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Magnetic properties of (γ-Fe₂O₃)ₓAg₂₀ nanocomposites prepared in reverse micelles

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The magnetic properties of nanoparticles of γ-Fe₂O₃ prepared by reverse micelles have been studied by dc magnetization, transverse ac susceptibility, and Mössbauer spectroscopy. The nanoparticles of γ-Fe₂O₃ in the nanocomposite (γ-Fe₂O₃)ₓAg₂₀ exhibit superparamagnetic behavior. The blocking temperatures determined by the three methods indicate the superparamagnetic nature of (γ-Fe₂O₃)ₓAg₂₀ above 70–80 K and show correlation with measuring time. The average particle diameter obtained by transmission electron microscopy of the γ-Fe₂O₃ particles is ~10 nm and that of the Ag particles is ~20 nm. The average particle size determined from the magnetic analyses for the γ-Fe₂O₃ particles is ~12 nm. Mössbauer spectra obtained between 4.2 and 295 K clearly reveal the presence of superparamagnetic relaxation at temperatures above ~80 K. The Mössbauer spectra reveal at most 1% of paramagnetic Fe²⁺ ions in the 295-K spectrum. © 2005 American Institute of Physics. [DOI: 10.1063/1.1847331]

I. INTRODUCTION

The magnetic properties of γ-Fe₂O₃ nanoparticles prepared by a variety of techniques have been reported by several groups.¹–⁷ Of interest is the superparamagnetic properties of the nanoparticles and their blocking behaviors. Knowing that such properties are sensitive to the measuring techniques, we present a study of the magnetic properties of nanoparticles of γ-Fe₂O₃ prepared by reverse micelles by dc magnetization, transverse ac susceptibility, and Mössbauer spectroscopy. The samples are silver/γ-Fe₂O₃ nanocomposites that we prepared to alter their transport properties near the percolation threshold.⁸ However, we focus on their magnetic properties in this paper.

II. SAMPLE PREPARATION AND STRUCTURAL CHARACTERIZATION

The (γ-Fe₂O₃)₁₋ₓAgₓ nanocomposites were prepared from particles synthesized in reverse micelles.⁹ Our previous study has shown that the percolation threshold of (γ-Fe₂O₃)₁₋ₓAgₓ is x=29, above which the Ag particles are connected and the samples are metallic.⁸ The present study focuses on (γ-Fe₂O₃)ₓAg₂₀, in which the conductance is in the insulating region. X-ray diffraction analysis was performed on the nanocomposite (γ-Fe₂O₃)ₓAg₂₀ using a Philips X’pert powder diffractometer. Average crystallite diameters were estimated using the Scherrer relationship and in (γ-Fe₂O₃)ₓAg₂₀ the resulting γ-Fe₂O₃ crystallite diameter was ~8 nm. The Ag crystallite diameter was found to be ~25 nm when the influence of strain was ignored. The x-ray diffraction indicates that the material has two distinguishable phases and is free of any impurity within the x-ray diffraction detection limits.

Both because maghemite and magnetite are nearly isostructural, and because peak broadening in a nanocrystalline phase obscures the separation of the diffraction lines of their two phases, their powder-diffraction patterns become nearly indistinguishable. To determine the presence of an impurity phase containing divalent iron, Mössbauer spectral analysis was performed on the (γ-Fe₂O₃)ₓAg₂₀ nanocomposite. The analysis of the spectra, see below, indicates that the sample contains at most traces of divalent iron.⁹

The morphology of the (γ-Fe₂O₃)ₓAg₂₀ nanocomposite was determined using transmission electron microscopy. The results indicate that the individual Ag and γ-Fe₂O₃ particles are both spherical before mixing. The typical particle diameters are ~10 nm for γ-Fe₂O₃ and ~20 nm for Ag, values which agree relatively well with the crystallite diameters obtained from the Scherrer analysis of the x-ray diffraction peak broadening.

III. MAGNETIC CHARACTERIZATION

Figure 1 shows the temperature dependence of the magnetization of (γ-Fe₂O₃)ₓAg₂₀ obtained with zero field and field cooling in various applied fields. The temperature dependence of the magnetization reveals the superparamagnetic behavior of the γ-Fe₂O₃ nanoparticles. By using the data obtained at the lowest field of 50 Oe, the blocking temperature T_b was found to be 70 K. The average particle diameter was estimated from this blocking temperature using the expression for noninteracting single domain particle
where \( K = 4.7 \times 10^4 \text{ erg/cm}^3 \) is the anisotropy constant for bulk \( \gamma\text{-Fe}_2\text{O}_3 \), \( V \) is the particle volume, and \( k_B \) is the Boltzmann constant. The resulting particle diameter of \( \approx 12 \text{ nm} \) for \( \gamma\text{-Fe}_2\text{O}_3 \) is reasonably consistent with the transmission electron microscopy and x-ray diffraction results. The broadness of the zero-field-cooled magnetization peak indicates a distribution of particle sizes.

The transverse susceptibility of \( s\gamma\text{-Fe}_2\text{O}_3d_{80}\text{Ag}_{20} \) was measured using a very sensitive method based on the tunnel-diode oscillator technique. The relative transverse susceptibility, obtained at 10, 20, and 30 K by ramping the magnetic field from positive saturation to negative saturation, the closed symbols, and from negative saturation to positive saturation, the open symbols, is shown in Fig. 2. At these temperatures the curves show two peaks located symmetrically about the zero field. These peaks have different heights, with the larger peak located at a positive field when the field is ramped from positive to negative values. In contrast, at higher temperatures, the irreversible character in the field variation of the transverse susceptibility disappears, i.e., both the \( \chi_T \) curves from the two opposite field sweeps coincide.

This technique clearly defines the blocked and superparamagnetic states of a magnetic material as a function of temperature. As the temperature increases the double-peak structure of \( \chi_T \) becomes less pronounced and merges into a single central peak. Above \( T_b \), the \( \chi_T \) curves for the opposite field sweeps are identical because of the equivalent switching probabilities of the magnetic moment between the two equilibrium positions in a superparamagnetic material. In other words, the blocking temperature is the temperature at which \( \chi_T \) is a maximum at zero applied field. The temperature dependence \( \chi_T \) is similar to that of the longitudinal susceptibility usually observed in magnetic nanoparticle systems, with a maximum that shifts towards lower temperatures as the magnetic field increases. This method yields a blocking temperature of \( \approx 80 \text{ K} \) for \( s\gamma\text{-Fe}_2\text{O}_3d_{80}\text{Ag}_{20} \). The dependence of \( \chi_T \) on both temperature and applied field is shown in Fig. 2, inset.

The Mössbauer spectra obtained at 295 and 100 K indicate that the \( s\gamma\text{-Fe}_2\text{O}_3d_{80}\text{Ag}_{20} \) particles are superparamagnetic at these temperatures, as would be expected for such fine particles. The 295-K spectrum (see the bottom portion) of Fig. 3 has been fitted with a distribution of symmetric quadrupole doublets and both the resulting average isomer shift of 0.354 mm/s and the average quadrupole splitting of 0.68 mm/s are characteristic of fine \( \gamma\text{-Fe}_2\text{O}_3 \) particles. We have studied the 295-K Mössbauer spectrum in detail to determine if it reveals the presence of any divalent iron. The center portion of Fig. 3 shows the spectrum of \( s\gamma\text{-Fe}_2\text{O}_3d_{80}\text{Ag}_{20} \) magnified by a factor of 10 and fitted with no high-spin divalent iron spectral component. The top portion of Fig. 3 shows the same spectrum fit with a possible divalent iron quadrupole doublet which has an isomer shift of 1.20 mm/s, a quadrupole splitting of 2.48 mm/s, and a
relative area of 1.3%. From this fit we conclude that, if $(\gamma$-$\text{Fe}_2\text{O}_3)_{80}\text{Ag}_{20}$ contains any divalent iron it is less than 1% of the total iron present.

Selected Mössbauer spectra obtained between 4.2 and 100 K are shown in Fig. 4. The Mössbauer spectrum obtained at 100 K indicates that $(\gamma$-$\text{Fe}_2\text{O}_3)_{80}\text{Ag}_{20}$ is still superparamagnetic at 100 K and exhibits hyperfine parameters characteristic of $\gamma$-$\text{Fe}_2\text{O}_3$. There is no evidence of any hyperfine field at 100 K. In contrast, the 78-K Mössbauer spectrum clearly indicates that, although many of the particles are still superparamagnetic, many of the $\gamma$-$\text{Fe}_2\text{O}_3$ small particles are beginning to show the onset of slow magnetic relaxation on the Mössbauer time scale of $10^{-8}$ s. The resulting average isomer shift of 0.46 mm/s and hyperfine field of 8.6 T is typical of superparamagnetic $\gamma$-$\text{Fe}_2\text{O}_3$ particles near their blocking temperature. At 78 K the quadrupole splitting of the superparamagnetic doublet has increased to $\sim 1$ mm/s, indicating the presence of the expected electronic distortions at the iron sites in the small particles. Again, there is no obvious indication of the presence of any divalent iron in the 78- and 100-K spectra.

Between 78 and 40 K, the Mössbauer spectra all show the obvious presence of a broad magnetic sextet, a sextet which is characteristic of the magnetic relaxation expected in small particles of $\gamma$-$\text{Fe}_2\text{O}_3$. This broad relaxation profile has been fitted with a distribution of hyperfine fields and, as needed, a paramagnetic doublet corresponding to the small particles still undergoing superparamagnetic relaxation. Below approximately 40 K, as expected for a compound with an average blocking temperature of 70–80 K, the spectral area of the superparamagnetic quadrupole doublet has decreased to essentially zero. Further, at 30 K and below the Mössbauer spectrum consists of the expected magnetic hyperfine sextet which is somewhat broadened because of the range of sizes of the small particles which are present in the $(\gamma$-$\text{Fe}_2\text{O}_3)_{80}\text{Ag}_{20}$.

IV. CONCLUSIONS

The blocking temperatures for the $(\gamma$-$\text{Fe}_2\text{O}_3)_{80}\text{Ag}_{20}$ nanocomposite depend on the experimental techniques used as expected, but are in general consistent with each other indicating the superparamagnetic nature of the $(\gamma$-$\text{Fe}_2\text{O}_3)_{80}\text{Ag}_{20}$ nanocomposites above 70–80 K. The dc zero-field and field-cooled magnetization measurements indicate that the maghemite particles are superparamagnetic with an average blocking temperature of 70 K. The particle diameter, as determined from this blocking temperature, is $\sim 12$ nm. The transverse ac susceptibility was measured over a full range of temperatures and applied fields, and the resulting blocking temperature is 80 K. Mössbauer spectroscopy indicates that $(\gamma$-$\text{Fe}_2\text{O}_3)_{80}\text{Ag}_{20}$ has a blocking temperature between 78 and 100 K. There exists a clear correlation between the blocking temperature and measuring time scale. The time scale for dc measurement, transverse susceptibility, and Mössbauer is $100, 10^{-7} –10^{-5}$, and $10^{-8}$ s, respectively. The measurement with a longer time scale obtains lower blocking temperature due to the relaxation of the magnetic particles.

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