High-temperature magnetic properties of noninteracting single-domain Fe$_3$O$_4$ nanoparticles

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Abstract

Magnetic measurements have been performed on 40-nm sphere-like Fe$_3$O$_4$ nanoparticles using a Quantum Design vibrating sample magnetometer. Coating Fe$_3$O$_4$ nanoparticles with SiO$_2$ effectively eliminates magnetic interparticle interactions so that the coercive field $H_C$ in the high-temperature range between 300 K and the Curie temperature (855 K) can be well fitted by an expression for noninteracting randomly oriented single-domain particles. From the fitting parameters, the effective anisotropy constant $K$ is found to be $(1.68\pm0.17)\times10^5$ erg/cm$^3$, which is slightly larger than the bulk magnetocrystalline anisotropy constant of $1.35\times10^5$ erg/cm$^3$. Moreover, the inferred mean particle diameter from the fitting parameters is in quantitative agreement with that determined from transmission electron microscope. Such a quantitative agreement between data and theory suggests that the assemble of our SiO$_2$-coated sphere-like Fe$_3$O$_4$ nanoparticles represents a good system of noninteracting randomly-oriented single-domain particles.
Ensembles of magnetic nanoparticles in various forms have been at the focus of scientific interest [1] since the days of Néel [2] and Brown [3], who developed a theory for noninteracting single-domain ferromagnetic particles. A complete understanding of the magnetic properties of ferromagnetic nanoparticles is not simple, in particular because of the complexity of real nanoparticle assemblies, involving magnetic interparticle interactions and magnetic anisotropy. An important contribution to the understanding of the magnetic behavior of nanoparticles was given by Bean and Livingston (BL) [4] who assumed an assembly of noninteracting single-domain particles with uniaxial anisotropy. This study was based on the Néel relaxation time \( \tau = \tau_0 \exp(KV/k_B T) \), where \( \tau_0 \) is the characteristic time constant, \( k_B \) is the Boltzmann constant, \( K \) is the uniaxial anisotropy constant, and \( V \) is the particle volume. \( KV \) represents the energy barrier between two easy directions. According to Bean and Livingston, at a given observation time \( \tau_{\text{obs}} \), there is a critical temperature, called the blocking temperature \( T_B \), given by [4]

\[
T_B = \frac{KV}{k_B \ln(\tau_{\text{obs}}/\tau_0)},
\]

above which the magnetization reversal of an assembly of identical single-domain particles goes from blocked (having hysteresis) to superparamagnetic-type behavior. Within this framework the coercive field \( H_C \) is expected to decrease with the square root of temperature:

\[
H_C = \alpha \frac{2K}{M_s} \left[ 1 - \left( \frac{T}{T_B} \right)^{1/2} \right],
\]

where \( M_s \) is the zero-temperature saturation magnetization and \( \alpha = 1 \) if the particle easy-axes are aligned [4] or \( \alpha = 0.48 \) if randomly oriented [5].

![FIG. 1: X-ray diffraction (XRD) spectrum of hydrothermally synthesized Fe\textsubscript{3}O\textsubscript{4} nanoparticles.](image-url)
The above equations have not been well tested by experiments due to the experimental difficulties in producing assemblies of noninteracting sphere-like nanoparticles. When magnetic nanoparticles are closely packed and/or aggregate, the interparticle interactions are expected to modify the magnetic behavior of the assembly. These interactions can have a dipolar, Ruderman-Kittel-Kasuya-Yosida (RKKY), or a superexchange character, depending on the character of an assembly. For magnetic nanoparticles embedded in an insulating matrix such as amorphous alumina [6] and amorphous SiO$_2$ [7–9], the dipolar interactions are the dominant ones [5]. Major theoretical and experimental efforts have been focused on the understanding of the role of the dipolar interactions [10]. In addition to granular metal solids [6–9, 11], frozen ferrofluids have been used to investigate the role of dipolar interactions [12–15]. In these systems, the magnetic particles are held fixed in a frozen insulating liquid. The degree of dilution in the liquid solvent controls the average particle distance and therefore the strength of the interactions. However, these studies have been limited to ultra-fine particles with a low $T_B$ and to a temperature region well below the Curie temperature ($T_C$) of the magnetic nanoparticles. Since the particles are so fine, the contribution of the surface anisotropy becomes significant and even dominant if they are not perfectly spherical particles [16].

Here we report magnetic measurements on 40-nm sphere-like Fe$_3$O$_4$ nanoparticles using a Quantum Design vibrating sample magnetometer. Coating Fe$_3$O$_4$ nanoparticles with SiO$_2$ effectively eliminates magnetic interparticle interactions so that the coercive field $H_C$ in the high-temperature range between 300 K and $T_C$ follows Eq. (2) for noninteracting randomly oriented particles. Fitting the data with Eq. (2) yields $K = (1.68 \pm 0.17) \times 10^5$ erg/cm$^3$, which is slightly larger than the bulk magnetocrystalline anisotropy constant of $1.35 \times 10^5$ erg/cm$^3$ (Ref. [17]). Moreover, the inferred mean particle diameter from the fitting parameters is in good agreement with that determined from transmission electron microscope. Such a good agreement between data and theory suggests that the assemble of our SiO$_2$-coated sphere-like Fe$_3$O$_4$ nanoparticles represents a good system of noninteracting randomly-oriented single-domain particles.

Samples were synthesized by an improved hydrothermal route [18] using the following reagents and solvents: iron(III) chloride hexahydrate, diethylene glycol, sodium hydroxide, and iron(II) chloride tetrahydrate. The as-grown Fe$_3$O$_4$ nanoparticles were then coated with SiO$_2$ following the method of Ref. [19]. Magnetization was measured using a Quantum Design vibrating sample magnetometer (VSM). The moment measurement was carried out.
FIG. 2: a) Transmission electron microscopy images of as grown Fe$_3$O$_4$ nanoparticles. b) Histogram of the particle size distribution. The mean diameter of the particles is found to be about 43 nm.

after the sample chamber reached a high vacuum of better than $9 \times 10^{-6}$ torr. The absolute measurement uncertainty in moment is less than $1 \times 10^{-6}$ emu.

Figure 1 shows x-ray diffraction (XRD) spectrum of hydrothermally synthesized Fe$_3$O$_4$ nanoparticles. The positions and relative intensities of all diffraction peaks match well with those of JCPDS card (19-0629) of magnetite with a lattice constant of 8.367 Å.

Figure 2a shows Transmission electron microscopy (TEM) images of as synthesized Fe$_3$O$_4$ nanoparticles. The TEM images were taken with a Hitachi model H-800 using an accelerating voltage of 80 kV. The pictures demonstrate high quality and monodispersity of the as synthesized nanoparticles. Fig. 2b displays a histogram of the particle size distribution. From the histogram, we determine the mean diameter of the particles to be about 43 nm.
FIG. 3: a) Temperature dependencies of the ZFC and FC susceptibilities for Fe$_3$O$_4$ nanoparticles coated with SiO$_2$, which were measured in a field of 50 Oe. The downward arrow indicates a Curie temperature $T_C$ of 855 K. b) The reciprocal of the susceptibility $1/\chi$ versus temperature. The Curie-Weiss fit (solid line) yields $T_C = 855$ K.

Figure 3a shows temperature dependencies of the ZFC and FC susceptibilities for Fe$_3$O$_4$ nanoparticles coated with SiO$_2$, which were measured in a field of 50 Oe. The susceptibility was calculated using the fact that the SiO$_2$-coated sample contains 75% Fe$_3$O$_4$ and 25% SiO$_2$ (in weight), which were determined from the measured room-temperature saturation magnetizations of both as-grown and SiO$_2$-coated Fe$_3$O$_4$ samples. One can clearly see that there are significant differences between the ZFC and FC susceptibilities in the whole temperature range between 300 K and $T_C$. This indicates that the blocking temperature of the nanoparticle assembly is higher than $T_C$. A Curie temperature of 855 K is inferred from the data (indicated by the downward arrow), which takes into account a small thermal lag. In Fig. 3b, we plot the reciprocal of the susceptibility $1/\chi$ versus temperature. It is apparent that the susceptibility data above the Curie temperature can be well fitted by the Curie-Weiss law (solid line): $\chi = C/(T - T_C)$ with $T_C = 855$ K and the Curie-Weiss constant $C$. 

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= 1.12 emu/K mole-Fe$_3$O$_4$. It is remarkable that the $T_C$'s determined from the data above and below $T_C$ are almost identical. The value of the Curie-Weiss constant corresponds to an effective moment $p_{eff} = 3.0 \mu_B$ per Fe$_3$O$_4$ (where $\mu_B$ is the Bohr magneton).

In Fig. 4a we plot magnetic hysteresis loops at four different temperatures. The magnetization at $H = 10$ kOe progressively decreases as the temperature increases and is almost saturated at 10 kOe. In order to see the low field data more clearly, we show an expanded view of the loops in Fig. 4b. It is clear that the coercive field $H_C$ also decreases progressively as the temperature increases.

Figure 5a shows the saturation magnetization $M_s$ as a function of temperature. The $M_s$ value at $T_C = 855$ K is set to zero. The solid line is a fitted curve by $M_s = A(T - T_C)^\beta$ with $\beta = 0.354$. The $M_s$ at room temperature is 86.6 emu/g-Fe$_3$O$_4$, which is slightly lower than the bulk value of 92 emu/g-Fe$_3$O$_4$. Then the zero-temperature $M_s$ should be about 90
FIG. 5: a) Temperature dependence of the saturation magnetization $M_s$. The solid line is a fitted curve by $M_s = A(T - T_C)\beta$ with $\beta = 0.354$ and $T_C = 855$ K. b) Temperature dependence of the coercive field $H_C$. The solid line is the fitted curve by Eq. (2) with the fitting parameters: $T_B = 1243\pm153$ K and $K/M_s = 361\pm37$ Oe.

In Fig. 5b, we plot $H_C$ versus $T$ for the sample. Since the $H_C$ values are found to be slightly different from the positive and negative field data due to a remanent magnetic field of about 10 Oe in the superconducting magnet of the equipment, we take $H_C$ to be the average of the two $H_C$ values obtained from the positive and negative field data, respectively. The solid line is a fitted curve by Eq. (2) with the fitting parameters $T_B = 1243\pm153$ K and $K/M_s = 361\pm37$ Oe. Using $M_s = 90$ emu/g and $K/M_s = 361\pm37$ Oe, we find $K = (1.68\pm0.17)\times10^5$ erg/cm$^3$, which is slightly larger than the bulk value of $1.35\times10^5$ erg/cm$^3$ (Ref. [17]). If we use $M_s = 77.8$ emu/g (Ref. [20]), we obtain $K = (1.45\pm0.14)\times10^5$ erg/cm$^3$, which is very close to the bulk value.

In order to further check whether our data are in quantitative agreement with the the-
oretical predictions [Eqs. (1) and (2)], we use Eq. (1), the bulk $K$, and the inferred $T_B$ to estimate the average particle diameter. Since the average measuring time for each data point is 0.5 s, we can set $\tau_{obs} = 0.5$ s. The value of $\tau_0$ for Fe$_3$O$_4$ nanoparticles was found [20] to be $9 \times 10^{-13}$ s. Substituting $\tau_{obs} = 0.5$ s, $\tau_0 = 9 \times 10^{-13}$ s, and $T_B = 1243 \pm 153$ K into Eq. (1), we find $d = 40.4 \pm 2.1$ nm, which is close to that (43 ± 2 nm) deduced from TEM. Using the diameter of 40 nm for as-grown Fe$_3$O$_4$ nanoparticles and the fact that the SiO$_2$-coated sample contains 75% Fe$_3$O$_4$ and 25% SiO$_2$ (in weight), we estimate the average thickness of the coated SiO$_2$ layers to be about 6 nm.

The quantitative agreement between our data and the BL theory suggest that the assembly of our 40-nm Fe$_3$O$_4$ nanoparticles coated with 6-nm SiO$_2$ layers represents a nearly ideal system of noninteracting single-domain particles. The diameter of 40 nm is well below the maximum diameter of single-domain particles of about 128 nm (Refs [21, 22]). The fact that the inferred $K$ value is close to the bulk one suggests that a contribution of the surface anisotropy is small, in agreement with the sphere-like shape of particles (see the TEM pictures in Fig. 2a).

In summary, we have made high-temperature magnetic measurements on hydrothermally synthesized Fe$_3$O$_4$ nanoparticles using a Quantum Design vibrating sample magnetometer. Coating 40-nm Fe$_3$O$_4$ nanoparticles with about 6-nm SiO$_2$ effectively reduces magnetic interparticle interactions so that the coercive field $H_C$ follows the BL expression for noninteracting single-domain magnetic particles. The quantitative agreement between our data and the BL theory [4] suggests that the assembly of our SiO$_2$-coated sphere-like Fe$_3$O$_4$ nanoparticles represents a nearly ideal system of noninteracting randomly-oriented single-domain particles.

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