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Low-Temperature Magnetic Properties of Nanocomposites Containing Superparamagnetic Fe_3C Particles

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Two nanopowders containing superparamagnetic Fe_3C particles, superparamagnetic Fe_3O_4/γ-Fe_2O_3 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 Fe_3C 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 Fe_3C content [2–4].

In the present paper we study samples containing superparamagnetic Fe_3C and Fe_3O_4/γ-Fe_2O_3 particles, i.e. with thermally fluctuating orientation of the particle magnetic moment (superspin) at room temperature.

2. Experimental

Two types of Fe_3C-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 C_2H_2 and in the case of FCB3N then NH_3 was added. SF_6 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 d_{XRD} for a given phase [6].

Mössbauer spectra (MS) were obtained at standard transmission geometry with ^{57}Co 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 shift ε_{Q}, quadrupole splitting ΔE_{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-Fe_3C (ICSD No. 16593) and magnetite Fe_3O_4 (ICSD No. 43001) [6]. The Rietveld refinement yielded in the case of the FCB1 sample for Fe_3C the values $d_{\mathrm{XRD}} = 3$ nm, $F = 74$ wt%, and for Fe_3O_4 the values $d_{\mathrm{XRD}} = 4$ nm, $F = 26$ wt% [5]. Correspondingly, in the case of the FCB3N sample for Fe_3C there were obtained the values $d_{\mathrm{XRD}} = 10$ nm, $F = 33$ wt%, and for Fe_3O_4 the values $d_{\mathrm{XRD}} = 3$ nm, $F = 67$ wt% [5]. The presence of maghemite γ-Fe_2O_3 could not be excluded because γ-Fe_2O_3 and Fe_3O_4 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 so the presence of carbon black in the samples (result of the C_2H_2 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 Fe_3C ($\delta = 0.18$ mm/s, $\Delta E_{\mathrm{Q}} = 0.42$ mm/s, $A = 0.36$), a broad doublet of superparamagnetic γ-Fe_2O_3 ($\delta = 0.30$ mm/s, $\Delta E_{\mathrm{Q}} = 0.91$ mm/s, $A = 0.53$) and a superposition of three sextets ($B_{\mathrm{HF}} = 19.2$ T, 12.3 T, 15.9 T; $A = 0.11$). In the corresponding MS measured at 27 K (Fig. 1) the sextet of ferromagnetic Fe_3C ($B_{\mathrm{HF}} = 24.5$ T, $\varepsilon_{\mathrm{Q}} = 0.07$ mm/s, $\delta = 0.36$ mm/s, $A = 0.74$) dominated the spectrum [3]. The absence of the characteristic ferromagnetic Fe_3C sextet at 293 K and its appearance at lower temperatures is the consequence of the superparamagnetism of Fe_3C nanoparticles at 293 K.

In the case of FCB3N sample the MS measured at 293 K exhibited very low absorption (the lowest value of

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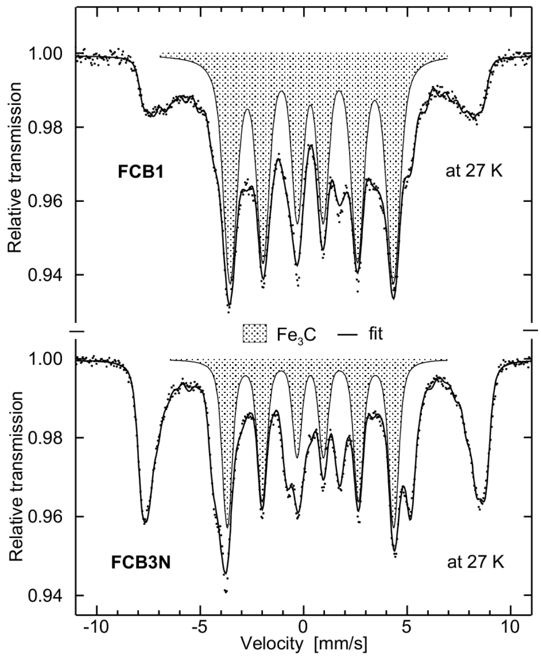

Fig. 1. Mössbauer spectra for the as-prepared nanopowders.

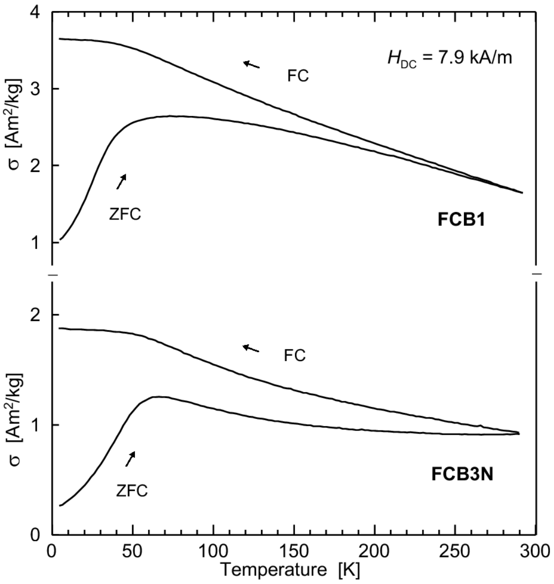

Fig. 2. ZFC and FC curves for the as-prepared nanopowders.

relative transmission was 0.994) [8]. This spectrum was fitted with the ferromagnetic Fe_3C 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_3O_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_3C 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_3O_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 (σ_{ZFC}, σ_{FC}) in Fig. 2 were measured under the same conditions as for the nanopowder with nonsuperparamagnetic Fe_3C particles reported in [3]. Present σ_{ZFC} and σ_{FC} values substantially differ from those given in [3]: σ_{ZFC} exhibits a maximum (72 K for FCB1 and 67 K for FCB3N) and σ_{FC} grows upon cooling and reaches saturation below ~ 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 ~ 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_3C particles at room temperature was proved in the studied samples synthesized by the laser pyrolysis method for the first time.

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