Low-Temperature Magnetic Properties of Nanocomposites

Containing Superparamagnetic Fe₃C Particles

B. DAVID a,∗, O. SCHNEEWEISS a, E. ŠANTAVÁ b and I. MORJAN c

a Institute of Physics of Materials, AS CR, Žižkova 22, CZ-61662 Brno, Czech Republic
b Institute of Physics, AS CR, Na Slovance 2, CZ-18221 Praha 8, Czech Republic
c National Institute for Lasers, Plasma and Radiation Physics, P.O. Box MG-36, 077125 Bucharest, Romania

Two nanopowders containing superparamagnetic Fe₃C particles, superparamagnetic Fe₂O₃/γ-Fe₂O₃ particles and carbon black phase were synthesised by the method of laser-induced homogeneous pyrolysis of gaseous precursors. Both were characterised by X-ray diffraction, Mössbauer spectrometry and standard magnetic measurements. The mean crystallite size of Fe₃C was 3 nm for the first sample and 10 nm for the second sample. Mössbauer spectra measured at 27 K and zero-field cooled/field cooled curves measured down to 4 K are reported.

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1. Introduction

Among gas phase synthesis methods, the laser-induced homogeneous pyrolysis is a very powerful and versatile tool for the creation of nanoparticles with various chemical compositions and diameters ranging from a few nanometers to about 50 nm [1]. It has been demonstrated in our previous reports that this method can provide nanopowders with dominant Fe₃C content [2–4].

In the present paper we study samples containing superparamagnetic Fe₃C and Fe₂O₃/γ-Fe₂O₃ particles, i.e. with thermally fluctuating orientation of the particle magnetic moment (superspin) at room temperature.

2. Experimental

Two types of Fe₃C-based nanopowders were synthesised by the method of laser-induced pyrolysis of gaseous precursors [1]. The synthesis parameters for the two experiments resulting in the nanopowders labelled FCB1 and FCB3N are given in [5]. In the case of FCB1 the reactants used were Fe(CO)₅ vapour and C₂H₂ and in the case of FCB3N then NH₃ was added. SF₆ was used as a laser radiation absorber. After the synthesis nanopowders were stored in ambient atmosphere.

The composition of nanopowders was studied by X-ray diffraction (XRD) on a PANalytical X’Pert Pro MPD device. The XRD pattern fitting procedure was done with TOPAS software using ICSD database and it yielded weight fraction F and mean crystallite size dXRD for a given phase [6].

Mössbauer spectra (MS) were obtained at standard transmission geometry with ⁵⁷Co in Rh matrix. As a result of the fitting procedure done with CONFIT [7] we obtained the values of the relative spectrum area A for a given phase and spectral component parameters: hyperfine magnetic induction B_HF, quadrupole splitting Δ_E_Q and isomer shift δ_IS (against α-Fe).

A physical properties measuring system PPMS 9 from Quantum Design was employed for low temperature magnetic measurements.

3. Results and discussion

The XRD patterns of the samples were fitted with orthorhombic cementite θ-Fe₃C (ICSD No. 16593) and magnetite Fe₂O₃ (ICSD No. 43001) [6]. The Rietveld refinement yielded in the case of the FCB1 sample for Fe₃C the values d_XRD = 3 nm, F = 74 wt%, and for Fe₂O₃ the values d_XRD = 4 nm, F = 26 wt% [5]. Correspondingly, in the case of the FCB3N sample for Fe₃C there were obtained the values d_XRD = 10 nm, F = 33 wt%, and for Fe₂O₃ the values d_XRD = 3 nm, F = 67 wt% [5]. The presence of maghemite γ-Fe₂O₃ could not be excluded because γ-Fe₂O₃ and Fe₂O₃ have similar XRD patterns. On the other hand, well pronounced D peak at ≈ 1360 cm⁻¹ and G peak at ≈ 1580 cm⁻¹ were observed in the Raman spectra of both samples confirming the presence of carbon black in the samples (result of the C₂H₂ decomposition). The transmission electron micrographs pictures for the samples can be found in [5].

The Mössbauer spectrum (MS) of FCB1 sample measured at 293 K was fitted with three components [8]: a narrow doublet probably of superparamagnetic Fe₃C (δ = 0.18 mm/s, Δ_E_Q = 0.42 mm/s, A = 0.36), a broad doublet of superparamagnetic γ-Fe₂O₃ (δ = 0.30 mm/s, Δ_E_Q = 0.91 mm/s, A = 0.53) and a superposition of three sextets (B_HF = 19.2 T, 12.3 T, 15.9 T; A = 0.11). In the corresponding MS measured at 27 K (Fig. 1) the sextet of ferromagnetic Fe₃C (B_HF = 24.5 T, Δ_E_Q = 0.07 mm/s, δ = 0.36 mm/s, A = 0.74) dominated the spectrum [3]. The absence of the characteristic ferromagnetic Fe₃C sextet at 293 K and its appearance at lower temperatures is the consequence of the superparamagnetism of Fe₃C nanoparticles at 293 K.

In the case of FCB3N sample the MS measured at 293 K exhibited very low absorption (the lowest value of
Relative transmission was 0.994) [8]. This spectrum was fitted with the ferromagnetic Fe$_3$C sextet ($B_{HF} = 20.5$ T, $\varepsilon_Q = 0.01$ mm/s, $\delta = 0.19$ mm/s, $A = 0.28$) [7], a doublet ($\delta = 0.19$ mm/s, $\Delta E_Q = 0.51$ mm/s, $A = 0.64$) and the superparamagnetic Fe$_3$O$_4$ doublet ($\delta = 0.68$ mm/s, $\Delta E_Q = 0.70$ mm/s, $A = 0.08$). In the corresponding MS measured at 27 K (Fig. 1) the Fe$_3$C sextet ($B_{HF} = 25.0$ T, $\varepsilon_Q = 0.01$ mm/s, $\delta = 0.32$ mm/s, $A = 0.42$) was identified. The intense outer lines correspond to the sextets of Fe$_3$O$_4$ phase.

It is concluded that two effects strongly influenced the measured Mössbauer spectra: superparamagnetic (SPM) effect ( sextet representing magnetically ordered phase collapses to doublet above the blocking temperature $T_B$) [9] and soft bonding of Fe-based particles to the pyrolytic carbon matrix (recoilless factor $f$ strongly increases with decreasing temperature, i.e. relative transmission at 27 K is lower than at 293 K) [10]. The curves of the zero field cooled (ZFC) and field cooled (FC) temperature dependent magnetization ($\sigma_{ZFC}$, $\sigma_{FC}$) in Fig. 2 were measured under the same conditions as for the nanopowder with nonsuperparamagnetic Fe$_3$C particles reported in [3]. Present $\sigma_{ZFC}$ and $\sigma_{FC}$ values substantially differ from those given in [3]: $\sigma_{ZFC}$ exhibits a maximum (72 K for FCB1 and 67 K for FCB3N) and $\sigma_{FC}$ grows upon cooling and reaches saturation below $\sim 30$ K. Hence present curves resemble the curves characteristic for samples with SPM particles [9, 10]. Nevertheless, due to magnetic particle interactions, they do not overlap above $\sim 150$ K as it happens for noninteracting SPM particles with very low $T_B$.

It is summarized that the presence of the significant amount of superparamagnetic Fe$_3$C particles at room temperature was proved in the studied samples synthesized by the laser pyrolysis method for the first time.

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References