Ionic disorder and Néel temperature in $ZnFe_2O_4$ nanoparticles

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Abstract

Magnetic properties of ultrafine $ZnFe_2O_4$ particles obtained from mechanosynthesis of the precursor oxides are presented. The ordering temperature of *as-milled* sample is $T_N \approx 115(10)$ K, and extends over a $\Delta T \approx 60$ K range. This behavior can be explained by oxygen vacancies and local disorder at Fe sites resulting from the milling process. Magnetic coupling between ordered and disordered phases is discussed. © 1999 Elsevier Science B.V. All rights reserved.

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There is a growing number of theoretical and technological applications based on ultrafine ferrite particles. Several methods for obtaining nanoparticles have been developed, among which ball milling is being increasingly applied (see Ref. [1]). Nanosized ferrites can show unconventional magnetic phenomena regarding ordering temperature, enhanced coercivity and spin canting effects [2]. It is well known that in $ZnFe_2O_4$ ferrite, the ordering temperature of bulk samples ($T_N \approx 10$ K) can be raised by increasing Fe^{3+} population at A sites through mechanical activation [3]. This increase is originated in the stronger intersublattice (A–B) AFM superexchange interaction, as compared to intra-sublattice (A–A and B–B) ferromagnetic (FM) interactions. However, the final magnetic structures resulting from changes in site populations in nanoparticles are only partially known, since these configurations are obscured by many concurrent effects such as spin canting, Fe clustering and/or breakup of exchange paths by oxygen vacancies.

The starting powder was an equimolar mixture of α-Fe_2O_3 and ZnO powders (99.99%) ball-milled for 1320 h in closed hardened steel containers, with a ball-to-sample mass ratio 20 : 1. Acetone was used as a carrier liquid. X-ray diffraction measurements were performed using Cu-K_α radiation in the $10° \leq 2\theta \leq 80°$ range. Mössbauer measurements were performed with a constant-acceleration spectrometer in transmission geometry between $T = 4.2$ and 296 K. Isomer shifts are given relative to that of α-Fe at room temperature. Magnetization measurements were performed in a vibrating sample magnetometer between 4.2 and 300 K, in fields up to 9 T.

XRD pattern of *as-milled* sample (labeled ZM hereafter) showed that the main phase was $ZnFe_2O_4$, with a small amount of α-Fe_2O_3 which was close to the detection limit ($\leq 5\%$). The mean grain size estimated from the Scherrer equation was $\langle d \rangle = 20(4)$ nm. Thermogravimetric measurements showed a $\approx 7\%$ weight loss up to $T = 573$ K, which can be associated to desorption of the carrier liquid bound to the particles and the final stage of $ZnFe_2O_4$ formation. Accordingly, in samples annealed at $T \geq 573$ K for 1 h the XRD pattern showed only peaks corresponding to the spinel phase.

Room temperature Mössbauer spectra of sample ZM and crystalline $ZnFe_2O_4$ are shown in Fig. 1. A single doublet with quadrupole splitting $\Delta Q = 0.35(1)$ mm/s and isomer shift IS = 0.36(1) mm/s was found in bulk ferrite, coincident with previous findings [4]. For sample ZM two components, labeled $P1$ and $P2$, were needed to fit the central doublet, with $\Delta Q_1 = 0.62(2)$ mm/s, $IS_1 = 0.36(1)$ mm/s and $\Delta Q_2 = 1.0(1)$ mm/s, $IS_2 = 0.85$ mm/s values, respectively. The higher ΔQ_1 value compared with bulk ferrite is assigned to disordered Fe^{3+} environment caused by milling. The $P2$ component

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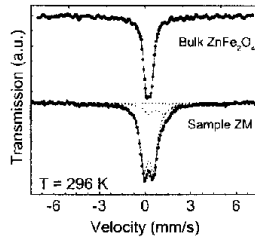
Fig. 1. Mössbauer spectra at $T = 295$ K for bulk $ZnFe_2O_4$ and sample ZM. Solid line is the total fitted spectrum, and dotted lines indiacte each component.
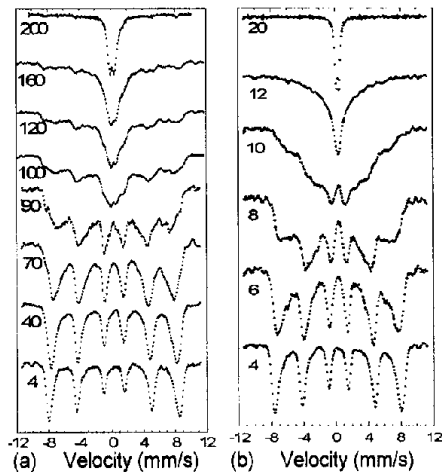

Fig. 2. Mössbauer spectra vs. temperature for (a) sample ZM and (b) bulk $ZnFe_2O_4$. The temperature of each spectrum is shown in the figure.

amounts $\approx 17\%$ of the total resonant signal, and its IS_2 value characterizes a Fe^2 oxidation state. This signal is no longer present in samples annealed in air at 573 K for 1 h. The additional sextet observed in ZM sample corresponds to α-Fe_2O_3, in agreement with XRD data.

Fig. 2 shows selected Mössbauer spectra taken for crystalline $ZnFe_2O_4$ and sample ZM at different temperatures near the AFM ordering. It can be seen that bulk $ZnFe_2O_4$ has a sharp transition at $T_N = 10(1)$ K, whereas for ZM sample the AFM ordering takes place within a wide range of temperatures, centered at $T_N \approx 115(10)$ K. This enhancement of the ordering temperature in ZM is associated to a higher Fe^{3+} population at A sites of the spinel structure, as previously observed in milled $ZnFe_2O_4$ [3]. The distribution of Fe^{3+} and Fe^{2+} ions and the oxygen vacancies resulting from milling can break the superexchange paths and induce spin disorder [2], yielding a broad distribution of hyperfine fields which relax at different temperatures, as can be seen from the complex shape of the spectra at temperatures near T_N.

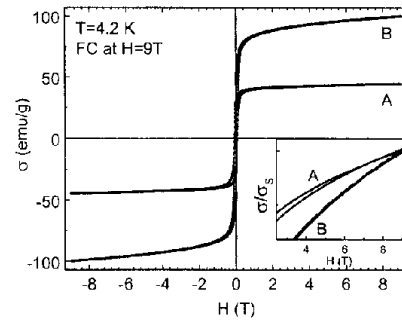Magnetization data taken at $T = 4.2$ K (Fig. 3) show lack of saturation for ZM sample, and irreversibility

Fig. 3. Field-cooled magnetization curves $\sigma(H,T)$ for (A) ZM sample and (B) sample ZM annealed in air at 573 K for 1 h. The inset shows the high-field region of both normalized curves σ/σ_s with $\sigma_s = \sigma(H = 9$ T). Notice the open hysteresis loop for curve A.

extending up to fields of $H \approx 6.5$ T. From the fitting of the $H \geq 6$ T region with the expression $\sigma = \sigma_0 + \chi H$, a value of $\sigma_0 = 41.6$ emu/g is obtained, which increases to 88.4 emu/g for sample annealed at 573 K. Assuming collinear alignment of the spins and that Fe^{2+} occupies only A sites, the effective moment per formula unit and inversion degree are $\mu_{eff} = 3.8\,\mu_B$ and $\delta = 0.11$, respectively. However, the lack of saturation at 4.2 K indicates that spin canting may result in these nanoparticles, and therefore the actual inversion degree may be higher. As shown in the inset of Fig. 3, the irreversible behavior disappears after annealing in air above $T = 573$ K. This feature may be therefore associated to the structural disorder observed in the as-milled sample. Similar behavior has been observed in γ-Fe_2O_3 [2] and $NiFe_2O_4$ [5] nanoparticles, and assigned to exchange coupling between an ordered ferrimagnetic core and a spin-glass-like surface layer. In our $ZnFe_2O_4$ samples, the local disorder observed from Mössbauer data suggests the possibility that also competing ferro- and antiferromagnetic exchange interactions arising from Fe clustering could be related to this irreversibility.

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