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Magnetic properties of $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ nanocomposites prepared in reverse micelles

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The magnetic properties of nanoparticles of γ-Fe_2O_3 prepared by reverse micelles have been studied by dc magnetization, transverse ac susceptibility, and Mössbauer spectroscopy. The nanoparticles of γ-Fe_2O_3 in the nanocomposite $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ exhibit superparamagnetic behavior. The blocking temperatures determined by the three methods indicate the superparamagnetic nature of $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ above 70–80 K and show correlation with measuring time. The average particle diameter obtained by transmission electron microscopy of the γ-Fe_2O_3 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-Fe_2O_3 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 Fe^{2+} ions in the 295-K spectrum. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1847331]

I. INTRODUCTION

The magnetic properties of γ-Fe_2O_3 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-Fe_2O_3 prepared by reverse micelles by dc magnetization, transverse ac susceptibility, and Mössbauer spectroscopy. The samples are silver/γ-Fe_2O_3 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 $(\gamma\text{-}Fe_2O_3)_{1-x}Ag_x$ nanocomposites were prepared from particles synthesized in reverse micelles.[9] Our previous study has shown that the percolation threshold of $(\gamma\text{-}Fe_2O_3)_{1-x}Ag_x$ is $x=29$, above which the Ag particles are connected and the samples are metallic.[8] The present study focuses on $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$, in which the conductance is in the insulating region. X-ray diffraction analysis was performed on the nanocomposite $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ using a Philips X'pert powder diffractometer. Average crystallite diameters were estimated using the Scherrer relationship and in $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ the resulting γ-Fe_2O_3 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 $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ nanocomposite. The analysis of the spectra, see below, indicates that the sample contains at most traces of divalent iron.[9]

The morphology of the $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ nanocomposite was determined using transmission electron microscopy. The results indicate that the individual Ag and γ-Fe_2O_3 particles are both spherical before mixing. The typical particle diameters are ~10 nm for γ-Fe_2O_3 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 $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ obtained with zero field and field cooling in various applied fields. The temperature dependence of the magnetization reveals the superparamagnetic behavior of the γ-Fe_2O_3 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

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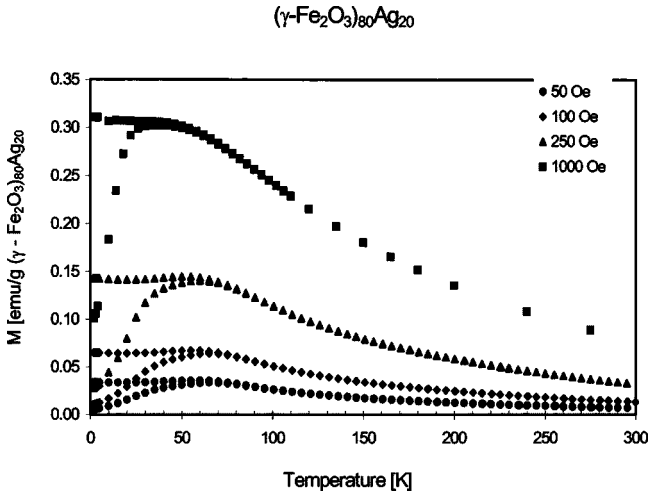

FIG. 1. The temperature dependence of the zero field and field cooled magnetic susceptibility of $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ obtained at four applied fields. Note the upward shift in T_b with decreasing field.

$$T_b = \frac{KV}{25k_B}, \tag{1}$$

where $K = 4.7 \times 10^4$ erg/cm^3 is the anisotropy constant for bulk γ-Fe_2O_3, V is the particle volume, and k_B is the Boltzmann constant.[10] The resulting particle diameter of ~12 nm for γ-Fe_2O_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 $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ was measured using a very sensitive method based on the tunnel-diode oscillator technique.[11] 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

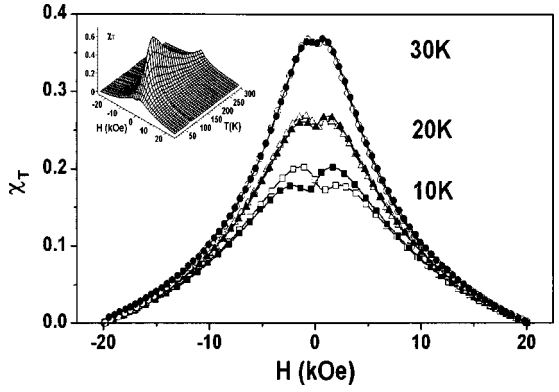

FIG. 2. The transverse magnetic susceptibility of $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ obtained at 10, 20, and 30 K by sweeping the magnetic field from positive saturation to negative saturation, closed symbols, and from negative saturation to positive saturation, open symbols. Inset: a three-dimensional plot of the experimentally determined $\chi_T(H,T)$ for $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$.

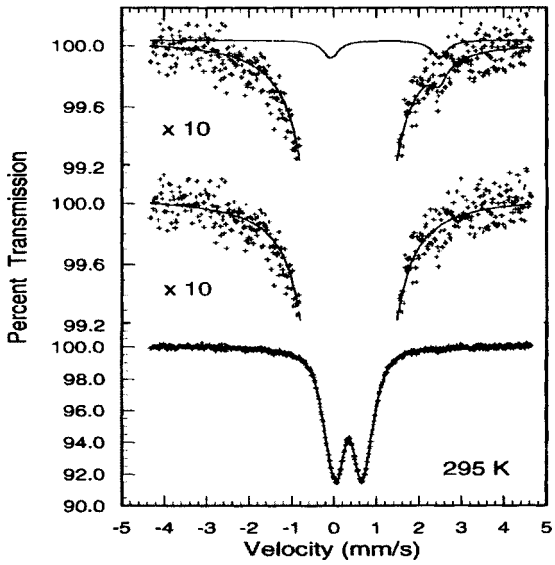

FIG. 3. The Mössbauer spectrum of $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ obtained at 295 K and fitted with a distribution of symmetric quadrupole doublets, bottom, and expanded by a factor of 10, middle. The same spectrum fit with a possible additional iron (II) quadrupole doublet is shown at the top.

higher temperatures, the irreversible character in the field variation of the transverse susceptibility disappears, i.e., both the χ_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 χ_T becomes less pronounced and merges into a single central peak. Above T_b, the χ_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 χ_T is a maximum at zero applied field. The temperature dependence χ_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 ~80 K for $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$.[12] The dependence of χ_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 $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ 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 quadruple 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 γ-Fe_2O_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 $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ magnified by a factor of 10 and fits 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

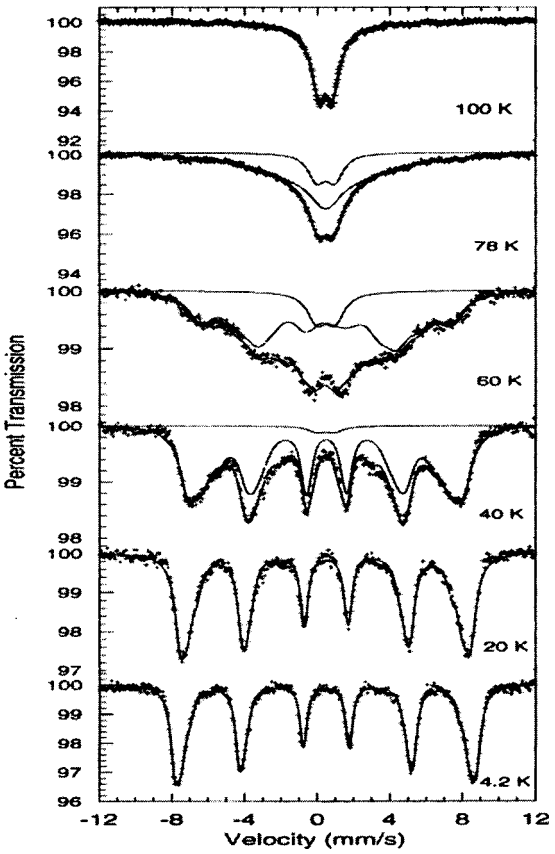

FIG. 4. The Mössbauer spectra of $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ obtained at several temperatures between 4.2 and 100 K and fitted with a distribution of hyperfine fields and, as needed, a superparamagnetic quadrupole doublet.

relative area of 1.3%. From this fit we conclude that, if $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ 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 $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ is still superparamagnetic at 100 K and exhibits hyperfine parameters characteristic of $\gamma\text{-}Fe_2O_3$. 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 $\gamma\text{-}Fe_2O_3$ 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 $\gamma\text{-}Fe_2O_3$ 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 $\gamma\text{-}Fe_2O_3$. 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 $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$.

IV. CONCLUSIONS

The blocking temperatures for the $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ nanocomposite depend on the experimental techniques used as expected, but are in general consistent with each other indicating the superparamagnetic nature of the $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ 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 $(\gamma\text{-}Fe_2O_3)_{80}Ag_{20}$ 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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