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Magnetic properties of Fe nanoparticle systems

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Abstract

The structure and magnetic properties of two systems of Fe-nanoparticles have been studied: (i) aerosol particles produced by a fast evaporation method and (ii) as-prepared particles dispersed in a silica aerogel matrix. The magnetic behavior of both samples is dominated by the long-range dipolar interparticle interactions but the confinement of Fe particle agglomerates in silica pores results in an enhancement of thermal fluctuation effects leading to a reduction of the remanence and coercivity.

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1. Introduction

Nanocomposites formed by particles trapped in porous media are a subject of interest since the structural confinement induced by the inorganic framework allows tailoring of the electronic, magnetic and optical properties of a nanocomposite [1–3]. Moreover, the use of an open-pore inorganic matrix provides an effective way for de-aggregation and confinement of airborne nanoparticles while still maintaining particle accessibility necessary in various applications such as magnetic separation or heterogeneous catalysis. Silica aerogels fulfill most of the required conditions demanded from a host such as chemical inertness, a large accessible surface area, a high porosity and pores in the nanometer range. To obtain the nanocomposite material, magnetic particles can either be synthesized in situ in the aerogel pores or the externally produced particles can be inserted into the matrix [2]. The latter method was used in this work to prepare the composite material of Fe nanoparticles hosted in a silica aerogel. The present study is aimed to investigate the magnetic properties of such nanocomposites and to relate them with those of the as-prepared Fe-particle powder.

2. Experimental

Aerosol Fe particles (sample A) were obtained by a fast evaporation of iron pentacarbonyl from a tungsten filament in an argon atmosphere at 3 Torr. After evaporation the particles were kept at a residual air pressure for 12 h to passivate their surfaces with a thin oxide shell allowing further handling of the powder at ambient conditions.

A composite material formed by Fe particles inside a silica matrix (sample B) was synthesized by dispersing the particles in a sol consisting of a water solution of ammonia and a mixture of methanol and tetramethoxysilane. The sol was forming a gel while continuously

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shaking a flask to avoid sedimentation of the particles and subsequent supercritical evacuation of the solvent. The density of the resulting nanocomposite aerogel was $0.11 \pm 0.02\,g\,cm^{-3}$ with an accessible surface area of $650\,m^2\,g^{-1}$. Pore diameters of the matrix range from 20 to 100 nm and the estimated volume fraction of Fe particles in silica matrix is ~0.45%.

Micrograph and electron diffraction pattern of the as-prepared Fe-particles were obtained with a 200 kV Hitachi H800MT transmission electron microscope (TEM). Magnetic properties have been studied with a vibrating sample magnetometer (VSM) (Oxford Instrument Ltd.) over the temperature range of 5–300 K. The materials were also characterized by Mössbauer spectroscopy (using a constant acceleration Mössbauer spectrometer with a $^{57}Co/Rh$ source) and powder X-ray diffraction (Siemens D5000 using CuKα radiation, $\lambda = 1.5406\,Å$).

3. Results and discussion

The bright field TEM image of sample A, presented in Fig. 1(a), shows that the particles are roughly spherical in shape and have a tendency to agglomerate. The histogram of the particle size distribution (Fig. 1(b)) was obtained by sampling of a minimum of 160 particles from the TEM image. The distribution, fitted using log-normal function, gives an average particle diameter $\langle D_1 \rangle \approx 15$ nm. The electron diffraction pattern of this sample (Fig. 1(c)) clearly displays the presence of α-Fe phase (distinct reflexes) as well as an iron oxide component (weak almost continuous rings). The former can be attributed to a metallic core of the particle while the latter, to a surface layer of iron oxides, mostly Fe_3O_4. Continuous rings of the oxide component indicate that the surface shell is formed by randomly oriented very small clusters. The core-shell structure found in the Fe aerosol particles studied has already been reported in the literature for similar particles [4–8].

The morphology as well as the size of Fe particles dispersed in the silica matrix were the same as those of sample A. However, in sample B, the size of agglomerates formed by interacting Fe particles was limited by the microstructure of the host material, i.e. the pore sizes.

Mössbauer measurements of the sample A were performed at 4, 80 and 300 K. The spectra, shown in Fig. 2, were fitted with two magnetically split subspectra. The hyperfine parameters obtained indicate the presence of: (i) α-Fe phase—sextet with sharp lines with $\langle B_{HF} \rangle \approx 34.4$ T at 4 K and the resonant area fraction of 60% of the total area (which does not change with temperature) and (ii) a broad component associated with the iron oxides (it was however not possible to make a univocal assignation to a given iron oxide) with $\langle B_{HF} \rangle \approx 50$ T at 4 K, which reduces with the temperature rise to $\langle B_{HF} \rangle \approx 33$ T at 300 K. Taking into account the Mössbauer resonant areas for both components and considering the different densities of Fe and Fe-oxides, it can be estimated that for particles ~15 nm in diameter, the average thickness of the oxide layer is $\delta \approx 2$ nm. This result is in agreement with the one obtained from powder X-ray diffraction (not shown) and analyzed using a Rietveld refinement program.

The sub-spectrum of the Fe-oxide phase at 300 K exhibits a reduced hyperfine field indicating the presence of thermal relaxation effects. Thus, the results obtained from the electron diffraction and Mössbauer investigations show that in aerosol Fe particles, passivated during the production process, the surface layer is not continuous but consists of very small clusters of Fe-oxides. These clusters, owing to their very small sizes, are affected by thermal fluctuations tending progressively to a superparamagnetic regime with the tempera-

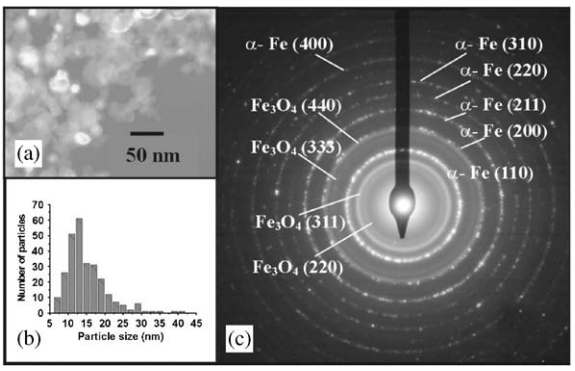

Fig. 1. The bright field TEM image of the particle assembly (a), histogram of the particle size distribution (b) and diffraction pattern (c) for sample A.

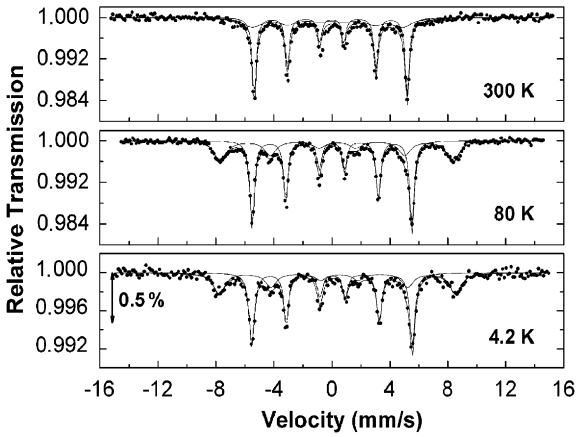

Fig. 2. Mössbauer spectra at 300, 80 and 4.2 K for sample A.