Low-Temperature Magnetic Properties of Nanometric Fe-Based Particles

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Fe-based nanoparticles were prepared by laser-driven pyrolysis. The as-synthesised powder consists of $\alpha$-Fe and $\text{Fe}_3\text{O}_4/\gamma$-$\text{Fe}_2\text{O}_3$ nanoparticles embedded in a pyrolytic carbon matrix. The crystallite size of 1.8 nm for $\alpha$-Fe was calculated using the Scherrer formula. The as-synthesised nanopowder was superparamagnetic. The maximum of the zero-field cooling curve was observed at 32 K and the distribution of blocking temperatures $g(T_B)$ peaked at 11 K. As a result of small particle sizes and the soft matrix, the Lamb–Mössbauer factor $f$ was significantly higher at 4 K than at 293 K.

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1. Introduction

The method of laser-induced pyrolysis of gases [1] has been recently used for the synthesis of various Fe-based nanopowders, either metallic (for instance $\alpha$-Fe, $\text{Fe}_3\text{C}$, $\text{Fe}_7\text{C}_3$) or oxidic (for example $\alpha$-$\text{Fe}_2\text{O}_3$, $\gamma$-$\text{Fe}_2\text{O}_3$, $\text{Fe}_3\text{O}_4$).

In the present article we describe the structural and low-temperature magnetic properties of a nanopowder with nanometer-sized $\alpha$-Fe, $\text{Fe}_3\text{O}_4$ and/or $\gamma$-$\text{Fe}_2\text{O}_3$ particles.
2. Experimental

The Fe–C-based nanopowder labelled CF26, which was obtained during the series of experiments reported earlier [2], was synthesised by the laser co-pyrolysis of the gas mixture \( \text{Fe(CO)}_5/C_2\text{H}_4/C_2\text{H}_2 \).

The powder X-ray pattern was obtained with the X’Pert Panalytical diffractometer (Co K\( \alpha \) radiation). The mean coherent domain length \( d_{\text{XRD}} \) (crystallite size) was calculated using the Scherrer formula.

Mössbauer spectra were measured in standard transmission geometry with \(^{57}\text{Co}\) in Rh matrix. Isomer shift was evaluated with respect to \( \alpha\)-Fe.

The physical properties measuring system PPMS 9 from Quantum Design equipped with the P500 AC/DC magnetometry system was used for low-temperature magnetic measurements.

3. Results and discussion

The X-ray diffraction (XRD) pattern of the CF26 sample exhibited very broad diffraction lines. The peak at \( 2\theta = 29.5^\circ \) belonged to (200) planes of graphite \( (d_{\text{XRD}} = 1.6 \text{ nm}) \) and the peak at \( 2\theta = 51.8^\circ \) was assigned to (110) planes of \( \alpha\)-Fe \( (d_{\text{XRD}} = 1.8 \text{ nm}) \). The peak of lower intensity at \( 2\theta = 40.5^\circ \) belonged to \( \text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3 \). The presence of Fe–C martensite was not excluded.

![HRTEM images (a) and (b) for the synthesised CF26 sample.](image)

The high resolution transmission electron microscopy (HRTEM) examination revealed fine morphology of the nanopowder (Fig. 1a) with very small nanoparticles embedded in a matrix. Nanometric particles were identified in the higher resolution image (Fig. 1b) where mainly iron oxide crystalline particles can be seen: the interplanar distance of 0.26 nm belongs to (311) planes of \( \text{Fe}_3\text{O}_4/\).
\(\gamma\)-Fe\(\sub{2}O\sub{3}\). The interplanar distance of 0.37 nm identified between particles is assigned to pyrolytic carbon which was generated by the decomposition of C\(\sub{2}H\sub{2}\) [2].

The hysteresis loop of the sample measured at 293 K exhibited zero coercivity \(H_C\), which was — due to phase composition and particle sizes — the sign of superparamagnetically behaviour [3]. After zero-field cooling (ZFC) we extracted the following values from the hysteresis loop measured at 4 K: \(H_C = 65\) kA/m, remanence \(\sigma_R = 7.6\) Am\(^2\)/kg, and saturation \(\sigma_S = 29.8\) Am\(^2\)/kg (at 7.2 MA/m).

The hysteresis loop measured at 4 K after cooling of the sample in the field of 7.2 MA/m was not displaced along the field axis with respect to the hysteresis loop measured at 4 K after ZFC. Hence core/shell exchange anisotropy effect [4] and spin glass behaviour [5] can be excluded.

![Fig. 2. Mössbauer spectra for the synthesised CF26 sample measured at specified temperatures. The position of the \(\alpha\)-Fe sextet at 4 K is indicated.](image)

![Fig. 3. ZFC and FC curves for the synthesised CF26 sample.](image)

The superparamagnetic character of the nanopowder expresses itself in the measured Mössbauer spectra through the transition to sextets below the blocking
temperature \( T_B \) [3]. Therefore the spectrum for our sample measured at 4 K (Fig. 2) is dominated by the sextets of \( \text{Fe}_3\text{O}_4/\gamma-\text{Fe}_2\text{O}_3 \) [6].

The significant feature of the Mössbauer spectra in Fig. 2 is the increase in the intensity of absorption after cooling down to 4 K. The intensity of the absorption of a given phase depends on its recoil-free fraction \( f \) (named the Lamb–Mössbauer factor) [7]. The factor \( f \) is a function of the Debye temperature, \( \Theta_D \), which decreases with decreasing particle size [8]. In our case, due to particle sizes and the soft pyrolytic carbon matrix [9], \( \Theta_D \) is significantly lower than 293 K and therefore \( f \) grows by cooling.

Because of particle size distribution, one has to consider the distribution of blocking temperatures \( g(T_B) \), which can be calculated from the measured ZFC and field cooled (FC) curves (Fig. 3). It holds that \( g(T_B) = d(\sigma_{ZFC} - \sigma_{FC})/dT \) [10]. In our case, the maximum of the \( g(T_B) \) curve is reached at 11 K. The highest value of \( \sigma_{ZFC} \) is observed at 32 K.

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References