Temperature dependence of magnetic anisotropy constant in manganese ferrite nanoparticles at low temperature

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The temperature dependence of the effective magnetic anisotropy constant, $K(T)$, of $MnFe_2O_4$ nanoparticles is obtained based on superconducting quantum interference device magnetometry measurements. The variation of the blocking temperature, T_B, as a function of particle radius, r, is first determined by associating the particle size distribution and the anisotropy energy barrier distribution deduced from the hysteresis curve and magnetization decay curve, respectively. Finally, the magnetic anisotropy constant at each temperature is calculated from the relation between r and T_B. The resultant effective magnetic anisotropy constant $K(T)$ decreases markedly with increasing temperature from 8.5×10^4 J/m^3 at 5 K to 0.35×10^4 J/m^3 at 125 K. © *2011 American Institute of Physics*. [doi:10.1063/1.3563068]

I. INTRODUCTION

Magnetic anisotropy has been a key issue in understanding the relaxation behaviors of nanosized particle systems.[1] Magnetization vector in a particle prefers a direction along a crystallographic axis, called the easy axis, which corresponds to the minimum of magnetic anisotropy energy. This anisotropy energy acts as an energy barrier that limits the rotation of magnetic moments away from the easy axis. At a finite temperature, it is possible for the moments of noninteracting, single-domain particles to escape over the energy barrier by means of thermal agitation with relaxation time, τ, given by the Néel–Arrhenius equation

$$\tau = \tau_0 \exp(\Delta E_a / k_B T), \tag{1}$$

where k_B is Boltzmann's constant, T is the absolute temperature, and τ_0 is the attempt time of the order of $10^{-9} - 10^{-13}$ s. In the simplest case, $\Delta E_a = KV$ is the anisotropy energy barrier for small applied field, where K is the effective uniaxial anisotropy constant and V is the particle volume. Any real nanoparticle systems necessarily have a distribution of particle sizes, which gives rise to a distribution of anisotropy energy barrier.

When the energy barrier is overcome thermally, the magnetization direction can change rapidly, exhibiting superparamagnetic relaxation. The threshold temperature at which the energy barrier is surmounted by thermal activation and the particle system goes into the superparamagnetic regime is the blocking temperature, T_B, whose characterization is closely dependent on the time scale of the measurement method used. In fact, the blocking temperature for a particle system of a given size is the temperature at which the relaxation time τ equals the measurement time τ_m.

Many works on magnetic nanoparticles treat the anisotropy constant as a constant independent of temperature, although the change of the magnetic anisotropy constant with temperature is a well-known[2,3] physical phenomenon in magnetic materials. It has already been pointed out that any analysis under the assumption that the magnetic anisotropy is constant in a temperature range where it is in fact changing can produce erroneous results.[4] In this study, a very simple but intuitive method for determining the temperature dependence of the anisotropy constant $K(T)$ is introduced, by associating the particle size distribution with the anisotropy energy barrier distribution, and then illustrated by applying it to manganese ferrite nanoparticles.

II. EXPERIMENT

$MnFe_2O_4$ nanoparticles were prepared in solution by the decomposition of metalorganic precursors.[5] The particles were dried and subsequently subject to magnetic characterizations. A superconducting quantum interference device magnetometer was used to measure the room-temperature dc magnetization curve and the temperature dependence of magnetization decay. For the latter measurement, the sample was initially cooled from room temperature down to 5 K in a magnetic field of 100 G. Then the applied field was turned off and the remanent magnetization was measured on stepwise increasing the temperature.

III. RESULTS AND DISCUSSION

The M versus H curve measured at room temperature shows a superparamagnetic behavior with no hysteresis. In order to estimate the particle size and its distribution, the first quadrant part of the hysteresis loop (Fig. 1) is fitted to the classical Langevin function weight-averaged with a modified log-normal distribution $f(r)$ (Ref. 6):

$$f(r) = \frac{1}{(r-\theta)\sigma\sqrt{2\pi}} \exp\left[\left(\ln\frac{r-\theta}{r_0}\right)^2 / 2\sigma^2\right]. \tag{2}$$

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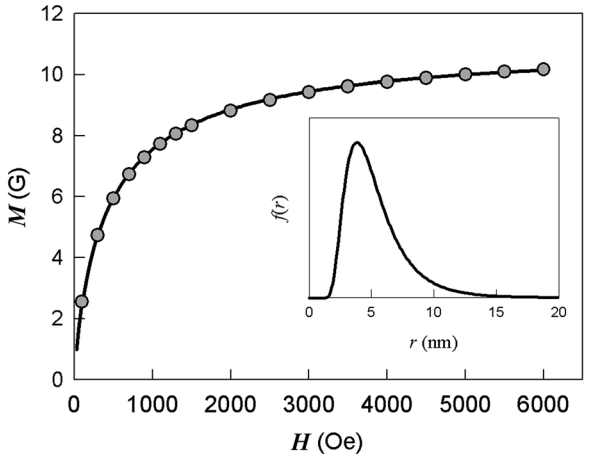

FIG. 1. Results of the M vs H curve analysis for the $MnFe_2O_4$ nanoparticles. Corresponding particle size distribution function, $f(r)$, is shown in the inset.

Best fit was obtained for $r_0 = 3.47$, $\theta = 1.26$, and $\sigma = 0.59$. The resultant distribution, $f(r)$, is shown in the inset of Fig. 1.

In order to get an anisotropy energy barrier distribution $f_A(T)$, the temperature dependence of magnetization decay M_{TD} of the sample was used. The result is depicted in Fig. 2, in which the magnetization decreases with increasing temperature and finally vanishes at 125 K. It is well known that the slope of the magnetization decay curve at any temperature gives the energy barrier distribution $f_A(T)$,[7]

$$f_A(T) \propto -\left.\frac{dM_{TD}}{dT}\right|_T. \tag{3}$$

The histogram in Fig. 2 shows the resultant energy barrier distribution $f_A(T)$. If the anisotropy constant were temperature independent, the anisotropy energy barrier distribution $f_A(T)$ would have been the same log-normal form as the size distribution $f(r)$. Actually, some studies report that this is indeed the case,[8] but, in general, this does not always hold.[9] It can be seen from the inset of Fig. 1 and the histogram in Fig. 2 that $f_A(T)$ skews to the right and shows a bimodal shape, whereas $f(r)$ skews to the left (ordinary log-normal distribution). This discrepancy can be explained if a temperature dependence is introduced into the anisotropy constant.

Now we have two different distribution functions at hand and the next step is to associate them together to extract the information about the temperature dependence of the anisotropy constant. As a first step, a relation between r and T_B is determined from the particle size distribution $f(r)$ and the anisotropy energy barrier distribution $f_A(T)$. Immediately after the cooling down to 5 K under an external magnetic field, most of the nanoparticle moments are blocked along the field direction. If the field is turned off and the temperature is slowly increased, larger and larger particles in the distribution $f(r)$ are unblocked and reverse their magnetization faster than the measurement time scale, τ_m. This means an increasing portion of the anisotropy energy barriers in the distribution $f_A(T)$ is gradually overcome. For a given distribution of anisotropy energy barriers, assume $x\%$ of the anisotropy energy barriers is thermally overcome at a temperature. Then one can obtain the corresponding particle radius by evaluating the critical radius at which the same $x\%$ of the particles in the distribution $f(r)$ are in the superparamagnetic state. Mathematically, this can be represented as

$$\int_0^r f(r')dr' = \int_5^{T_B(r)} f_A(T)dT, \tag{4}$$

where $T_B(r)$ is the blocking temperature of particles whose radius is r.

By taking two equal quantiles from each of the distributions, one can get a relation between the particle radius r and the corresponding blocking temperature T_B, which is shown in the inset of Fig. 3. If the anisotropy constant, K, is a constant in temperature, T_B should show a simple steep increase with increasing r. However, T_B shows a trend toward saturation, which strongly suggests the possibility that K must decrease with increasing temperature. Substituting the values of r and T_B into Eq. (1) with τ_m being 100 s, which is suitable for conventional magnetometry measurements, the anisotropy constant is estimated as a function of

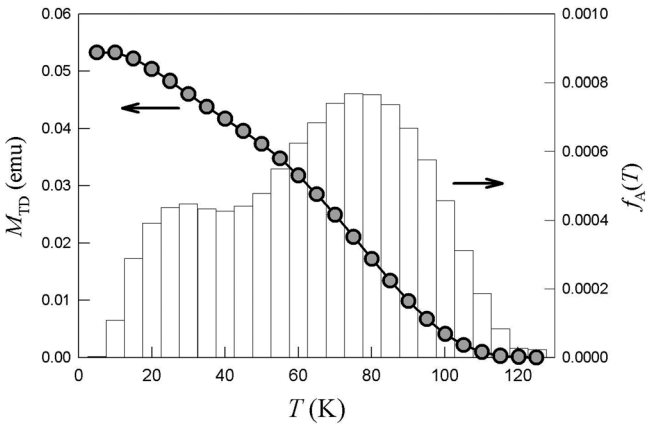

FIG. 2. Temperature dependence of magnetization decay for the $MnFe_2O_4$ nanoparticles cooled under a magnetic field of 100 G. The histogram is the anisotropy energy barrier distribution $f_A(T)$ deduced from Eq. (3).

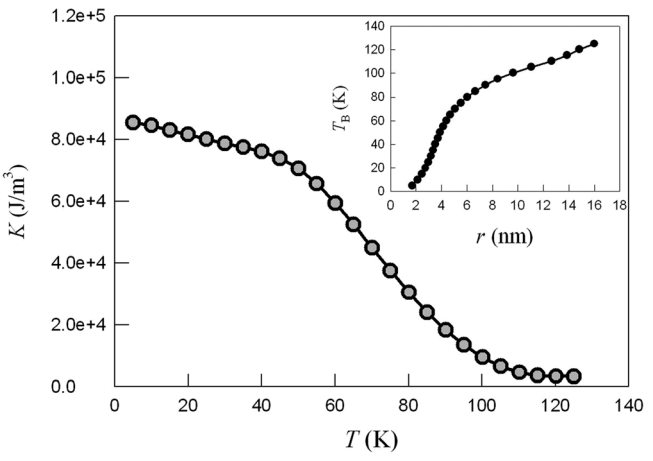

FIG. 3. Temperature dependence of the effective magnetic anisotropy constant $K(T)$ for the $MnFe_2O_4$ nanoparticles. The inset shows the variation of T_B as a function of r obtained programmatically from the analysis of Eq. (4).

temperature, as is represented in Fig. 3. During the programmatic process of obtaining $K(T)$, the other unknown parameter τ_0 is fixed to be 10^{-9} s. If this study is backed up by a complementary measurement with a different characteristic time scale, such as Mössbauer spectroscopy, one can get precise value of τ_0 as well.

The resultant effective magnetic anisotropy decreases with increasing temperature from 8.5×10^4 J/m^3 at 5 K to 0.35×10^4 J/m^3 at 125 K. If the decreasing trend of K with temperature is retained, a much lower anisotropy constant K value is expected at room temperature. The reported bulk value for K at room temperature in the literature is 0.25×10^4 J/m^3.[10] At this stage, the physical origin for the nontrivial variation in Fig. 3 is not clear. However, the temperature at which the anisotropy deviates from linear decrease in Fig. 3 ($\sim$50 K) corresponds to the temperature at which T_B/r^3 deviates from linear relationship in the inset of Fig. 3. In view of the reduced slope of the blocking temperature in the inset of Fig. 3, the reversal of magnetization in larger particles could take place through an incoherent rotation in the surface layer.[11] Moreover, since manganese ferrite has a cubic anisotropy, making it especially susceptible to surface effects, a contribution from the surface layer may result in more enhanced K in smaller particles, which are unblocked at lower temperature, and finally a nonlinear behavior in Fig. 3 is obtained. In fact, it was reported that materials with cubic anisotropy could show a behavior different from that of uniaxial materials, for which the linear temperature dependence is a good approximation.[12]

It is also worth noting that a high quality monodispersed sample is not needed for this study. Rather, a polydispersed sample with moderate size distribution width is preferred in order to get the anisotropy constant over a wider temperature range. This is why we can get the anisotropy constant at most up to 125 K in this study.

IV. CONCLUSION

The temperature dependence of the magnetic anisotropy constant, $K(T)$, of $MnFe_2O_4$ nanoparticles is determined from the particle size distribution and the anisotropy energy barrier distribution deduced from magnetometry measurements. The resultant magnetic anisotropy constant decreases with increasing temperature. The anisotropy constant at low temperatures is far more than one order of magnitude larger than that at 125 K, indicating the surface effects of smaller particles, which is particularly pronounced for materials with cubic anisotropy. Further experiments with nanocrystals of smaller size, to avoid incoherent rotation effects, and crystals with uniaxial anisotropy should validate this approach. Such work is in progress.

ACKNOWLEDGMENTS

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