Size-Dependent Curie Temperature in Nanoscale $MnFe_2O_4$ Particles

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We have determined the Curie temperature T_c of ferrimagnetic $MnFe_2O_4$ nanoscale particles by means of direct measurement of the magnetization. A considerable enhancement in T_c compared to the bulk was observed for particles in the size range 7.5 to 24.4 nm. At $d=7.5$ nm, T_c is 97 K higher than for the bulk material. The shift in Curie temperature is well described by the finite-size-scaling formula $[T_c(d)-T_c(\infty)]/T_c(\infty)=(d/d_0)^{-1/\nu}$ with $\nu=0.71\pm0.07$ and $d_0=2.0$ nm.

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The general question of what happens to the bulk properties of a macroscopic body as one or more of its dimensions is reduced to atomic size has engendered intense interest in the past several years. This question is relevant not only to our fundamental understanding of nature, but also to our current technology as efforts continue to create useful devices of small size. Recent work has uncovered novel behavior in electronic, optical, and magnetic properties as the system size declines [1]. Relevant to the work reported here are studies of magnetism in films or layered materials [2–7] where one of the dimensions may be brought down to the atomic scale. Of fundamental importance is the behavior of the transition temperature, either the Curie temperature (T_c) in ferromagnetic systems or the spin freezing temperature (T_g) in spin-glass systems, which in all studies has been found to be significantly lower than in the bulk. The behavior in the spin-glass systems is well described by finite-size scaling for layers several monolayers thick or greater [4,7]. Still unexplored, however, is the behavior of the magnetic transition temperature when all three dimensions are limited, i.e., what is T_c in a particle? In this Letter we describe direct measurements of the Curie temperature of ferrimagnetic manganese ferrite particles and show that considerable *enhancement* in T_c is obtained. We find that this enhancement is well described by a finite-size-scaling formula with proper exponent and amplitude.

The selection of $MnFe_2O_4$ for size-dependent Curie temperature studies is an important aspect of our work. Its selection was based on (1) controllable size with uniform morphology and stoichiometry, (2) relative inertness to atmospheric oxygen compared to metallic particles, (3) the moderate Curie temperature to avoid particle sintering during measurement, and (4) a large magnetic period spacing which may make it easier to enter the size range which is comparable to the correlation length without the particle size being so small that a superparamagnetic transition results. Our major task in what follows is to demonstrate that our synthetic technique yielded particles with only one independent variable, the particle size, which then solely controlled the Curie temperature.

The synthetic technique is described in detail elsewhere [8]. Briefly, aqueous solutions of Mn^{+2} and Fe^{+3} chloride salts were coprecipitated with NaOH. After digestion at 100 °C for 90 min, roughly spherical particles, as seen by transmission electron microscopy, of $MnFe_2O_4$ were obtained. The mean diameter d of these particles could be controlled between 5 and 25 nm with the reactant molar ratio $[Me]/[OH^-]$, where [Me] is the total Fe^{+3} plus Mn^{+2} concentration.

Figure 1 shows an x-ray-diffraction (XRD) pattern for our particles with mean diameter $d=24.4$ nm. For all diameters d the patterns fit $MnFe_2O_4$ well with little noise. No systematic changes are seen with d. Size was measured with gas adsorption BET (Brunauer, Emmett, Teller) measurements which yield the specific surface area. This was converted to d by assuming spherical particles with $\rho=5.0$ g/cm^3, the density of bulk $MnFe_2O_4$. The Scherrer formula has also been used to determine the crystal size from the width of the XRD (311) line. We found that these sizes approximately agreed with each other and were consistent with transmission electron mi-

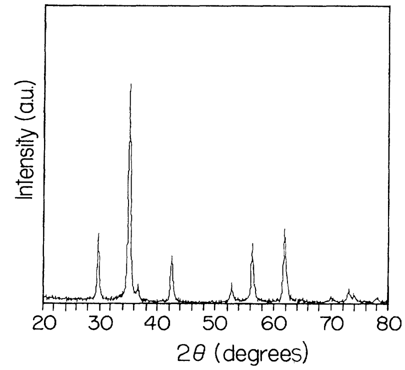

FIG. 1. X-ray-diffraction pattern for the particles. All lines correspond to $MnFe_2O_4$.

TABLE I. Chemical analysis results for four different particle sizes.

d (nm)	Mn (wt.%)	Fe (wt.%)	Atomic Mn/Fe	Missing mass (wt.%)
24.4	21.99	45.66	0.493	6.4
12.0	21.13	44.43	0.485	9.3
9.1	20.31	42.61	0.485	12.3
7.5	20.42	42.01	0.495	13.6

crographs for all sizes in our range. This implies that our particles are single crystals, a result consistent with electron microscope lattice imaging of similarly prepared particles by Sato *et al.* [9].

Table I gives chemical analysis data for four different sizes. The atomic ratio Mn/Fe is within experimental error of the stoichiometric value, 0.5, and there are no systematics with d. Oxygen analysis has not been done, but from the known compositions of Mn and Fe, the expected mass of $MnFe_2O_4$ could be determined. This value was not 100%; hence a missing (unknown) mass was present in our particles, and its calculated percent is given in Table I. Given the XRD results and the correct stoichiometry of Mn/Fe, we propose this missing mass is due to the surface adsorption of extra ions, such as OH^-, Cl^-, Na^+, and H^+, from the aqueous solution where the particles were made.

Figure 2 displays the saturation magnetization $\sigma_s(S)$ at room temperature versus surface area S from BET adsorption for our particles. σ_s is substantially lower than the bulk value $\sigma_s(0)=80$ emu/g. The missing mass can account for only part of this decreasing saturation magnetization. σ_s also varies linearly with $d^{-1}\propto S$ and this extrapolates to the known bulk value of $MnFe_2O_4$ as $d\rightarrow\infty$. This linear behavior can be obtained if one assumes a core-shell structure in which the shell layer has a constant thickness Δr and has lower saturation magnetization than the bulk. The straight line in Fig. 2 can be described by

$$\sigma_s(S)=\sigma_s(0)(1-aS)=\sigma_s(0)\left[1-\frac{\Delta\sigma\rho_2}{\sigma_s(0)}\Delta r\,S\right], \tag{1}$$

with $a=3.3\times10^{-7}$ g/cm^2 from a fit to the data. Then the surface shell thickness is $\Delta r=a\sigma_s(0)/\Delta\sigma\rho_2$, where $\Delta\sigma$ (emu/g) is the difference in magnetization between the core and the shell and ρ_2 is the density of this layer. As a rough estimation, we assume this layer has zero magnetization, and then $\Delta\sigma=80$ emu/g. Then using the bulk density value for $MnFe_2O_4$ ($\rho_2=5.0$ g/cm^3), the nonmagnetic layer is 0.7 nm thick. This is about the lattice constant of $MnFe_2O_4$ and hence implies the magnetic nature of the first crystalline layer on the particles is destroyed by the surface or surface adsorption. The surface layer thickness may have been underestimated by this analysis. For our purpose here, however, the point of this analysis is that while a weak magnetic layer exists on our particles, the most reasonable conclusion is that it does not affect the magnetic properties of the core $MnFe_2O_4$.

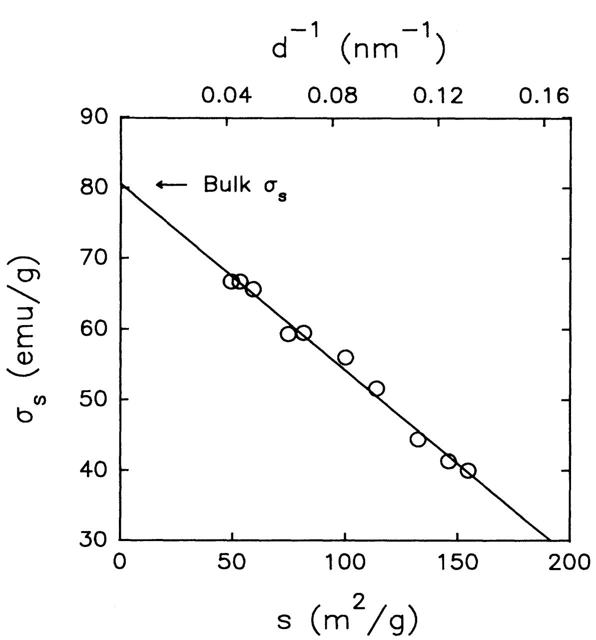

FIG. 2. Saturation magnetization σ_s vs specified surface area S for our particles. The upper abscissa is inverse mean particle diameter which is proportional to S. The bulk saturation magnetization is 80 emu/g.

Room-temperature Mössbauer spectroscopy using a ^{57}Co(Rh) source was applied to our particles. This spectroscopy allowed us to probe the atomic environment of the iron ions. The spectra showed both a sextet due to the magnetic iron ions and a doublet due to superparamagnetic particles. The relative intensity of the doublet increased as the average particle diameter fell, from single sextet at $d=24.4$ nm to single doublet at $d=5.0$ nm. Analysis of these relative intensities has led us to conclude that the superparamagnetic diameter was 8 nm.

Figure 3 displays the Mössbauer parameters for the magnetically split sextets. The isomer shift is reported relative to metallic iron. Importantly, no systematics are seen with size and the measured values are equal to those obtained for the bulk. A small shift of 12 kOe (2.5%) as d varies from 24.4 to 7.5 nm is seen in the hyperfine internal field. Its increase with declining d can be qualitatively explained from the fact that the internal field increases with core magnetization which in turn will increase with our observation, below, that T_c increases with decreasing d.

In summary, our characterization of these particles leads us to conclude that the major fraction core of our particles is stoichiometric, single-crystal $MnFe_2O_4$ wherein the magnetic iron ions see no change in environment as the particle size changes. The shell is well represented as weakly magnetic and noninteracting. We now

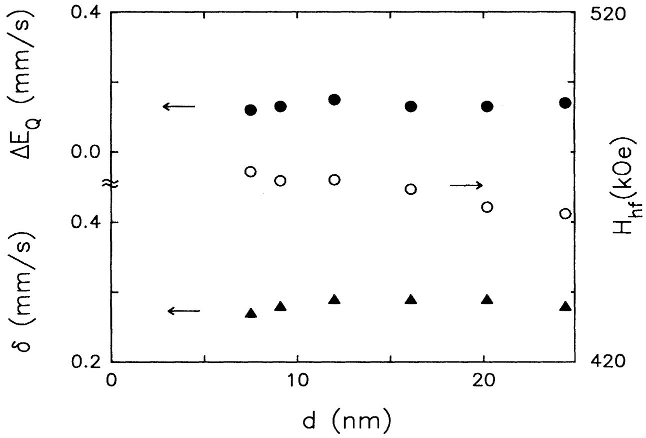

FIG. 3. The Mössbauer parameters isomer shift δ (relative to α-Fe), quadrupole splitting ΔE_Q, and hyperfine internal field H_{hf}, as a function of particle size.

explore this size dependence of the Curie temperature.

We measure the Curie point in the most direct and unambiguous manner possible, by watching the spontaneous change in magnetization as the temperature is varied through T_c with the sample in a small applied field. Figure 4 plots the magnetization σ vs T measured with a vibrating-sample magnetometer in an applied field of 20 Oe for four particle sizes. For bigger particles, the demagnetization effect appears at lower temperature (below 500 K) where a plateau is observed. This effect disappears for size $d \lesssim 12$ nm because of their lower saturation magnetization. T_c was determined from the intersection of extrapolations of the greatest slope and flat region above T_c. Methods to determine T_c involving scaling equations of state such as the Arrott and Noakes plot [10] could not be used because the particle size distribution led to a T_c distribution and hence curved isotherms on such plots. Only one transition has been observed for any sample, supporting the nonmagnetic shell model we have described above. T_c is seen to increase with declining d. The smallest particles, $d = 5.0$ nm, were all superparamagnetic as shown by the Mössbauer spectrum. Their σ was ~ 10 times less than when $d \gtrsim 7.5$ nm and showed no sharp features in the region of T_c. Therefore, the superparamagnetic fractions known from Mössbauer to exist for mean size $d \lesssim 7.5$ nm do not affect our determination of T_c for these samples. Given our characterization above, we conclude that the increase in T_c is due to the decrease in size in some fundamental way.

Some rounding of the expected jump at T_c is seen due to, for the most part, the finite size distribution. The size distribution, which can be inferred from the relative intensities of the ferrimagnetic and superparamagnetic Mössbauer lines [11], has a geometric width of ~ 1.7, for an assumed log-normal distribution. No extra broadening due to fluctuations induced by the declining particle size is seen. Hence the enhanced T_c is not due to fluctuation broadening. This can be reinforced by the fact that if T_c were determined from the midpoint of the jumps in Fig. 4, T_c would still increase with decreasing d.

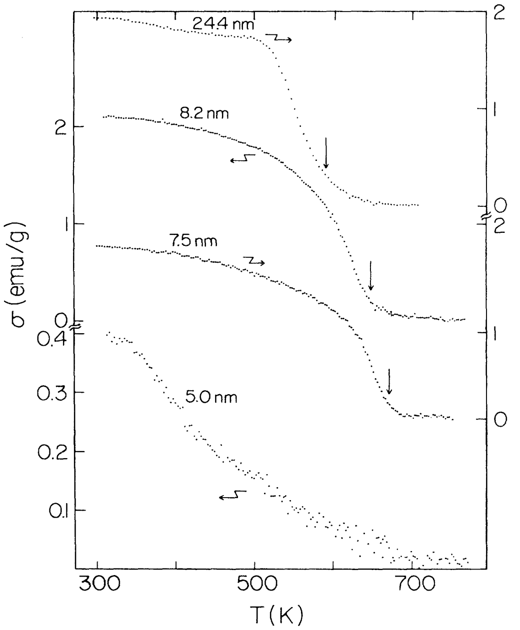

FIG. 4. Magnetization σ in an applied field of 20 Oe vs temperature for four different particle sizes. Note the smallest system with $d = 5.0$ nm was superparamagnetic. Verticle arrows designate T_c.

We find that finite-size scaling [12] can be used to explain the behavior of T_c. This theory predicts that the shift in the transition temperature from that of the bulk should depend on a dimension of the system in the following manner:

$$[T_c(d) - T_c(\infty)]T_c^{-1}(\infty) = \pm (d/d_0)^{-\lambda}. \qquad (2)$$

The exponent is predicted to be related to the correlation length exponent by $\lambda = 1/\nu$, the system-dependent sign may be either positive or negative, and d_0 should be of the order of the characteristic microscope dimension of the system. Figure 5 displays a log-log plot of $[T_c(d) - T_c(\infty)]T_c^{-1}(\infty)$ vs d $[T_c(\infty) = 573$ K$]$. The plot is linear, supporting Eq. (2), and $\lambda = 1.42 \pm 0.13$ to imply $\nu = 0.71 \pm 0.07$. This value of ν agrees well with those predicted by the isotropic three-dimensional Heisenberg model [13] which are in the range from $\nu = 0.65 \pm 0.07$ to 0.733 ± 0.020. The value of d_0 we find is 2.0 nm. This is roughly twice the lattice spacing of $MnFe_2O_4$ and hence fulfills its identification as a microscopic length scale. Thus we conclude finite-size scaling describes the shift in T_c well.

Also drawn in Fig. 5 is a line of slope -1.0. In many cases purely surface effects are proportional to d^{-1} because surface/volume $\sim d^{-1}$, e.g., Fig. 2. The data in Fig. 5 are not described by this dependency. This, coupled with the fact that the finite-size-scaling fit yields

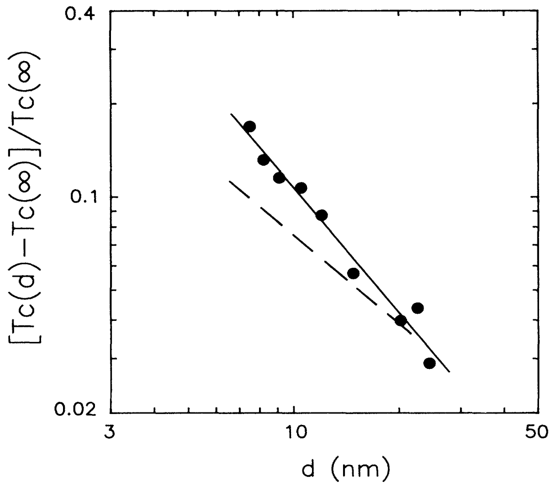

FIG. 5. Reduced Curie temperature shift vs particle diameter. Solid line is fitted by Eq. (2) with $\lambda = 1.42$ and $d_0 = 2.0$ nm; dashed line has slope of -1.0.

both a reasonable exponent and amplitude, leads us to conclude finite-size scaling is the best description of our data.

All other investigations have shown T_c (or T_g) to decrease with declining size in contrast to our measurement. All have also been on film or layered systems, however, in which only one of the three spatial dimensions went to atomic size. Our system, being particulate, has all three dimensions decreasing uniformly. The different geometries may be the reasons for the different T_c behavior. This proposition is supported by theoretical work of Ferdinand and Fisher [14] who saw T_c increase in 2D Ising systems in which the lattice was roughly square (aspect ratio less than 3.14), but decrease when the lattice became rectangular with aspect ratio larger than 3.14.

To summarize, we have observed, for the first time, a considerable enhancement in T_c as all dimensions of a ferrimagnetic system ($MnFe_2O_4$) are reduced to the nanoscale without changing composition and crystal structure. The shift in Curie temperature from that of the bulk is well described by the finite-size-scaling formula with proper exponent and characteristic microscopic dimension. The geometry of particulates, such as our nanoscale $MnFe_2O_4$ particles, in which all three dimensions are limited offers a different system to study the finite-size scaling compared with thin films. Further research should be directed to expand the experimental scope, including other metallic oxides, metals, and alloys in the geometry of spherical, acicular, and platelike shapes.

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