentrations (up to 5.6% of Fe_2O_3) a typical fan-shaped texture is observed in the SmA phase (see Fig. 3a). Such a texture is also found for the pure compound 9HL and indicates a common tendency of molecules to orient along the sample surface (planar alignment). It results in a sample structure with the smectic planes perpendicular to the sample surface (bookshelf geometry). In the planar texture, slightly elongated dots are visible, which represent defects decorated by clusters of MNPs (see ESI,[†] Fig. S6). For higher MNP concentrations, a homeotropic texture is preferred, with molecules perpendicular to the sample surface, which is seen as a black area in Fig. 3b. From this fact, one can speculate that there is modification of the anchoring at the surface, from the planar to the homeotropic texture, due to the presence of MNPs. For intermediate concentrations, both types of textures can coexist in one sample (see Fig. 3).

2.3. Dielectric properties

In the ferroelectric SmC^* phase, which is present for mixtures up to a concentration of 5.6% of Fe_2O_3 , the direction of the spontaneous polarization, P_s , can be switched by an electric field. The spontaneous polarization was evaluated by the integration of the peak area in the switching current profile (Fig. 4a). The temperature dependencies $P_s(T)$ have been measured for nanocomposites with 1.4% and 2.8% of Fe_2O_3 in 9HL, and compared with the $P_s(T)$ of pure 9HL (Fig. 4b). All dependencies show a typical increase in P_s on cooling from the SmA to the SmC^* phase. The decrease on the low temperature side reflects a gradual crystallization. The results also reveal a significant decrease of P_s with increasing MNP concentration.

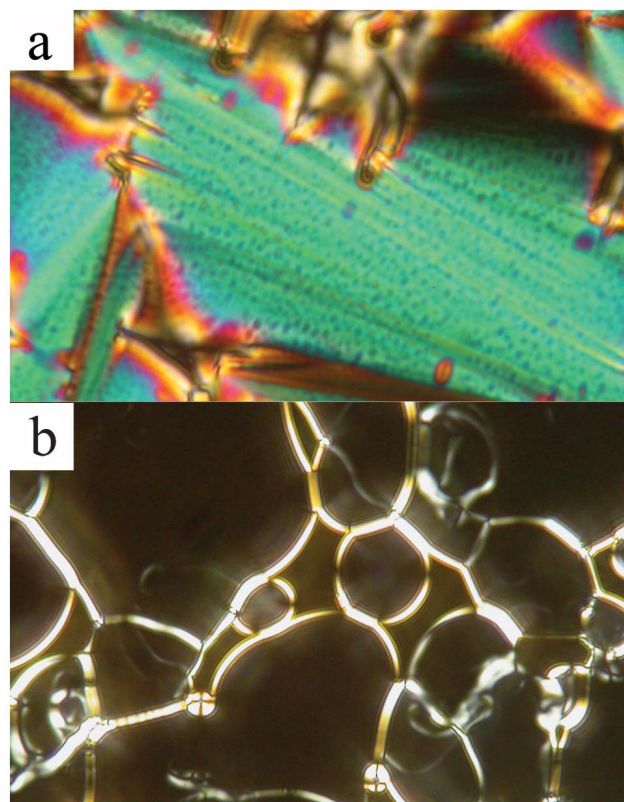


Fig. 3 Microphotograph of the studied 5.6% Fe_2O_3 in 9HL, embedded into a commercial $6\ \mu\text{m}$ thick cell. (a) A fan-shaped texture observed below the Iso-SmA phase transition; (b) homeotropic texture with birefringent bands. Both textures coexist in different parts of the cell. The width of the photograph is $120\ \mu\text{m}$.

The results of dielectric spectroscopy show that both the Goldstone and the soft modes are suppressed and smeared with increasing MNPs concentration. A similar effect is also observed when inserting another type of nanoparticle into the LC species.¹⁵ We have studied the dielectric properties of hybrid nanocomposites under a magnetic field of 9 T, directed along the sample surface. We established the effect of the magnetic particles on the complex permittivity, measured at 1 kHz. Generally, the permittivity in the ferroelectric liquid crystalline compound is given by the Goldstone mode (director-azimuthal fluctuations) besides the vicinity of the SmA-SmC^* phase transition, where a peak due to the soft mode (fluctuations of the tilt angle) can be observed. Under a sufficiently high magnetic field, the helix in the SmC^* phase is unwound and thus the Goldstone mode is suppressed.¹⁶ A comparison of the temperature dependencies of the real, ϵ' , and imaginary, ϵ'' , parts of the permittivity without a magnetic field and under a magnetic field of 9 T is shown in Fig. 5. For all studied samples, pure 9HL and the hybrid nanocomposite, the effect of the magnetic field is very similar. In all samples the applied magnetic field strongly suppresses the permittivity in the SmC^* phase. In the temperature dependence range, where the Goldstone and soft modes are not active or are suppressed by the applied electric or magnetic field, the losses are very small showing a low concentration of impurities.

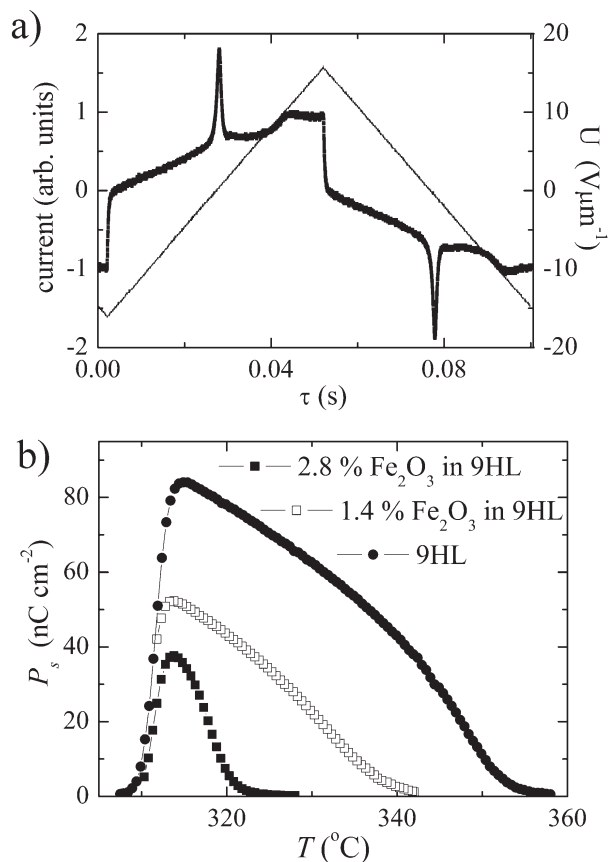


Fig. 4 (a) Switching current profile versus intensity of an applied triangular electric field, U , for the composite 1.4% Fe_2O_3 in 9HL host. (b) Temperature dependencies of the spontaneous polarization, P_s , for pure 9HL and the composite systems 1.4% Fe_2O_3 in 9HL and 2.8% Fe_2O_3 in 9HL.

2.4. X-ray scattering data

Small angle X-ray diffraction studies were performed on cooling from the isotropic phase. The layer spacing, d , was evaluated from the peak on diffracted intensity. The temperature dependencies of d , shown in Fig. 6, exhibit a gradual increase in d in the SmA phase. A negative thermal expansion coefficient is common for the SmA phase and is usually explained by the increase of the orientational order on cooling and by the molecular conformation changes due to the ending-chain prolongation. At the SmA–SmC* phase transition, a decrease in d is observed, which is related to the tilt of the molecules in the SmC* phase. An additional significant decrease occurs in the crystalline phase. Qualitatively similar behavior is found for pure 9HL, as well as for the composite with MNPs. The presence of MNPs increases the layer spacing, the increase being more pronounced in the SmC* and crystal phases. One can expect that the presence of nanoparticles influences the process of ending-chain prolongation in the liquid crystalline phase.

2.5. Magnetic properties

The magnetic response of the original maghemite nanoparticles and the nanocomposites in the studied hybrid system with LC was investigated by means of the temperature

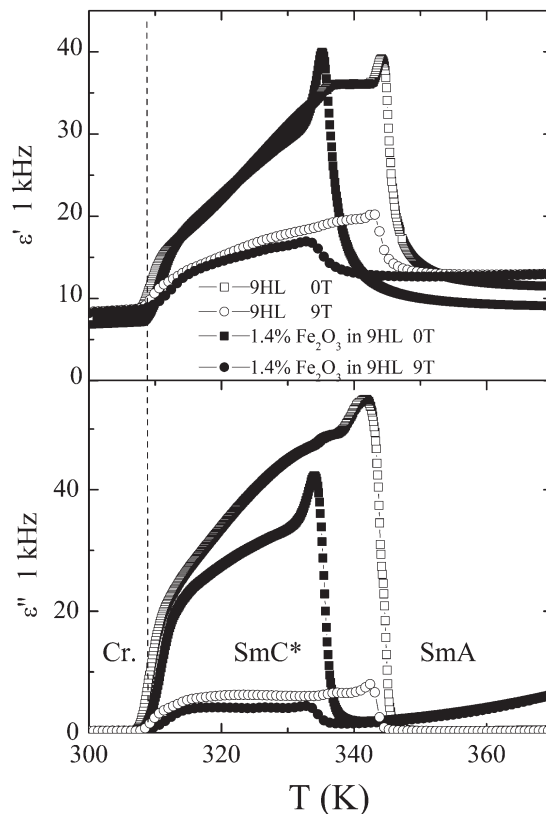


Fig. 5 Temperature dependencies of (a) the real part of permittivity, ϵ' , and (b) the imaginary part of permittivity, ϵ'' , taken at a frequency of 1 kHz for the pure liquid crystal 9HL (empty symbols) and a mixture 1.4% w/w of Fe_2O_3 in 9HL (full symbols) without a magnetic field and under a 9 T magnetic field. The studied samples are heated from R.T. to 400 K and then cooled down.

dependence of magnetization, magnetization isotherms and a.c. susceptibility. The typical temperature dependence of the zero field cooled (ZFC) and field cooled (FC) curves is shown in Fig. 7. The bifurcation point ($T_B \sim 15$ K) of the ZFC-FC curves attributed to the blocking temperature of the MNPs, is slightly

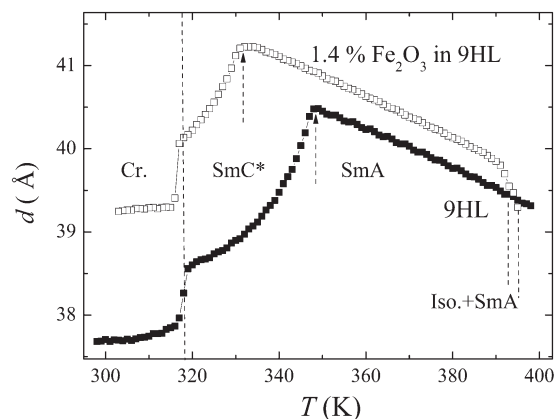


Fig. 6 Temperature dependence of the layer spacing value, taken from the X-ray scattering data, for pure 9HL and composite 1.4% of Fe_2O_3 in 9HL. The SmA–SmC* phase transitions are marked by dashed arrows.

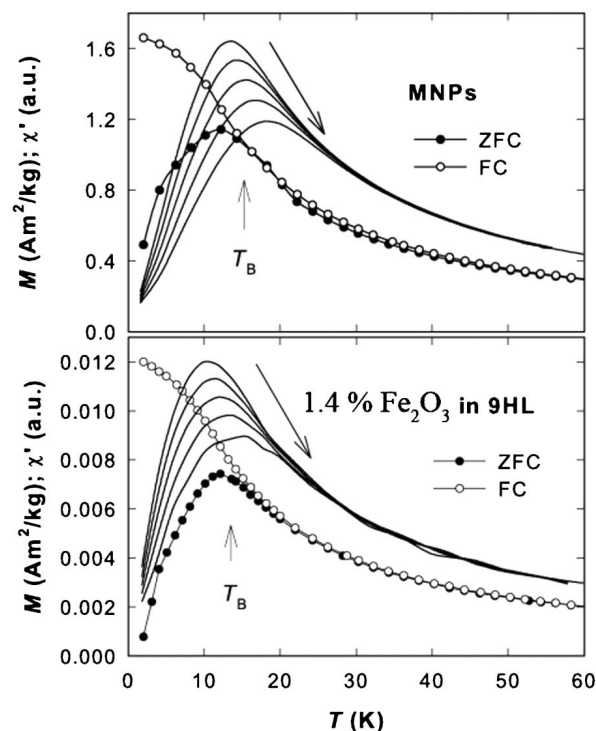


Fig. 7 Temperature dependence of the zero field cooled (ZFC) and field cooled (FC) magnetization, M , of the MNPs and the composite containing 1.4% of the Fe_2O_3 in 9HL. The vertical arrows depict the blocking temperature, T_B . The solid lines correspond to the real part of the a.c. susceptibility, χ' ; the shift of the maximum with frequency of the applied a.c. magnetic field, increasing from 0.1 to 1 kHz, is schematically shown by the long arrow.

above the maximum on the ZFC curve (at ~ 12 K for all studied samples). The saturation of the FC curve at low temperatures points to dipolar interactions among the MNPs in all studied samples.

The magnetization isotherms of the original MNPs and the sample containing 1.4% Fe_2O_3 in 9HL are depicted in Fig. 8. The loops recorded in the block state show a net hysteresis due to the blocked state (Fig. 9), while those above the T_B show the expected Langevin character. All curves exhibit a linear paramagnetic-like contribution, which can be attributed to the disordered surface spin layer response; however, the saturation value, M_s , and remnant magnetization, M_r , values are almost comparable to the bulk value (when normalized to Fe_2O_3 content), suggesting the suppression of the surface spin disorder by the oleic acid coating in the MNPs and the nanocomposite. At the temperature 10 K, the M_s (determined after subtraction of the linear spin-disorder contribution at high magnetic fields) and the M_r values for the MNPs sample are about 12.0 and 4.2 $\text{A m}^2 \text{ kg}^{-1}$, respectively. The corresponding M_s/M_r values for the samples containing 5.6% and 1.4% of Fe_2O_3 in 9HL are 1.3/0.32 $\text{A m}^2 \text{ kg}^{-1}$ and 0.48/0.12 $\text{A m}^2 \text{ kg}^{-1}$, respectively. These values are in a very good agreement considering the expected MNP content in the composite samples. The important feature observed on the hysteresis loops in the blocked state is the reduction of the coercivity, H_c , in the composite samples to about $\frac{1}{2}$ of the pure MNP value (from 0.1 T to 0.05 T at 2 K, as shown in Fig. 9a). In

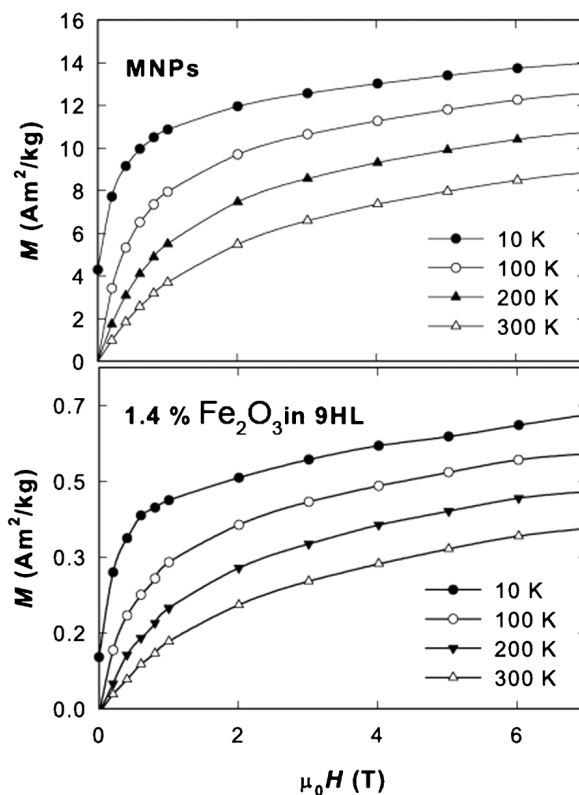


Fig. 8 Magnetization isotherms at selected temperatures for the MNPs and the sample containing 1.4% of Fe_2O_3 in 9HL.

Fig. 9b the magnetization isotherms recorded at 300 K are shown in order to demonstrate the superparamagnetic nature of the MNPs and the hybrid system. This effect can be attributed to the weakening of the inter-particle interactions. Usually, the dilution of the dipolar interaction is also evidenced by a decrease in the blocking temperature, however, considering the size of our MNPs (4 nm) and the temperature scale, where the transition to the blocked state occurs, the potential shift of the T_B would be hardly detectable by analyzing the ZFC-FC dependencies.

The superspin relaxation phenomena are inspected by the a.c. susceptibility measurements. The typical temperature dependencies of the real part of the a.c. susceptibility, χ' , are shown in Fig. 7 (solid lines). The maxima of the χ' curves for the equivalent frequencies occur at slightly lower temperatures for the composite sample, suggesting a modification of the interaction strength between the MNPs. This observation is consistent with the reduction of the H_c . Because the saturation of the FC curve at low temperature suggested the presence of weak inter-particle interactions, the evolution of temperature of χ' maxima with frequency was inspected using the Vogel-Fulcher (VF) law¹⁷ describing the (super)spin relaxation among the weakly interacting MNPs:

$$\ln f = \ln f_0 - \frac{E_A}{k_B(T - T_0)} \quad (1)$$

where the characteristic parameters are: frequency f_0 , activation energy E_A k_B^{-1} and VF temperature, T_0 , that is the

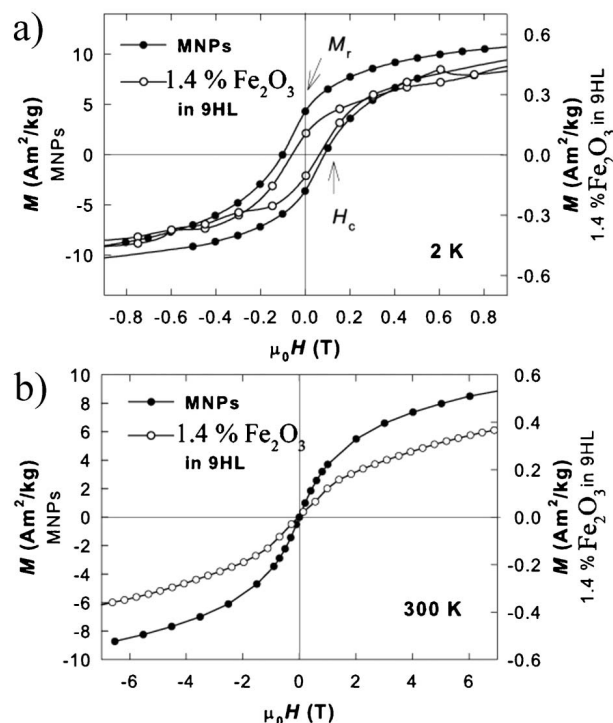


Fig. 9 Hysteresis loops (a) in the blocked state at $T = 2$ K and (b) at $T = 300$ K for the MNPs (full symbols) and the sample containing 1.4% of Fe_2O_3 in 9HL (empty symbols). The left-side scale corresponds to the MNPs and the right-side to the composite. The magnetization isotherms recorded at 300 K are shown in order to demonstrate the superparamagnetic nature of the MNPs and the hybrid system.

correction of the well-known Arrhenius–Nell law (valid for a system of non-interacting MNPs), and representing the inter-particle interaction. The resulting values for relaxation times are $\tau_0 = 2 \times 10^{-9}$ s, $T_0 = 12$ K, $\tau_0 = 6.8 \times 10^{-10}$ s, $T_0 = 10$ K and $\tau_0 = 4.2 \times 10^{-10}$ s, $T_0 = 9$ K for the MNPs, composites 5.6% and 1.4% Fe_2O_3 in 9HL, respectively. The obtained values of the relaxation time correspond well to those expected for superparamagnetic (SPM) nanoparticles. The observed decrease of both the VF temperature and the relaxation times supports the scenario of the inter-particle interactions weakening in the composite samples. In general, the magnetic response of the composites shows all the attributes of the MNPs, so the embedding of the MNPs in the LCs does not affect their unique SPM properties.

3. Conclusions

The admixture of magnetic nanoparticles, coated by oleic acid, to ferroelectric liquid crystal 9HL, which exhibits the SmA–SmC* phase sequence on cooling from the isotropic phase, gradually suppresses the SmC* temperature range and at about 5.6 w% concentration this phase disappears and only the SmA phase persists on cooling, till crystallization. The crystallization temperature is not affected by the presence of

MNPs. In the SmC* phase, the values of the spontaneous polarization, as well as the permittivity, gradually decrease with the particle concentration. A typical *planar* anchoring of the LC molecules at the sample surface is changed to the *homeotropic* one, due to the presence of MNPs. The layer spacing in the smectic phase is increased due to the MNP presence, the effect being stronger in the SmC* phase. We present a new hybrid system exhibiting both ferroelectric and superparamagnetic properties. Moreover, we are able to modify the ferroelectric properties by applying a magnetic field. The magnetic behavior is typical for a system of superparamagnetic nanoparticles with inter-particle dipolar interactions and surface spin disorder. The magnetic response of the MNPs in the composite is observed and the unique SPM properties preserved. The magnetic properties are modified due to the reduction of the dipolar interaction strength between the MNPs, which is evidenced by the decrease of the coercivity, superspin relaxation time and VF temperature.

4. Experimental section

4.1. Preparation of MNPs and nanocomposites

Magnetic nanoparticles, covered with oleic acid ($\gamma\text{-Fe}_2\text{O}_3$), were synthesized following the published hydrothermal procedure¹⁸ with some modifications: 10 mmol of NaOH was dissolved in 2 ml of water, 10 ml of ethanol and 12 mmol of oleic acid was added with stirring, which led to a clear solution. It was transferred to an autoclave tube and an aqueous solution of 1 mmol of Fe(III) nitrate and 1 mmol of Fe(II) nitrate was added with vigorous stirring and sonication. In total, 20 ml of distilled water was added. The autoclave was closed and placed into a pre-heated, 180 °C oven for 10 h. After cooling, the final mixture was composed of an upper organic phase, a lower aqueous phase and sedimented particles. The liquid phase was discarded. The remaining particles were washed four times by re-dispersion in 5 ml of hexane and precipitation by 15 ml of ethanol. After washing they were re-dispersed in 10 ml of hexane and the dispersion was centrifuged at 4500 rpm to remove large agglomerates.

The maghemite particles coated by oleic acid (MNPs) and liquid crystalline material 9HL were dissolved in 5 ml of hexane (p.a.) under heating and stirring. The relative concentrations of the components were adjusted to give 20 mg of the final composite, having an Fe content from 1% to 8% w/w. The hexane solution was then heated up to 60 °C and the solvent was gradually evaporated. The composite was then dried in a vacuum oven for 2 h at room temperature. The content of Fe in the composite was determined by atomic absorption spectroscopy. Samples were mineralized in a mixture of HCl and HNO_3 with the addition of a small amount of H_2O_2 . The absorption of the solution was measured on an atomic absorption spectrometer AA240 (Varian) at a wavelength of 248 nm. A flame technique, using an air–acetylene mixture and a deuterium background correction was used. A standard iron stock solution was prepared from iron nitrate. Various hybrid composites were prepared with concentrations

of 1.4, 2.8, 5.6 and 11.2% w/w of Fe_2O_3 , which correspond to 5, 10, 20 and 40% w/w of MNPs with the oleic acid admixture.

4.2. Mesomorphic and electro-optical studies

The texture observations and the measurements of the spontaneous polarizations, P_s , were carried out on planar samples, 7 or 12 μm thick, with a $5 \times 5 \text{ mm}^2$ electrode area. The cells consisted of two glasses provided with transparent ITO electrodes and polyimide layers, ensuring a planar geometry (the layers were perpendicular to the sample surface). The cells were filled by means of capillary action in the isotropic phase. Liquid crystalline samples were examined under a polarizing optical microscope, Nikon Eclipse E-600, equipped with a Linkam heating stage. The temperature was stabilised within $\pm 0.1^\circ\text{C}$.

4.3. Switching properties and dielectric spectroscopy measurements

The dielectric properties were studied using a Schlumberger 1260 impedance analyser. The frequency dispersions were measured at a cooling rate of about 0.2 K min^{-1} , keeping the temperature of the sample stable during the frequency sweeps in the range of 10 Hz–10 MHz. Details of the fitting procedure are in the ESI.† The spontaneous polarisation, P_s , was determined from the switching current, detected under a triangular electric field profile at a frequency of 50 Hz and an electric field of $20 \text{ V } \mu\text{m}^{-1}$. The current profile was detected with the memory digital oscilloscope, Tektronix.

The temperature dependencies of the real and imaginary parts of the dielectric permittivity under an external magnetic field were determined at a frequency of 1 kHz using an ultra-precise capacitance bridge Andeen-Hagerling 2500 A implemented in PPMS 9 T (Physical Property Measurement System).

4.4. Magnetic properties measurements

Magnetic measurements of the samples in the solid state were performed using a commercial SQUID magnetometer MPMS 7XL (Quantum Design, San Diego). The samples, of a typical mass in the order of milligrams, were placed into a gelatine capsule and fixed with glue to avoid rotation of the particles in the direction of the external magnetic field. To determine the values of the blocking temperature, T_B , the temperature dependencies of the zero field cooled (ZFC) and field cooled (FC) magnetization were measured in the temperature range of 10–300 K in an external magnetic field equal to 0.01 T. The magnetization isotherms were recorded at selected temperatures in magnetic fields varying up to 7 T in both polarities. The temperature dependencies of the real, χ' and imaginary, χ'' parts of the a.c. susceptibility were collected at different frequencies of the altering magnetic field (0.1 Hz–1 kHz) with an amplitude of 0.3 mT in a zero external magnetic field.

4.5. X-ray measurements and TEM studies

X-ray studies were performed using the Bruker D8 Discover system ($\text{Cu-K}\alpha$ radiation) equipped with an Anton Paar DCS-350 heating stage (temperature stability 0.1 K), working in the reflection mode. Samples were prepared as one-surface free droplets on a heated surface. The smectic layer thickness, d , was determined using Bragg's law $n\lambda = 2d\sin\theta$, where d is

calculated from the diffraction angle θ of the (001) smectic layer peak in the small angle regime.

A TEM Libra 120 from Zeiss was used with the highly flexible Koehler illumination system, together with the in-column OMEGA filter, providing an excellent image contrast.

Acknowledgements

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3.2.2 Izolované nanočástice magnetitu a maghemitu

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V této části jsou zahrnuty práce věnující se přípravě nanočástic oxidu železitého zejména pro biomedicínské aplikace. První práce [94] se zabývá novou metodou přípravy hydrofilních nanočástic Fe_2O_3 s CM-dextranem, který je vhodným pokrytím pro následné modifikace. Nanočástice byly charakterizovány standardním spektrem fyzikálních metod a bylo potvrzeno, že je možné měnit velikost částic v rozmezí 6 - 10 nm při zachování úzké distribuce jejich velikosti.

Další dvě práce se zabývají porovnáním magnetických vlastností nanokrystalů Fe_2O_3 , resp. Fe_3O_4 o stejné velikosti, které jsou pokryty kyselinou olejovou nebo SiO_2 (pozn. nominální složení má odpovídat magnetitu, nicméně z důvodu topotaktické transformace jsou částice silně zoxidované). V prvním případě se jedná o nanokrystaly připravené dekompozicí organického prekursoru v přítomnosti kyseliny olejové, ve druhém jsou částice získány koprecipitací v bazickém prostředí. Porovnání vlivu krystalinity a pokrytí nanočástic na sklonění spinů v povrchové vrstvě je předmětem studia práce [95]. Dva typy částic o stejné velikosti byly, kromě standardních metod, detailně studovány pomocí měření Mössbauerovy spektroskopie v závislosti na teplotě a magnetickém poli. V případě vysoce krystalických částic s kovalentně vázanou kyselinou olejovou jsou pozorovány vysoké hodnoty saturované magnetizace a koercivity, společně se zanedbatelným skloněním spinů. U částic připravených koprecipitací s amorfni vrstvou SiO_2 , vyloučenou na povrchu pomocí dodatečné modifikace, je pozorován významný nárůst neuspořádaných spinů společně s poklesem saturované magnetizace a koercivity. Výsledky měření střídavé susceptibility potvrdily přítomnost defektního magnetitu v nanokrystalech s vysokou krystalinitou.

Související práce [96] se zabývá mezičásticovými interakcemi v obdobných systémech jako [95], zejména možným vznikem meziklastrových interakcí v nanokrystalech dodatečně pokrytých amorfní vrstvou SiO_2 o různé tloušťce. Kromě standardních experimentů byl provedena měření teplotní závislosti střídavé susceptibility v magnetických polích a data byla analyzována pomocí modelu pro kritickou dynamiku v silně interagujících systémech. Společně s výsledky teplotní závislosti Mössbauerových spekter bylo potvrzeno, že s rostoucí tloušťkou vrstvy SiO_2 mírně klesá vliv dipolárních interakcí, nicméně všechny vzorky vykazují chování superspinového skla, tj. silně interagujícího systému.

Poslední práce v této sekci se věnuje problematice spinového ne-uspořádání ve vysoce krystalických nanočásticích maghemitu o různé velikosti (7 - 20 nm) připravených dekompozicí organického prekurzoru v přítomnosti kyseliny olejové. Ukazuje, že standardně používané postupy vedou k velmi rozdílným výsledkům a neumožňují rozlišit mezi povrchovým a objemovým efektem. Nanočástice použité v této studii byly vyvinuty jako optimální magnetické nosiče pro teragnostické aplikace v rámci projektu 7RP Multifun a vykazují velmi úzkou distribuci velikostí částic (index polydispersity menší než 0.2), proto lze velmi dobře eliminovat vliv distribuce velikosti na spektrální parametry. Naše práce navrhuje nový přístup, kdy je uvažován vývoj hyperjemného, resp. efektivního magnetického pole jednotlivých podmříží v závislosti na aplikovaném vnějším magnetickém poli. Ukázkovým příkladem je srovnání dvou typů částic o stejné fyzické velikosti (určené z transmisní elektronové mikroskopie), kdy jedny vykazují tzv. strukturu core-shell, zatímco druhé obsahují vrstevnaté chyby, tj. celkový podíl krystalograficky uspořádané fáze ve vzorku je větší. Mössbauerova spektra měřená v nulovém a ve vnějším magnetickém poli v saturovaném režimu jsou však identická, což ukazuje, že ustálená metodika bez znalosti mikrokystalické struktury nanočástic nerozliší, v jaké části nanokrystalu dochází k dekoherenci magnetického uspořádání. Dále bylo pozorováno, že u nanočástic o velikosti 7 nm nedochází ke sklonění spinu, pokud jsou vysoce krystalické, zatímco u nanočástic o velikosti 15 nm je spinové neuspořádání signifikantní.

Hydrothermal preparation of hydrophobic and hydrophilic nanoparticles of iron oxide and a modification with CM-dextran

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Abstract Hydrophobic and hydrophilic particles of iron oxide (magnetite/maghemite) with diameter of 6–10 nm were prepared by hydrothermal hydrolysis of iron oleate in water/pentanol/oleic acid system at 180 °C. The hydrophobic/hydrophilic nature of resulting particles was controlled by the presence of sodium oleate and by manipulating the ionic strength (with NaCl). The final particle size was controlled by additional organic solvent (octanol or toluene) and by seed growth. Hydrophilic particles (6 nm) were further modified by carboxymethyl-dextran in water to obtain stable and well-dispersed superparamagnetic nanoparticles suitable for biomedical application. The

prepared particles were characterized by transmission electron microscopy, thermogravimetry, Fourier-transform infrared spectroscopy, magnetic measurements, Mössbauer spectroscopy, dynamic light scattering, and zeta-potential measurement.

Keywords Superparamagnetism · Magnetite · Carboxymethyl dextran · Hydrothermal synthesis · Nanocrystals

Introduction

Superparamagnetic particles of magnetite/maghemite ($\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$) are intensively studied materials due to their application as ferrofluids, mainly in biomedical area as MRI contrast agents (Jun et al. 2005), constituents of biosensors (Geng et al. 2007), and for hyperthermic treatment of tumors (Duguet et al. 2006). In order to fulfill the requirements on biocompatibility and stability against agglomeration and flocculation, they are usually prepared by the coprecipitation method and subsequently covered with dextran. However, the coprecipitation leads to particles of poor crystallinity and wide size distribution. To improve the magnetic properties of the nanoparticles, progressive methods of preparation must be involved. The methods usually employed to produce well-dispersed particles of narrow size distribution are

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either thermal decomposition in organic solvents (Sun and Zeng 2002; Sun et al. 2004) or, less frequently, hydrothermal method (Liang et al. 2006). However, these particles are hydrophobic and thus they need to be modified to become hydrophilic and usable for biomedical purposes. The surface modification involves either coating by silica layer, using controlled hydrolysis of silanes (De Palma et al. 2007), or by carboxylic acids (Jun et al. 2005). To our knowledge, there are almost no reports of dextran coating of particles of this type; one multi-step modification (using 3-aminopropyl trimethoxysilane) was reported by Barrera et al. (2009), and another one, involving thermal treatment with inert salt (Na_2SO_4), was reported by Park et al. (2011).

Our previous work (Repko et al. 2011) dealt with the mechanism of hydrothermal synthesis of CoFe_2O_4 nanoparticles. In the present work, we summarize further enhancement of the procedure in order to obtain high batch yield (400 mg) and one-pot synthesis of hydrophilic particles of iron oxide.

The prepared hydrophilic particles were then subjected to modification with carboxymethyl dextran (CM-dextran), which was chosen as a polymer with better affinity to iron oxide than dextran (through carboxylate groups), and its attraction to the surface of the nanoparticles leads to their better stability in solution due to lower isoelectric point (Liu et al. 2011). The optimized procedure is fully reproducible for high-yield preparation of highly crystalline iron oxide nanoparticles stabilized by CM-dextran desired in various biomedical applications.

We also demonstrate seed-mediated growth in hydrothermal conditions. Here, the as-prepared hydrophobic particles dispersed in octanol or toluene act as seeds and their growth in subsequent preparation leads to larger particles, up to 10 nm.

Experimental

Materials

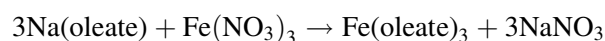
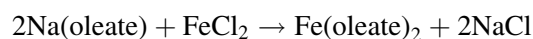
Oleic acid (PhEur) was obtained from Fluka; iron(III) nitrate pentahydrate (puriss. p.a., ACS reagent), chloroacetic acid (99 %), and 1-octanol (ACS reagent) from Sigma-Aldrich; dextran (from *Leuconostoc mesenteroides*, average mol wt 9,000–11,000) from Sigma; iron(II) chloride tetrahydrate from Merck;

hexane (pure) and sodium hydroxide (p.a., micro-pearls) from Lach-Ner; ethanol (absolute, p.a.), 1-pentanol (*n*-amylalcohol, p.a.), and sodium chloride (p.a.) from Penta-chemicals.

Reaction mixture for hydrothermal treatment

General strategy

The formation of the hydrophilic particles is maximized when water phase contains only sodium oleate and no salts, according to the growth mechanism depicted in Fig. 1. For this aim, a solution of sodium oleate first reacted with iron(II) chloride and iron(III) nitrate:



After the water phase containing sodium salts was removed, more sodium oleate and water was added in order to obtain final reaction mixture (Table 1).

Organic phase

The following items were added to a 100 ml beaker with stirring: NaOH (14 mmol, 560 mg), water (4 ml), pentanol (5 ml), oleic acid (18 mmol, 5.08 g), and a clear solution was obtained. Then, a water solution of $\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (2 mmol, 0.808 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (4 mmol, 0.795 g) was added, so the total amount of water was 15 ml. The mixture was stirred under sonication for 3 min and then left for 15 min to separate the colorless water phase and dark brown organic phase. The water phase was discarded and the

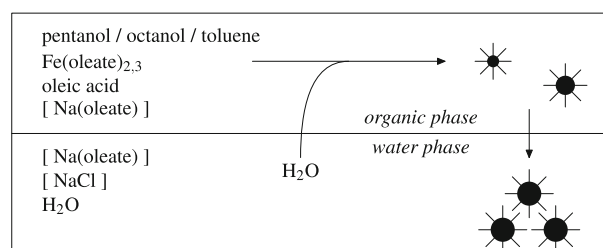


Fig. 1 Mechanism of the nanoparticle formation: iron oleates in organic phase, composed of pentanol or toluene, undergo hydrolysis at hydrothermal conditions and grown hydrophobic particles precipitate into water phase depending on polarity of the organic phase (more polar organic phase leads to smaller particles)

Table 1 Reaction mixtures for hydrothermal preparation of Fe₃O₄ nanoparticles contained 2 mmol of iron(III) oleate, 4 mmol of iron(II) oleate, 4 mmol of oleic acid, 10 ml of water and additional components (2nd column)

Sample	Additional components in reaction mixture	Diameter (nm)			Loss on ignition (%)
		TEM	XRD	DLS/PDI	
A	Pentanol (20 ml), Na(oleate) (2 mmol), NaCl (8 mmol)	5.9 ± 1.0	5.4	8.5/0.19	22.4
B	Pentanol (20 ml), Na(oleate) (2 mmol)	6.1 ± 0.9	5.3	71/0.44 (oleate)	52.3
C	Pentanol (20 ml)	6.3 ± 1.2	5.8	9.8/0.22	19.4
D	Pentanol (10 ml), octanol (10 ml) with 150 mg of C	7.9 ± 1.6	7.3	11.2/0.21	14.9
E	Pentanol (10 ml), toluene (10 ml) with 150 mg of D	10.4 ± 2.2	8.5	12.3/0.14	12.4

Next columns list particle size obtained by the transmission electron microscopy, an estimate from the strongest spinel phase X-ray diffraction (311), and Z-average size with polydispersity index from dynamic light scattering. Last column lists the mass of organic layer obtained by thermogravimetry. Sample B was hydrophilic, the rest was hydrophobic. DLS measurement of sample B was performed before modification with CM-dextran, while TEM, XRD, and TG after modification

organic phase (containing 5 ml of pentanol and iron oleates) was moved into 50-ml Teflon autoclave tube.

Seeds (samples D, E)

150 mg of dry particles was dispersed in 5 ml of octanol (with the help of 0.2 ml of hexane and heating) or in 5 ml of toluene and added to the autoclave tube.

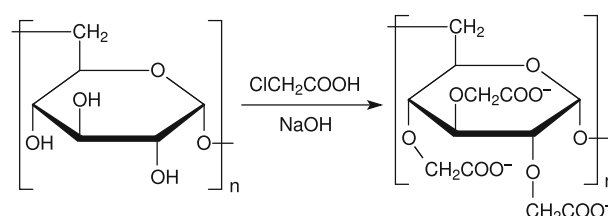
Water phase (samples A, B)

Solution of sodium oleate and NaCl was prepared by mixing NaOH (2 mmol, 80 mg), NaCl (8 mmol, 468 mg; only for sample A), water (5 ml), pentanol (5 ml), and oleic acid (2 mmol, 565 mg). The mixture was added to the autoclave tube.

Total volume of added pentanol/octanol/toluene was 20 ml and water 10 ml. The tube was sealed under flow of nitrogen, enclosed in a stainless steel autoclave (Berghof DAB-2), briefly shaken and put horizontally into oven, pre-heated to 180 °C, for 10 h.

Isolation of hydrophobic particles (samples A, C, D, E)

After cooling, the liquid phases were discarded while Fe₃O₄ was held by magnet. The particles were dispersed in hexane (10 ml), precipitated by ethanol (10 ml), separated by magnet, again dispersed in hexane (10 ml) and precipitated by ethanol (8, 7, 5.5, or 5 ml for A, C, D, E, respectively). The precipitate isolated by magnet was dried in hot air, weighted, and dispersed in hexane (4 ml). The obtained dispersion was centrifuged at 3,000 rpm for 5 min to remove

**Fig. 2** Preparation of carboxymethyl dextran from dextran and chloroacetic acid. The achieved degree of substitution is usually lower than what is shown (0.5–1 instead of 3)

larger particles (e.g., of goethite phase), and stored for further experiments. Bare particles were obtained by drying the hexane dispersion in hot air as a fine black powder, easily re-dispersible in hexane or toluene. The yield was around 400 mg (ca. 80 %) for A, C, D and 150 mg for E.

Preparation of CM-dextran solution

Preparation of CM-dextran (Fig. 2) was adapted from Huynh et al. (1998) and Liu et al. (2011). Water (2.5 ml), NaOH (10 mmol, 400 mg), chloroacetic acid (5 mmol, 473 mg), and dextran (6 mmol of OH groups, 324 mg) were mixed and sonicated until dissolution, and then stirred at 70 °C for 90 min.

We did not use commercial carboxymethyl dextran, because its degree of substitution tends to be very low or even not specified. Procedure used in this work should lead up to 1.0 COOH group per glucose unit (Huynh et al. 1998). By titration, our CM-dextran contained 0.5 COOH groups per glucose (solid CM-dextran as a sodium salt was isolated by precipitation with methanol).

Isolation and treatment of hydrophilic particles (sample B)

Hydrophilic particles (sample B) were isolated differently, avoiding the magnetic separation. The reaction mixture after the hydrothermal treatment was left for 30 min to separate into a black water phase and a slightly colored organic phase. The water phase was carefully moved to glass tubes and centrifuged at 3,000 rpm for 5 min to remove large aggregates and solid sodium oleate. Black supernatant with hydrophilic particles was mixed with CM-dextran solution (volume of the resulting turbid solution is around 15 ml) and mechanically stirred for 26 h. After the first 6 h, 80 mg of NaOH in 2 ml of water was added (this was necessary for the complete ligand exchange). The resulting brownish-black dispersion was centrifuged 5 min at 3,000 rpm to remove upper soap-like layer and then transferred to a dialysis membrane and dialyzed against 1 l of distilled water for 72 h. The water was changed after 24 h. A solution of 10 mg NaOH in 1 ml of water was added to the resulting water dispersion (dark brown, 40 ml) and it was centrifuged 10 min at 6,000 rpm to remove agglomerated particles.

Drying at room temperature resulted in 14 mg of solid phase per 1 ml of the dispersion. Thermogravimetry of this phase showed weight loss of 52.3 % after heating to 800 °C (see Fig. 5). Yield of the hydrophilic particles can be then estimated as $40 \times 14 \times 0.48 \approx 270$ mg of iron oxide (ca. 55 %).

Characterization

Transmission electron microscopy (TEM)

A drop of ca. 0.05 % dispersion of the particles in hexane (samples A, C, D, E) or water (B) was dried on carbon-coated copper grid. The particles were studied by JEOL 200CX at 200 kV (TEM) and high resolution TEM images were obtained with a JEM 2010 UHR equipped with a Gatan Imaging Filter (GIF) and a 794 slow scan CCD camera. The average particle size was obtained by visual measurement of 100 particles for each sample.

Powder X-ray diffraction (XRD)

The XRD was carried out on PANalytical X'Pert PRO using Cu K α radiation (1.5418 Å), secondary monochromator and PIXcel position-sensitive detector. The range was 10°–80° with step 0.039° and integration time of 5,000 s (or 3,000 s for sample E). The peaks were fitted by Gnuplot 4.6 by a sum of gaussian and lorentzian (with the same full width at half maximum, FWHM, in reciprocal space) and the size (diameter) was obtained by Scherrer equation,

$$d = \frac{0.94\lambda}{B \cos \theta}, \quad (1)$$

where d is the size of crystallites, and B is full width at half maximum. Peak widths were constrained in groups 311-511-422-222, 440-220-531, 400.

Thermogravimetry

Thermogravimetical analysis was performed on NIETZSCH STA 449F1 in air atmosphere with heating rate 10 K/min. Amount of the samples was 2.5–12 mg.

Fourier transform infrared spectroscopy (FT-IR)

Reflectance infrared spectra were recorded on a Thermo Nicolet Magna 6700 FTIR spectrometer. The spectra were processed using Omnic (version 8) software. The reflectance DRIFTS method was applied (128 scans, 4 cm⁻¹ resolution, 4,000–400 cm⁻¹ spectral range, Happ-Genzel apodization). The powdered sample A and CM-dextran were mixed with potassium bromide. Sample B was measured directly without KBr dilution (drying led to thin leaves which could not be ground to fine powder).

Magnetic measurements

Temperature dependences of zero-field-cooled (ZFC) and field-cooled (FC) magnetizations (at the field of 10 mT) and hysteresis loops (at 10 and 300 K, maximum field of 7 T) were measured on Quantum Design MPMS7XL (SQUID magnetometer). Samples were put into a gelatin capsule and fastened by a drop of instant glue to avoid rotation of particles when being magnetized.

Mössbauer spectroscopy

Mössbauer spectroscopy of ^{57}Fe was done on Wissel spectrometer using transmission arrangement and scintillating detector ND-220-M (NaI:Tl^+). An $\alpha\text{-Fe}$ foil was used as a standard and fitting procedure was done using NORMOS program. Measurements at low temperature (4 K) under magnetic field of 6 T were done in perpendicular arrangement.

Light scattering

Hydrodynamic diameter (size) and ζ potential were measured on Malvern Zetasizer NANO-ZS ZEN3600. The sample B was measured in ca. 0.05 % dilution in 0.01 M KNO_3 without filtering, and pH was adjusted by 0.01 M KOH and 0.01 M HNO_3 , respectively. Dynamic light scattering took place in a plastic cell with optical path of 1 cm and at focus position of 4.65 cm. Zeta potential was measured in a plastic zeta cell.

To measure hydrophobic particles in hexane, we prepared new samples with no drying during the synthesis and separation of the products, to avoid agglomeration. Dispersions were diluted to ca. 0.05 % with hexane and measured in glass cell with optical path of 1 cm at focus position of 4.65 cm.

Results and discussion

Choice of the reaction mixture

In order to obtain high yield of magnetite, we found the optimal ratio of $\text{Fe}^{2+}:\text{Fe}^{3+}$ in initial reaction mixture as 2:1. To introduce precise amount of Fe^{3+} , we had to use iron(III) nitrate instead of chloride or sulfate due to their non-stoichiometric composition. After the preparation of oleates, water phase was discarded to remove sodium nitrate as a potential oxidant.

TEM and XRD measurements

The phase composition and the particle size were obtained by both the transmission electron microscopy (Fig. 3) and by the powder X-ray diffraction (Fig. 4); the values are summarized in Table 1. Majority of the samples show dominant contribution of the spinel

(iron oxide) phase, only the sample B contains small amount of $\text{FeO}(\text{OH})$ (goethite). The samples prepared without seeds in octanol + pentanol would have the same size as in the case of the synthesis using pure pentanol (therefore, we used seed-growth). The correspondence of the particle size revealed by the TEM and XRD for the A–D samples points to great crystallinity of the particles. In the case of the sample E (seed-grown particles), the difference between the TEM and XRD size can be explained as follows. The size determined by the XRD corresponds to that of the coherently scattering domain (related to its volume). Therefore, the particle can be considered as a well-crystalline core and a disorder shell, which grows mainly in the second step of preparation. However, the TEM image represents the 2D projection of the physical size of the particles.

Thermogravimetry and infrared spectroscopy

Thermogravimetry was performed on all samples to estimate the amount of oleic acid or CM-dextran (for sample B) on the surface of the particles (see Fig. 5 and Table 1), and resulted in decreasing ratio of organic matter, in agreement with the increasing size of the particles. Sample B modified with CM-dextran showed more significant loss of weight, 52 %, due to the presence of excess CM-dextran.

Infrared spectroscopy was used to confirm surface modification of sample B (see Fig. 6). Its spectrum in the region $2,000\text{--}800\text{ cm}^{-1}$ is similar to pure CM-dextran (sodium salt), which was prepared as described in “[Preparation of CM-dextran solution](#)” section. Peaks were assigned according to Dean (1999), Liu et al. (2011). Although overall shape of the spectrum is influenced by the different measurement method (no KBr dilution), it confirms the absence of oleate (no sharp CH_2 stretching vibrations around $2,900\text{ cm}^{-1}$).

Magnetic measurements and Mössbauer spectroscopy

Magnetization measurements by SQUID magnetometry (see Table 2; Fig. 7) confirmed the superparamagnetic nature of the particles at room temperature, with the mean blocking temperature (estimated from the maximum on the ZFC curve in Fig. 7) increasing

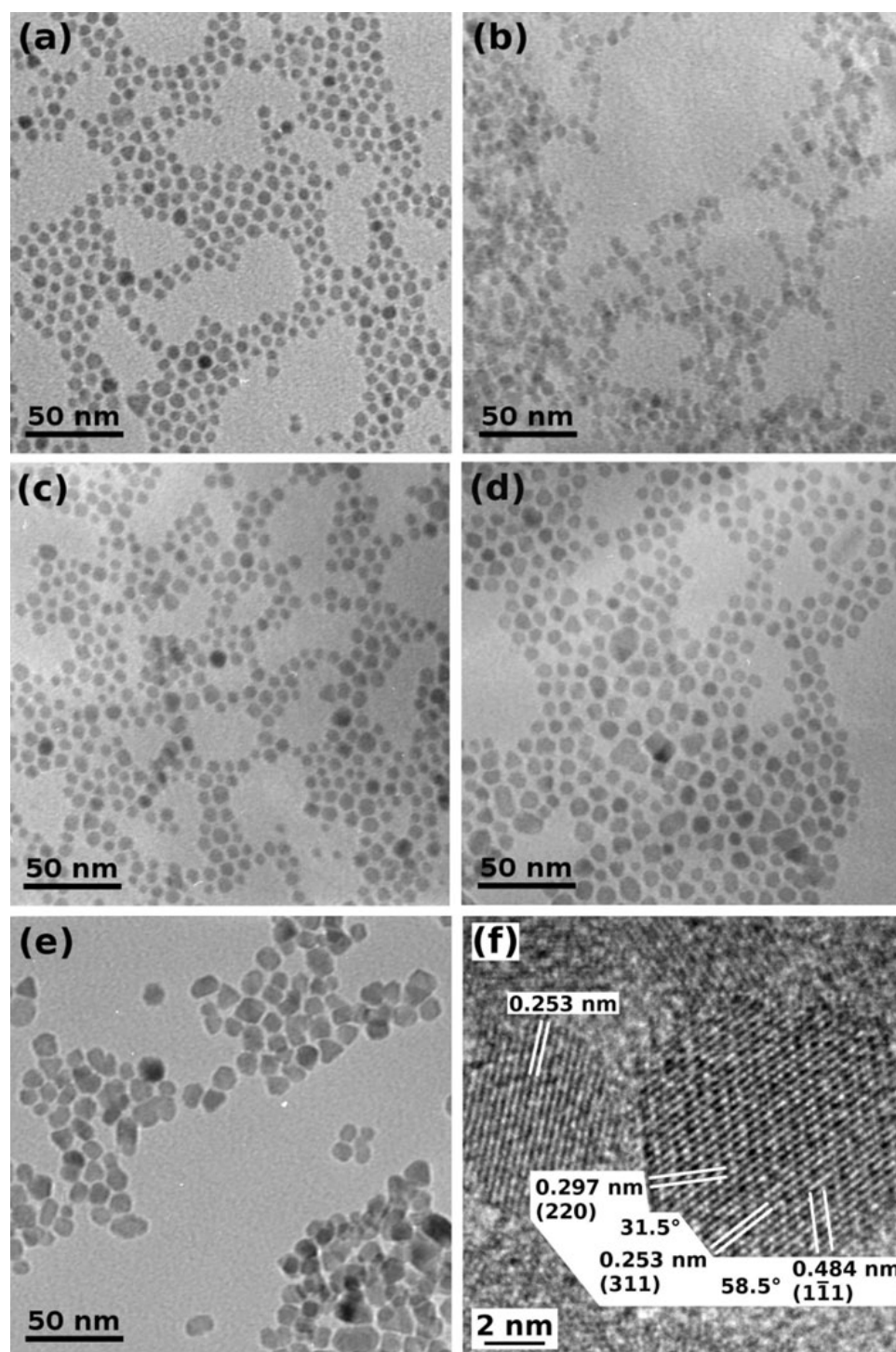


Fig. 3 TEM images of sample A (a), B coated with CM-dextran (b), C (c), D (d), E (e), and sample C observed by HRTEM (f). HRTEM image shows inter-plane distances and angles which agree well with expected values

with the particle diameter from 45 K for 6 nm up to 290 K for 10 nm. Even in the blocked state, the nanoparticles show magnetically soft behavior, with the coercitive field of ca. 10 mT at 10 K. However, they exhibit relatively high magnetization at 7 T,

reaching over 80 Am²/kg at 10 K, or over 70 Am²/kg at 300 K, respectively, which is in correspondence with high crystallinity of the particles. The specific magnetization was corrected for the mass of organic layer. The reason of the lower magnetization of the

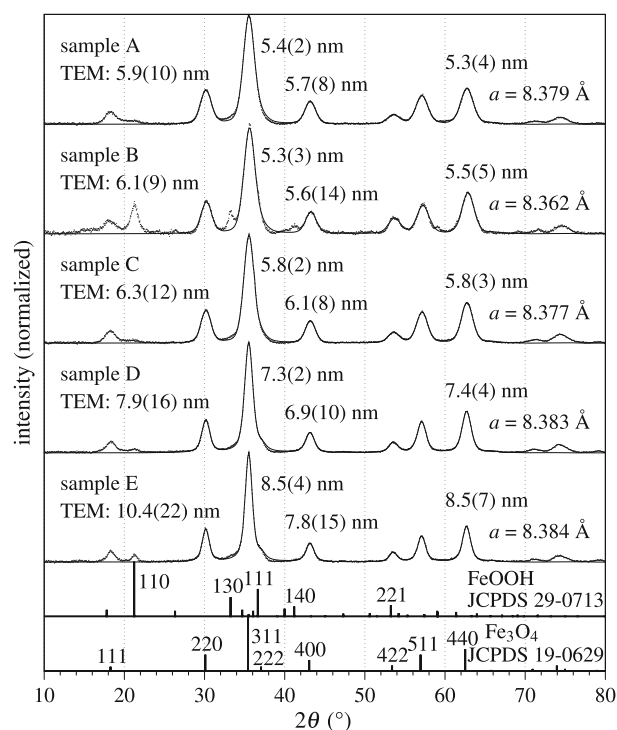


Fig. 4 X-ray diffraction of samples A–E. Size of the crystallites and their lattice parameter (a) were obtained from FWHM and positions of the peaks

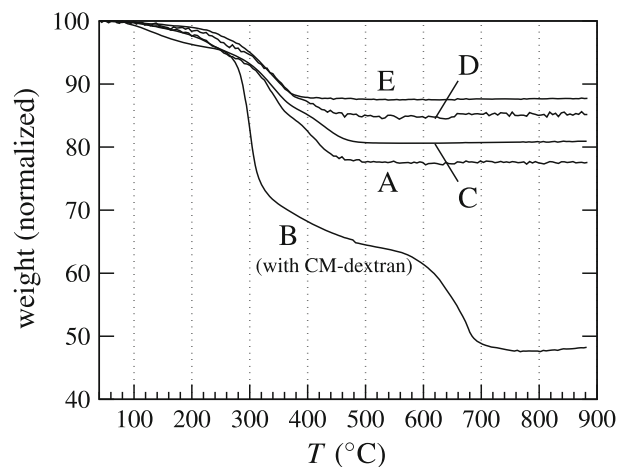


Fig. 5 Thermogravimetry of hydrophobic samples A, C–E and hydrophilic sample B. Hydrophobic samples are expected to contain oleic monolayer on their surface. Sample B contains considerable amount of carboxymethyl dextran

sample B (containing CM-dextran) could be the higher degree of oxidation to maghemite.

Mössbauer spectroscopy (see Table 3; Fig. 8) gives us the information about magnetic ordering at given temperature and also about occupancy of the

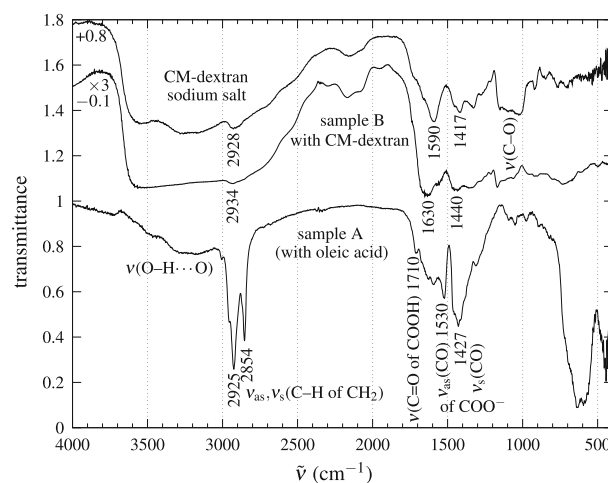


Fig. 6 FT-IR spectra of hydrophobic sample A, CM-dextran-modified sample B, and pure carboxymethyl dextran (sodium salt) measured in KBr using DRIFTS arrangement. The presence of CM-dextran is demonstrated mainly by asymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations of COO^- at 1,630–1,400 cm^{-1} , by the stretching vibrations of C–OH and C–OR at 1,150–1,000 cm^{-1} and by the absence of sharp stretching vibrations of CH_2 . Protonated carboxylate shows stretching vibrations of C=O at around 1,700 cm^{-1}

Table 2 Magnetic properties of the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ particles: blocking temperature from ZFC curve and parameters of hysteresis loops ($T = 10$ K) corrected for the mass of organic layer

Sample	T_B (K)	$\mu_0 H_{c,10\text{ K}}$	$M_{r,10\text{ K}}$	$M_{\max}$ (Am^2/kg)	
		(mT)		10 K	300 K
A	45	5	4	87	73
B	47	12	6	52	44
C	60	5	5	89	75
D	180	17	11	79	68
E	290	17	13	79	70

All samples exhibit $H_c = 0$, $M_r = 0$ at 300 K

tetrahedral and octahedral sites in the iron oxide spinel structure. The sample C measured at room temperature shows relatively broad doublet. It means that the sample is in superparamagnetic state at this temperature. Low temperature measurements carried out at 4 K exhibit sextets, which means that the sample is already in a magnetically blocked state. The subspectra for iron in tetrahedral sites and octahedral sites are overlapped. For this reason, the sample was measured also in external applied field of 6 T in order to split these two sextets. It was found that 35 % of the iron cations are located in tetrahedral positions and 58 % are located in octahedral positions. It fits

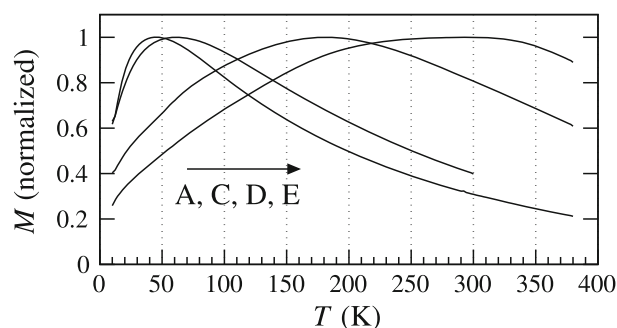


Fig. 7 Zero-field magnetization of the samples A, C–E showing gradual rise of blocking temperature

Table 3 Mössbauer parameters of the sample C at 4 K: isomer shift δ , quadrupole splitting ΔE_Q , hyperfine field B and canting angle θ

Fe	Tetrahedral	Octahedral	Paramagnetic
Area (%)	35	58	7
δ (mm/s)	0.37	0.49	0.33
ΔE_Q (mm/s)	0.01	0.01	0
$B_{\text{hf},0\text{T}}$ (T)	52.40	51.68	0
$B_{\text{hf},6\text{T}}$ (T)	57.50	46.87	6
θ (°)	33	35	

perfectly with the ratio found in $\gamma\text{-Fe}_2\text{O}_3$ where the theoretical value $\text{Fe}_{\text{oct}}:\text{Fe}_{\text{tet}}$ corresponds to 1.66. Mössbauer spectra measured at applied field permit us to calculate a canting angle of the moments both in tetrahedral and octahedral sites (Roca et al. 2009). The values were found to be 33° and 35° for tetrahedral and octahedral positions, respectively. Taking into account the resolution of Mössbauer spectra, we can consider them to be the same. This canting angle could be attributed to the surface spin disorder commonly found in magnetic oxide nanoparticle systems.

Hydrophilic particles

The hydrophilic particles obtained for the case B (before modification with CM-dextran) are quite stable in water, but precipitate quickly after addition of ethanol or solution of NaCl. The precipitated and dried particles are not hydrophilic anymore, but can be dispersed in hexane (i.e., they are hydrophobic and similar to the samples A, C, D, E). We can attribute this change of hydrophilicity to the presence of some

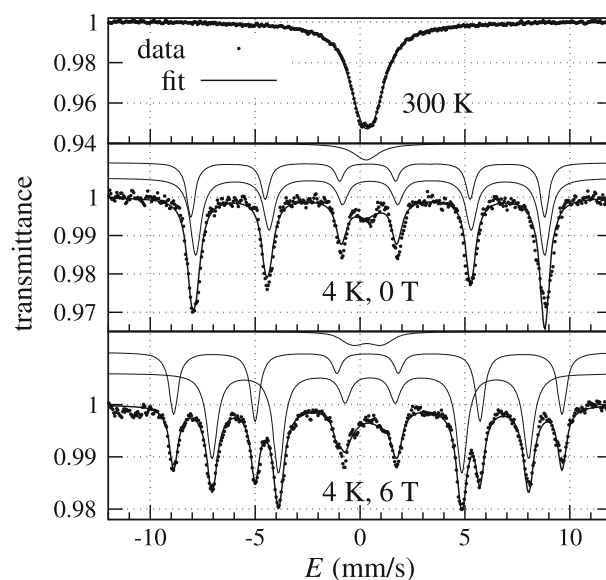


Fig. 8 Mössbauer spectroscopy of the sample C demonstrating magnetically blocked state at 4 K, and no ordering at room temperature

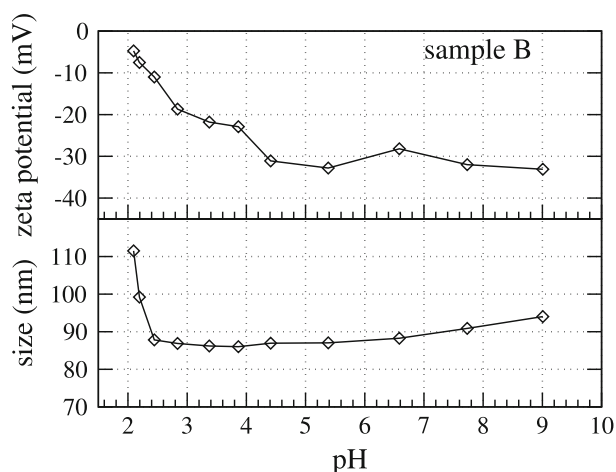


Fig. 9 Dynamic light scattering and zeta-potential measurements for sample B and at various pH

sodium oleate (with COO^- pointing outwards) on the surface of oleate-coated nanoparticles. This type of hydrophilic particles is not suitable for direct application, because the solution contains excess sodium oleate and its removal leads to precipitation of the particles. However, the particles modified by CM-dextran form a stable dispersion in water up to 0.3 M of NaCl or in the presence of ethanol.

Hydrophilic particles were further characterized by the dynamic light scattering. The zeta potential and hydrodynamic size was measured for the pH range:

2–9. As can be seen in Fig. 9, hydrodynamic diameter of the particles is under 100 nm for pH down to 2.5. At even lower pH they become unstable and gradually precipitate.

Relatively higher hydrodynamic diameter (90 nm) indicates that the hydrophilic particles are not perfectly dispersed. This behavior can be caused either by binding of the CM-dextran to more particles at once or by not-so-ideal conditions during surface modification—we observed temporary precipitation during the addition of CM-dextran solution (that contained some NaCl as a by-product). To circumvent the precipitation, we also tried to use the pure CM-dextran (prepared as described in “[Preparation of CM-dextran solution](#)”), but the procedure did not lead to substitution of the oleic acid shell—even after 3 days of stirring, the particles could be precipitated by ethanol and then dispersed in hexane.

Conclusion

In this work, we prepared 6–10 nm nanoparticles of magnetite/maghemite, both hydrophobic and hydrophilic, by the hydrothermal process in water/pentanol/oleic acid. The final particle size is controlled by additional organic solvent (octanol or toluene) and by the seed growth. The formation of the hydrophilic particles was achieved by the presence of sodium oleate in the reaction. The product can be reverted back to hydrophobic by increasing the ionic strength (with NaCl) during the reaction or by subsequent precipitation by ethanol. The hydrophilic particles were further stabilized by carboxymethyl dextran. The prepared particles are well dispersed and show very good magnetic properties, therefore the proposed synthesis is suitable as an environmentally friendly and much more simple alternative to the organic-decomposition methods.

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Magnetite nanoparticles with no surface spin canting

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Surface spin canting has been studied for high quality magnetite nanoparticles in terms of size and shape uniformity. Particles were prepared by thermal decomposition of organic precursors in organic media and in the presence of oleic acid. Results are compared to spin canting effect for magnetic iron oxide nanoparticles of similar size prepared by coprecipitation and subsequently coated with silica. Magnetic characterization and Mössbauer spectroscopy at low temperature and in the presence of a magnetic field have been used in this study. Transmission electron microscopy images and x-ray diffractograms show that iron oxide nanoparticles synthesized by thermal decomposition are more uniform than those prepared by coprecipitation, and they have higher crystal order. Magnetic measurements show superparamagnetic behavior for both samples at room temperature but particles synthesized by thermal decomposition shows higher saturation magnetization and lower coercivity at low temperature. The imaginary part of the ac susceptibility has been used to support the presence of mainly magnetite instead of maghemite in these iron oxide nanoparticles. Mössbauer measurements with and without field demonstrate surface spin canting, only in the octahedral positions for the coprecipitation particles. However, high synthesis temperature and the presence of oleic acid molecules covalently bonded at the particle surface, accounting for the lack of spin canting in particles prepared by thermal decomposition, which justifies the high saturation magnetization and low coercivity at low temperature. © 2009 American Institute of Physics.

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I. INTRODUCTION

For the past century, submicron magnetic iron oxide particles, in the magnetite or maghemite phase, have been the subject of numerous studies because of their interesting properties.¹ They have been used in several applications such as motor seals, magnetic ink for bank cheques, or magnetic recording devices.² Below 50 nm, nanoparticles could be used for biomedical applications such as hyperthermia, magnetic resonance imaging, and drug delivery.³ The main advantage of these materials is the possibility of being manipulated by an external magnetic field without aggregation after its removal because of its superparamagnetic character.

When magnetic nanoparticles sizes go down to the multidomain-monodomain limit, surface and finite size effects become more important and interesting physical properties appear⁴ such as the increase in anisotropy due to the surface contribution leading to high coercivities at low temperature.⁵ Unfortunately, spin canting at the surface has also been observed and it was demonstrated that it is responsible for saturation magnetization reduction limiting material applications.^{6,7}

In this work, structural and magnetic characterizations of iron oxide nanoparticles have been carried out by different techniques, including Mössbauer spectroscopy. Mössbauer is

a powerful tool for studying structural, physical, and magnetic properties and the best for iron oxide nanoparticles.^{8,9} This technique could estimate stoichiometry of iron oxide nanoparticles, order degree, structural site occupancy, and magnetic dipolar interactions. It is also possible to analyze the spin orientation at the nanoparticles surface when measuring in the presence of a magnetic field.⁸ The aim of this work is to analyze surface spin canting effect for high quality magnetite nanoparticles in terms of size and shape uniformity. Particles were prepared by thermal decomposition of organic precursors in organic media and in the presence of oleic acid.^{10,11} Results are compared to spin canting effect for magnetic iron oxide nanoparticles of similar size prepared by coprecipitation and subsequently coated with silica. It has been previously reported that structural, physical, and magnetic properties of nanoparticles greatly depend on the synthesis route and therefore it is predicted to affect surface spin canting.⁷ Silica and oleic acid coatings are chosen to keep particles apart, reducing magnetic dipolar interactions and surface effects.

II. EXPERIMENTAL SECTION

A. Synthesis of magnetite nanoparticles by coprecipitation and coating with silica (M and MSi)

Sample M was prepared by precipitating iron salts with sodium hydroxide.¹² The salt solutions used were at

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0.0352M (FeSO_4) and they were mixed with constant stirring. A mixture of ferric and ferrous salt solutions, 0.048M of $\text{Fe}(\text{NO}_3)_3$ and 0.0352M (FeSO_4), was added to 1M Na(OH) solution of ethanol and water (1:1 ratio). Average particle size prepared by this process was 5 nm (sample M).

A silica layer was deposited on 5 nm magnetite nanoparticles (sample MSi).¹³ First of all, 30 mg of magnetite nanoparticles were added to a stirred mixture of 12 mL distilled water, 60 mL of 2-propanol, and 1.5 mL of ammonia. The solution was maintained in an ultrasonic bath for 1 h. Then, 0.36 mL of tetraethoxysilane was added to the solution and left in the ultrasonic bath for 12 h. The solution was filtered, and the nanoparticles were washed with 2-propanol and dried at 20 °C for 1 day.

B. Synthesis of magnetite nanoparticles coated by oleic acid (MO)

Sample MO was synthesized by thermal decomposition method.¹¹ A mixture of 5.32 g $\text{Fe}(\text{acac})_3$ (15 mmol), 16.93 g 1,2-dodecanediol (75 mmol), 14.19 g oleic acid (45 mmol), and 17.27 g oleylamine (45 mmol) were added to 150 mL of benzyl ether. The temperature of the resulting mixture was increased by 3 °C/min⁻¹ up to 200 °C with mechanical stirring and nitrogen flow. The reaction was maintained at this temperature for 2 h, and then, the solution was heated up to reflux (298 °C) for 30 min under nitrogen atmosphere. Once the reaction stopped, it was cooled down to room temperature and impurities (unbounded surfactants) were removed by washing with ethanol. The powder was obtained by precipitation with ethanol, centrifugation, and finally dried under nitrogen flow.

C. Characterization

Particle size, shape, and polydispersity degree (standard deviation/mean size) were analyzed by transmission electron microscopy (TEM) using a 200 keV JEOL-2000 FXII microscope. TEM samples were prepared by placing one drop of a dilute suspension of magnetite nanoparticles on a carbon coated copper grid and allowing the solvent to evaporate at room temperature. Average particle size (D_{TEM}) and distribution were evaluated by measuring the largest internal dimension of at least 300 particles. Size data were fitted with a log-normal distribution function and the logarithmic standard deviation was calculated.

The iron oxide phase was identified by powder x-ray diffraction. The x-ray patterns were collected between 10°–80° (2 θ) using a PHILLIPS 1710 diffractometer with Cu $K\alpha$ radiation. Lattice parameters and crystal size (D_{XRD}) were calculated from the position and the broadening of the (311) reflection of the spinel structure following standard procedures.¹⁴ Thermogravimetric (TG) analysis was carried out in a SEIKO TG/ATD 320 U, SSC 5200 (Seiko Instruments) to evaluate the organic coating percentage. Samples were heated at 10 °C/min in air atmosphere from room temperature to 700 °C. Silica percentage was evaluated by elemental analysis [inductively coupled plasma (ICP)] after digestion with HF.

Mössbauer spectra were recorded in the transmission mode with ⁵⁷Co diffused into a Rh matrix as the source moving with constant acceleration. The spectrometer was calibrated by means of a standard α -Fe foil and the isomer shift (IS) was expressed with respect to this standard at 293 K. The samples were measured at room temperature and in cryostat at the temperature of 4.2 K without field and under the external field of 5 T perpendicular to the γ -ray. The fitting of the spectra was performed with the help of the NORMOS program using Lorentzian profiles.

Magnetic characterization of the samples was carried out in a 7 T superconducting quantum interference device magnetometer (SQUID, MPMS7XL, Quantum Design). Magnetization curves were recorded by first saturating the sample in a field of 7 T; then, the saturation magnetization (M_s), remanence (M_r), and the coercive field (H_c) were determined for each sample. M_s values were evaluated by extrapolating to infinite field the experimental results obtained in the high field range where magnetization linearly increases with 1/H. For the zero field-cooled (ZFC) and field-cooled (FC) measurements the sample was cooled down to 2 K in zero field, and the magnetization was recorded as the sample was heated to 350 K in a field of 5 mT (ZFC). Then, the sample was cooled to 2 K under a field of 5 mT, and the magnetization was recorded as the sample was heated to 350 K in the same field. The ac susceptibility was recorded in zero magnetic field in the temperature range 2–350 K using the amplitude of the ac field of 0.3 mT and varying frequency from 0.1 Hz to 1 kHz.

III. RESULTS AND DISCUSSION

A. Morphological and Structural characterizations

TEM images of the iron oxide nanoparticles are shown in Fig. 1 and the morphological characteristics are collected in Table I. Nanoparticles prepared by decomposition are very uniform in size and shape, and they are arranged on the TEM grid forming arrays due to the presence of oleic acid molecules coating the nanoparticle [Fig. 1(b)]. Self-assembling process is the result of the equilibrium between the attracting magnetic dipolar forces between nanoparticles and the repulsive steric barrier of the surfactant hydrophobic chains.¹⁵ The mean size for sample MO was 6.4 nm and the polydispersity degree was 0.12, well below the monodispersed limit (0.2). Nanoparticles prepared by coprecipitation, sample M, had a mean particle size of 5.0 nm with a standard deviation of 0.2 [Figs. 1(a) and 1(d)]. This is the best that can be obtained by coprecipitation without any size selection process.¹⁶ Silica coated nanoparticles are shown in Fig. 1(c) (sample MSi), where a thick silica layer is observed around particle aggregates. The particle size histograms fitted to a log-normal distribution are shown in Fig. 1(d).

The x-ray diffraction peak positions and intensities correspond to an inverse spinel structure similar to magnetite-maghemite¹⁷ (Fig. 2). Lattice parameters calculated for the (311) reflection are 8.38 Å for sample MO and 8.36 Å for sample M, suggesting certain degree of oxidation for sample M (magnetite lattice parameter 8.39 Å and maghemite lattice parameter 8.33 Å). Additionally, crystal

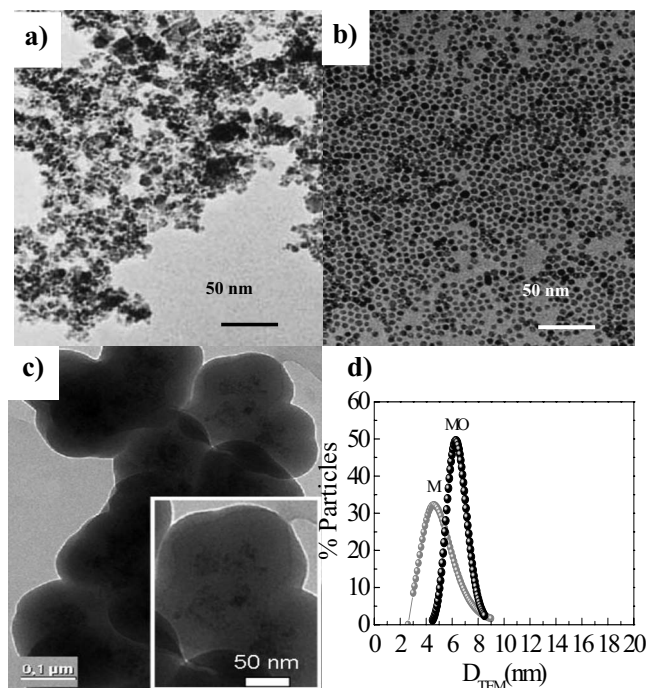


FIG. 1. TEM images of (a) Magnetite nanoparticles prepared by coprecipitation (M); (b) Magnetite nanoparticles coated by oleic acid prepared by thermal decomposition (MO); (c) Sample M coated by silica (MSi); and (d) Particle size histograms fitted to a log-normal distribution for samples M and MO.

size calculated from Scherrer equation was 7.4 nm for sample MO and 5.6 nm for sample M. These measurements are in good agreement with TEM data indicating that each particle is a single crystal. TG analysis reveals that 1 g of sample consists of 0.84 g of iron oxide and 0.16 g of surfactant for sample MO. The percentage of silica on sample MSi is 80% as calculated by elemental analysis (ICP).

B. Magnetic properties

Representative ZFC and FC measurements are shown in Fig. 3. They clearly demonstrate different superspin arrangements in both types of materials, mainly affected by particle size distribution in the samples. Samples M and MSi show almost identical behavior, illustrated by a broad maximum on ZFC at around 100–120 K together with a furcating point on the ZFC and FC curves in the region of 250–270 K. Moreover, FC curves show an inflection point at $T_{\text{infl}} \sim 150$ K. However, ZFC and FC curves of sample MO show a maxi-

TABLE I. Morphological characteristics of the magnetite nanoparticles: M=Magnetite nanoparticles prepared by coprecipitation; MSi=Aggregated M particles coated with silica; and MO=individual oleic coated particles prepared by thermal decomposition in organic media.

Sample	Morphological characteristics			
	D_{TEM} (nm)	Polydispersity	Coating	Thickness (nm)
M	5.0	0.20	...	...
MSi	5.0	0.20	Silica	40
MO	6.4	0.12	Oleic acid	2

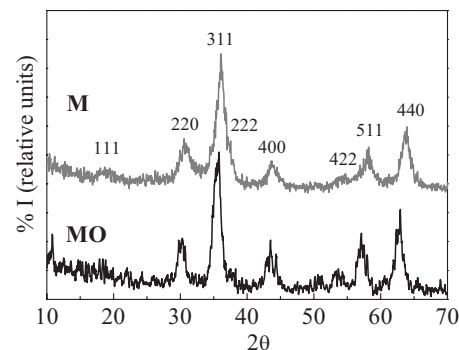


FIG. 2. X-ray diffraction patterns for magnetite nanoparticles prepared by coprecipitation (sample M) and by thermal decomposition (sample MO).

um at higher temperature, 198 K and a furcating point coincident with the maximum temperature of the ZFC curve (Table II).

The behavior of samples M and MSi is characteristic for a superparamagnet (SPM) with considerable dipolar interactions, probably leading to a collective phenomena known as super-spin-glass (SSG) order.¹⁸ The identical behavior of samples M and MSi, suggests a minor influence of the silica coating in suppressing undesirable dipolar interactions between the magnetic nanoparticles. Thus, for the silica-coated sample (MSi) we are looking at aggregates of several particles. In the case of sample MO, saturation of FC curve at low temperatures also suggests considerable dipolar interactions between iron oxide particles despite of the oleic acid coating.¹⁹ Therefore, the main difference between samples MO and MSi is the size distribution. Particles obtained by coprecipitation exhibit considerably broader size distribution in comparison to particles prepared by decomposition. As a

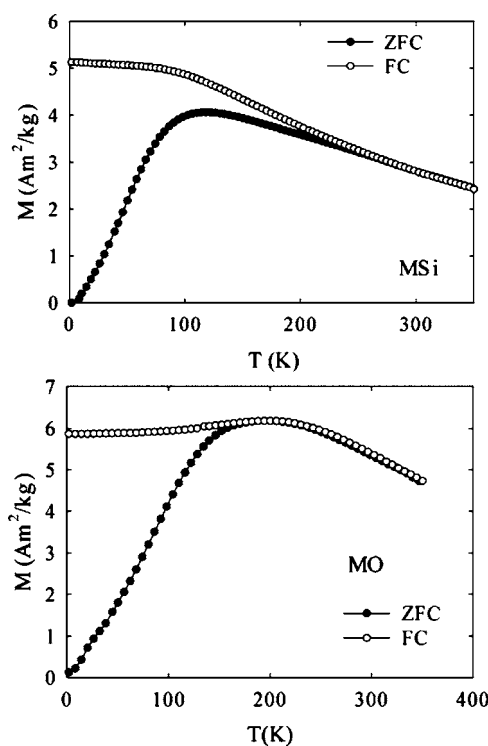


FIG. 3. The temperature dependence of the ZFC and FC magnetization recorded at 5 mT for samples MSi and MO.

TABLE II. Magnetic and Mössbauer parameters of the magnetite nanoparticles. [Saturation (M_s) and remanence magnetization (M_r), coercive field (H_c), ZFC maximum temperature ($T_{\max}^{\text{ZFC/FC}}$), FC inflection point ($T_{\text{infl}}^{\text{ZFC/FC}}$), ac susceptibility maximum temperature ($T_B^{\chi'}$, recorded at $f=100$ Hz), angle between Fe magnetic moments in tetrahedral ($\alpha \text{ Fe}_T$) or octahedral ($\alpha \text{ Fe}_O$) positions with the external magnetic field.]

Samples	Magnetic parameters						Mössbauer data 4 K, 5 T	
	$T_{\max}^{\text{ZFC/FC}}$ (K)	$T_{\text{infl}}^{\text{ZFC/FC}}$ (K)	$T_B^{\chi'}$ (K)	$M_s^2 \text{ K}$ (A m ² kg)	$M_s^{300 \text{ K}}$ (A m ² kg)	$H_c^2 \text{ K}$ (T)	$\alpha \text{ Fe}_T$ (°)	$\alpha \text{ Fe}_O$ (°)
M	118	250	130	55	46	0.05	0	140
MSi	106	270	137	53	44	0.05	0	143
MO	198	198	240	96	84	0.04	0	169

result, the ZFC of samples M and MSi exhibits an extended tail from the maximum toward higher temperatures.

Hysteresis loops were recorded at room temperature and 2 K, as shown in Fig. 4 and the obtained magnetic characteristics for all samples are summarized in Table II. Sample MO shows larger values of saturation magnetization M_s and remanence M_r , as a consequence of the higher synthesis temperature (of ~ 300 °C), which leads to particles with higher crystal order. However, the coercivity trend at low temperature is not straightforward to understand. Considering Stoner–Wohlfarth criterion for switching of single-domain particles with similar effective anisotropy K_{eff} , the expected coercivity for samples M and MSi would be double of that for sample MO rather than only 20% larger ($H_c=0.05$ T) than for sample MO ($H_c=0.04$ T) (Fig. 5, Table II). A simple interpretation of this difference in the view of the Stoner–Wohlfarth model would be a noticeably larger K_{eff} for sample MO. However, the calculation of the effective anisotropy constant from the irreversibility field¹⁹ H_{irr} , (above which is the magnetization cycle reversible), as $K_{\text{eff}}=1/2M_sH_{\text{irr}}$, yields K_{eff} values of 8.3, 8, and 7.2 $\times 10^5$ erg/cm³ for samples M, MSi, and MO, respectively (H_{irr} values=0.3, 0.3, and 0.6 T). It has been recently

shown, in agreement with these results, that magnetite nanoparticles prepared by thermal decomposition in organic media have lower anisotropy constant than magnetite nanoparticles prepared by coprecipitation.²⁰ Factors accounting for larger coercivity values for magnetite nanoparticles are: stress anisotropy at the particle-matrix interface,²¹ shape anisotropy coming from irregular morphology, interactions, and surface anisotropy. These factors usually increase the irreversibility field and they are probably responsible for the enhanced H_c values at low temperatures for samples M and MSi. On the other hand, the oleic acid molecules, coating the nanoparticles surface in sample MO, keep the particles isolated from each other reducing interactions, spin canting, and surface anisotropy, leading to lower H_c values.

Real (χ') and imaginary (χ'') parts of the ac susceptibility of samples M and MSi, show a single broad maximum, which position and amplitude are sensitive to the applied ac magnetic field frequency. Both samples are almost identical and results for sample M are shown in Fig. 6(a). The peak amplitude of χ' increases, and the position shifts to lower temperatures with decreasing frequency. The shift in the χ' -maxima can be attributed to the SPM or SSG phenomena.¹⁸ Considering the limited range of the applied frequencies, we cannot provide clear evidence of the presence of SSG phenomena. The broad particle size distribution often originates a mixture of single-superspin relaxation and collective dissipation phenomena, so the obtained values would be booting for further interpretation.^{22,23}

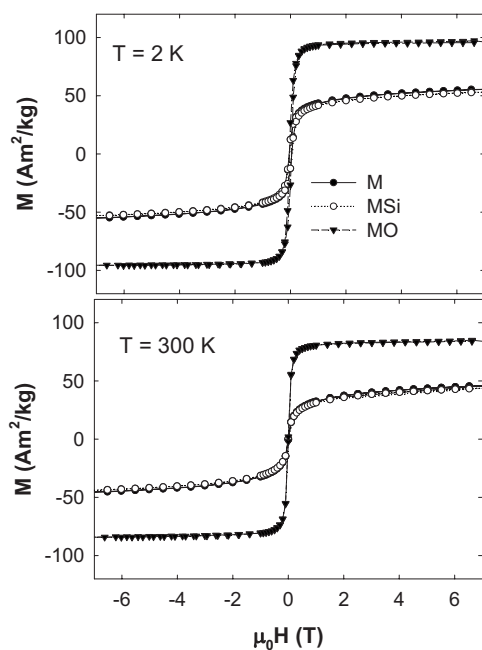


FIG. 4. Comparison of the hysteresis loops recorded at 2 and 300 K for samples M, MSi, and MO.

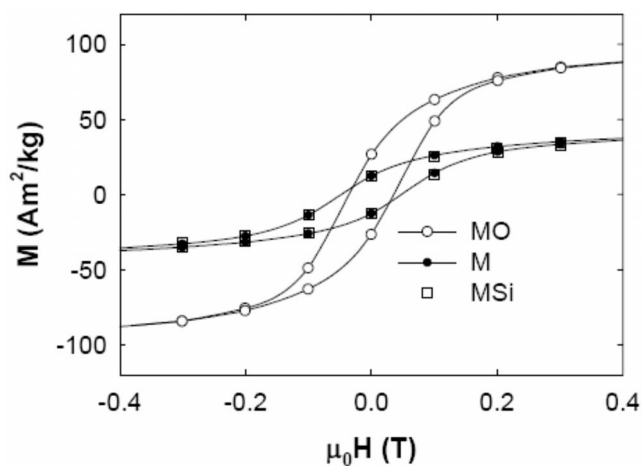


FIG. 5. Detail of the hysteresis loops measured at 2 K for M, MSi, and MO samples.

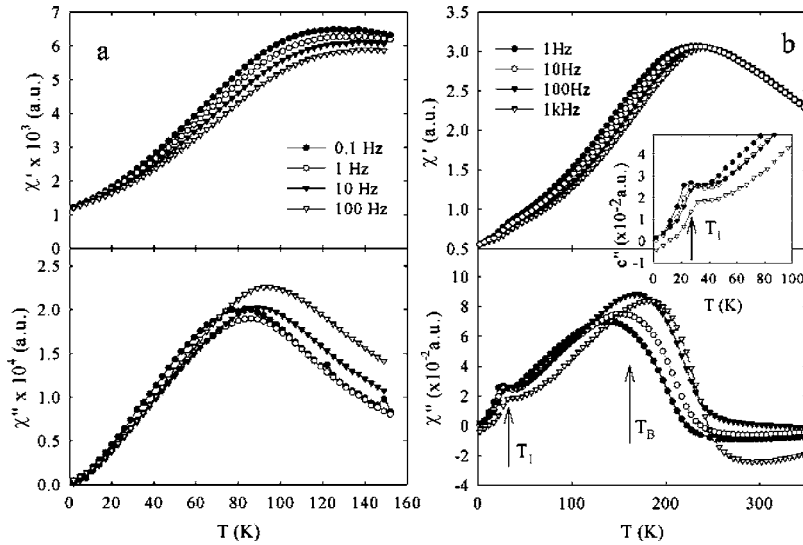


FIG. 6. Temperature variation in the real and imaginary parts of the ac susceptibility for samples M (a) and MO (b). The inset in panel (b) demonstrates the detail of the contribution of the incoherent tunneling in defected magnetite at T_1 (T_1 =incoherent tunneling temperature and T_B =maximum susceptibility temperature).

Real (χ') and imaginary (χ'') parts of the ac susceptibility of sample MO is presented in Fig. 6(b). Beside the broad maximum expected near the T_B , an additional pronounced anomaly was observed mainly on the χ'' versus T curve at $T_1 \sim 25$ K, depending just slightly on the applied frequency. The T_1 -related feature can be attributed to the unusual phenomena observed by magnetic after-effect (MAE) spectroscopy in disordered magnetite for the B -site vacancy concentration ($\text{Fe}_{3-\delta}\text{O}_4$): $\delta < 0.01$ associated with incoherent electron tunneling.^{23,24} The dissipation of magnetic energy related to the complex electron processes can be observed as an anomaly on the imaginary part of the ac susceptibility, and may serve as a strong argument for having magnetite instead of maghemite in sample MO and in general in iron oxide nanoparticles.

C. Spin canting effect

Mössbauer spectroscopy can give useful information on the oxidation state of iron but the situation is not so clear in the case of magnetite. Stoichiometric magnetite is an inverse spinel having both Fe^{2+} and Fe^{3+} in octahedral positions. Above Verwey transition, there is very quick electron exchange between Fe^{2+} and Fe^{3+} , which leads to ISs of approximately 0.65 mm/s for Fe in the octahedral positions, just between IS values for Fe^{3+} (0.1–0.4 mm/s) and Fe^{2+}

(0.8–1.5 mm/s).²⁵ During oxidation of magnetite, the IS shifts toward lower values down to 0.3 mm/s for fully oxidized maghemite ($\gamma\text{-Fe}_2\text{O}_3$). It is worth to note that magnetite nanoparticles prepared in this work are in the superparamagnetic state at room temperature and the Mössbauer spectra of all three samples were represented only by doublets with ISs δ (millimeter per second) of 0.32 for sample M, 0.33 for sample MSi, and 0.4 for sample MO. From the IS values, it can be concluded that the degree of oxidation of Fe^{2+} in magnetite nanoparticles is relatively high. At the same time, it is shown that silica layer forms a slight barrier to the oxidation while the protection by oleic acid is much more effective.

Spin canting effect was analyzed from the Mössbauer spectra at low temperature without and with an external magnetic field (Figs. 7 and 8). These measurements give information about magnetic properties of the magnetic sublattices in magnetite. From the hyperfine and effective field values, measured at zero field and at 5 T, respectively, the angle (α) between the external field and the hyperfine field can be calculated using the cosine equation²⁶

$$B_{\text{eff}}^2 = B_{\text{hf}}^2 + B_{\text{app}}^2 - 2B_{\text{hf}}B_{\text{app}}\cos(180^\circ - \alpha). \quad (1)$$

Mössbauer spectrum of magnetite below Verwey transition is very complex. From our 4.2 K in field measurements, both tetrahedral and octahedral subspectra are well separated and each of them can be well fitted by one sextet with Lorentzian shape (supporting information). Each sextet represents Fe in tetrahedral and octahedral positions. From in-

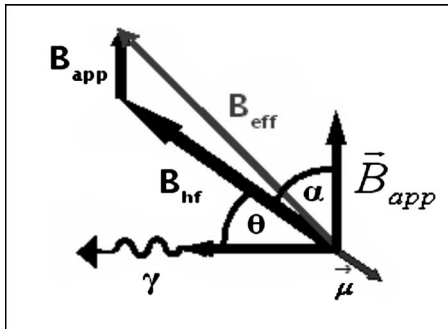


FIG. 7. Schematic representation of the magnetic moment, hyperfine, and effective field directions respect to the γ radiation in the Mössbauer experiment.

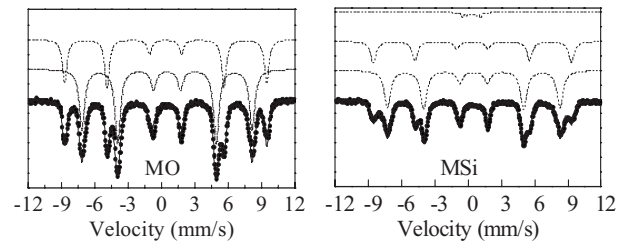


FIG. 8. In-field Mössbauer spectra of samples MO (left) and MSi (right) at 4 K.

field measurements, the values of ISs, quadrupole splitting, and width at half heights (full width at half maximum) of the sextets were taken for the fitting of the corresponding zero-field Mössbauer spectra (these parameters are unchanged when a magnetic field is applied) in order to minimize the number of free parameters. When comparing the spectra for samples M and MSi, the second one shows an additional doublet originated from iron that is not magnetically ordered (about 4% of total iron), which could be due to iron “dissolved” in the silica shell or iron at the interface silica-magnetite nanoparticle that is “magnetically disordered” due to influence of Fe–O–Si bonds (Fig. 8).

Canting angle of the Fe magnetic moments in tetrahedral positions and Fe in octahedral positions with respect to the external magnetic field for the three samples are presented in Table II. For all samples, magnetic moments of Fe in tetrahedral positions are antiparallel (180°) to the external magnetic field while magnetic moments of Fe in octahedral positions are forming a smaller angle (α) with respect to external magnetic fields of 140° and 143° , which means that the magnetic moments are canted by 40° for the case of sample M and 37° for sample MSi (Table II).

In the case of sample MO, Fe magnetic moments in tetrahedral positions are antiparallel (180°) to the external magnetic field while Fe magnetic moments in octahedral positions are located at 169° with respect to external magnetic field, which means that they are canted only by 11° and therefore nearly parallel, taking into account the possible error of the fitting procedure. It must be noted, that due to the strong overlap of the components, angle values had to be taken as a rough values (standard deviation of about 10°).

From the above-mentioned results it could be concluded that octahedral positions are more susceptible to be canted than tetrahedral ones, and both crystallinity and surface coating influence the canting angles of magnetic moments of Fe atoms in its magnetic sublattice. The protection by oleic acid leads to magnetite nanoparticles (MO) with practically no magnetic moment canting. It is clear that the surface spin disorder arises from reduced coordination of surface cations and broken exchange bonds between surface spins, giving rise to magnetic frustration. However, the effect of the coupling agent, i.e., the inorganic-organic interactions, is still unclear. Thus, it has been recently published that phosphonated nanoparticles of 40 nm diameter behave as a collinear ferrimagnet,⁷ whereas a canted ferrimagnetic structure occurs in the case of these magnetite nanoparticles grafted with carboxylated molecules, in opposition to our results for sample MO. The angle values were found to be about $25(8)^\circ$ for both tetrahedral and octahedral Fe magnetic moments. It should be noted that a different method for the evaluation of canting angle was used in that paper (the ratio of surface area of 2/5 and 1/6 lines of sextets in parallel arrangement of in field Mössbauer measurement), and it was concluded that the particles have a well defined “dead surface layer” (thickness of 2.8 nm reported by Daou *et al.*⁷). In our particles, the lack of canting in the 6 nm particles coated with oleic acid suggests the absence of dead layer but a solid solution of Fe_3O_4 - γ - Fe_2O_3 could be present, as reported by Schmidbauer and Keller²⁷ for much larger particles.

IV. CONCLUSIONS

It can be concluded that both crystallinity and surface coating influence the canting angles of magnetic moments of Fe atoms in its magnetic sublattice, being the octahedral positions more susceptible to be canted than tetrahedral ones. The high crystallinity and the oleic acid protection of particles prepared by high temperature decomposition lead to magnetite nanoparticles with practically no canting of magnetic moments. This justifies the high saturation magnetization values, close to the bulk value, measured for these particles in spite of the high surface/volume ratio.

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INFLUENCE OF AGGREGATE COATING ON RELAXATIONS IN THE SYSTEMS OF IRON OXIDE NANOPARTICLES

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We have investigated properties of systems of strongly interacting magnetic nanoparticles in order to estimate the influence of the inter-aggregate interactions on the collective phenomena. We have compared two systems composed of γ -Fe₂O₃ nanoparticles, prepared by thermal

decomposition of an organic precursor and coprecipitation, respectively; with those prepared by coprecipitation, containing the particle aggregates coated by SiO_2 layer of different thickness. Detailed magnetic studies of all samples such as the temperature dependence of magnetization and frequency-dependent a.c. susceptibility, recorded also in external magnetic field, revealed the blocking temperature close to 300 K and super-spin glass (SSG) or SSG-like nature of the systems. The slight minimization of the interaction strength in the system with increasing thickness of the SiO_2 coating has been observed.

Keywords: Magnetic nanoparticles; aggregates; inter-particle interactions; coating; relaxation time.

1. Introduction

Technologies using superparamagnetic (SPM) iron oxide nanoparticles (NPs) as magnetic carriers are promising in a lot of aspects improving our life, because of their ability to be magnetically resuspended, aggregated and collected, as desired.¹ The targeted surface modification allows them to be used for many different purposes in medicine²: MRI contrast agents,³ drug carriers,⁴ smart biosensors,⁵ hyperthermia,⁶ industry,^{7,8} and data storage technologies as recording media.⁹ The principal physical properties of the carriers are usually very precisely studied, but the crucial question is if and how the desired surface modification affects the final magnetic attributes of the material. The correlation between reduction of the inter-particle distances, strength of the inter-particle interactions (of either exchange or dipolar origin) and formation of a super-spin-glass-like (SSG-like) and super-spin-glass (SSG) states have been described in detail theoretically.^{10–16} Also the works experimentally studying the inter-particle interactions in the systems of NPs covered with a nonmagnetic, SiO_2 layer of different thickness has appeared recently.¹⁷ The evolution of the systems from weakly up to the strongly interacting ones with decreasing thickness of the insulating nonmagnetic layer has been observed, as was consistent with the theoretical predictions. The critical inter-particle dipolar energy, E_{dip} , fundamental for the observation of the SSG phenomena, has been elicited as 10^{-22} J. Decreasing the E_{dip} down to 10^{-24} J, the SPM behavior has been observed. Considering creation of aggregates in the strongly interacting SSG or SSG-like systems, the question is whether the collective phenomenon is mainly a consequence of the interaction between individual particles, or whether any interaction between the aggregates plays the role.

Thus this article mainly treats the effect of the inter-aggregate interaction on the collective phenomena, which seems to be important mainly because of the increasing importance and investigation of the composite materials. The studies of such kind, focused on the effect of inter-aggregate forces on evolution of the SSG phenomena has not been performed yet, thus we have focused on the experimental point of view with the attempt to suppress collective behavior via the isolation of the aggregates (with subsequent minimization of the inter-aggregate interaction).

Considering systems of densely packed collections of thousands of NPs, where the aggregates are considered as the groups of NPs in a defined volume with a preferential orientation of magnetization with respect to their environment, the limiting factors of suppression of the collective effects are the size of aggregates and the thickness of coating that separates them.^{17,18} Because of that, we have focused on experimental study of interactions in ensembles of pure and modified $\gamma\text{-Fe}_2\text{O}_3$ NPs, supported by basic calculations of the inter-particle and inter-aggregate dipolar energies, based on qualitative inspection of data. The effect of suppression of the interactions via covering the aggregates by SiO_2 layer of various thicknesses has been examined by advanced a.c. susceptibility measurements and supported by analysis of the Mössbauer spectra. The magnetic behavior of the $\gamma\text{-Fe}_2\text{O}_3$ NPs, prepared by coprecipitation and subsequently coated by SiO_2 to dispel two extra samples with different thickness of the aggregate- SiO_2 cover have been compared to those of the reference sample — particles of the same size prepared by decomposition of organic precursor, covered with the oleic acid. The evolution of the collective phenomena caused by the suppression of the inter-aggregate interactions should therefore be observable at (i)

the low temperature part of the field-cooled (FC) temperature dependence of the magnetization, (ii) difference between the relaxation time of the systems, τ_0 and (iii) evolution of the line-widths of the Mössbauer spectra within the series of the samples.

2. Experimental Section

2.1. Sample preparation

2.1.1. Oleic acid coated γ - Fe_2O_3 nanoparticles

The sample labeled as MD (maghemite decomposition) was prepared by a thermal decomposition of an organic precursor in the presence of oleic acid. Detail description of the preparation method is in paper by Roca *et al.*¹⁹ The resulting nanocrystals exhibit high degree of crystallinity and they are naturally covered by the oleic acid.

2.1.2. γ - Fe_2O_3 nanoparticles with SiO_2 cover

The γ - Fe_2O_3 nanoparticles were prepared by coprecipitation method often used for preparation of magnetite.¹⁹ The sample containing uncoated maghemite nanoparticles is labeled as MC (consistent with 2.1.1.: Maghemite Coprecipitation). Two fractions of the original sample were subsequently coated by SiO_2 layer (MCS1 and MCS2) of different thickness.

2.2. Characterization

The composition, structure and estimation of size of NPs in samples were characterized using the powder X-ray diffraction (PXRD), the particle size and morphology were inspected by the transmission electron microscopy (TEM). The PXRD patterns were taken with Bruker diffractometer working with the parafocusing Bragg-Brentano geometry, recorded using $\text{Cu K}\alpha$ radiation at room temperature. Particle size was analyzed using advanced profile analysis implemented in the FullProf program which is based on fit of convolution of the instrumental function and the intrinsic sample profile to the experimental data.²⁰ The TEM was used for direct observation of the nanocomposites, average particle size of at least 100 NPs in each sample was estimated using IMAQ Vision Builder software.

The Mössbauer spectra measurement was done in the transmission mode with ^{57}Co diffused into a Rh matrix as the source moving with constant acceleration. The spectrometer was calibrated by means of a standard α -Fe foil and the isomer shift was expressed with respect to this standard at 293 K. The samples with the average mass of approximately 50 mg were measured in cryostat at the temperatures varying from 293 K to 4.2 K. The fitting of the spectra was performed with the NORMOS program.

The temperature dependencies of the magnetization, a.c. susceptibility (both in zero and nonzero external magnetic field) and hysteresis loops were measured using the MPMS7 — SQUID device (Quantum Design) up to magnetic field of 7 T in the temperature range from 2 to 350 K. The zero-field-cooled, ZFC and field-cooled, FC curves were recorded in external magnetic field of 10 mT, 5 mT and 2 mT, respectively. The temperature dependence of the a.c. susceptibility (with the alternating field amplitude of 3 mT) was measured both in zero (with frequencies ranging from 0.1 Hz up to 1 kHz) and nonzero (0.4–50 mT, with frequencies belonging to the 0.1–100 Hz interval) external magnetic fields. The amount of measured samples was at least 35 mg.

3. Results and Discussion

3.1. Structure and morphology determination

The TEM images of the MD and MC series samples are shown in Fig. 1. It is obvious that the MD-nanocrystals have well defined size and shape whether the NPs in MC series show considerable size and shape distribution, with the strong sign of aggregation. The diffraction patterns correspond to those of the inverse-spinel (γ - Fe_2O_3) structure (Fig. 2, Table 1). The mean particle diameters, d_{XRD} obtained from this procedure are comparable with those evaluated from the TEM data, d_{TEM} suggesting that the NPs are single-crystalline^a (Table 1).

3.2. Static magnetic properties

The temperature dependencies of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization (M) for all samples recorded at 10 mT exhibit the

^aBecause the MCSx samples were prepared as the modification of the MC sample and the TEM pointed at the same size of the particles within all series, only the XRD of one representative sample has been performed.

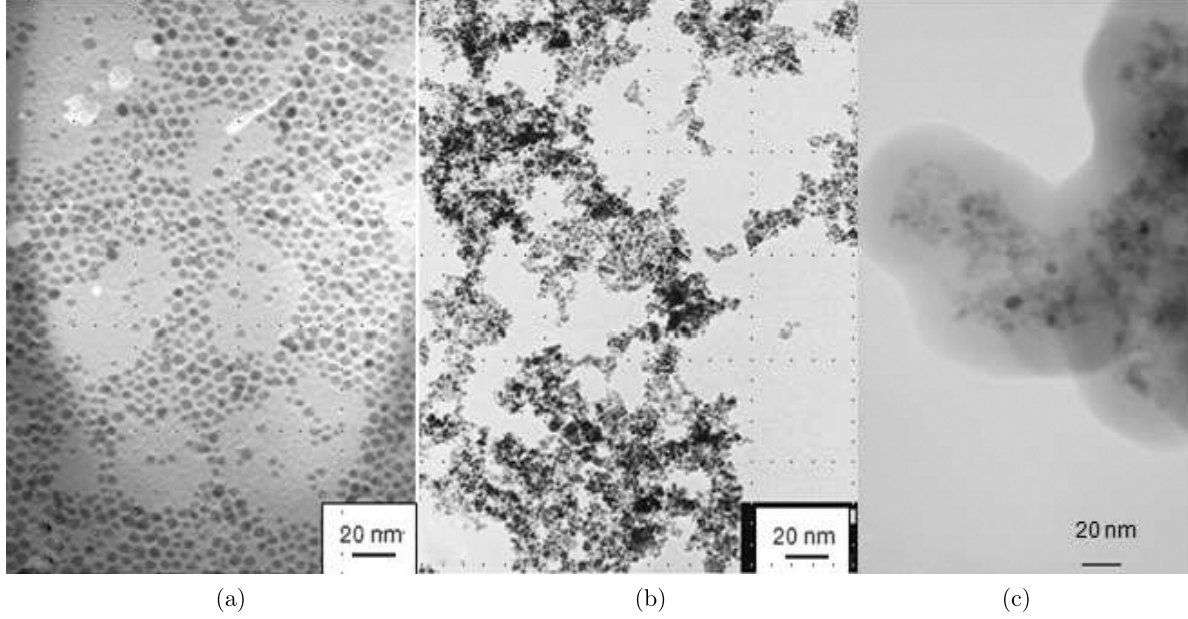


Fig. 1. TEM images. From left: MD, MC and MCS1 samples, respectively.

transition from the blocked to the SPM state. The blocking temperature, T_B belonging to the major fraction of NPs in the sample, T_{MAX} , varies from 44 K (MD) up to 118 K (MC series), respectively. Shift between the T_{MAX} and the temperature of furcation, T_{DIFF} is attributed to the distribution of particle size in the sample together with presence of the inter-particle interactions. The broad maximum at the low-temperature part of the FC curve and a jump in the ZFC magnetization at 2 K together with the nonlinear temperature dependence of the inverse M above the T_{MAX} signalize that we are dealing with a system of interacting NPs, with the interactions of dipolar origin (Fig. 3). The strength of the interactions will be treated further.

The qualitative inspection of the ZFC curves suggests that (i) the values are nearly the same for the MC series abstractedly from the thickness of the cover and (ii) the strongest inter-particle interactions were observed in the sample made by decomposition, MD. Both points can be explained in the following manners: the net magnetic moment of the sample (after cooling down in random orientation without magnetic field from the RT) is given by the alignment of super-spins affected by the local environment. Thus the higher value of the magnetic moment of the sample reflects the stronger inter-particle interactions, leading to the higher order of the super-spin alignment. Applying these to the data, it is obvious that there is a minimal observable

reduction of the strength of the inter-particle interactions within the MC series which could simply means that the differences in strength of such order could not be revealed inspecting the M curves.

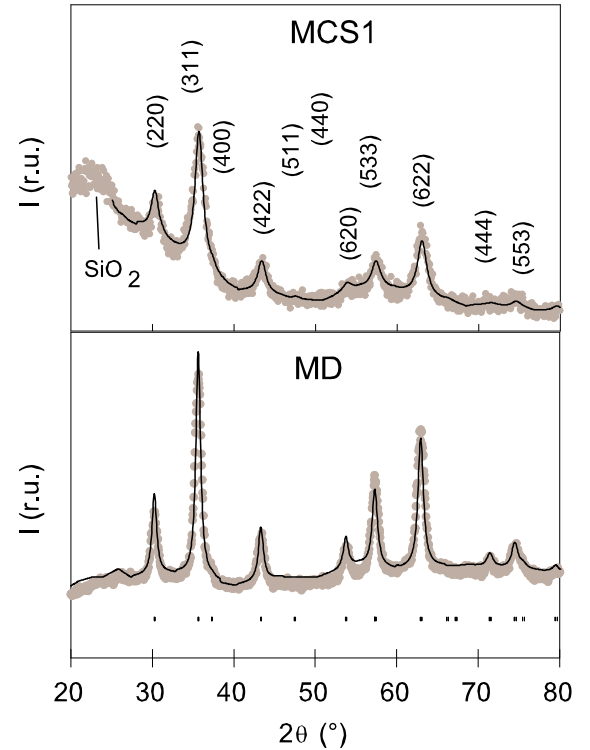


Fig. 2. XRD patterns (gray) and results of the Rietveld Refinement (black line) for the MCS1 and MD sample, respectively.

Table 1. List of the samples containing method of preparation, material used for particle coating, amount of magnetic carrier in the particle (obtained from EDX), average diameter of the particle, $d_{\text{carrier}}^{\text{TEM}}$ and $d_{\text{carrier}}^{\text{XRD}}$ determined from TEM and XRD measurements and average thickness, t of the particle (aggregate) cover.

Sample	Method	Coating	% of $\gamma\text{-Fe}_2\text{O}_3$	$d_{\text{carrier}}^{\text{TEM}}$ (nm)	$d_{\text{carrier}}^{\text{XRD}}$ (nm)	t_{layer} (nm)
MD	dec.	oleic acid	67	5.1	3.2	0.6
MC	cop.	—	100	4.9	—	—
MCS1	cop.	SiO_2	27	4.9	4.5	25
MCS2	cop.	SiO_2	17	4.9	—	40

We have also measured magnetization isotherms for all samples at 2 K, 150 K and 300 K in the magnetic field varying up to 7 T in both polarities. The value of the saturated magnetization, M_s in case of the MD sample is 1.3 times higher than for the MC sample (Fig. 4). The hysteresis (typical feature of the blocked state) has been observed in all samples at 2 K. The loops exhibit symmetric values of the coercivity, H_c , for opposite polarities of the magnetic field, 85 mT for the MC series samples and 80 mT for the MD sample, respectively.

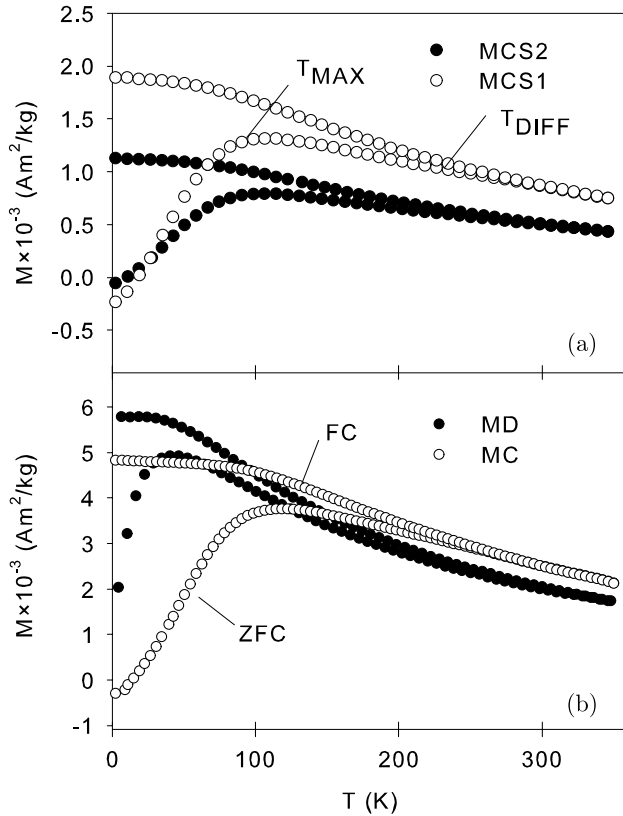


Fig. 3. (a) Temperature dependence of the ZFC-FC magnetization of the MCS1 and MCS2 samples measured in field of 10 mT and (b) temperature dependence of the ZFC-FC magnetization of the MD and MC samples measured at 10 mT.

The moderately larger H_c value in the MC series in comparison with the MD sample can be interpreted as the consequence of the larger crystalline part of the NPs in the MC series samples, as has been proven by the XRD measurements. The hysteresis vanishes above the T_{DIFF} in case of the MC series, but survives for the MD sample. It points at the existence of the non-negligible fraction of particles with the blocking temperature above the 300 K or it is simply the consequence of the formation of a collective cluster-glass-like state, more significant in the MD sample.²¹ To have the estimation of the inter-particle dipolar interaction energy, E_{dip} for the systems, the average magnetic moments, μ_m per particle were calculated fitting the un-hysteretic magnetization curves to a generalized Langevin function,¹⁶ considering the distribution of magnetic moments of particles within the samples (Fig. 4). The results are summarized in Table 2. The calculated values of the E_{dip} of all samples (Table 2), considering the direct contact between particles, are of the same order as was the proposed one for the strongly interacting systems.¹⁷ Now the question is how large should be the aggregates to keep also the strength of the inter-aggregate interactions at this value. Taking the real thickness of the SiO_2 coating, the estimated limiting amount of NPs in the aggregate are approximately 10 NPs for the MCS1 and 50 NPs for the MCS2 sample. Having these estimations, the real strength of the interactions and their evolution within the systems has to be examined via dynamic magnetic measurements.

3.3. Dynamic magnetic properties

3.3.1. a.c. susceptibility in zero external field

To examine the effect of the SiO_2 coating on the possible suppression of the collective phenomena,

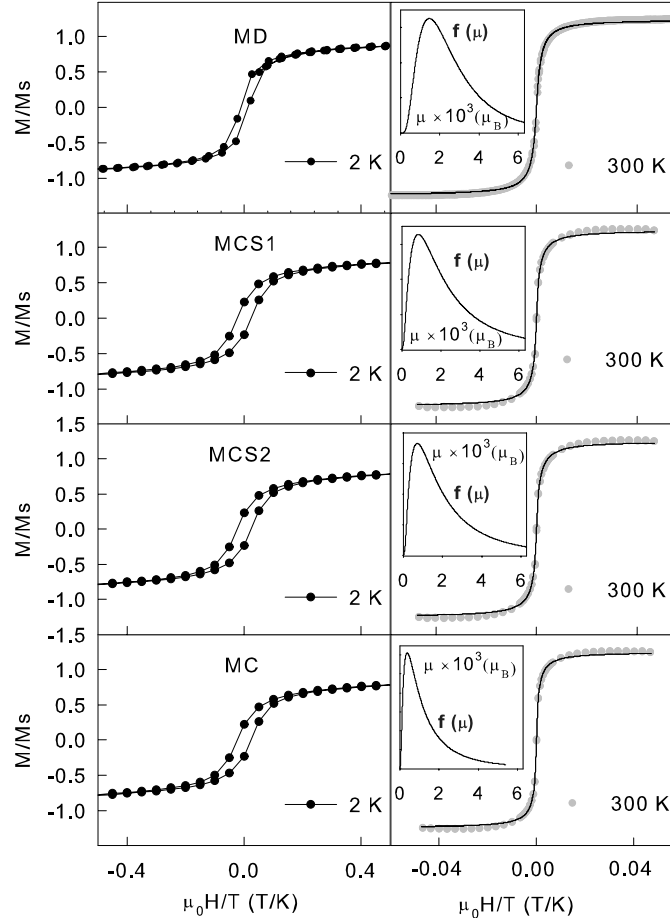


Fig. 4. Magnetization versus applied field for all samples measured at 2 K (left) and 300 K (right) together with the line representing the fit of the universal M/M_s versus $\mu_0 H/T$ curve (right) with the distribution of the magnetic moments in the insets.

the spin relaxation in the samples was inspected using a.c. susceptibility measurements. Both the real (χ') and imaginary (χ'') parts of the a.c. susceptibility were measured in different frequencies of the alternating magnetic field with the amplitude of 3 mT in zero external field. The shifts of the χ'

maxima are considered as a consequence of the super-spin relaxation, possibly of a super-spin-glass nature. Even if it has been suggested we are dealing with the strongly interacting systems, we have analyzed the experimental data by the Vogel-Fulcher²² law^b fitting the three parameters:

Table 2. List of characteristic parameters obtained from the magnetic measurements: T_{MAX} — temperature of ZFC maxima curve, T_{DIFF} — temperature of furcation at ZFC-FC curve, μ_0 — median and μ_m — mean magnetic moment per particle, connected by the relation $\mu_0 = \mu_m \exp(-\sigma/2)$. T_0 — Vogel-Fulcher characteristic temperature, τ_0 — Vogel-Fulcher relaxation time and E_{dip} — inter-particle dipolar energy.

Sample	T_{MAX} (K)	T_{DIFF} (K)	T_0 (K)	$\mu_0 \times 10^3$ (μ_B)	σ	$\mu_m \times 10^3$ (μ_B)	$\tau_0 \times 10^{-11}$ (s)	$E_{\text{dip}} \times 10^{-22}$ (J)
MD	44	345	35	2.25	0.67	1.63	1.3	0.9
MC	118	255	85	1.08	1.04	0.64	2.5	0.3
MCS1	110	280	84	2.02	0.93	1.27	1.1	1.2
MCS2	106	315	85	1.82	0.97	1.11	2.5	0.9

^bThe law was proposed for the weakly interacting systems, but the value of τ_0 lies in the aforesaid interval no matter if we are dealing with the strongly interacting system. Also if there is any observable evolution in the strength of inter-particle interactions within the series of samples, there should be a detectable change in the τ_0 parameter. So this approach is valid as the qualitative estimation of possible evolution of relaxation phenomena in the series of related systems.

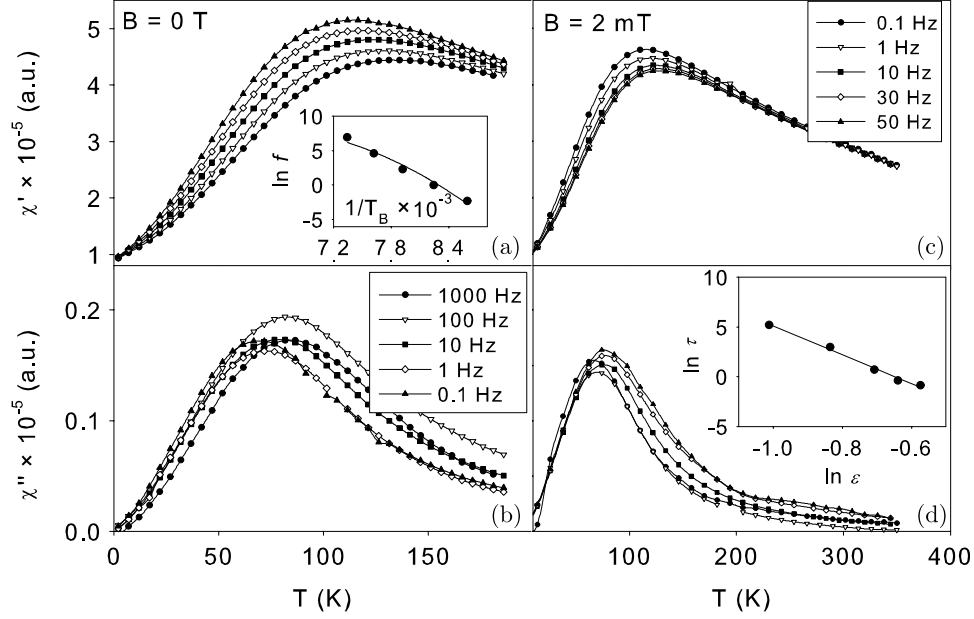


Fig. 5. MCS1 sample (a), (b) χ' and χ'' versus T in zero external field, the inset shows the fit according to the V-F law, (c) and (d) χ' and χ'' versus T in field of 2 mT, $\tau = (2\pi f)^{-1}$ versus $T_m/T_g - 1$ in the inset.

characteristic frequency, f_0 , activation energy, E_A/k_B and Vogel-Fulcher temperature, T_0 in order to estimate the relaxation time, τ_0 . To get physically relevant result, we have used the value of the anisotropy constant, K_{eff} measured by Fiorani *et al.*²³ as a $8.6 \times 10^{-2} \text{ J/cm}^3$ for 4.6 nm particles (Fig. 5). Calculated relaxation times, τ_0 and Vogel-Fulcher temperatures of all samples are summarized in Table 2.

The fitting procedure leads to the results that correspond with the values typical for SSG systems, $\tau_0 = 10^{-9} - 10^{-12} \text{ s}$.^{10,11} The values of the τ_0 of the MC series samples are in range of the fit error, no evolution has been observed. It is not physically relevant to conclude whether the relaxation processes are different or the dipolar interactions are considerably suppressed in any of the samples in comparison to the others. Also the τ_0 of the sample with the strongest inter-particle interactions, MD, does not significantly deviate from the series. If there is any mediation of the relaxation phenomena due to the SiO_2 layer, it is not so strong to be detectable in this manner.

3.3.2. a.c. susceptibility in nonzero external field

Because the strong dipolar interactions in our powder samples were assumed, we have investigated

one of them using a proper approach to evaluate properties of such a system. The additional susceptibility measurements in moderate external magnetic fields were done with the MCS1 sample. The constant frequency (50 Hz) scans were measured in the field of 0.4 mT, 1 mT, 2 mT, 4 mT, 7 mT, 10 mT and 50 mT, respectively. An overall suppression of the phase transition in field of 50 mT was observed. The temperature of the transition into the super-spin-glass state, T_g , was obtained from the scans taken at different frequencies in the field of 2 mT, using the equation²⁴ $\tau_0 = (T_m/T_g - 1)^{zv}$, where τ_0 is the relaxation time, zv is the critical exponent, T_m is the temperature of the curve maxima and T_g is the temperature of transition to the glassy state. Values derived from the best fit for the MCS1 sample are $T_g = 85 \text{ K}$, $zv = 15$ and $\tau_0 = 8.2 \times 10^{-5} \text{ s}$, respectively; those ones usually founded in literature^{11,14,24} are $zv = 5 - 11$ and 12.5 , τ_0 is ranging from 10^{-5} up to 10^{-11} s .^{14,25,26} This experiment finally confirms that even in case of sample containing the silica covered aggregates, the observed relaxation agrees with those of the strongly interacting systems. With respect to the previously presented magnetic measurements, this could be extended on the whole MC series. Based on the results, one can conclude that the dominant interaction in our systems of NPs is the inter-particle one, acting inside the aggregates, not the inter-aggregate one.

Table 3. Characteristic parameters obtained from the fits of the Mössbauer spectra. Isomer shift — δ , quadrupole splitting — ΔE_Q and linewidth — Γ .

Sample	δ (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	Interpretation
MC	0.32	0.66	0.83	SPM Fe ³⁺
MCS1	0.32	0.58	0.74	SPM Fe ³⁺
MCS2	0.33	0.63	0.70	SPM Fe ³⁺

3.4. Mössbauer spectroscopy

Further inspection of the Mössbauer spectra has been done to finally clarify the possible suppression of interactions with increasing thickness of the aggregate coating. The room temperature Mössbauer spectra were measured for all samples, the temperature evolution of the spectra has been investigated for MCS and MCS1 samples, respectively. The characteristic parameters together with the interpretation of the data are summarized in Table 3.

The comparison of the MC and MCS1 samples (Fig. 6) demonstrates that temperature evolution of the spectra for both samples is similar. There is obviously a transition from the superparamagnetic to blocked state between 200 K and 100 K, which is in the agreement with the magnetic measurements.^c

Figure 7 represents the comparison of the MC and MD sample, respectively. The interpretation of the spectra with respect to the magnetic properties of the samples is following: the linewidths of the doublets could serve as a probe of the magnetic interaction. A broader line corresponds to the stronger magnetic interaction between particles, which causes the slowing of the movement of free magnetic moment due to transition into blocked state. Thus the much broader lines of the MD samples in comparison to those of the MC series point at the stronger inter-particle interactions, as has been suggested by the d.c. magnetization measurements. We can also follow a slow decrease of the

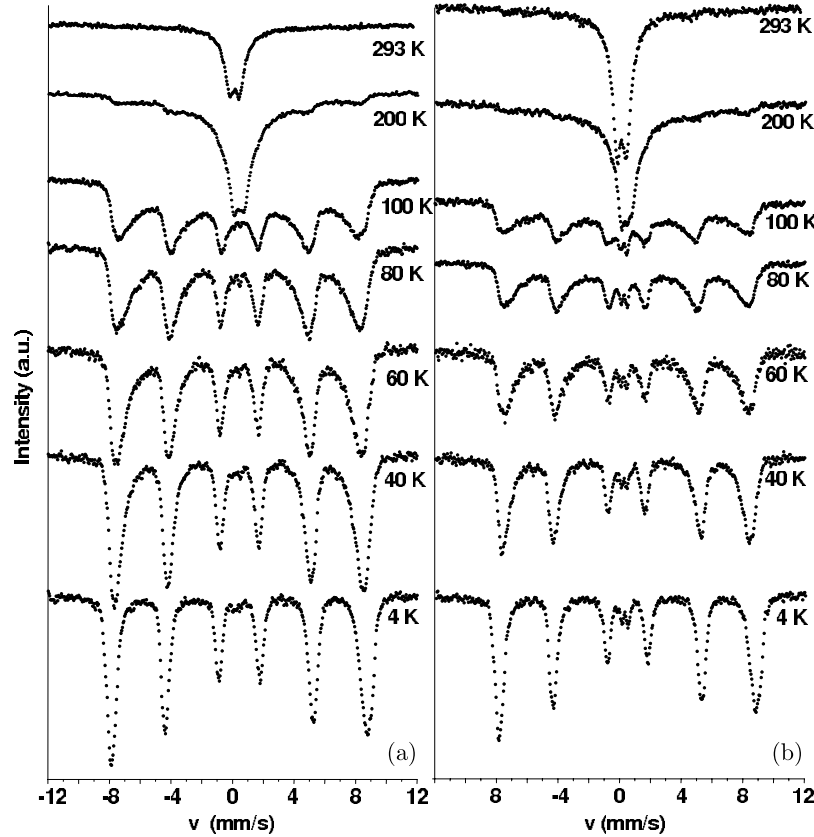


Fig. 6. The Mössbauer spectra for the MC (a) and the MCS2 (b) samples taken at different temperatures.

^cThe difference between the samples MC (a) and MCS2 (b) is represented only by an additional doublet (MCS2) that originates from iron that is not magnetically ordered. This doublet represent about 4% of total iron and could be due to iron dissolved in the silica shell or iron at the interface silica-maghemite nanoparticle due to influence of Fe-O-Si bonds.

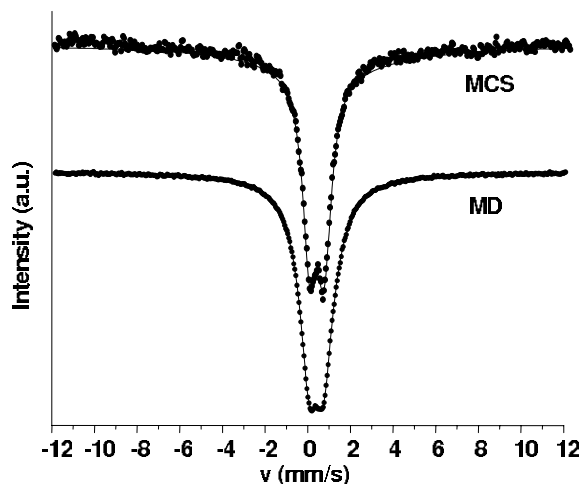


Fig. 7. Comparison of the Mössbauer spectra of the MC and MD samples, measured at room temperature.

linewidth in the series of MCS — MCS1 — MCS2, which is the final evidence that the presence of the SiO₂ — aggregate coating results in a slight weakening of the magnetic interactions in the system.

4. Conclusion

We have focused on investigation of evolution of relaxation phenomena in samples of pure and surface-modified γ -Fe₂O₃ (maghemite) nanoparticles. The particles covered with oleic acid, un-covered ones and the samples containing the aggregates coated by the SiO₂ layer of different thickness have been prepared. Particle structure and size were determined using PXRD and TEM complementarily. It has been proven by static and dynamic studies of magnetization, that all samples exhibit properties of strongly interacting systems of magnetic nanoparticles. Examination of the Mössbauer spectra confirmed slight weakening of inter-particle interactions with increasing thickness of the aggregate coating. With regards to the limit of detection of this effect by comparison of the relaxations in the systems, no measurable evolution of the relaxation time, τ_0 determined from the a.c. susceptibility measurement, even for the strongest interacting MD sample has been observed. The resulting weakening of the interaction strength within the system with increasing thickness of inter-aggregate coating could not be observable on change of the relaxation time τ_0 , determined from the studies of dynamic properties and only Mössbauer spectroscopy serves as the only valuable probe to expose this phenomenon.

Acknowledgments

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Structural disorder versus spin canting in monodisperse maghemite nanocrystals

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Monodisperse maghemite nanoparticles with diameter ranging from 7 to 20 nm were examined by the In-field Mössbauer Spectroscopy (IFMS) in varying external magnetic field up to 6 T. Surprisingly, the small-sized particles (7 nm) exhibit nearly no spin canting in contrast to the larger particles with lower surface-to-volume ratio. We demonstrate that the observed phenomenon is originated by lower relative crystallinity of the larger particles with different internal structure. Hence, the persistence of the 2nd and 5th absorption lines in the IFMS cannot be unambiguously assigned to the surface spins. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4881331>]

Iron oxide nanoparticles (NPs) attracted significant attention of numerous researchers due to variety of applications in nanomedicine, data storage, and other magneto-responsive technologies.^{1–3} However, their performance in practical applications is conditioned by the optimized magnetic response for a given particle size, which is believed to imprint the magnetic properties of the NPs. Reduction of the NP size to the nanometer scale leads to pronounced increase of the surface-to-volume spin ratio resulting in undesirable effects such as the lowering of the volume saturation magnetization. First attempts to treat the surface effects were done by Coey^{4,5} who proposed the so-called *magnetic* core-shell structure. The NP consists of a core with aligned spins and a disordered shell with the surface spins inclined at the so-called spin canting angle. This model was supported by the presence of non-zero intensity of the 2nd and 5th absorption lines in In-field Mössbauer Spectroscopy (IFMS) and was further confirmed by Morrish *et al.*⁶ who investigated maghemite NPs with ⁵⁷Fe-enriched surface. Since that time, a couple of studies have determined the spin canting angle from IFMS and assigned its origin to the presence of the inclined surface spins without any deeper insight into the internal structure of the NPs.^{7,8} Contrary to these reports, several theoretical or experimental studies claim that the spin canting angle determined by IFMS is not caused by the inclined surface spins, but it is a finite-size effect, hence a volume effect especially in NPs larger than 10 nm.^{9–12}

Most of the studies discussing the surface effects have not performed the proper characterization of the examined samples, such as determination of the relative crystallinity by comparison of the particle diameter determined by Powder X-ray Diffraction (PXRD) and Transmission Electron Microscopy (TEM). A deeper insight into the internal structure of the NPs by High Resolution TEM

(HR-TEM) is rarely carried out. Moreover, the studies are typically performed on samples with a significant particle size distribution that broadens the absorption lines precluding the observation of the surface effects. Therefore, the aim of this study is to investigate the presence of the spin canting in strictly monodisperse NPs and its influence on the IFMS spectra. For this purpose, four samples of maghemite, γ -Fe₂O₃ were prepared by the thermal decomposition (Np7, Np15a, Np15b, and Np20)¹³ with low particle size distribution ($\sigma < 0.2$). The preparation conditions were changed in order to obtain well-crystalline NPs (Np7), two samples with the same NPs sizes but different internal structure (Np15a, Np15b) and a sample with large NPs size (Np20).

The samples were investigated by PXRD, TEM, HR-TEM, magnetic measurements, and IFMS. The IFMS measurement was performed in the transmission mode at 4.2 K and the applied magnetic field of 0–6 T in perpendicular direction to the direction of γ -rays. The details are given in supplementary material.¹⁴ The particle diameter, d_{XRD} (expressed as the size of a coherently diffracting domain), d_{TEM} (represents the mean particle size fitted by the log-normal distribution), and the saturation magnetization at 300 K, M_{s}^{300} are summarized in Table I.

The PXRD measurement confirmed the presence of the spinel structure only, with the lattice parameters matching the 8.36 Å value, corresponding to the maghemite phase

TABLE I. Characterization of the samples: diameter determined by PXRD, d_{XRD} ; by TEM, d_{TEM} , saturation magnetization at 300 K, M_{s}^{300} .

Sample	d_{XRD} (nm)	d_{TEM} (nm)	M_{s}^{300} (A · m ² · kg ^{−1})
Np7	6.6 ± 0.3	6.5 ± 0.3	67.5
Np15a	7.2 ± 0.5	15.0 ± 0.4	51.0
Np15b	7.4 ± 0.5	14.1 ± 0.4	66.0
Np20	15.9 ± 1.0	19.9 ± 0.2	80.2

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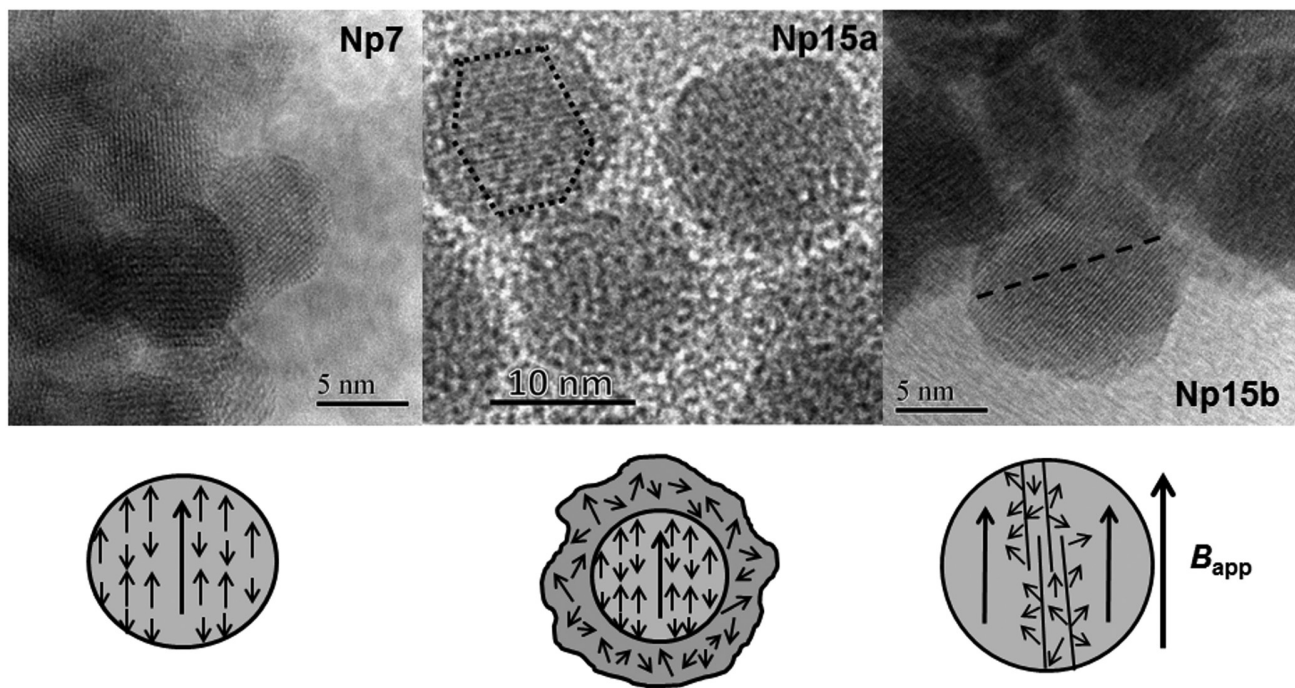


FIG. 1. The HR-TEM images of the samples. The well-crystalline Np7 sample on the left. The *structural* core-shell structure of the Np15a sample is depicted by dotted lines, the Np15b sample possesses stacking faults, the one propagating through the whole particle is depicted by dashed line. The simple sketch of the possible orientation of the spins in the high applied field, B_{app} is shown below.

(PDF2 database, card no. 83-0112). The presented parameters clearly pointed to the differences in the relative crystallinity of the NPs. Nearly the same d_{XRD} and d_{TEM} of the Np7 sample indicated the well-crystalline NPs that was further confirmed by the HR-TEM measurement (see Figure 1). On the other hand, both the Np15 samples exhibited large differences in the d_{XRD} and d_{TEM} indicating that more than 80% of the NP volume is not crystalline. The HR-TEM images revealed that the Np15a particles consist of a crystalline core embedded in an amorphous shell, which can be described as a *structural* core-shell model, whereas the Np15b sample possesses stacking faults through the whole particle that divide the particle into at least two crystallographic single domain parts and affect its magnetic properties (Figure 1). The Np20 sample consists of NPs with relatively large volume of the crystalline core in comparison to the disordered fraction evidenced by the discrepancy in the d_{XRD} and the d_{TEM} . The conclusions based on the PXRD and TEM results were further supported by the magnetic measurements, where the relatively small M_s^{300} for the Np15a sample can be interpreted in terms of the *magnetic* core-shell model.⁴

The IFMS was performed in order to determine the evolution of the hyperfine parameters and the spin canting angle with varying external applied field of 0–6 T, B_{app} . The individual spectra are depicted in supplementary material.¹⁴ The relative areas of the tetrahedral (T_d) to the octahedral (O_h) sites were fixed to 1.67 according to the theoretical occupancy of the spinel crystallographic sites, and further refinement of the occupancy in the 6 T-spectra was in agreement with those values within the experimental error for all samples. The values of the isomer shift, $\delta = 0.36\text{--}0.37\text{ m}\cdot\text{s}^{-1}$ and $0.49\text{--}0.50\text{ m}\cdot\text{s}^{-1}$ for the T_d and O_h sites, respectively, correspond to the Fe^{3+} ions in high-spin state and did not change with the varying B_{app} . The nearly zero quadrupolar shift, 2ϵ (values ranging from -0.02 to $0.02\text{ m}\cdot\text{s}^{-1}$) is consistent with the cubic symmetry of the T_d and O_h sites of the $\gamma\text{-Fe}_2\text{O}_3$ phase.

The evolution of the effective field, B_{eff} with the increasing B_{app} is depicted in Figure 2, and the exact values are summarized in supplementary material.¹⁴ The linear increase of the B_{eff} with step of 1 T with the increasing B_{app} of 1 T in high-field regime indicates the complete alignment

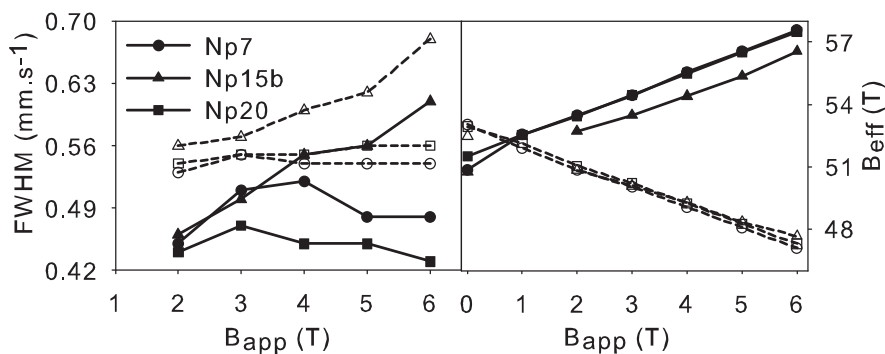


FIG. 2. The evolution of the FWHM (left panel) and the B_{eff} (right panel) with the increasing B_{app} . The T_d -sites are depicted with the full symbols and full lines and the O_h -sites with the open symbols and dashed lines.

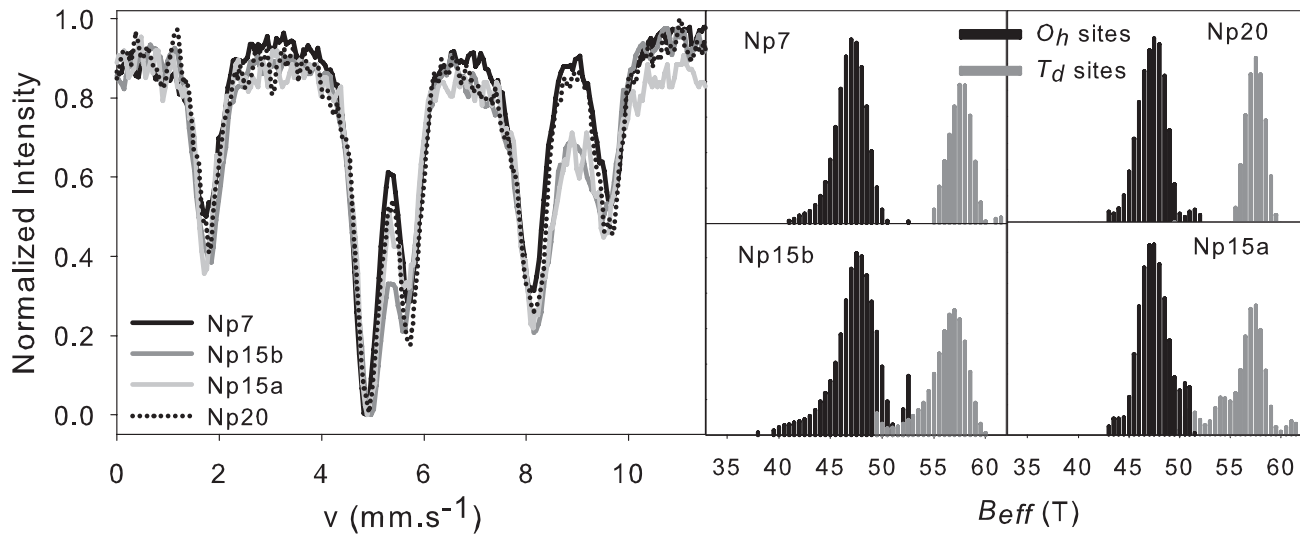


FIG. 3. The part of normalized 6 T-spectra of all samples on the left. The distribution of the B_{eff} of all samples on the right.

of the hyperfine field, B_{hf} and B_{app} for the well-crystalline Np7 and Np20 samples. In the Np20 sample, the contribution of the crystalline core dominates and the disordered spins exhibit only negligible contribution. In ferrite oxides, only the Fermi contact term (proportional to the magnetic moment, μ) is considered. Our results show the parallel orientation of the μ with the B_{app} , resulting in zero spin canting (discussion in supplementary material¹⁴). On the other hand, the Np15b sample exhibits a non-linear increase of the B_{eff} with the increasing B_{app} pointing to the incomplete alignment of the μ with respect to the B_{app} ; therefore, the determined spin canting angle should be non-zero. Moreover, the evolution of the FWHM (full width at half maximum) is nearly constant in high-field regime for both the Np7 and Np20 samples confirming the complete alignment of the μ with the B_{app} . On the other hand, the FWHM increases with the increasing B_{app} for the Np15b sample suggesting the continuous disorder of magnetic moments with the increasing B_{app} (see Figure 2). The smaller values of all B_{eff} for both the Np15 samples can be attributed to the higher FWHM of the peaks that shifts the centre of the absorption lines to lower values. The increasing FWHM is consistent with the observed paramagnetic contribution of the disordered spins that is superimposed on the magnetization isotherms at 300 K for both the Np15 samples (supplementary material¹⁴).

All 6 T-spectra were normalized in order to compare the shape of the absorption lines, and part of the spectra (0–12 mm · s⁻¹) is depicted in Figure 3 together with the distribution of the B_{eff} for individual sites that was fitted using the Gaussian distribution of the Lorentzian profiles of the absorption peaks.¹⁵ The wider asymmetric peaks of both the Np15 samples are observed in comparison with other samples indicating the presence of the disordered spins, thus lowering the B_{eff} .

The calculation of the so-called spin canting angle is very disputable and inaccurate in the case of small NPs. The mostly used approach is the calculation from the ratio of the 2nd to the 3rd peak areas given by the equation (B_{app} perpendicularly to the γ -rays):

$$4 \left(\frac{2}{\sqrt{1 + \sin^2 \theta}} - 1 \right) : 1. \quad (1)$$

However, this angle θ corresponds to the angle between the B_{app} and the B_{eff} that is not collinear with the direction of the μ , because the μ points oppositely to the direction of the B_{hf} in the case of the ferrite oxides; therefore, this approach is not appropriate for determination of the exact value of the spin canting angle.¹⁶ An alternative approach leading to the relevant angle, α between the B_{hf} and the B_{app} requires both the measurement of the zero-field spectrum together with the in-field spectrum, yielding the B_{hf} and B_{eff} , respectively. The spin canting angle can be then calculated using the following expression (supplementary material¹⁴):

$$\cos \alpha = \frac{B_{\text{eff}}^2 - B_{\text{app}}^2 - B_{\text{hf}}^2}{2B_{\text{app}}B_{\text{hf}}}. \quad (2)$$

This procedure can be accurate only in the cases, where both the B_{hf} and B_{eff} can be precisely determined, otherwise the angle is only estimative. We have calculated the spin canting angle using both approaches; the results are summarized in Table II. The first approach leads to much higher θ for the

TABLE II. Evolution of the spin canting angles, θ and α determined by both approaches. The experimental error is about 10°.

θ/α (°)	2 T	3 T	4 T	5 T	6 T
<i>T_d</i> -site					
Np7	32/-	24/-	21/-	22/-	19/-
Np15a	...	...	...	...	32/15
Np15b	35/12	34/26	28/25	31/24	27/15
Np20	23/17	18/13	16/5	21/4	9/4
<i>O_h</i> -site					
Np7	6/-	10/-	14/-	10/-	8/-
Np15a	...	...	...	...	23/28
Np15b	36/33	34/36	33/35	32/33	30/34
Np20	24/19	23/24	19/22	16/20	15/19

T_d -sites than the O_h -sites in both the Np7 and Np20 samples, that is in contrast with general observation that the O_h -sites should possess higher θ due to the presence of vacancies.¹⁷ Moreover, it is not consistent with the evolution of the B_{eff} that suggested parallel direction of the μ and B_{app} , thus zero spin canting.

On the other hand, the α cannot be determined for Np7 and Np20 because the difference between the B_{eff} at 6 T and B_{hf} is higher than 6 T owing to the only estimative values of the B_{hf} caused by completely overlapped sextets. Fixing all other hyperfine parameters to the high-field spectra values did not cause any significant changes in the B_{hf} . Setting the B_{hf} value of the T_d -sites in any way is connected with the strong change of the B_{hf} of the O_h -sites without any significant change of the error (χ^2) of the fit. This approach is thus only estimative and just the evolution of the B_{eff} with the increasing B_{app} can be discussed in relevant way. The values of the θ and α differ significantly, however, the in-field evolution of these angles is nearly the same they decrease with the increasing B_{app} for the Np7 and Np20 samples, on the other hand, they remain more or less constant for the Np15b sample, that is consistent with the evolution of the FWHM.

Finally, the difference in IFMS of both the Np15 samples possessing different internal structure was examined. The normalized IFMS at 6 T did not reveal any significant differences in the profile of both spectra, the asymmetric broadening at the lower values of the B_{eff} is pronounced in both spectra in equal way. The θ and α values are identical within the experimental error; therefore, the IFMS cannot distinguish the origin of the spin canting angle. This observation has demonstrated that the determined spin canting angle cannot be dedicated either to the presence of surface spins or to the low crystallinity of the particles without any deeper insight into the internal structure of the NPs.

To conclude, we have demonstrated that the IFMS is not an unambiguous method to study the surface effects in the NPs as the IFMS is sensitive only to the average value of all spins and does not distinguish between the surface and core effects. The non-zero spin canting angle can only indicate the presence of low crystallinity of the NPs, but for precise determination of the origin of the spin disorder, the support of the HR-TEM experiments is essential. The exact calculation

of the spin canting is disputable and both presented approaches are not precious. We strongly propose to measure the evolution of the B_{eff} with the B_{app} in order to obtain the complex behavior of the spins in individual sublattices. Finally, we have shown that the spin canting angle is negligible in the well-crystalline NPs with sizes larger than 6.5 nm.

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- ¹⁶Furthermore, the peak area is sensitive to the fitting procedure (with or without distribution of the B_{eff}) or to experimental setup such as thick samples resulting in saturation of absorption lines.
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3.3 Další systémy s magnetickými nanočásticemi

V této sekci jsou zahrnuty tématicky odlišné práce. První část obsahuje výsledky studia granulárních multivrstev s nanočásticemi železa a kobaltu, druhá část se věnuje magnetickým a strukturním vlastnostem nanočástic reziduálního katalyzátoru v uhlíkových nanotubách.

3.3.1 Granulární multivrstvy $\text{SiO}_2-(\text{Co}/\text{Fe}/\text{CoFe}_2)$

- B. Pacakova Bittova, J. Lancok, M. Klementova, J. Vejpravova, Appl. Surf. Sci. (2014), 289, 257. [C1-107] [97]

Dalšími typovými systémy, ve kterých byl potvrzen významný vliv mezičásticových interakcí na magnetické vlastnosti, jsou tenké filmy a multivrstvy s nanočásticemi Co, Fe a slitiny CoFe_2 deponované pomocí magnetronového naprašování na křemíkový substrát [97]. K dispozici byly filmy o nominální tloušťce 3, 5 a 10 nm s ochranou vrstvou SiO_2 (10 nm). Vzorky byly charakterizovány pomocí elektronové mikroskopie, měřením RTG reflektivity a mikroskopie atomárních sil a bylo zjištěno, že filmy jsou polykrystalické se střední velikostí (poloměrem) částic 6 nm. Z teplotní závislosti magnetizace v protokolu ZFC-FC bylo zjištěno, že vzorky vykazují chování systému silně interagujících SPM částic. Měření magnetizace s využitím torzního magnetometru ukázalo, že nad teplotou 200 K vykazuje systém uniaxiální anizotropii se snadnou osou magnetizace v rovině filmu. Pod teplotou 50 K dochází k potlačení tvarové anizotropie a snadná osa magnetizace je stočena mimo rovinu filmu o úhel 40 až 150 ° v závislosti na orientaci nanočástic uvnitř vrstvy. Tento jev lze interpretovat jako tzv. kooperativní reorientaci superspinu, kdy je výsledná orientace magnetizace určena silnou dipolární interakcí mezi částicemi, která zprostředkuje orientaci jejich superspinů ve směru snadné osy majoritní frakce částic.



Temperature dependent rotation of the uniaxial easy axis of magnetization in granular $\text{SiO}_2\text{--}(\text{Co/Fe/CoFe}_2)\text{--Si}(1\ 1\ 1)$ multilayers

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High temperature in-plane easy axis

Low temperature rotation of easy axis

ABSTRACT

We have observed temperature dependent rotation of the uniaxial easy axis of magnetization and introduced the phenomenon of the superspin reorientation transition (SSRT) for the nanogranular thin films and multilayers. The effect is demonstrated on the nanogranular $\text{SiO}_2\text{--}M(x)\text{--Si}(1\ 1\ 1)$ multilayers, where M is the metal (Co, Fe or CoFe_2) of the nominal thickness $x=3, 5$ and 10 nm, respectively. The morphology and layer thickness have been examined using the transmission electron microscopy, X-ray reflectivity measurement and atomic force microscopy. Magnetic property measurements demonstrated that the orientation of the uniaxial in-plane easy axis of magnetization given by the film shape anisotropy was thickness independent at temperatures above 200 K. Below 50 K, the film shape anisotropy has been overcome and the uniaxial easy axis was rotated into different directions for each samples series, forming an angles from 40° up to 150° with respect to the film plane. Such effect of the low temperature magnetization rotation has been attributed to the specific arrangement of the nanoparticles in the individual layers and has been assigned to the SSRT phenomena.

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1. Introduction

The electronic devices are subjected to the miniaturization in recent decade and the research in the field is highly focused on the development of suitable incorporated magnetic components. Miniaturization requires operation at high frequencies (HF), in applications such as the high-density recording, production of HF inductors or transformers [1–3]. The most promising materials in the field are granular thin films and multilayers with soft magnetic properties [4]. The important parameters that determine suitability of material for the specific application are the magnetization (M) value, its direction at selected temperature and strength which keeps it in the given direction. Because the M direction in the thin film is driven by the anisotropy energy, E_A , which is defined as the energy required for rotating the M from easy into the hard direction [5], investigation of the temperature dependence of the sample magnetic anisotropy is essential. There are many anisotropy components of different origins and in general, M follows direction of the dominant component either of intrinsic or extrinsic origin [6].

The main intrinsic component arising from the spin–orbit coupling, directly influenced by the nanoparticle (NP) crystallinity and crystallographic structure, is the magnetocrystalline anisotropy energy (MCA); extrinsic components originating from dipole interactions depend on the parameters such as shape, thickness, quality of surface and interfaces, strain caused by the lattice misfit of the substrate and layer. It has been demonstrated in the epitaxial thin films that the strain anisotropy is one of the leading terms besides MCA and the shape anisotropy (SA). Furthermore, the interface and surface anisotropies, originating from the roughness of layers are several orders of magnitude lower [6] and contribute negligibly to the final anisotropy of the sample. The anisotropy mechanism in the granular films composed of magnetic NPs in direct contact differs from that of epitaxial layers: the strain anisotropy is not important because the lattice misfit, typical for epitaxial layers, is not so pronounced. The SA, anisotropy due to the interparticle interactions and MCA of the layer (which is not determined only by the crystallographic structure of individual NPs, but also by their arrangement) compete together [7,8].

There have been published many works that are focused on the magnetic properties of Co or Fe single-domain superparamagnetic-like granular thin films [9–12], but the magnetization rotation with temperature from parallel (in-plane) to perpendicular (out-of-plane) direction has been investigated in detail only for epitaxial layers [6]. Typical crystallographic structures in which the Co and Fe could be found in thin films are depicted in Table 1.

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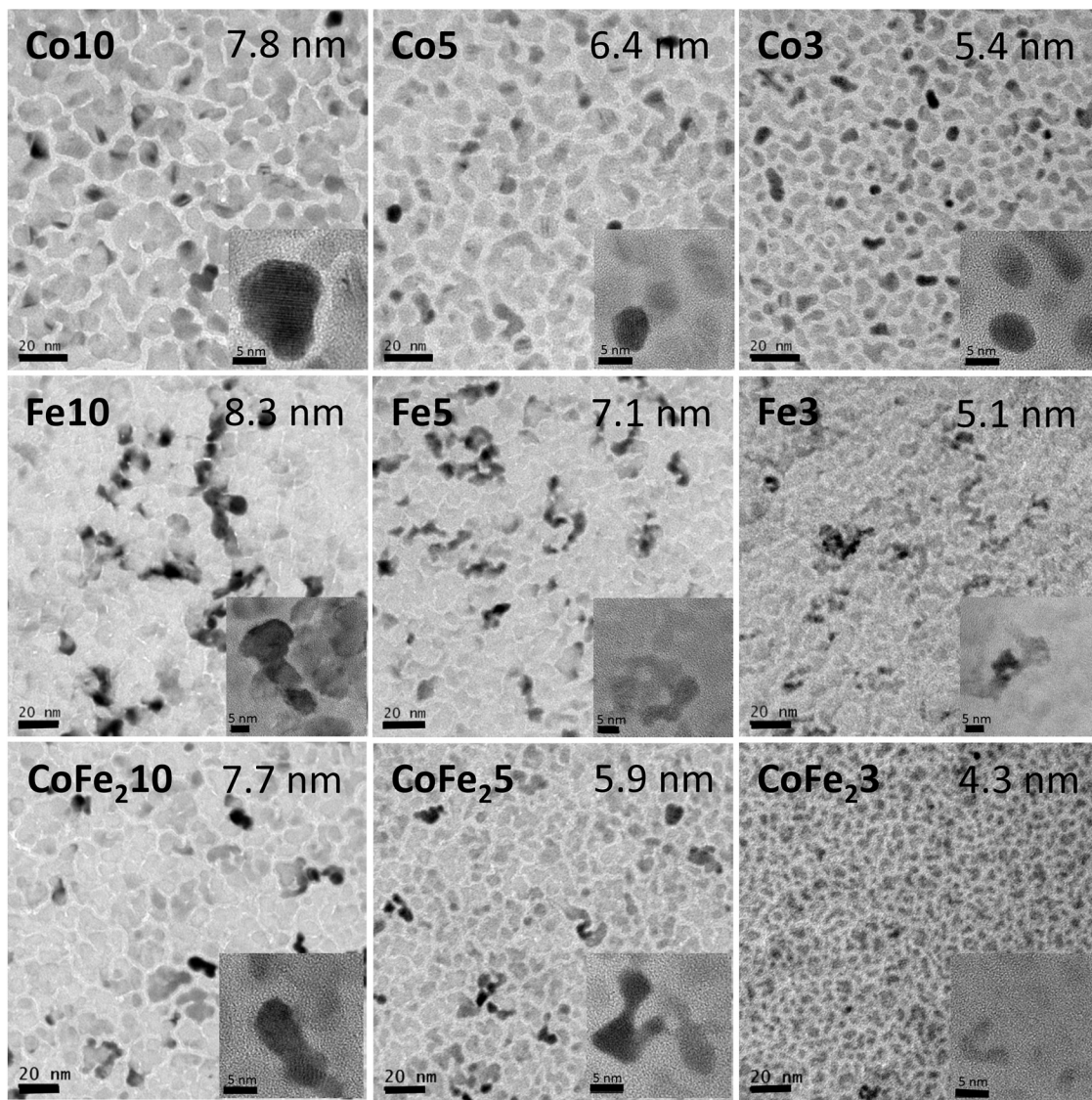


Fig. 1. The HRTEM images of the single metal layers capped with the SiO₂ layer, respectively. The granular nature of the layers and high crystallinity of particles is clearly visible. Even if capturing of the HRTEM images of the individual layers in our multilayer samples is not possible, we assume that their character corresponds well with observed granular structure of the single metal layers, as has been suggested by other experiments. The mean size of the particles in single layers has been evaluated from refining the log-normal distribution of the particle sizes and is written directly in individual images. The distribution width is $\sigma = 0.22, 0.19$ and 0.15 for the Co10, Co5 and Co3 samples, respectively; $\sigma = 0.1, 0.17$ and 0.09 for the Fe10, Fe5 and Fe3 samples; and finally $\sigma = 0.13, 0.12$ and 0.19 for the CoFe₂10, CoFe₂5 and CoFe₂3 samples, respectively.

It has been shown that soft magnetic materials are magnetized due to the spin rotation rather than domain wall motion [13]. Different anisotropy terms are usually temperature dependent [5], thus the temperature dependent rotation of M in epitaxial films and multilayers has been assigned to the spin reorientation transition (SRT) [13–16]. In order to have an analogous formalism for description of the temperature dependent rotation of M in granular thin films, we introduced the term superspin reorientation transition (SSRT). In this formalism, single spins of epitaxial layer are substituted by the spin of whole NP (superspin) for granular layer. Direction of single superspin is driven by the orientation of the single NP easy axis of magnetization, which is determined either by the NP SA [17] or the MCA. To describe the anisotropy of layer composed of these NPs (means to define easy and hard axes of the layer), we need to consider all contributions of individual anisotropies. If all competing magnetic anisotropies in granular film are uniaxial, then the total anisotropy energy, E_{uni} is written as [5,17]:

$$E_{uni} = K_u \sin^2 \theta, \quad (1)$$

with

$$K_u = K_{LP} + K_{SA}, \quad (2)$$

where K_{SA} is the film SA constant and K_{LP} is the NP layer anisotropy (LPA) constant. Final direction of easy axis is given by the vector sum of easy axes attributed to distinct anisotropies [18].

If we take only the sum of the single NP anisotropies (SPA) neglecting the SA, and if there is the preferential fraction of NPs with parallel easy axes pointing in direction D , the layer easy axis is uniaxial and keeps D direction, supposing the remaining superspins rotate to the D direction due to the strong interparticle interactions. We could say that internal arrangement of NPs within the layer (hence orientation of grains in case of anisotropic NPs or texture of layers for isotropic ones) determines the low temperature easy axis direction [18,19], as has been already observed by Zhao et al. on preferential distribution of antiferromagnetic easy axis of individual grains [20].

Table 1

The crystallographic structure in which the Co and Fe could be found in thin films. Orientation of easy axis is given with respect to the basal plane.

	Easy axis	Orientation	Metal	Material
hcp	c-axis [0001]	90°	Co	Co/Si(001) [11], Au/Co/Au(111) [29]
fcc	[111]	30°	Co	Co/Ni/Cu(001) [30], Co/Cu(111), Co/Cu(001) [31]
			Fe	Fe/Cu(001) [32]
bcc	[100]	0° (180°)	Fe	Fe/Ag(001) [33], Fe bcc[110]/fcc[111]

In our work, we have investigated temperature dependent magnetization rotation in nanogranular $\text{SiO}_2\text{--M}(x)\text{--Si}(111)$ multilayers, where M is the metal (Co, Fe or CoFe_2) of the nominal thickness $x=3, 5$ and 10 nm, respectively. The morphology and quality of the interfaces of the samples were characterized by the transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray reflectivity measurements (XRR), atomic (AFM) and magnetic force microscopies (MFM). Magnetic properties were investigated using vibrating sample magnetometry (VSM) in parallel and perpendicular orientation of the film plane with respect to the applied field direction, and by torsion magnetometry (TqM). The M -rotation is discussed in terms of the temperature dependent competition of SPA considering NP arrangement and effect of interparticle interactions that compete with the film SA. Results are supported by the theories on behavior of interacting single domain magnetic NPs.

2. Experimental

2.1. Preparation of layers

Multilayers were prepared using dual radio-frequency (RF) magnetron sputtering with alternating targets, in the chamber evacuated down to 6×10^{-4} Pa and filled with Ar of pressure 1 Pa. The samples were composed of ten metal (Co, Fe or CoFe_2)/ SiO_2 sandwich layers, deposited on the Si(111) substrate and capped with the 10 nm thick SiO_2 layer. The nominal thickness based on the calibration of the deposition equipment was 3, 5 and 10 nm for metal layers and 10 nm for the SiO_2 layer, respectively. The samples are labeled as $M(x)$, where M is the metal and x is the thickness of the metal layer. The details on preparation and schematic figures could be found in Ref. [21]. Testing samples containing only one metal layer of the same thickness as in the multilayer samples were prepared for investigation of the granular structure by TEM and HRTEM, respectively.

2.2. Characterization

The samples containing single metal layer capped with the SiO_2 were investigated by TEM and HRTEM (images were captured with the JEOL JEM 3010 microscope) by means of direct visualization of the granular nature of metal layers and high crystallinity of individual NPs. The TEM images of vertically cut multilayers could be found in [21].

XRR measurements were performed on the X-Pert Pro MRD diffractometer in the parallel beam setup with the incident angles lower than 3° and analyzed in the X-Pert software. The size of the sample used in experiment was 1 cm^2 .

Magnetic measurements have been performed on the PPMS14 device in the VSM (with samples of average size $0.5 \text{ cm} \times 0.5 \text{ cm}$) and TqM (sample average size $1 \text{ mm} \times 1 \text{ mm}$) modes. The temperature dependencies of magnetization, $M(T)$ measured after cooling without and with external magnetic field (ZFC–FC curves) and magnetization isotherms, $M(B)$ were measured in parallel orientation of the film plane with respect to the field direction in the temperature ranges 2–350 K and 300–600 K. TqM was

measured in the orientation $0\text{--}365^\circ$ with respect to the external magnetic field direction, at temperatures down to 5 K.

The AFM and MFM images were captured with the Veeco Multimode V microscope. Topography imaging was done with the SNL-10 probes, imaging of magnetic forces with the MESP and MESP-HM probes by Veeco Inc. The images have been processed in the Nanoscope and Gwyddion software's, surface roughness has been evaluated from the topography images. MFM imaging has been performed after magnetizing the sample in the field of 1 T or 5 T, respectively.

3. Results and discussion

3.1. Multilayers structure

As is demonstrated in Ref. [21], TEM images showed that the metal and SiO_2 layers are well separated, without the observable diffusion of layers. The granular nature of our metal layers could be demonstrated on single metal layers capped with the SiO_2 prepared under similar conditions as the multilayer samples, as is depicted in Fig. 1. It has been observed that the NP size varies from 4.3 to 8.3 nm and increases with the increasing layer thickness, as is consistent with the multilayer data, as will be shown further.

The surface morphology examined via AFM (see Supplementary) visualizes the granular structure of the upper SiO_2 layer, also the root-mean-square (rms) roughness, σ_q^{AFM} of the surface has been determined for each sample (Table 2). In selected cases, the σ_q^{AFM} values do not correlate with the roughness values obtained from the XRR measurement, σ_q^{XRR} , thus σ_q^{AFM} does not directly serve as the parameter indicating quality of the layer which enables proper measurement of reflectivity (Table 2 and Supplementary file). To predict the X-ray scattering from the layer using the statistical analysis of the AFM images, deeper analysis of the surface fractal properties has to be done, as is discussed in detail in Supplementary. We have demonstrated, that the surfaces deviating significantly from the Gaussian relief described by the height–height correlation function [22] exhibit large diffuse scattering and strongly limit the measurements of reflectivity (the case of the Fe(3), CoFe_2 (3) and CoFe_2 (5) samples).

MFM images of the thickest films captured after magnetizing the sample in the external field gradient of 1 T showed areas of different contrast, which represents the perpendicular components of M belonging to domains composed of NPs, as is expected for the film which is not in saturation (example in Fig. 2). Also no sign of macroscopic periodic domain structure has been observed, as is typical for films of larger than nm thickness [11]. Exposure of the film to 5 T led to the homogeneous unidirectional magnetization of the layer. MFM phase contrast disappeared and magnetic probe has been strongly attracted to the sample surface during scanning (data are not presented).

Dependence of the reflected intensity on the angle of incidence has been measured for all samples, but as has been already mentioned, three samples exhibited large diffuse scattering with the strong decrease of intensity at low angles, disabling proper measurements of the XRR curve (example in Fig. 3). The critical angle, α_c , density of individual layers, ρ and the σ_q^{XRR} have been evaluated

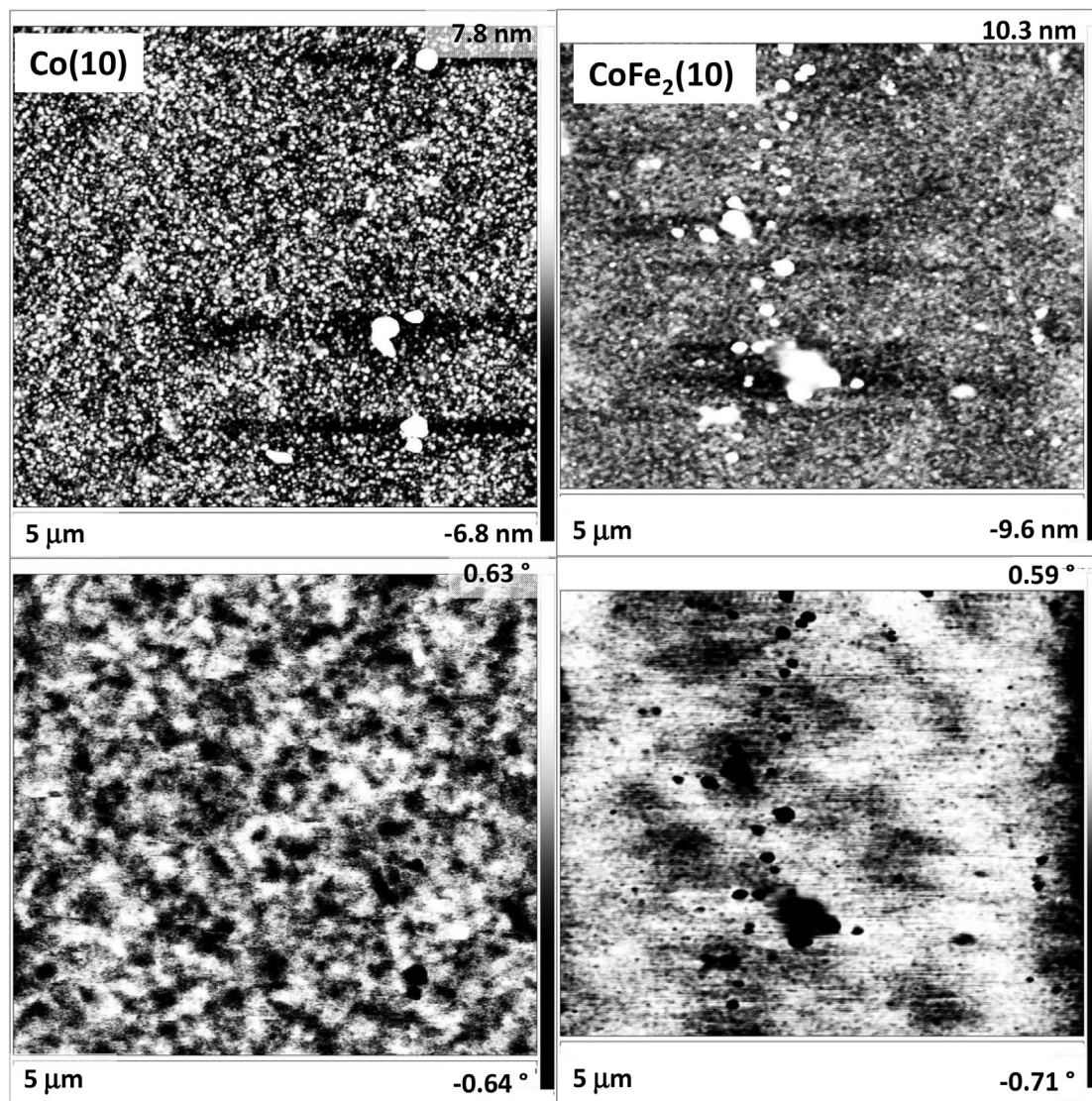


Fig. 2. Topography (up) and magnetic phase (down) images of the Co(10) and CoFe₂(10) samples, respectively, after magnetizing the sample in gradient of 1 T. The images were taken with the MESP (Co(10)) and MESP-HM (CoFe₂(10)) probes in the 30 and 70 nm lift scan height, respectively. The dark and bright areas in the magnetic phase images, let us say domains, belong to the magnetized areas with an overall perpendicular component of magnetization pointing down and up, respectively. The domain size is one to several orders of magnitude larger than the grain size, which is the consequence of strong magnetic interactions among NPs.

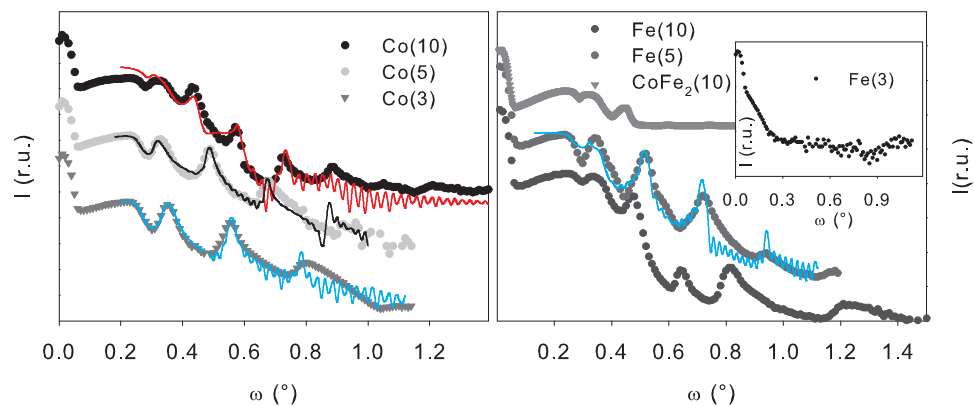


Fig. 3. The experimental and refined reflectivity curves for the samples with low diffuse scattering with an example of the sample possessing high diffuse scattering in the inset.

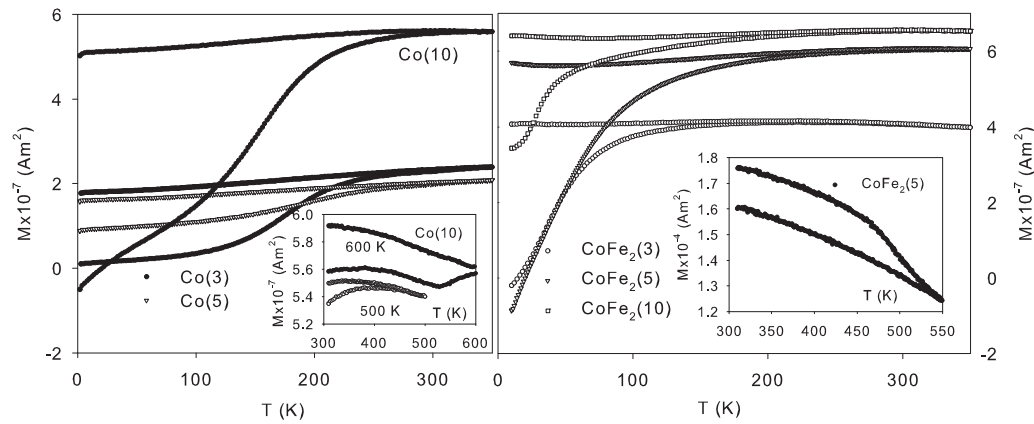


Fig. 4. The ZFC–FC curves for the Co(*x*) and CoFe₂(*x*) series of samples measured in 20 mT. The high temperature *M*(*T*) curves in the insets demonstrate sintering of NPs after heating the samples above 500 K, as is manifested by shift of *T*_{DIFF} to higher temperatures.

Table 2

Parameters of the layers obtained from the reflectivity curves refinement and the AFM. *a_c* is the critical angle, *t_N* and *t_M* are the nominal and mean thickness of the metal layer determined from the reflectivity curves refinement. The σ_q^{XRR} is the XRR rms roughness of upper layer, σ_q^{AFM} is the AFM rms roughness, calculated from the reflectivity curves and AFM topography data, respectively.

Sample	<i>a_c</i> (°)	<i>t_N</i> (nm)	<i>t_M</i> (nm)	σ_q^{XRR} (nm)	σ_q^{AFM} (nm)
Co(3)	0.25	3	3.7	1.9	1.3
Co(5)	0.25	5	5.5	1.3	1.4
Co(10)	0.26	10	11.4	1.4	1.5
Fe(3)	0.20	3	–	–	2.1
Fe(5)	0.26	5	5.4	0.8	1.3
Fe(10)	0.26	10	11.6	1.4	4.3
CoFe ₂ (3)	0.23	3	–	–	3.2
CoFe ₂ (5)	0.23	5	–	–	1.8
CoFe ₂ (10)	0.27	10	11.6	1.4	5.5

from the simulations of the measured reflectivity curves. It has been observed that ρ decreased with increasing distance from the substrate, which is consistent with the granular nature of individual layers. Results are summarized in Table 2 and Fig. 3.

3.2. Magnetic properties

Magnetic property measurements suggested that the metal layers are composed of the strongly interacting superparamagnetic-like NPs. The NP nature of the samples has been manifested by [17]: (1) zero hysteresis for the *M*(*B*) curves measured above blocking temperature (example in the inset of Fig. 5), (2) magnetic moment values, μ calculated from the unhysteretic magnetization isotherms in Langevin scaling in order of tens thousands of μ_B , with corresponding average magnetic size of NPs,¹ *d_m* reaching approximately 6–12 nm [23] (Table 3), which corresponds well with the grain size obtained from HRTEM images of the single layers. (3) Increase of the temperature of the ZFC curve maxima, *T*_{MAX} and the temperature of coincidence of the ZFC–FC curves labeled as *T*_{DIFF} with increasing layer thickness (due to the different NP sizes, Figs. 4 and 5 and Table 3) and their decrease with increasing magnetic field (example in the inset of Fig. 4).

Evidence of the strong interparticle interactions has been demonstrated by the (4) non-Curie–Weiss dependence of the FC curves and (5) strong saturation of the low temperature part of FC curves (Figs. 4 and 5).

¹ The unit cell parameters were used in the calculation, bcc for Fe(*x*) and fcc for Co(*x*) structures. The hcp structure has been used for the CoFe₂(*x*) sample, similar as for the Co, replacing the Co with Fe in desired ratio.

Table 3

Parameters of the layers obtained from the magnetic property measurements. *T*_{DIFF} is the furcation temperature, $\mu_0 H_C^{10}$ is the coercivity measured at 10 K, μ and *d_m* are the magnetic moment and the magnetic diameter of NPs, respectively, calculated from the un-hysteretic Langevin curves [34]. The unit cells have been considered as the BCC for Fe and HCP for the Co and CoFe₂ thin films.

Sample	<i>T</i> _{DIFF} (K)	$\mu_0 H_C^{10}$ (mT)	μ (μ_B)	<i>d_m</i> (nm)
Co(3)	335	133	75	7.0
Co(5)	340	120	47	6.1
Co(10)	>350	86	54	6.4
Fe(3)	260	22	63	8.8
Fe(5)	346	26	78	9.8
Fe(10)	441	16	155	11.8
CoFe ₂ (3)	314	110	45	5.8
CoFe ₂ (5)	>350	75	118	7.9
CoFe ₂ (10)	>350	69	131	8.2

Table 4

The *M_s* measured at 10 and 300 K, respectively

Sample	<i>M_s</i> ¹⁰ × 10 ^{−6} (Am ²)	<i>M_s</i> ³⁰⁰ × 10 ^{−6} (Am ²)
Co(3)	3.3	3.6
Co(5)	2.1	2.5
Co(10)	2.0	2.3
Fe(3)	1.7	1.8
Fe(5)	1.3	1.3
Fe(10)	3.8	3.9
CoFe ₂ (3)	4.6	5.0
CoFe ₂ (5)	6.3	6.5
CoFe ₂ (10)	6.5	6.7

The $\mu_0 H_C$ has been symmetric for both polarities of magnetic field for all samples series and decreases with increasing layer thickness, as has been observed for similar multilayers by Li and Wang [24]. Saturation magnetization, *M_s* of individual samples measured in 1 T slightly decreases with decreasing temperature (Table 4), which supports hypothesis that the low temperature magnetization rotation is connected with the specific internal grain arrangement.²

² The NPs in our samples are above or close to the *T_B* at room temperature (RT), thus their superspins rotates almost freely and are oriented in the direction of external magnetic field. If we now cool the sample down to the low temperature, the superspins are either oriented in the NP easy axis direction in non-interacting system of NPs or are pinned to the specific direction which is given by the internal arrangement of the layer for the interacting system. In both cases, stronger field is required for rotating all superspins into its direction. Because we have not increased external magnetic field during cooling, the *M_s* value at LT is lower than at RT. The superspins in a non-interacting system of NPs at low *T* point in the direction of the NP easy axis. Now if we cool down from RT the sample with switched interparticle

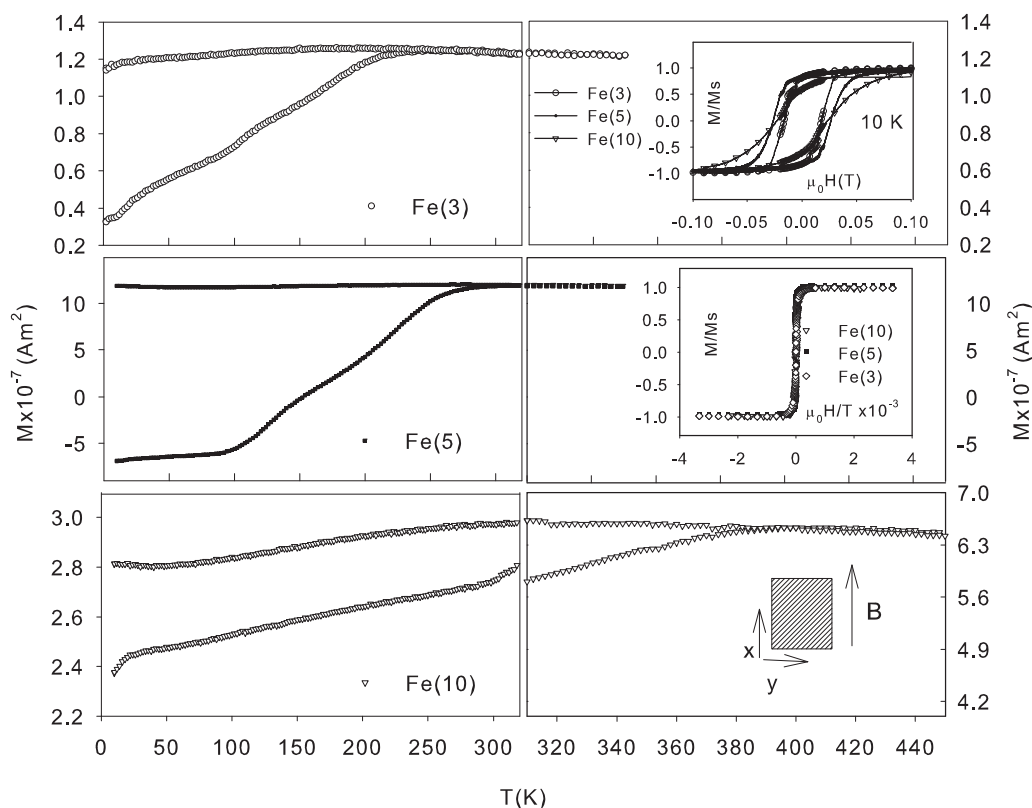


Fig. 5. The ZFC–FC curves for the Fe(*x*) series of samples measured in 20 mT. The *M*(*B*) curves measured at 10 K and the unhyseteric ones are in the insets. The sketch of the sample orientation with respect to the external field, in which the measurements on all samples has been performed, is on the bottom right.

The T_{MAX} , $\mu_0 H_C$ and μ were unchanged upon heating the samples up to 450 K, as has been demonstrated on the Co(*x*) and CoFe₂(*x*) series. NPs sintered after heating the samples above 500 K, as was manifested by the increase of the T_{DIFF} and the $\mu_0 H_C$ value (insets of Fig. 4).

3.3. Torque magnetometry

Measurements of Tq curves have demonstrated uniaxial magnetization nature of the samples in the whole temperature range. The torque extorted on the sample exhibiting the E_{uni} is written as [18]:

$$T = \frac{-dE}{d\theta} = K_u \sin 2\theta. \quad (3)$$

The experimental Tq curves of the M(10) samples measured at 300 and 200 K are plotted together with the low temperature curves in Fig. 6. Simulated theoretical Tq curves demonstrates that the uniaxial easy axis lies in plain at the temperatures above 200 K and is rotated at low temperatures, forming the different angles with respect to the film plane for each sample series – 150° for the Co(10), 140° for the Fe(10) and 40° for the CoFe₂(10) samples, respectively.

As has been introduced, total magnetic anisotropy could be simply viewed as the superposition of anisotropies of different origins, the SA and LPA in case of our multilayers. Thus the low temperature rotation of the easy axis could be explained by the suppression of

the SA,³ that is overcome by LPA (which is similar with the phenomenon observed in epitaxial layers in which the SA is overcome by MCA) [25–27].

Origin of the LPA which causes different orientations of the low temperature easy axis for each examined sample is following. The smooth and symmetric shape of the low temperature Tq curves could be either attributed to presence of the one single uniaxially magnetized phase, or several phases of the NPs with their easy axes rotated 90° with respect to each other, finally giving the signal of the uniaxially magnetized layer. As has been stated in the introduction, the orientation of the single phase uniaxial easy axis arises from the internal arrangement of the NPs within the individual layers. If there is the preferential fraction of the NPs with parallel easy axis, the rotation of remaining superspins to this preferential direction is mediated by the strong interparticle interactions and the layer becomes uniaxially magnetized. The origin of the effect has been discussed by Bushow and de Boer [7], when the NPs with sizes smaller than is the exchange length of exchange interactions between the NPs were forced to orient their magnetizations in parallel. It has been also shown on collection of interacting hematite NPs that not only the rotation of whole superspin, but also the rotation of selected sub-lattice magnetization out of the magnetic anisotropy direction is possible [28]. Thus the fact that the layer composed of the NPs could posses uniaxial easy axis at LT even if

interactions, superspins are pinned to the specific direction given by the internal arrangement of layer (Fig. 8) as is discussed and presented below.

³ Normally, K_{SA} of the layer is the temperature dependent term and decreases with decreasing temperature, not as in the former case. But as has been observed, differences of its values at high and low temperatures are not so significant, thus we could assign the temperature dependent superspin rotation to the origin of this effect.

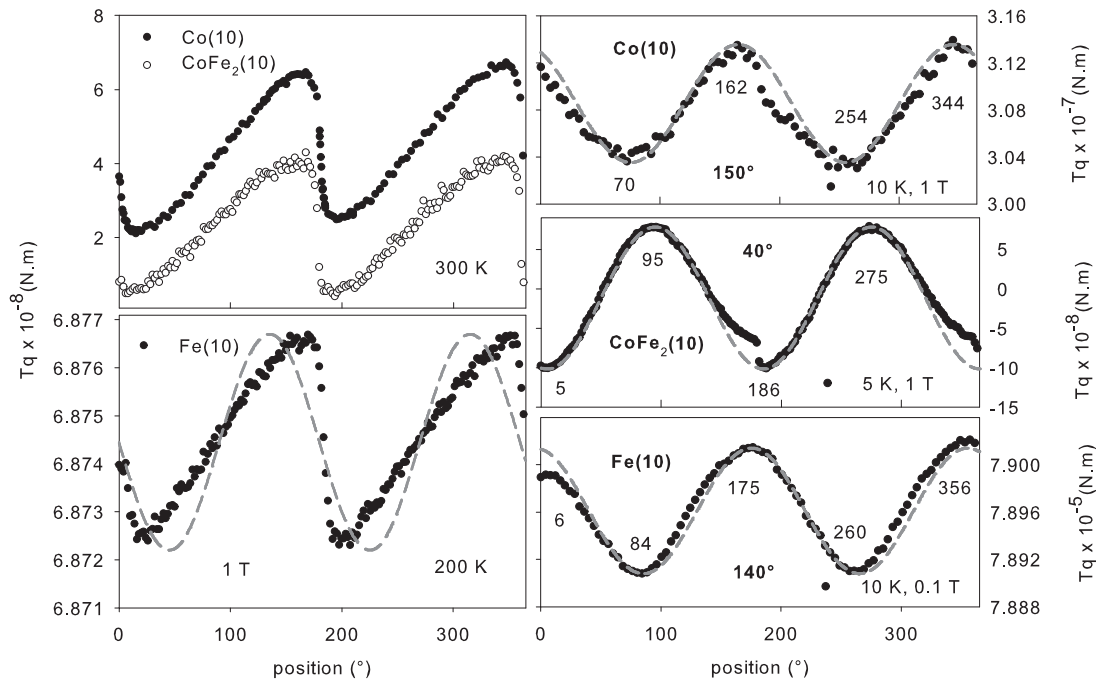


Fig. 6. Dependence of the torque on the angle of film orientation with respect to the applied field, measured in 1 T at high temperature (HT) and 1 and 0.1 T at low temperature (LT), respectively. Dashed curves represents ideal Tq curve for sample with given orientation of easy axis of magnetization, 180° for HT measurements (left) and 150°, 140° and 40° for the Co(10), Fe(10) and CoFe₂(10) samples at LT (right), respectively. Asymmetry of the curves is consequence of un-saturation of the film magnetization, as is explained by Cullity and Graham [18].

all single-particle easy axes are not oriented in the same direction is not surprising.

Let us discuss now the possible arrangement of the NPs in the layer possessing uniaxial easy axis, with respect to the SPA. As has been already mentioned, SPA either originates from the anisotropic NP shape or it is simply the MCA of single isotropic NP. If we have an individual phase composed of the NPs possessing unique direction of the uniaxial easy axis of magnetization and consider these two options, there is a major fraction of the NPs that are either all oriented in same direction (anisotropic NPs, Fig. 8 left) or to the direction given by the preferential texture of layer (isotropic NPs, Fig. 8 right). Direction of the easy axes of such unique fraction of NPs determines the easy axis of the whole layer, which could be extended into other layers via dipolar interactions and the total direction of the multilayer easy axis is the projection of the sum of single layer easy axes. The observed SSRT is thus not the consequence of the film thickness, like rotation of easy axis from in-plane to perpendicular direction with decreasing thickness, as has been observed in ultra-thin films, but it is the consequence of the intermediate size effect – arrangement of the anisotropic NPs or the layer texture. The problem of multiple texture or NP orientation could not be treated using only TqM data [18] and further experiments, such as the texture measurements or the neutron diffraction would be helpful.⁴

The last question is if the LT orientation of easy axis is elemental dependent (same elements would grow with the same texture or orientation of NPs, depending on the substrate properties and the average grain size), size dependent, result of random arrangement of the NPs within the layers or it is the combination of multiple

effects. The thickness (thus the NP size) dependence of the easy axis direction for the samples from one series has been tested only for the Fe(5) sample (the only one which had sufficiently high signal to evaluate the data). The asymmetric shape of the Tq curve (Fig. 7) indicates either the SA contribution is not suppressed by the LPA even at low temperature or there are more phases possessing uniaxial easy axes shifted with respect to each other. Reason for this could be the incomplete rotation of remaining superspins into the direction of easy axis of major fraction of NPs, arising from the size effect on NPs. A control experiment on the single layer of the Co10 films was unsatisfactory; signal was too poor to make any serious conclusions. Because neither the exact orientation of the individual NPs within the layer nor the texture of the layers is known, any further influence of NP size or layer thickness on the easy axis

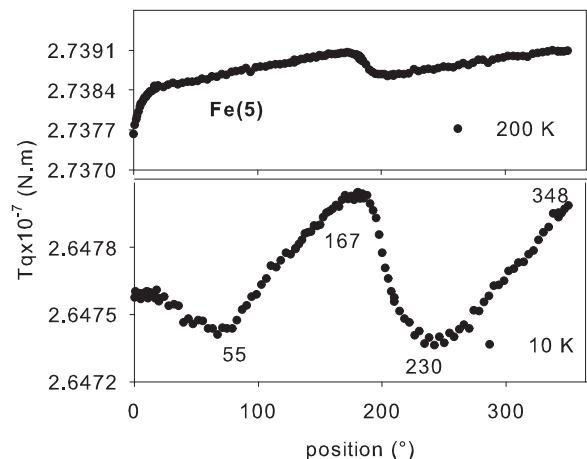


Fig. 7. The torque curve for the Fe(5) sample measured at 200 and 10 K, respectively.

⁴ Unfortunately, it was even impossible to perform the synchrotron X-ray diffraction due to the low signal quality, thus the samples are inappropriate for further examination and layers with much higher thickness of M layer should be prepared.

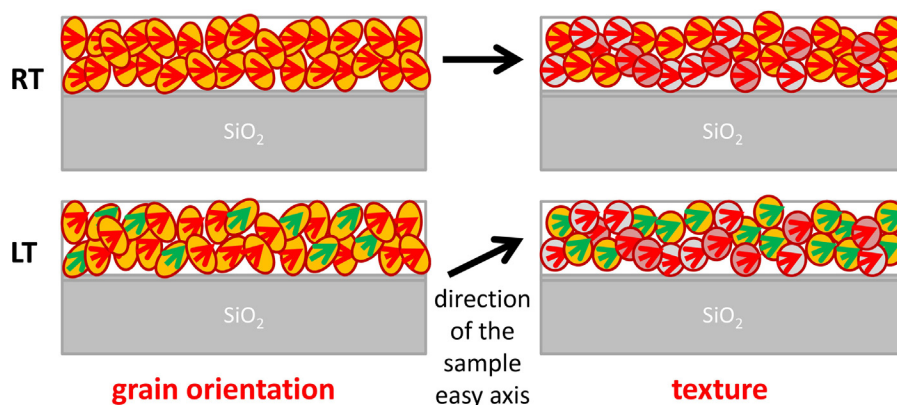


Fig. 8. The mechanism of the SSRT explained by internal arrangement of the NPs within the layers, demonstrated on the single layer for the simplicity. Left: the layer composed of the anisotropic NPs. The significant amount of NPs is oriented in the similar direction, as well as their easy axes if we consider that there are no interparticle interactions. Right: same example for the layer composed of isotropic NPs, with the preferential texture of the layer. Detail explanation of illustration and magnetization direction represented by the red and green arrows is following. At room temperature (RT), all superspins in the layer are allowed to rotate almost freely, which is the presumption of the SPM state, thus point in the direction of in-plane easy axis, as a result of the sample shape anisotropy. From the single particle point of view, superspins follow the direction of hard axis of NP in the extreme case, which is represented by red arrow (considering for simplification that no NP is oriented to have its easy axis parallel with the film plane). At low temperature (LT), neglecting action of interparticle interactions, each superspin is oriented in the direction of single NP easy axis (represented by the green arrow). Switching the interactions on, the fraction of NPs that are not oriented in parallel with the preferential fraction of NPs from the beginning revert their superspins into the direction which is parallel with such easy axis of the preferential fraction of NPs. Thus the layer could possess LT uniaxial magnetization direction both for the NPs with similar orientation or texture. (For interpretation of the references to color in the text, the reader is referred to the web version of the article.)

orientation could not be treated and just the general mechanism responsible for the LT easy axis orientation has been introduced.

4. Conclusion

We have observed temperature dependent rotation of the magnetization direction in the multilayer sandwiches of $\text{SiO}_2\text{--M}(x)\text{--Si}(111)$ with the M as the metal (Fe, Co or CoFe_2) of nominal thickness $x=3, 5$ and 10 nm, respectively. Sample series have been investigated by complementary methods such as TEM, XRR, AFM, MFM and magnetic property measurements. It has been demonstrated that the films are polycrystalline, composed of approximately $6\text{--}12$ nm large NPs obeying properties of strongly interacting SPM system. The NP size is increasing with the increasing layer thickness for each sample series. The multilayers possess room temperature in-plane uniaxial easy axis of magnetization. The rotation of the magnetization out of the film plane direction during the sample cooling has been observed. At temperatures below 50 K, the easy axis is oriented into the direction given by the internal particle arrangement, 150° for the $\text{Co}(10)$, 140° for $\text{Fe}(10)$ and 40° for the $\text{CoFe}_2(10)$ samples, respectively. The origin of the observed phenomena has been attributed to the superspin reorientation transition, when all superspins are pointing in the direction of the easy axis of major fraction of particles, that are either oriented in the same direction (for anisotropic particles) or with the preferential texture (for isotropic particles). Final orientation of the film easy axis and its uniaxiality is result of the strong interparticle interactions acting among particles, that rotate rest of superspins into the direction of easy axes of the major fraction of particles.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.japsusc.2013.10.147>.

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3.3.2 Magnetické částice v uhlíkových nanotubách

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Speciálním případem superparamagnetického chování jsou jednotěnné uhlíkové nanotuby (SWCNT, z ang. single-wall carbon nanotubes) připravených metodou depozice chemických par s využitím nanočástic železa jako katalyzátoru. Intrinsecké magnetické vlastnosti uhlíkových nanostruktur, zejména mechanismus vzniku spontánních magnetických momentů a jejich magnetické uspořádání, patří mezi atraktivní témata současného nanomagnetismu. Možnost magnetického uspořádání v SWCNT byla sice již teoreticky předpovězena, bohužel se ale zatím nikomu nepodařilo experimentálně prokázat existenci lokalizovaného magnetického momentu na atomech uhlíku. Hlavní překážkou je přítomnost (magnetického) kovového katalyzátoru jako rezidua přípravy pomocí CVD. Studie [39] ukázala na specifickou strukturu zbytkového katalyzátoru ve vzorcích nanotub. V současnosti je tedy kladen velký důraz na efektivní odstranění tohoto katalyzátoru a následné prokázání čistoty SWCNTs. Pomocí Mössbauerovy spektroskopie a difrakce synchrotronového záření bylo poprvé ukázáno, že původní nanočástice železa přecházejí během CVD na fázi Fe_3C . Průměr částic byl určen analýzou výsledků difrakce a činil 1.9 nm. Měřením teplotní závislosti magnetizace (protokol ZFC-FC), magnetizačních izoterm a střídavé susceptibility bylo pozorováno, že nanočástice zbytkového katalyzátoru vykazují vlastnosti slabě interagujícího souboru SPM částic, což dokázalo velmi nízkou koncentraci katalyzátoru ve vzorku. Analýza magnetizačních izoterm poskytla informaci o distribuci velikostí nanočástic a jejich magnetickou velikost. Na základě získaných výsledků bylo možno usoudit, že částice katalyzátoru tvoří tzv. strukturu jádro-slupky ve smyslu magnetického a strukturního uspořádání. V případě čištěných vzorků došlo k částečnému sintrování a v případě vysokoteplotního žíhání rekrystalizaci nanočástic a odstranění neuspořádané slupky. Vzhledem k velmi malému množství katalyzátoru ve vzorcích byla magnetická měření jedinou metodikou jak určit reálnou strukturu zbytkových částic katalyzátoru a optimalizovat purifikační metody, jak je shrnuto v práci [98].

Navazující práce se zabývá studiem fázového složení a magnetické odezvy SWCNT, které podstoupily různé purifikační postupy. Žíhání SWCNT na 400 °C a následný reflux ve slabě kyselém prostředí vedl k vzniku 10-18 nm nanočástic $\alpha\text{-Fe}_2\text{O}_3$, přičemž po následné filtraci zbyly ve vzorku pouze největší z nich. Žíhání SWCNT při 1000 °C vedlo ke snížení množství

katalyzátoru o 10 %, frakce zbylých nanočástic se transformovala na γ -Fe₂O₃ a jejich obsah v původním vzorku se zmenšil díky odstranění paramagnetické slupky. Pouze SWCNT vystavené teplotě 2200 °C nevykazovaly při makroskopických měřeních přítomnost katalyzátoru (synchrotronová prášková difrakce, termogravimetrie, magnetometrie), měřením absorpce na Fe-K hraně pomocí metody EXAFS (z angl. Edge X-ray Absorption Fine Structure) byla ale potvrzena přítomnost zbytkového Fe ve formě α -Fe₂O₃. Bylo tedy ukázáno, že makroskopické metody standardně používané pro charakterizaci nanotub zbavených katalyzátoru nejsou dostačující pro prokázání jejich čistoty a možná přítomnost zbytkového katalyzátoru musí být ověřena lokálně sensitivní sondou (např. EXAFS).

Výše uvedené postupy byly v letošním roce dále aplikovány pro studium nanotub připravených laserovou ablací. Vzorky, které obsahovaly nejmenší množství magnetického katalyzátoru byly vhodné pro studium pomocí Ramanské spektroskopie v magnetickém poli, které ukázalo na přítomnost magneto-oscilační složky v intenzitě charakteristických módů, podobně jako u grafenu.

Magnetic Properties of Iron Catalyst Particles in HiPco Single Wall Carbon Nanotubes

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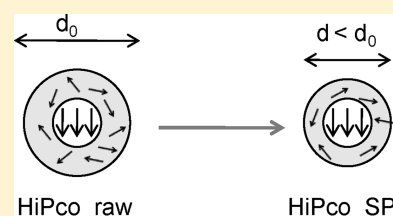
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ABSTRACT: We have investigated the magnetic response of residual metal catalyst in the raw and super purified HiPco single wall carbon nanotubes (HiPco_raw and HiPco_SP SWCNTs). It has been shown that the residual metal catalyst is in the form of nanoparticles, even in the HiPco_SP SWCNTs that should contain a minimal amount of the metal. Mössbauer spectroscopy of the HiPco_raw SWCNTs proved the catalyst nanoparticles are in the form of Fe₃C. Analysis of the synchrotron X-ray diffraction data provided an average diameter of nanoparticles about 1.9 nm. Magnetic studies by means of temperature dependence of magnetization, magnetization isotherms and susceptibility suggested that the nanoparticles obey the behavior of weakly interacting superparamagnetic systems in both samples. Further analysis of the data revealed a core–shell structure of the nanoparticles in the HiPco_raw nanotubes, with a magnetically oriented core and a paramagnetic shell, which is almost removed in the case of the HiPco_SP catalyst nanoparticles.



1. INTRODUCTION

Because the magnetism and superconductivity of the pure carbon materials has been theoretically predicted and already observed in special cases (magnetic ordering in the proton-irradiated graphite,¹ pressure induced magnetism in fullerenes²), the possibility to study and utilize the magnetic response of carbon nanotubes (CNTs) for further applications in spintronics has appeared recently.

The CNTs could possess not only the semiconducting and metallic properties,³ depending on their chirality, but it has been also proven theoretically that the metallic CNTs could exhibit a ferromagnetic ground state.^{4,5} In spite of these studies discussing the defect-induced magnetism in CNTs, this phenomenon has not been experimentally observed yet. It is mainly because of the presence of the residual metal catalyst in the nanotubes and its very difficult removal. Because of the great interest in many research areas, we have focused on studies of the basic properties of nanosystems composed both of the single wall carbon nanotubes (SWCNTs) and metallic nanoparticles (residues of the preparation of SWCNTs).

One of the preparation methods of the SWCNTs in large quantities is the so-called HiPco process; the metal catalyst (Fe, Co, Ni) based growth of CNTs by the gas phase chemical vapor deposition (CVD).^{6–8} To obtain the pure CNTs, the metal has to be removed afterward. Unfortunately, most of the purification methods do not lead to complete removal of the remaining metal catalyst,^{9–15} and if so, there are only a few studies that

significantly analyze the purity of CNTs.¹⁶ However, to determine the mass content of the metallic fraction in the SWCNTs is not sufficient, it is important to investigate the form in which the metal is presented. If the metal is in the form of nanoparticles (not just single atoms or clusters distributed within the sample), the impurity-induced magnetism exceeds the signal from the pure CNTs in several orders of magnitude, even if the proportional amount of the metal in the sample is low, and it disables reliable studies of magnetic properties of CNTs. The amount and nature of the catalyst can be determined complementarily via magnetic measurements but as a reference, magnetic properties of the catalyst in raw SWCNTs have to be investigated in detail. Despite few reports on magnetic properties of the SWCNTs containing magnetic catalyst (discussing magnetic hysteresis and susceptibility qualitatively^{16,17}), the comprehensive quantitative studies concerning the magnetism of the catalytic particles are still lacking. Because of that, we have focused on investigation of magnetic properties of the metal catalyst in the raw and superpurified HiPco SWCNTs purchased by Unidym Inc. It has been proven that both samples contain magnetic nanoparticles, the magnetic behavior has been discussed in the terms of the superparamagnetism (SPM) phenomenon.

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The superparamagnetic state is defined for a system of non-interacting single domain nanoparticles, whose susceptibility follows the Curie law and its magnetization curve can be described by the Langevin function.^{18,19} The critical size of a single domain nanoparticle is determined by microstructural parameters of the material (atomic composition and crystallographic structure) and reaches the size of 10^{-8} – 10^{-9} m. The characteristic parameters that define the SPM state are the blocking temperature T_B , particle magnetization (the so-called superspin) μ and magnetocrystalline anisotropy, E_A . The T_B , analogy of the Curie temperature T_C in a ferromagnet, is the blocking temperature of the superspins, when the particles anisotropy energy E_A is overcome by the energy of thermal fluctuations and particles get into the blocked state, in which the stable magnetization cannot be established.

The magnetic state of nanoparticles in the blocked state (below the T_B) is characterized by a nonzero coercivity, H_C .²⁰ Considering a real sample, the pure superparamagnetism has been observed so far in very diluted samples, such as in ferrofluids with low density or nanoparticles diluted in a nonmagnetic matrix.^{21–24} In most of the real systems, when the particles are close enough, considerable interparticle interactions (mainly of dipolar origin) that affect the macroscopic magnetic properties, has to be taken into account.^{21,25} Because the catalyst particles in the HiPco nanotubes are supposed to be diluted enough, we expected them to obey either the SPM or weakly interacting SPM behavior.

2. EXPERIMENTAL METHODS

2.1. Sample Characterization and Measurement of Magnetic Properties. The samples have been characterized by several methods to gain comprehensive amount of data enabling analyzing properties of the metal catalyst properly.

Thermogravimetry (TG) has been used for setting the mass content of the metal precursor in the SWCNTs. The samples were heated up to the 800 °C with the heating rate of 10 K/min in atmosphere containing 80% of He and 20% of O₂.

We have used complementary methods for the phase analysis and particle size determination, respectively. The synchrotron radiation diffraction (S-XRD) was used for the determination of the catalyst phase and for estimation of the mean diameter of the particle size, respectively. The diffraction data has been taken at PDFIF beamline in ANKA Karlsruhe, using the radiation with wavelength of 1.24 Å. The diffraction patterns were collected within the range of 3–63° with the step of 0.02°. Further analyses have been done using the FullProf software.²⁶

The Mössbauer spectra were employed as a complementary experiment to determine the iron phase(s) in the sample. The measurement was done in the transmission mode with ⁵⁷Co diffused into the Rh matrix as the source moving with constant acceleration. The spectrometer was calibrated by means of a standard α -Fe foil and the isomer shift was expressed with respect to this standard at 293 K. The HiPco_raw sample (by Unidym Inc.) was measured in cryostat at the temperatures varying from 293 to 4.2 K. The fitting of the spectra was performed with the help of the NORMOS program. The HiPco_SP sample (by Unidym Inc.) seems to be not suitable for the experiment because of the undetectable amount of the metal catalyst.

Magnetic measurements on HiPco nanotubes were performed using MPMS7-SQUID device (Quantum Design) up to magnetic field of 7 T in the temperature range 2–400 K. The

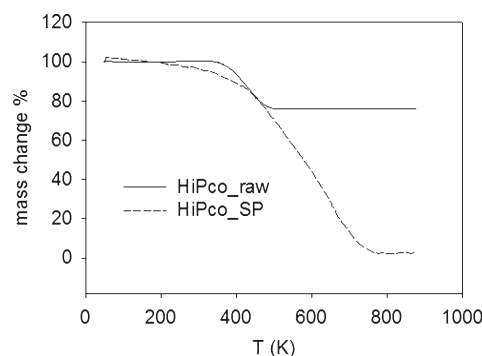


Figure 1. Thermogravimetry data for the HiPco_raw and the HiPco_SP samples.

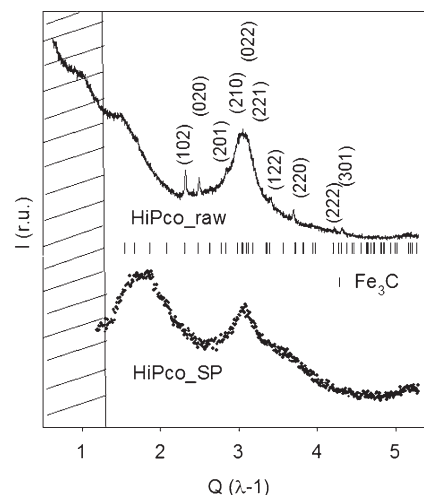


Figure 2. S-XRD patterns for the HiPco_raw and the HiPco_SP SWCNTs. The vertical marks correspond to the positions of the Fe₃C Bragg reflections, the cross-hatched area illustrates expected positions of the SWCNTs reflections.

zero-field-cooled (ZFC) and field-cooled (FC) curves were measured in low external magnetic fields (from 5 to 50 mT). The magnetization isotherms were measured at 10 and 300 K up to field of 7 T in both polarities. The temperature dependence of the a.c. susceptibility (with the alternating field amplitude of 3 mT) was measured in a zero magnetic field (1–100 mT) in the frequency range of 0.1–100 Hz.

3. RESULTS AND DISCUSSION

3.1. Analysis of Compound and Structure. The thermogravimetry provided the mass content of metal precursor in the samples leading to the values of 75 wt % for the HiPco_raw and 5 wt % for the HiPco_SP SWCNTs (Figure 1). The weight percentage set by the producer should be less than 35 and 5 wt % in the HiPco_raw and HiPco_SP SWCNTs, the measured discrepancy is the result of the small starting mass of the sample, with the possibly higher local concentration of metal in such a sample than is the average for the higher amounts.

The S-XRD pattern of the HiPco_raw SWCNTs reveals the peak positions corresponding to those of the cementite, Fe₃C (Figure 2), which crystallizes in the orthorhombic *Pnma* space group with the four units in the unit cell (*Z* = 4).²⁷ Eight of the

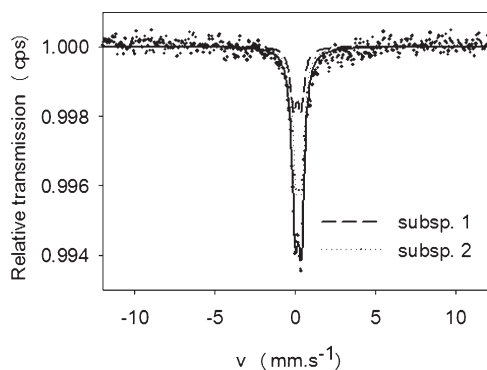


Figure 3. Fit of the Mössbauer spectra measured at room temperature by the two subspectra, representing the two special positions of iron in Fe_3C .

Table 1. Room Temperature Mössbauer Parameters. Isomer Shift δ , Quadrupole Splitting ΔE_q , Full Width in the Half Maxima FWHM, Together with the Real Area Under the Peak and the Interpretation of Simulated Spectra

	δ (mm/s)	ΔE_q (mm/s)	fwhm (mm/s)	rel. area (%)	interpr.
HiPco_raw					
subsp. 1	0.14	0.47	0.46	33.3	F_s (4c)
subsp. 2	0.21	−0.35	0.45	66.7	F_g (8d)

iron atoms are in 8d positions (F_g), four are placed in 4c positions (F_s), and the four carbon atoms sit in the interstitials. Because the quality of the diffraction pattern has not been suitable for the full profile fitting procedure by the Rietveld method, the mean size of the Fe_3C particles was calculated from the (102) and (201) reflections, leading to the value of 1.9 nm, considering the resolution function.

The quality of the data collected for the HiPco_SP SWCNTs has not been suitable for further analysis of the particle diameter, only the highest peak created by broadening of significant Fe_3C peaks similar to the HiPco_raw SWCNTs was observed (Figure 2).

The Mössbauer spectroscopy confirmed the presence of Fe_3C -cementite phase in the HiPco_raw sample. No metal iron (zero isomer shift) has been detected. The room temperature spectrum consists of doublet indicating the superparamagnetic state of the sample that can be attributed to the small size of Fe_3C particles in nanotubes. The spectrum was fitted with two doublets representing the two types of sites for iron atoms – the general (F_g) and special (F_s) sites (Figure 3). The intensities of lines were fixed up to 2:1. The obtained parameters are in good agreement with those presented by other authors.^{28,29} The results are summarized in Table 1.

3.2. Magnetization Studies and Hysteresis. The ZFC and FC curves (Figure 4) exhibit the main attributes of the superparamagnetic (SPM) system in case of both samples. The ZFC curve exhibits sharp maximum at the temperature T_{MAX} and both the ZFC and FC curves coincide at high temperatures – the temperature of deviation is labeled as T_{DIFF} . The discrepancy between T_{MAX} and T_{DIFF} , that should be equal in the ideal case of a SPM system, usually signals the particle size distribution in the sample. Thus, the majority of particles are blocked at the T_B corresponding to T_{MAX} (35 K at 10 mT in case of the HiPco_raw and 26 K at 10 mT for the HiPco_SP samples, respectively),

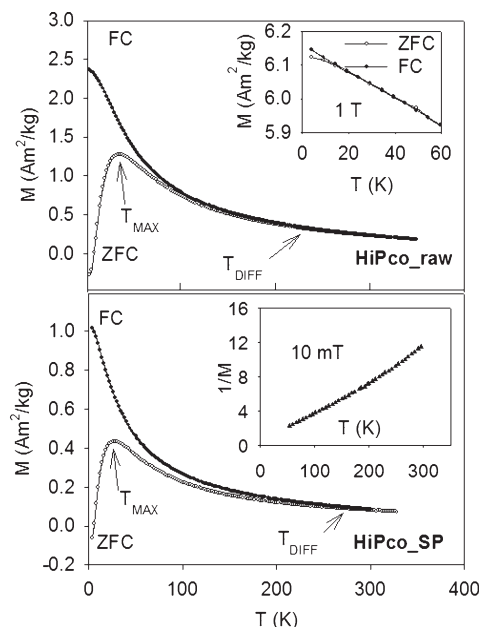


Figure 4. Temperature dependence of ZFC and FC magnetization measured at 10 mT for the HiPco_raw and the HiPco_SP samples, respectively. The magnetization measured at 1 T and the inverse dependence of magnetization as the function of temperature are shown in the insets.

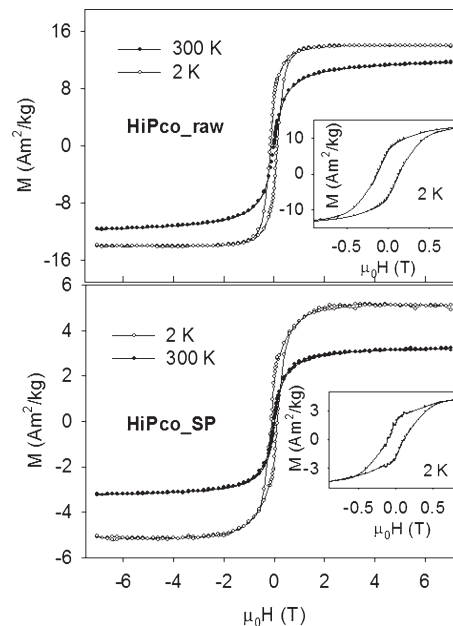


Figure 5. Magnetization isotherms measured at different temperatures for the HiPco_raw and the HiPco_SP samples, respectively. The detail of the loops measured at 2 K in the inset.

whereas the largest particles are blocked at temperature T_{DIFF} (202 K for the HiPco_raw and 278 K for the HiPco_SP samples, respectively). Also, the reduction of the T_B in increasing magnetic field, typical for such a system, has been observed (inset in Figure 4). Shift of the T_{MAX} to the lower temperature in case of the HiPco_SP sample could be attributed to the reduction of particle size or weakening of interparticle interactions.

Table 2. Median, μ_0 , and Mean, μ_m , Magnetic Moment with the Median, d_0 , and Mean, d_m , Magnetic Diameters, Respectively; Compared with Particle Diameters Obtained from XRD Measurements, d_{RTG} , and Blocking Temperatures, d_{TDIFF} and d_{TMAX}

	$\mu_0 \times 10^3$ (μ_B)	d_0 (nm)	σ	$\mu_m \times 10^3$ (μ_B)	d_m (nm)	d_{TMAX} (nm)	d_{TDIFF} (nm)	d_{RTG} (nm)
HiPco_raw	1.3 (2)	2.6 ± 0.8	0.59	0.9 (2)	2.4 ± 0.3	2.4 ± 0.4	4.3 ± 0.5	1.9 ± 0.2
HiPco_SP	2.0 (2)	3.0 ± 0.7	0.58	1.5 (2)	2.7 ± 0.3	2.2 ± 0.5	4.7 ± 0.7	

Inspecting the low temperature part of the FC curve of the HiPco_raw SWCNTs, the small saturation of the magnetization was observed, signaling the presence of weak interparticle interactions. Saturation of the FC curve of the HiPco_SP sample is negligible, which is not surprising because the amount of magnetic metal is at least six times lower than in case of the HiPco_raw sample, suggesting better dilution of particles within the sample leading to the minimization of interparticle interactions. In an ideal case of a SPM system without interaction, the FC curve should obey the Curie–Weiss law. Thus, plotting the temperature dependence of inverse magnetization (result for HiPco_SP is illustrated in the Figure 4), the resulting curve should be linear. The nonlinearity of such a curve was observed for both samples, as a consequence either of interparticle interactions (more significant for the HiPco_raw sample), particle size distribution (HiPco_SP sample), or combination of both of these effects. To estimate the strength of the interparticle interactions, the magnetic response has been examined by a.c. susceptibility measurements, as mentioned further.

The magnetization isotherms provided additional information about nature of magnetic nanoparticles in both samples. The hysteresis (typical feature of the block state below the T_B) was observed at 2 K with the symmetric values of coercivity, H_C , for opposite polarities of magnetic field, reaching values of 150 mT for the HiPco_raw and 102 mT for the HiPco_SP samples, respectively (Figure 5). The decrease of the coercivity points at the reduction of the nanoparticle size or interparticle interactions in the HiPco_SP sample.

The magnetization isotherms above the T_B were analyzed by using the fit of generalized Langevin function. The total magnetization, M , of the SPM system can be described by equation valid for system of monodispersed noninteracting nanoparticles:

$$M = M_s L(x) \quad x = \frac{\mu B}{k_B T} \quad (1)$$

where M_s is the saturated magnetization of N particles with the magnetic moment μ and $L(x)$ is the Langevin function. In real systems with non-negligible dispersion of magnetic moments, $f(\mu)$ the total magnetization is given by a weighted sum of Langevin functions²⁵

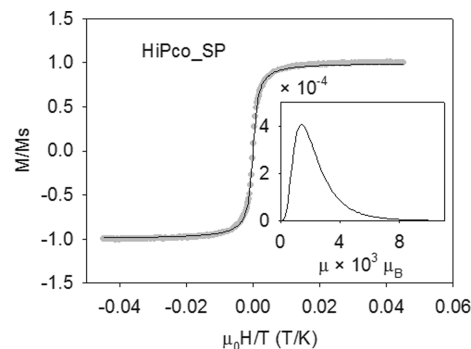
$$M(H, T) = \int_0^\infty L(\mu) M_s = \int_0^\infty \mu L\left(\frac{\mu H}{k_B T}\right) f(\mu) d\mu \quad (2)$$

with the distribution function

$$f(\mu) = \frac{N}{\sqrt{2\pi}} \exp\left(\frac{-\ln^2(\mu/\mu_0)}{2\sigma^2}\right) \quad (3)$$

where σ is the log-normal distribution width and μ_0 is the median of the distribution from which the average magnetic moment μ_m can be calculated as

$$\mu_m = \mu_0 \exp\left(\frac{-\sigma^2}{2}\right) \quad (4)$$

**Figure 6.** Example of the fit of the weight sum of the Langevin function to the data at 300 K in Langevin scaling for the HiPco_SP sample, the moment distribution function in the inset.

The parameters obtained from the fitting to the weighted sum of Langevin functions to the unhysteretic magnetization curves measured at 300 K are summarized in Table 2 and illustrated in the Figure 6.

Knowing both the magnetic moment of the particle and that of the unit cell, it is possible to calculate the volume and subsequently the “magnetic” size of the particle. The magnetic moments of the Fe_g and Fe_s atoms calculated by Shine, Medvedeva, and Ivanovski²⁷ are 1.74, 1.98 μ_B , respectively; with the total magnetic moment of the Fe_3C unit cell, μ_c , equal to 21.6 μ_B . Thus, using the equations

$$d = 2\sqrt[3]{\frac{3V}{4\pi}} = \frac{\mu_c}{\mu} V_c \quad (5)$$

where μ_c and V_c are the magnetic moment and volume of the unit cell, respectively; the value of median and mean magnetic diameters of the particle, d_0 and d_m can be calculated. Resulting values for the HiPco_raw and the HiPco_SP samples are depicted in Table 2.

It is obvious that the “magnetic size” of the particle in the HiPco_raw sample is larger than the size of the particle calculated from the diffraction pattern. The discrepancy could be explained by the so-called core–shell model of the particle with the well-crystalline and magnetically ordered core (which contributes to the diffraction) and an amorphous shell, which only increases magnetic moment of the particle by a linear, paramagnetic-like term. Increase of the “magnetic size” of the nanoparticles of the HiPco_SP sample in comparison to the HiPco_raw sample could be either the result of the real increase of particle size in the HiPco_SP sample or more probably it means that the shell part of the particles in the HiPco_raw sample (which decreases the resulting magnetic moment) has been removed. This explanation is valid whether the part of the shell of the HiPco_raw nanoparticles is not only amorphous, but also paramagnetic.³⁰ This presumption could be simply proved considering the extreme cases in which the metal nanoparticles in the HiPco_SP

sample could differ from those in the HiPco_raw sample (Figure 7): (1) possible recrystallization of the amorphous paramagnetic shell, conserving the size of the particle (which lead to the increase of coercivity, H_C), (2) sintering of particles with the unchanged core–shell structure (increases H_C), and (3) removal of the part of paramagnetic shell with unattached crystalline core (decreases H_C and increases magnetic moment of the particle). Comparison of the shape of the unhysteretic magnetization isotherms measured for both samples (Figure 6) exhibit the presence of linear paramagnetic contribution only in the case of the HiPco_raw sample and support the idea that the

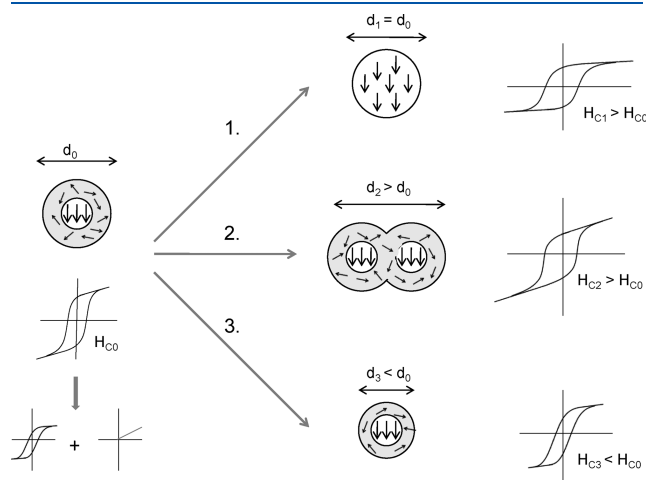


Figure 7. Scheme of the structure of nanoparticles and the model of hysteresis loops of collections of such particles below T_B for the HiPco_raw (left) and the HiPco_SP (right) samples. There are three extreme cases how the structure of NPs changes after the process resulting into the HiPco_SP SWCNTs: (1) The recrystallization of whole particle, (2) Particle sintering without change of the core–shell structure, (3) Removal of part of the amorphous paramagnetic shell.

real particle size in the HiPco_SP sample has been reduced, but the “magnetic size” has been effectively enhanced. All previously mentioned together with the decrease of coercivity in the HiPco_SP sample suggests the exclusive explanation of observed phenomena is the reduction of paramagnetic shell of nanoparticles in the HiPco_SP with respect to the HiPco_raw sample.

3.3. Relaxation Phenomena. Relaxation phenomena in both samples were inspected using a.c. susceptibility measurements. Both the real (χ') and the imaginary (χ'') parts of the a.c. susceptibility were measured in different frequencies of the alternating magnetic field with the amplitude of 3 mT in zero external field (Figure 8).

The shifts of the χ' maxima to the higher temperatures with increasing frequencies are considered as a consequence of a super spin relaxation. Because the saturation of the FC curve at low temperature suggested the presence of weak interparticle interactions in both samples, more significant for the HiPco_raw sample, the evolution of temperature of χ' maxima with frequency was inspected using the Vogel-Fulcher law describing the relaxation among the weakly interacting particles,

$$\ln f = \ln f_0 - \frac{E_A}{k_B(T - T_0)} \quad (6)$$

where the characteristic parameters are frequency f_0 , activation energy E_A/k_B , and Vogel-Fulcher temperature T_0 that is the correction of the well-known Arrhenius–Nell law representing the interparticles interaction.³¹ The resulting values for the HiPco_raw sample are: the relaxation time $\tau_0 = 1.8 \times 10^{-10}$ s, the effective anisotropy constant $K_{\text{eff}} = 1.69 \times 10^6$ J/m³, obeying relation $E_A = K_{\text{eff}} \cdot V$, and Vogel-Fulcher temperature $T_0 = 15$ K. The value of the K_{eff} is higher than that for the 7 nm Fe₃C particles measured by Zhang and Yu,³² 3.54×10^5 J/m³; the value of relaxation time, τ_0 lies in the interval typical for SPM systems, 10^{-9} – 10^{-12} s.^{33–35} The value of the K_{eff} was calculated using the resulting anisotropy energy E_A and the particle size,

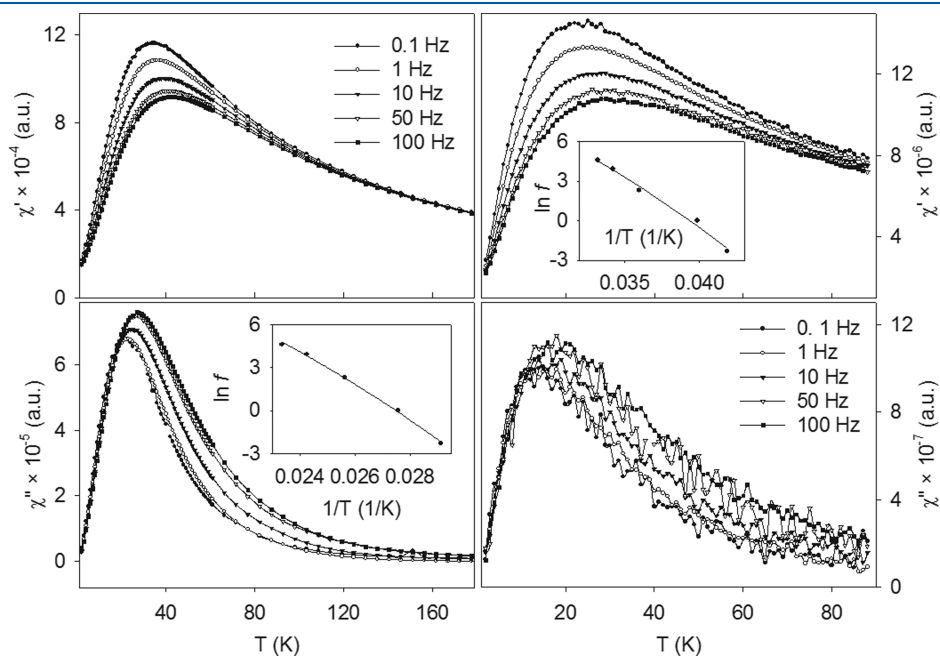


Figure 8. Temperature dependence of the real and imaginary part of susceptibility, χ' and χ'' in zero external field, the inset shows the fit according to the V–F law.

d_{RTG} . Applying the same procedure to the HiPco_SP sample, resulting value of relaxation time is $\tau_0 = 5.4 \times 10^{-11}$ s, which is lower than that of the HiPco_raw sample that confirms the faster relaxation of superspins, as was expected due to the lower concentration of particles in the HiPco_SP sample (it has been demonstrated by Dormann et al.²¹ that with increasing concentration of particles, the strength of the interparticle interactions also increases, which results to prolongation of relaxation time in the system). The value of the anisotropy energy E_A/k_B decreased from 435 K for the HiPco_raw to 429 K for the HiPco_SP samples, respectively. The effective anisotropy constant has not been calculated because the particle size in HiPco_SP sample was not possible to be determined by S-XRD.

Using the formula valid for a system of uniform noninteracting superparamagnets,²⁵ $T_B = K_{\text{eff}}V/25k_B$, the estimation of the nanoparticle mean diameter, d , could be obtained. As the T_B , we have used both the T_{MAX} and T_{DIFF} to obtain the diameters of the mean, $d_{T_{\text{MAX}}}$, and largest, $d_{T_{\text{DIFF}}}$, fraction of particles in the sample, leading to the values of 2.4 and 4.3 nm for the HiPco_raw and 2.2 and 4.7 nm for the HiPco_SP samples, respectively (K_{eff} of the nanoparticles in the HiPco_raw samples has been used in both cases). Decrease of the size $d_{T_{\text{MAX}}}$ in the HiPco_SP sample either additionally supports the presumption of the reduction of particle size by removal of paramagnetic shell and it is the result of reduction of interparticle interactions.

4. CONCLUSION

We have investigated structural and magnetic properties of the residual Fe catalyst in the HiPco_raw and the HiPco_SP (superpurified) SWCNTs, respectively. The S-XRD and Mössbauer spectroscopy confirmed presence of Fe in the HiPco_raw SWCNTs, most in the form of cementite, Fe_3C . Size of the nanoparticles in the HiPco_raw sample was determined from the S-XRD, leading to the mean diameter value equal to 1.9 nm. The magnetic measurements proved the metal particles in HiPco_raw sample obey presumption of the weakly-interacting SPM system, with the blocking temperature of the mean fraction of particles at 35 K. The mean magnetic moment and “magnetic” diameter of particles were determined as $0.9 \times 10^3 \mu_B$ and 2.4 nm, respectively. Results pointed at the core–shell structure of the particles, with the amorphous paramagnetic shell and the crystalline core. Advanced studies of relaxation in the systems done via a.c. susceptibility measurements provided the values of the characteristic relaxation time typical for SPM systems, $\tau_0 = 1.8 \times 10^{-10}$ s and effective anisotropy constant, $K_{\text{eff}} = 1.69 \times 10^6 \text{ J/m}^3$.

Even if the HiPco_SP sample should contain less than 5 wt % of metal, as it has been demonstrated, this metal is also in the form of weakly interacting SPM nanoparticles with the blocking temperature at 26 K, pointing either at the decrease of particle size with respect to the HiPco_raw sample or reduction of interparticle interactions. The increase of mean magnetic moment and “magnetic” diameter of particles that were determined as $1.5 \times 10^3 \mu_B$ and 2.7 nm together with the decrease of coercivity and reduction of linear paramagnetic part in magnetization isotherms measured at 300 K finally confirmed the decrease of particles size due to the removal of paramagnetic shell. Studies of the relaxation phenomenon result in decrease of relaxation time to $\tau_0 = 5.4 \times 10^{-11}$ s, which suggested better dilution and lower concentration of particles within the sample in comparison with the HiPco_raw SWCNTs. Besides that, it has

been demonstrated that HiPco_SP SWCNTs are not suitable for reliable studies of CNTs magnetism because further removal of metal catalyst particles is required.

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Structure and magnetic response of a residual metal catalyst in highly purified single walled carbon nanotubes

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This article presents methods for detailed physical analysis of partial steps leading to the removal of residual metal catalyst nanoparticles (NPs) from single walled carbon nanotubes (SWCNTs) and options for detecting negligible amounts of metal in samples possessing diamagnetic response. Based on the previous knowledge of the composition, structure and magnetic properties of NPs included in the commercial HiPco_raw and HiPco_SP SWCNTs, the properties of remaining NPs after the multi-step purification (oxidation followed by mild acid treatment) and annealing both under static and dynamic vacuum have been investigated. Thermogravimetry, X-ray diffraction, static and dynamic magnetic property measurements and the Extended X-ray Absorption Fine Structure (EXAFS) experiments have been performed. The data provide information about the nature of the residual NPs in purified SWCNTs, which is crucial for further understanding of the purification processes and their improvement. It has been demonstrated that even if all macroscopic methods indicate a high purity of the treated sample, a non-negligible amount of the metal may still be present and the metal content has to be examined using local and element sensitive probes such as EXAFS.

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1 Introduction

Formation of the ferromagnetic ordering in carbon nanotubes^{1,2} (CNTs) and other carbon-based materials such as graphene and their usage in spintronic devices led to huge efforts being devoted to the preparation of the highly pure material without the presence of magnetic metal.^{3,4} However, a lot of CNT preparation methods are based on the CVD growth on the metal containing (Fe, Ni) nanoparticles, NPs.⁵ Removal of residual metal from CNTs is highly important and many reports concerning the chemical and physical methods of purification have been published in the last decade.^{6–10} The determination of the purity of CNTs is usually supported by the methods such as Transmission Electron Microscopy (TEM), Thermogravimetry (TGA) and spectroscopic methods: Raman and Ultraviolet Visible

(UV-VIS) spectroscopies and^{11,12} Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).^{13,14} There are also a few studies highlighting the necessity of magnetic measurements (dc magnetization, ac susceptibility) in order to properly examine the purified CNTs.¹⁵ Our purpose is to demonstrate that even if all of the macroscopic methods point at high purity of treated CNTs, a non-negligible amount of the metal is still present and more reliable processes of characterization have to be used. We also perform the characterization of the purification processes step by step to determine the nature of remaining metal after exposure of CNTs to treatment.

If one is wondering theoretically about capturing the magnetic response of the intrinsic or induced magnetic moments in CNTs that are in the order of tenths of Bohr magnetons,² μ_B , this could be suppressed by the signal of sole magnetic atoms (single μ_B), magnetic clusters (tens of μ_B) or even totally screened out by magnetic NPs (thousands of μ_B). If the purification process is not entirely successful and some amount of catalyst still remains, knowledge of the structure of metal NPs in the treated sample provides information crucial for enhancement of further processes of purification and leads to the higher purity of CNTs. The magnetic response of the metal precursor in the untreated SWCNTs,¹⁶ which is in the

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form of the non-interacting single domain magnetic particles in the order of 10^{-8} – 10^{-9} m,¹⁷ is described by the theory of superparamagnetism, SPM. The characteristic parameters that define the SPM state are the blocking temperature, T_B , particle magnetic moment (the so-called superspin), μ , and magneto-crystalline anisotropy, E_A . The blocking temperature, T_B , is determined from the particle volume, V :

$$T_B = K_{\text{eff}} V / (25 k_B), \quad (1)$$

where k_B is the Boltzmann constant and K_{eff} is the effective anisotropy constant. The behavior of real systems of magnetic NPs differs from the SPM model and additional effects have to be considered, namely: (1) the interparticle interactions and (2) the particle size distribution. The interparticle interactions influence the blocking of particles, which is not independent on the local environment and is not controlled only by the particle size together with the K_{eff} of individual particles, as in the SPM case. Depending on the strength of the interactions, behavior of such a system is described by different models that distinguish between weakly and strongly interacting systems.¹⁷ The interactions in the weakly interacting systems are introduced in the form of the additional variable and modified relaxations of particles are described by the Vogel–Fulcher law:¹⁸

$$\tau = \tau_0 \exp(E_a / (k_B(T - T_0))), \quad (2)$$

where T_0 is the constant representing the correction of the weak interactions to the Néel–Arrhenius law and has no physical meaning. The particle size of the collection of NPs prepared by standard preparation routes (gas or chemical vapour deposition, laser ablation, wet chemical methods, *etc.*) is usually non-uniform and obeys the log-normal distribution,¹⁷ which is also preserved when these standard routes are applied again to the collection of already prepared particles.¹⁹ The distribution of magnetic moments of ensembles of crystalline monodomain NPs is in the first approximation the same as the distribution of particle size and the magnetization of such a system could be described by the generalized Langevin function, $L(\mu)$, with the superspin, μ , instead of the single spins as in the classical paramagnetic case:¹⁷

$$M(H, T) = \int_0^\infty L(\mu) M_S d\mu = \int_0^\infty \mu L(x) f_L(\mu) dx, \quad x = \frac{\mu H}{k_B T} \quad (3)$$

with the log-normal distribution function:

$$f_L(\mu) = \frac{N}{\sqrt{2\pi}} \exp\left(\frac{-\ln^2(\mu/\mu_0)}{2\sigma^2}\right), \quad (4)$$

where N is the number of particles, σ is the log-normal distribution width and μ_0 is the median of the distribution from which μ can be calculated as:

$$\mu = \mu_0 \exp\left(\frac{-\sigma}{2}\right). \quad (5)$$

Besides mentioned effects, magnetism of systems of small particles is a complex phenomenon which is influenced by

additional factors such as the structural and magnetic inhomogeneities of individual NPs, canting of the surface spins²⁰ and others that finally change the magnetic response of the investigated sample with respect to the ideal SPM case. Even if the macroscopic magnetic properties of bulk materials are usually unambiguously characterized by specific parameters such as the saturated and remanent magnetizations at given temperatures, M_S and M_r , the situation for nanosystems is not so simple and the above-mentioned effects have to be taken into account. One simple example could be the decrease of the metal content in the CNTs after purification, which is not to be strictly observed upon the decrease of M_S , which could rise in contrast (as was the case of the NPs in the HiPco_raw and less contaminated HiPco_SP SWCNTs¹⁶). Thus to determine the sample purity, different approaches have to be used and special attention has to be paid to both the complex characterization and interpretation of the data in context. To test possibilities and principles of detailed specification of the properties of residual magnetic NPs in purified CNTs, we have examined samples treated by three different methods (multi-step purification, oxidation under static and dynamic vacuum) and investigated them by TGA, X-ray diffraction (XRD), dc magnetization and ac susceptibility measurements and Extended X-ray Absorption Fine Structure (EXAFS) techniques. The main emphasis of this work is put on the proper characterization of the treated SWCNTs by means of magnetism and supported by the mass and phase analysis in order to gain comprehensive valid information about the structure of metal NPs. Interpretation of data is supported by previous work dealing with properties of metal catalysts in untreated raw and super-purified SWCNTs, HiPco_raw and HiPco_SP, respectively.¹⁶ The discussion on magnetism is based on the SPM theory and models considering weak inter-particle interactions.¹⁷

2 Experimental section

2.1 Treatment of SWCNTs

All purification treatments have been performed on the SWCNTs grown by the HiPco process⁵ and HiPco_raw SWCNTs distributed in the wet form by Unidym Inc. These SWCNTs should contain less than 35 wt% of the nanometer sized Fe NPs that serve as the catalyst. The basic properties are declared to be a diameter of 0.8–1.2 nm, a length of 100–1000 nm and a maximum density of 1.6 g cm^{-3} . Three different treatments were done, such as the (1) low temperature annealing (400 °C) followed by the refluxing in a mixture of HCl and H_2O_2 (ref. 21) (sample labelled HiPco_400), (2) annealing at 1000 °C under static vacuum (HiPco_1000) and (3) high temperature vacuum annealing at 2200 °C (HiPco_2200).

2.1.1 Annealing at 400 °C followed by mild acid treatment (the HiPco_400 sample). The procedure was performed several times with a slight modification of the partial steps; the best process giving a measurable significant yield was done as follows. At first, the sample placed in a glass boat was annealed at 400 °C for 45 min in an ambient atmosphere (labelled HiPco_400^{ann}). The aim was to partially damage the carbon

shells encapsulating the metal catalyst particles to prepare them for further mild acid removal. Then 1 mg of the HiPco_400^{ann} sample was sonicated in 4 ml of distilled H₂O and refluxed for 2 h after addition of 6 ml of 30% H₂O₂ (Sigma Aldrich). 4 ml of the supernatant were decanted and replaced by 4 ml of 12 M HCl (Sigma Aldrich) followed by additional 2 h reflux. The resulting sediment was diluted in a sufficient amount of distilled H₂O and filtered through the 200 nm pore filter (sample labelled HiPco_400^{acid}).

2.1.2 Annealing at 1000 °C under static vacuum (the HiPco_1000 sample). The HiPco_raw sample was placed in the SiO₂ tube which was sealed for 24 hours at a vacuum level of 10⁻⁷ Torr. Then the sample was placed in the oven and kept at 1000 °C for two days. Normally, the heating of the dry sample under static vacuum would not have any oxidation effect and would not result in the reduction of the residual metal content. Because the HiPco_raw SWCNTs are originally stored in the wet form (ethanol), the oxidation of the carbon shells and subsequently of the metal NPs after the sealing of the tube was possible.

2.1.3 Annealing at 2200 °C under dynamic vacuum (the HiPco_2200 sample). The sample was packed into the tantalum folio and kept at 2200 °C for 3 hours under dynamic vacuum. The idea was to let the iron evaporate and pump it out from the chamber (see Appendix for details of the melting temperatures of the individual iron phases).

2.2 Characterization of the samples

The samples have been characterized by several methods to gain a comprehensive amount of data to analyze properly properties of the residual metal catalyst, if there was any. TGA has been used for setting the mass content of the metal precursor in the purified SWCNTs. The samples were heated up to 800 °C at a heating rate of 10 °C min⁻¹ in an atmosphere containing 80% of He₂ and 20% of O₂. XRD was used for determination of the catalyst phase and for estimation of the mean diameter of the catalyst NPs in the samples, if it was possible. Diffraction data were obtained using a Rigaku diffractometer, with the Cu and Mo K α radiation. Diffraction patterns were collected in transmission mode and finally transformed into the standard 2 θ scale. Further processing of data was done using FullProf software; profile fitting provided the phase analysis and average particle diameter, d_{XRD} . Magnetic measurements on all purified HiPco SWCNT samples were performed using a MPMS7-SQUID device (Quantum Design) up to a magnetic field of 7 T in the temperature range of 2–350 K. The zero-field-cooled (ZFC) and field-cooled (FC) temperature dependencies of magnetization, $M(T)$, were measured at low external magnetic fields (from 5 to 50 mT). Magnetization isotherms, $M(B)$, were measured at 10 and 300 K up to the field of 7 T in both polarities. The temperature dependence of the ac susceptibility (with the alternating field amplitude of 3 mT) was measured in zero external magnetic field in the frequency range of 0.1–100 Hz. EXAFS experiments have been performed on synchrotron radiation source ANKA, Karlsruhe, in the transmission mode at Fe K-edge and captured

using a diode detector. Data analysis was carried out using the IFFEFIT software (Athena, Artemis).

3 Results and discussion

3.1 Phase analysis

TGA provided the mass content of the metal precursor in the samples: 25 wt% for the HiPco_1000 and 0 wt% for the HiPco_2200 SWCNTs (Fig. 1).

The final HiPco_400^{ann} sample was not analyzed because of the insufficient yield. Also the data for the HiPco_raw (75 wt%) and HiPco_SP (5 wt%) samples are presented as the reference of the precursor and commercially purified samples, respectively.

To discuss properties of the metal NPs and principles of the purification process of treated SWCNTs, the nature of NPs in the precursor, untreated HiPco_raw SWCNTs, has to be considered. The untreated and also insufficiently treated CNTs contain Fe-based NPs that could be theoretically present in the form of pure iron, α -Fe, carbide, Fe₃C or one of the allomorphs of the iron oxide, Fe₂O₃ or Fe₃O₄. The crystallographic structure of individual phases is described in Appendix. It has been already explored that the metal NPs in the precursor are in the form of 1.9 nm Fe₃C particles, with a highly crystalline magnetically oriented core and a paramagnetic shell, encapsulated in carbon.¹⁶ The XRD patterns of the HiPco_400^{ann} and HiPco_1000 samples showed the presence of both the Fe₃C and Fe₂O₃ phases (Fig. 2), confirming the attack of carbon shells and subsequent oxidation of the metal particles.

The major phase (>90%) in the HiPco_400^{ann} sample was the α -Fe₂O₃ phase in the form of 10 nm nanoparticles, with the lattice parameters $a = 5.033$ Å and $c = 13.730$ Å. Also the γ -Fe₂O₃ (<5% of 5 nm nanoparticles) and a negligible amount of Fe₃C phases were detected (Fig. 2a). The presence of the α -Fe₂O₃ phase is the expected consequence of the fast annealing, which usually leads to the stabilization of iron trioxide. The amount of the HiPco_400^{acid} sample was insufficient for capturing a reliable diffraction pattern. The data for the HiPco_1000 sample showed the major presence of both the Fe₃C and γ -Fe₂O₃ phases (Fig. 2b).

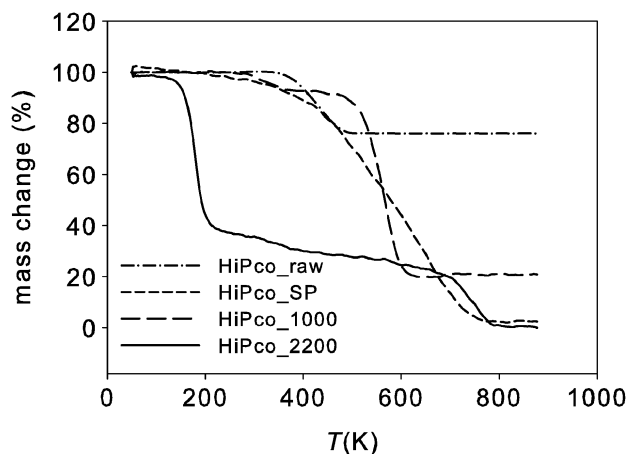


Fig. 1 TGA data of the HiPco_raw, HiPco_SP, HiPco_1000 and HiPco_2200 samples, respectively.

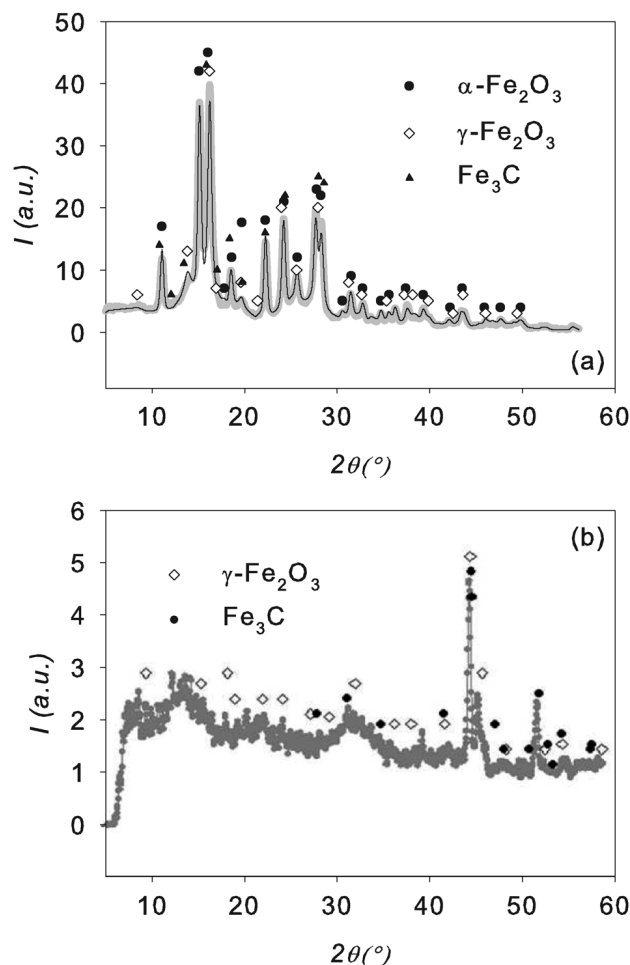


Fig. 2 The XRD patterns for: (a) the HiPco_400^{ann} sample (Mo K α) together with the refined structure (black line) and (b) the HiPco_1000 sample (Cu K α).

The size of the NPs in the HiPco_raw sample was considered as the upper bound of the particle diameter of the HiPco_1000 sample. This approach is adequate in comparison with magnetic data, as will be shown further. No diffraction was observed in the HiPco_2200 sample, pointing again at the low content of the iron phases in the sample, as has been suggested by TGA.

3.2 Magnetization, ac susceptibility and magnetization isotherms

The analysis of the ZFC–FC curves revealed whether the detectable amount of NPs is still present in the samples or not.

Table 1 The blocking temperatures of the mean, T_{MAX} , and the largest fraction of particles, T_{DIFF} , for all samples

Sample	T_{MAX} (K)	T_{DIFF} (K)
HiPco_400 ^{ann}	102	322
HiPco_400 ^{acid}	340	>350
HiPco_1000	11	>350
HiPco_2200	Diamag	Diamag

The maximum of the ZFC curve, labelled T_{MAX} , represents T_{B} of a major fraction of particles, whereas the point of coincidence of both curves, T_{DIFF} , belongs to the fraction of the largest particles (Table 1). The $M(B)$ curves captured above the T_{B} were analyzed using the fit of the generalized Langevin function (eqn (3)),¹⁷ if it was possible, and the average magnetic moments per particle were calculated. If one knows both the magnetic moment of the particle, μ , and that of the unit cell, μ_{C} , it is possible to calculate the volume and subsequently the magnetic size of the particle, d_{m} (Table 2).

The measurements of the real χ' and imaginary χ'' parts of the ac susceptibility in zero magnetic field provided the value of the E_{A} of the particles and their relaxation times, τ_0 , using the Vogel–Fulcher law,¹⁸ eqn (2). The K_{eff} value was calculated using the formula $E_{\text{A}} = K_{\text{eff}}V$, where V is the volume of particle (which was calculated assuming spherical particles using observed d_{XRD}). In the ideal case, when the whole particle is crystalline and magnetically oriented, the real and magnetic sizes of the particles, d_{XRD} and d_{m} , are equal. But even if the particle is crystalline, the spins in the thin surface layer are canted, which minimizes μ as has been proposed by Coey;²⁰ thus the d_{XRD} and d_{m} do not coincide. Because of this reason, we use d_{XRD} rather than d_{m} in calculations requiring the value of the particle size. The particle size determined by the blocking temperatures, $d_{T_{\text{MAX}}}$ and $d_{T_{\text{DIFF}}}$, was calculated using eqn (1) and corresponds well with the other data (Table 2). The detailed interpretation of data is summarized in the following part of the article, and the illustration of purification processes for all samples is depicted in Fig. 8 at the end of the article.

4 Interpretation of the purification process

4.1 The HiPco_400 sample

The ZFC–FC curves of the HiPco_400^{ann} and HiPco_400^{acid} samples (Fig. 3) exhibit sharp maxima at the temperature T_{MAX} of 102 and 340 K, respectively.

Table 2 Median, μ_0 and mean, μ magnetic moments with the appropriate magnetic diameters, d_0 and d_{m} , compared with particle diameters calculated from the blocking temperatures, $d_{T_{\text{DIFF}}}$ and $d_{T_{\text{MAX}}}$

Sample	$\mu_0 \times 10^3$ (μ_{B})	d_0 (nm)	σ	$\mu \times 10^3$ (μ_{B})	d_{m} (nm)	$d_{T_{\text{MAX}}}$ (nm)	$d_{T_{\text{DIFF}}}$ (nm)
HiPco_400 ^{ann}	2.1 ± 0.02	12 ± 1.0	0.85	1.1 ± 0.03	9.8 ± 1.0	12.5 ± 1.0	18.3 ± 1.0
HiPco_400 ^{acid}	—	—	—	—	—	18.6 ± 1.0	>18
HiPco_1000 ^N	4.05 ± 0.06	3.8 ± 0.5	249	1.3 ± 0.5	2.5 ± 0.3^a	1.7 ± 0.5^b	4.7 ± 0.9^b
HiPco_1000 ^L	6.43 ± 0.21	4.4 ± 0.6	0.48	5.1 ± 0.3	4.1 ± 0.4	1.7 ± 0.5	4.7 ± 0.9

^a The value was calculated considering the $\gamma\text{-Fe}_2\text{O}_3$ particles. The calculation for the Fe_3C NPs gives a similar result, $d_{\text{m}} = 2.4$ nm, which is in the range of the fitting error. ^b The volume of particle taken is the same as for the HiPco_raw NPs.¹⁶

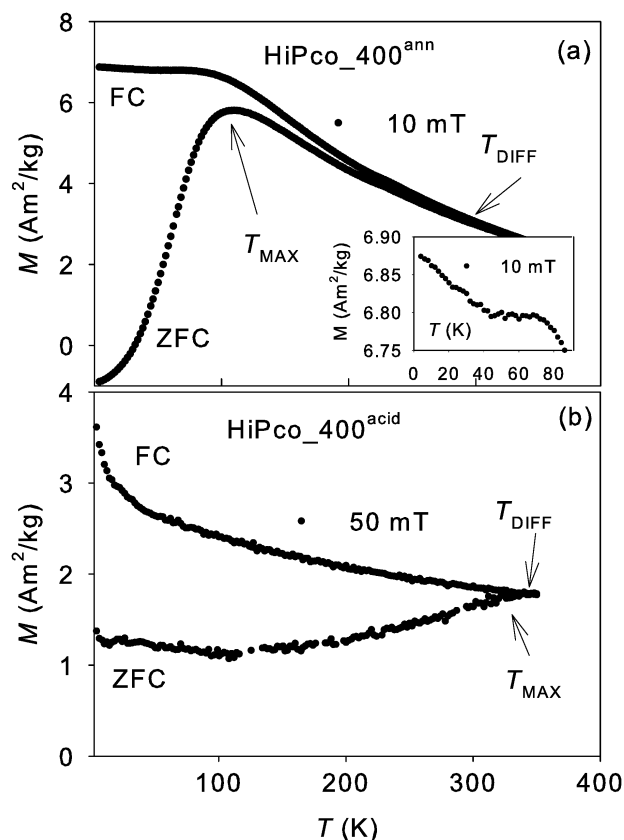


Fig. 3 (a) The temperature dependence of the ZFC and FC magnetization measured for the HiPco_400 sample after the annealing step, together with the details of the low temperature part of the FC curve in the inset, and (b) after the mild acid treatment and subsequent filtration. Anomaly at the low temperature part of FC magnetization could be explained as follows. The bulk α -Fe₂O₃ exhibits antiferromagnetic (AFM) ordering below the Neel temperature, $T_N = 955$ K and the spin-flop transition which changes the orientation of the AFM ordering from perpendicular to parallel to the c -axis below the so-called Morin transition temperature, $T_M = 260$ K. In the NPs, the T_M decreases with the decreasing particle size and could reach very low temperatures for NPs below 20 nm.²² Furthermore, it has been observed that the long range magnetic ordering, such as the creation of aggregates of particles increases T_M , could be manifested by a slight increase of magnetization at 44 K with maxima attributed to the change of AFM ordering at 72 K in our case.

The calculated particle size of the HiPco_400^{ann} sample, $d_{T_{MAX}} = 12.5$ nm, increases at least 5 times in comparison with the particles in the HiPco_raw sample, 1.9 nm (Table 2), and is in the range of the fitting error in agreement with the size obtained from the XRD, $d_{XRD} = 10$ nm. The strong saturation at the low temperature part of the FC curve confirms the sintering of particles that are liable to this effect. An explanation for this is that with the increase of particle size the magnetic moment increases the dipolar interaction among the particles, preserving their constant number and leading to the saturation of the FC curve.

Because of the linear dependence of T_B on the particle volume, V , there is a shift of the T_{MAX} from 102 up to 340 K for the HiPco_400^{ann} and the HiPco_400^{acid} samples, respectively, suggesting that only the largest particles persisted in the sample after mild acid treatment and subsequent filtration.

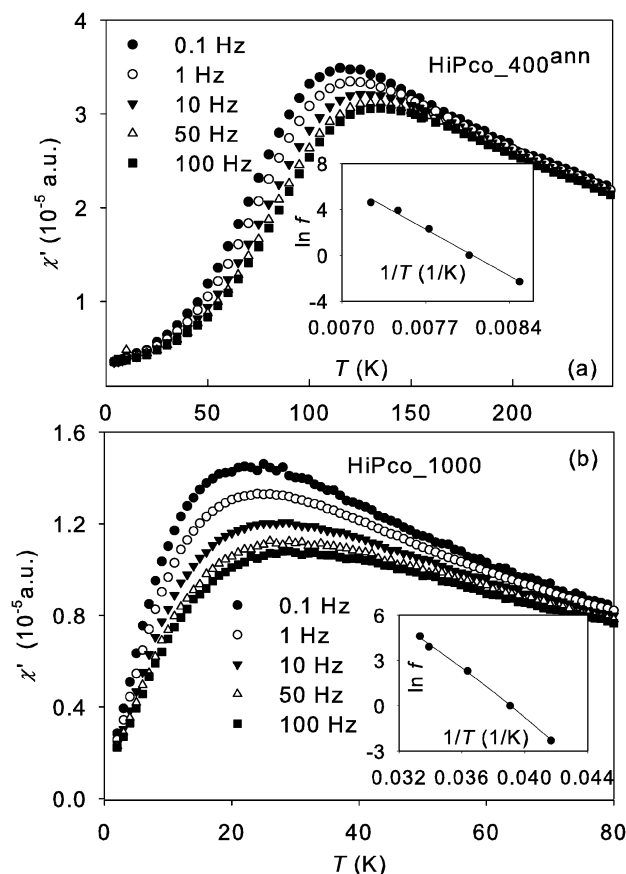


Fig. 4 The temperature dependence of the real part of susceptibility, χ' , in zero external field: the insets show the fit according to the Vogel-Fulcher law for the (a) HiPco_400^{ann} sample and (b) HiPco_1000 sample.

This has been also confirmed by the suppression of the extreme saturation of the FC curve (Fig. 3b) as a result of minimization of the interparticle interactions relying on better dilution and lower concentration of NPs within the treated sample. The relaxations in the system have been examined for the HiPco_400^{ann} sample (Fig. 4a). The temperature dependence of the χ' exhibits a characteristic maximum, T_m , which shifts to the higher temperatures with increasing frequency. Examining the data, relatively low values of $\tau_0 = 2.3 \times 10^{-9}$ s supported the existence of strong interactions among particles as the consequence of suggested particle sintering. K_{eff} was determined to be 3.47×10^4 J m⁻³ which is in agreement with the value obtained for 10 nm α -Fe₂O₃ particles diluted in the SiO₂ matrix, as has been observed by Bødker *et al.*²³

The calculated median magnetic size of the NPs in the HiPco_400^{ann} sample, d_0 , perfectly corresponds to the $d_{T_{MAX}}$ (Table 2). Because the structure of the HiPco_raw NPs before annealing was a core-shell structure, with a ferromagnetically oriented core and a paramagnetic shell, these results demonstrated that sintered particles in the HiPco_400^{ann} sample were completely crystalline and magnetically oriented. The mean magnetic moment of the weakly ferromagnetic α -Fe₂O₃ unit cell at room temperature was taken as $3.8 \times 10^{-2} \mu_B$.²³ As the quality of magnetization isotherms for the HiPco_400^{acid}

sample was poor because of the low metal content, further processing of data was impossible. The magnetic size of the particles was estimated only for the T_{MAX} and T_{DIFF} (Table 2) and confirmed the presence of the largest fraction of the sintered particles introduced by annealing.

4.2 The HiPco_1000 sample

Examination of the dc magnetization curve suggested that annealing of SWCNTs at 1000 °C leads to three effects. At first, the number of particles was reduced, which is proven by only little saturation of the FC curve in comparison with the FC curve of the untreated HiPco_raw sample.¹⁶ Also the reduction of the particle size is demonstrated by a decrease of T_{MAX} down to 11 K, which is lower than that for the HiPco_raw sample, 35 K. The last observed result is the partial removal of the paramagnetic shell of particles, as could be deduced from an almost similar course of $M(B)$ curves measured at 2 and 300 K, respectively. If the magnetic structure of particles would be the same as in the HiPco_raw sample (a magnetically oriented core with a paramagnetic shell), the $M(B)$ at room temperature would exhibit unsaturation of the curve, with linear paramagnetic contribution and the value of the M_{S} would be lower than M_{S} at low temperatures¹⁶ (Fig. 5a). The absence of such behavior simply suggests that the whole particle is homogeneously magnetically oriented. Indication of partial sintering of a minor fraction of particles is manifested by the shift of the T_{DIFF} to the higher values than was the T_{DIFF} for the HiPco_raw sample (202 K). Examination of the collective phenomenon (Fig. 4b) provided values of $E_{\text{A}} = 4.69 \times 10^{-21}$ J (the value observed for NPs in the HiPco_raw sample was $E_{\text{A}} = 6.06 \times 10^{-21}$ J), $\tau_0 = 1.2 \times 10^{-9}$ s and $T_0 = 9.3$ K. The K_{eff} value was calculated using d_{XRD} of the HiPco_raw NPs as 1.9 nm, the resulting value is 1.31×10^6 J m⁻³ which is approximately 20% lower than that for the HiPco_raw NPs, an expected consequence of minimization of interparticle interactions due to the lower concentration of NPs in the purified HiPco_1000 sample.

As has been claimed in the introduction, the standard size distribution of NPs prepared by classical routes is the log-normal distribution.¹⁹ Examining the $M(B)$ of the HiPco_1000 sample measured at room temperature, the fit of the generalized Langevin function with the log-normal distribution did not correspond well with the data. Because the high temperature annealing probably does not affect the whole particle equally, which is the presumption of preservation of log-normality impinged by the preparation process of the raw sample, we have tested different types of distribution of particle sizes. The best result was obtained for the binomial distribution, $f_{\text{b}}(\mu)$, composed of 92% of normal, $f_{\text{N}}(\mu)$, and 8% of log-normal, $f_{\text{L}}(\mu)$, distributions (Fig. 5b), using the relation:

$$f_{\text{b}}(\mu) = \alpha f_{\text{N}}(\mu) + (1 - \alpha) f_{\text{L}}(\mu) \quad (6)$$

with

$$f_{\text{N}}(\mu) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(\mu - \mu_0)^2}{2\sigma^2}\right). \quad (7)$$

Calculated magnetic moments for both distributions with appropriate magnetic sizes are summarized in Table 2.

4.3 The HiPco_2200 sample

Magnetic measurements performed on the HiPco_2200 sample demonstrated that the magnetic response was purely diamagnetic (Fig. 6), as is illustrated by plotting the temperature dependence of the M/H ratio, which is constant. Regarding the result from the TGA and XRD measurements that indicated an undetectable amount of metal in the sample, one should state that the sample is of perfectly high purity.

As was claimed in the introduction, to study magnetism on SWCNTs, the sample should contain no metal. Thus the EXAFS experiment has been performed on this sample to exclude any contamination of the sample by residual iron, which is undetectable by macroscopic measurements. As could be seen from the energy dependence of the normalized absorption

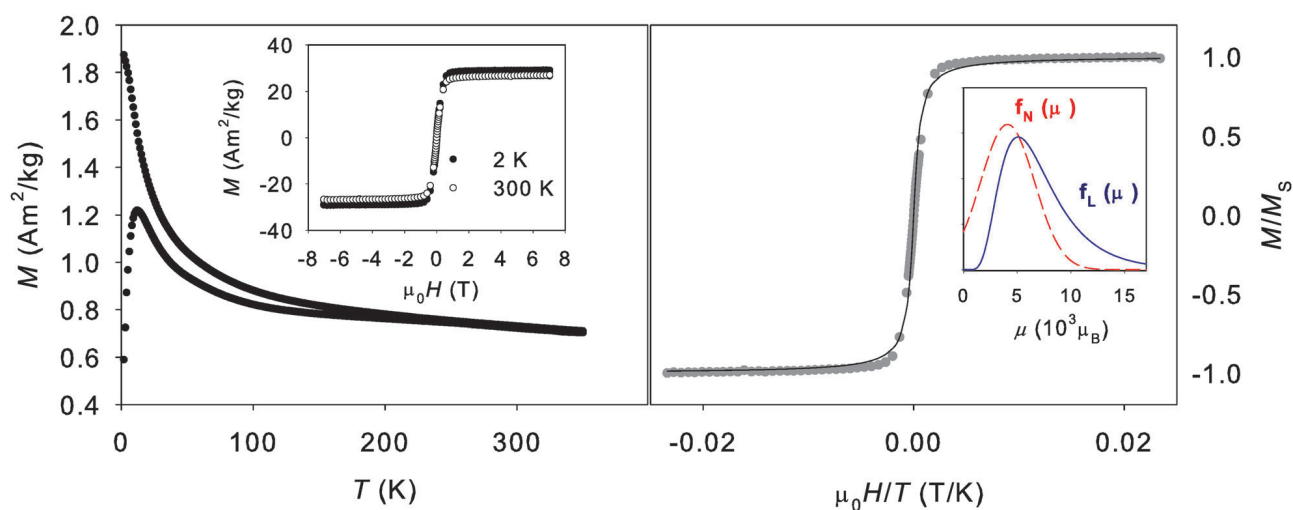


Fig. 5 (a) The temperature dependence of the ZFC–FC magnetization measured at 10 mT for the HiPco_1000 sample with the magnetization isotherms in the inset. (b) The fit of the weighted sum of the Langevin function to the data at 300 K in Langevin scaling with the moment distribution functions is shown in the inset.

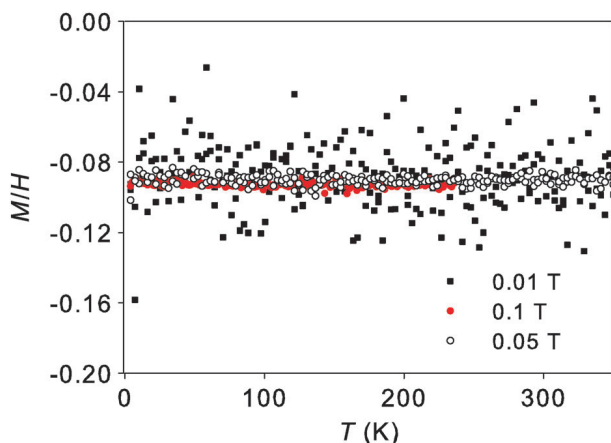


Fig. 6 The temperature dependence of the M/H for the HiPco_2200 sample.

coefficient, $\mu(E)$ (Fig. 7a), there is obvious absorption at the Fe K -edge, pointing at the unambiguous presence of iron. The course of the $\mu(E)$ curve is similar to those of the random environment around iron atoms, suggesting that no ordered structures are present and low concentration of atomic iron is dispersed within the sample. Further qualitative analysis of the $k\chi(R)$ data (Fig. 7b) provided information about first coordination shells (nearest neighbors) of absorbing iron atoms. The structures of Fe, Fe_3C and $\gamma\text{-Fe}_2\text{O}_3$ have been tested, as demonstrated in Fig. 7b. It is clearly evident that the first maximum corresponds well to the first single-scattering path of the iron oxide representing the nearest Fe–O bonds.²⁴ The presence of Fe_3C and pure Fe has been strictly elided.

5 Conclusion

We have presented possible routes of detailed detection, examination and interpretation of the properties of low-size and low-concentration metal catalyst NPs in the SWCNTs. The three different model approaches of purification have been

tested on the HiPco_raw SWCNTs in order to examine the ability of precise determination of the nature and amount of residual metal within the samples. The samples have been investigated by the TGA, XRD, and static and dynamic magnetic property measurements. The EXAFS technique has been used for determination of purity of the purest sample. The annealing of SWCNTs at 400 °C in an ambient atmosphere led to the transformation of the Fe_3C NPs into at least five times larger $\alpha\text{-Fe}_2\text{O}_3$ NPs, and subsequent mild acid treatment followed by filtration caused significant minimization of the number of particles, where only the largest ones persisted in the sample. The annealing of SWCNTs at 1000 °C under static vacuum led to removal of the paramagnetic shell of particles, where only magnetically oriented cores persisted, and to subsequent partial sintering of these cores, with average magnetic diameters two times higher than was the size of the NPs in the HiPco_raw SWCNTs. Also the total amount of residual metal was reduced down to 25%. Annealing of SWCNTs at 2200 °C under dynamic vacuum seemed to result in complete removal of metal, as has been suggested by undetectability of any iron phase by TGA and XRD, supported by the diamagnetic response of the sample. However, EXAFS confirmed absorption at the iron K -edge, with the presence of little amount of residual iron in the form of iron oxide, as is reflected by the examination of the Fourier transformed EXAFS data. As has been demonstrated, complementary methods have to be used in order to clarify purity of treated CNTs in detail and interpretation of magnetic data is essential for specification of the structure and form of the residual magnetic metal. The standard routes used for the characterization of bulk material are insufficient and the analysis has to be more complex. It has been demonstrated that even if all macroscopic methods confirm high purity of the sample, it could contain a non-negligible amount of metal, which is absolutely undesirable for some applications such as further studies of carbon magnetism. Thus a great emphasis should be placed on the examination of samples by local probes to elide the low-level presence of metal.

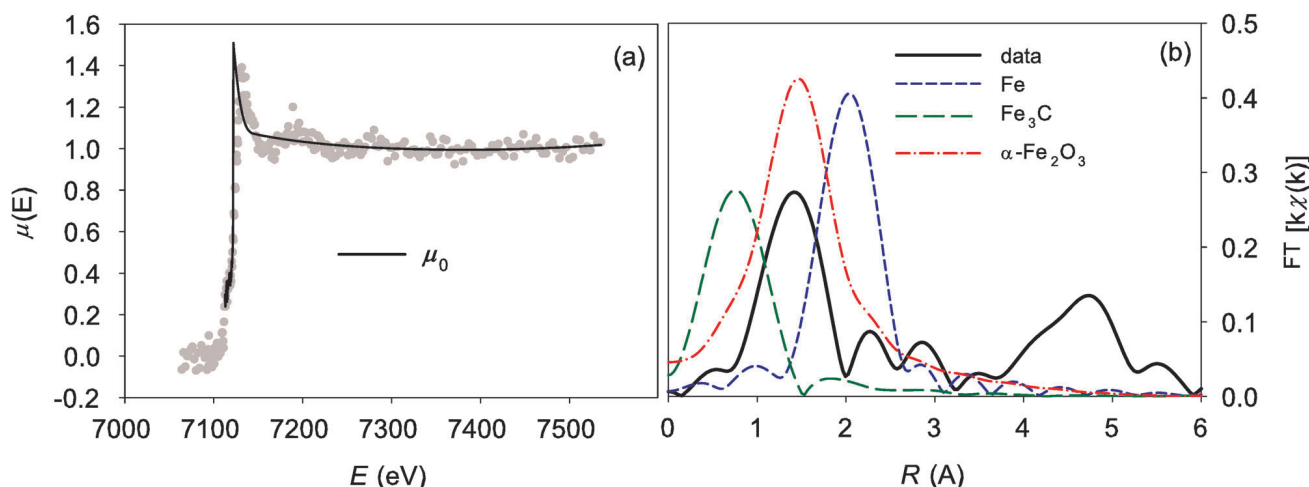


Fig. 7 (a) The XAFS normalized data with the indication of absorption of embedded atoms, μ_0 . (b) Magnitude of the Fourier transformation of the $k\chi(k)$ with the lines representing the Fe–O (dashed dotted line), Fe–C (long dashed line) and Fe–Fe first paths (short dashed line).

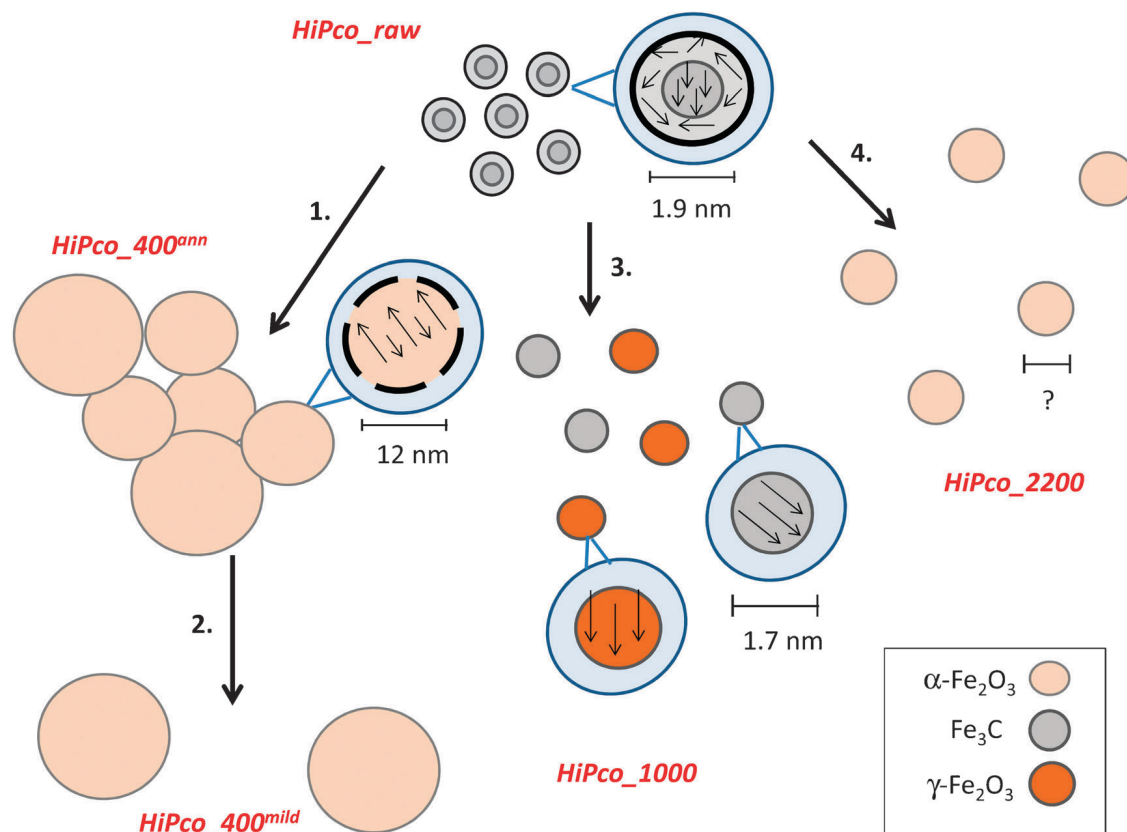


Fig. 8 Scheme of the purification processes in detail, the internal structure of nanoparticles is magnified and indicated in blue circles. (1) Heating in ambient air at 400 °C. (2) Mild acid treatment in H_2O_2 and HCl . (3) Annealing under static vacuum at 1000 °C. (4) Annealing under dynamic vacuum at 2200 °C.

6 Appendix

A iron catalyst in the HiPco SWCNTs could be theoretically present in the three different forms:²⁵

(1) The pure α -Fe with the melting temperature of 1536 °C, which crystallizes in the $Im\bar{3}m$ space group.

(2) The iron carbide, Fe_3C , phase with a melting temperature of 1227 °C, which crystallizes in the orthorhombic $Pnma$ space group with the four units in the unit cell ($Z = 4$). The eight of the iron atoms are in 8d positions, four are placed in 4c positions and the four carbon atoms sit in the interstitials.

(3) The iron oxide (melting temperature 1460 °C) which could be present in one of the three possible allomorphs, mostly occurring in the spinel structure composed of closed packed oxygen ions with the Fe sitting in the tetrahedral (T_d) and octahedral (O_h) sites:

(A) The magnetite, Fe_3O_4 , with the inverse spinel structure (space group $Fd\bar{3}m$), where the eight Fe^{2+} ions sit in the O_h (16d) sites and the Fe^{3+} ions in the remaining eight O_h (16d) and all T_d (8a) sites. The particles exposed unprotected to the air oxidize to

(B) Maghemite, $\gamma\text{-Fe}_2\text{O}_3$, crystallizing in the non-stoichiometric spinel structure with the 8/3 vacancies per unit cell distributed among the O_h (16c) and T_d (8b) sites. Depending on the ordering of vacancies, the structure changes from cubic ($Fd\bar{3}m$) for vacancies distributed over the T_d and O_h sites to tetragonal ($P4_12_12$) with the vacancies only in the O_h sites, lowering the

symmetry of structure. At high temperatures, the maghemite transforms into the most stable

(C) Hematite, $\alpha\text{-Fe}_2\text{O}_3$, crystallizing in the rhombohedral ($R\bar{3}c$) structure with the Fe^{3+} atoms occupying 2/3 of the O_h (4c) sites.

Acknowledgements

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Kapitola 4

Závěr

Tato habilitační práce se zabývá studiem magnetických vlastností a struktury izolovaných nanočástic a nanokompozitů v kontextu reálných jevů a jejich dopadu na modifikaci superparamagnetického, resp. blokovaného stavu. Vznikla na základě několikaleté intenzivní spolupráce s kolegy z několika pracovišť Univerzity Karlovy v Praze (katedra anorganické chemie PřF, katedra fyziky kondenzovaných látek MFF), Ústavu anorganické chemie AVČR a Ústavu fyzikální chemie JH AV ČR, dále s významným přispěním kolegů z Instituto de Ciencia de Materiales de Madrid. Výsledky, které tvoří základ habilitační práce, byly převážně získány při řešení bakalářských, diplomových a dizertačních prací studentů, které jsem vedla jako školitel nebo konzultant v letech 2003 - 2014. Zároveň tvoří zásadní výstupy několika projektů Grantové agentury ČR, Grantové agentury UK aj. Výzkumné aktivity v oboru vedly ke vzniku několika nových kurzů v oblasti fyziky nanorozměrových materiálů na MFF UK a PřF UK a přednesení série populárních přednášek pro středoškolské pedagogy a studenty.

Dosavadní spolupráce a související pedagogická činnost iniciovaly úspěšný rozvoj navazující problematiky a vznik nových výzkumných směrů. Na prvním místě bych zmínila účast naší skupiny ve velkém konzorciálním projektu 7RP MULTIFUN (2011 - 2015), jehož cílem je příprava multimodálních terapeutik na bázi magnetických částic. Expertýza v interpretaci reálných efektů v souborech nanočástic nám umožnila formulovat modely pro korelaci velikosti a spinové struktury individuálních nanočástic vzhledem k jejich efektivitě při magnetické fluidní hypertermii.

Zájem ze strany biomedicínských oborů deklaruje i nedávno navázaná spolupráce s kolegy z 2. lékařské fakulty UK, kteří se věnují využití magnetických nanočástic pro přípravu nosičů k zesílené proliferaci buněk.

Zcela novou problematikou, řešenou ve spolupráci s UFCh JH, je využití nanorozměrových částic pro přesnou kontrolu zvrásnění grafenu, kde řízené rozmístění nanočástic na vhodném substrátu umožňuje selektivně indukovat napětí spojené s posunem Fermiho meze a vznikem lokálních magnetických pseudopolí. Zájem o pilotní práce v oblasti nanorozměrových chromitů nedávno vyústil ve spolupráci s European High-field Magnetic Laboratory.

Je tedy zřejmé, že problematika magnetických nanorozměrových částic je stále aktuálním tématem a její multidisciplinární charakter tak umožňuje synergetický výzkum vědeckých týmů z různých oborů. Proto je velmi žádoucí v mezioborovém duchu rozvíjet i související výuku nejen na úrovni studentských prací, ale i přednášek a cvičení, čemuž bych se chtěla i do budoucna věnovat.

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