Suppression of the Néel temperature in hydrothermally synthesized α-Fe₂O₃ nanoparticles

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Magnetic measurements up to 1000 K have been performed on hydrothermally synthesized α-Fe₂O₃ nanoparticles (60 nm) using a Quantum Design vibrating sample magnetometer. A high vacuum environment (1×10⁻⁵ torr) during the magnetic measurement up to 1000 K leads to a complete reduction of α-Fe₂O₃ to Fe₃O₄. This precludes the determination of the Néel temperature for the α-Fe₂O₃ nanoparticles. In contrast, coating α-Fe₂O₃ nanoparticles with SiO₂ stabilizes the α-Fe₂O₃ phase up to 930 K, which allows us to determine the Néel temperature of the α-Fe₂O₃ nanoparticles for the first time. The Néel temperature of the 60-nm α-Fe₂O₃ nanoparticles is found to be 945 K, about 15 K below the bulk value. The small reduction of the Néel temperature of the α-Fe₂O₃ nanoparticles is consistent with a finite-size scaling theory. Our current results also show that coating nanoparticles with SiO₂ can effectively protect nanoparticles from oxidation or reduction, which is important to technological applications.

There are finite-size effects of ferromagnetism, antiferromagnetism, superconductivity, and other physical properties when the dimensions of solids are reduced to the nanoscale. For a magnetic system, the growth of the spin correlation length will be limited by the smallest dimension and the system will exhibit a reduced magnetic transition temperature following a finite-size scaling theory [1]. So far, experimental observations of finite-size effects in magnetic systems have been mostly limited to quasi-two-dimensional ferromagnetic systems such as ferromagnetic thin films of Ni [2, 3], Fe [4, 5], Co [6], and Gd [7]. Experimental observation of finite-size effects in antiferromagnetic (AF) thin films has been very challenging because it requires very thin layers and because the magnetic response of an AF material is much weaker than that of a ferromagnet. One study of finite-size effects in an AF material is through the indirect measurement of resistivity in thin layers of Cr, which is an incommensurate spin-density-wave AF metal [8]. Since the results were observed in Fe/Cr multilayers, the interlayer coupling through the Cr layers and the ferromagnetic ordering of the Fe layers complicate the analyses of the finite-size scaling of Cr layers. The second study of finite-size effects in an AF material is through the direct magnetic measurement of antiferromagnetic thin films of CoO that has an ideal Néel temperature (T_N) near room temperature [9]. This study shows a finite-size scaling relationship with a scaling exponent ν of 0.65.

Recently, finite-size effects have been investigated in antiferromagnetic hematite (α-Fe₂O₃) nanowire arrays with a mean diameter d of about 150 nm [10]. A magnetic transition at 852 K has been assigned to the Néel temperature T_N of the α-Fe₂O₃ nanowire arrays [10]. Then the speculated T_N of 852 K for the nanowires is over 100 K below the bulk value (960 K [10]). Such a T_N reduction in these nanowires (d = 150 nm) is too large to be compatible with the finite-size scaling relations inferred from both ferromagnetic thin films [2] and antiferromagnetic thin films [6]. Moreover, the assigned T_N value [10] happens to be the same as the Curie temperature of Fe₃O₄. Therefore, it is likely that the magnetic transition at 852 K is not associated with the antiferromagnetic transition of the 150-nm α-Fe₂O₃ nanowires but with the minor phase of Fe₃O₄.

Here we report magnetic measurements (up to 1000 K) on hydrothermally synthesized α-Fe₂O₃ nanoparticles (60 nm) using a Quantum Design vibrating sample magnetometer. A high vacuum environment (1×10⁻⁵ torr) during the magnetic measurement up to 1000 K leads to a complete reduction of α-Fe₂O₃ to Fe₃O₄. This precludes the determination of the Néel temperature of the α-Fe₂O₃ nanoparticles. In contrast, coating α-Fe₂O₃ nanoparticles with SiO₂ almost stabilizes the α-Fe₂O₃ phase up to 930 K, which allows us to determine the Néel temperature of the α-Fe₂O₃ nanoparticles for the first time. The Néel temperature of the 60-nm α-Fe₂O₃ nanoparticles is found to be 945 K, about 15 K below the bulk value. The small reduction of the Néel temperature of the α-Fe₂O₃ nanoparticles is consistent with the finite-size scaling theory [1]. Our current results also show that coating nanoparticles with SiO₂ can effectively protect nanoparticles from oxidation or reduction, which is important to technological applications of nanoparticles.

Samples of α-Fe₂O₃ nanoparticles were synthesized by a hydrothermal route [11]. 4 mL of 0.5 mol/L FeCl₃.6H₂O solution was mixed with 12 mL of 0.5 mol/L CH₃COONa aqueous solution to form a mixture solution and 2 mL of C₂H₅OH was slowly added into the mixture solution under vigorous stirring for 10 min. The whole mixture was filled with 2 mL of H₂O and stirred for 30 min to form homogeneous solution. Then the solution was transferred into a Teflon lined stainless steel autoclave, sealed, and maintained at 200 °C for 12 h. After the heating treatment, the autoclave was cooled to room temperature naturally. Red product was obtained and collected by centrifugation, washed with water several times, and finally dried at 60 °C under vacuum. The
α-Fe₂O₃ nanoparticles were then coated with SiO₂ according to the method of Ref. [12]. Hematite particles were dispersed in 75 mL of ethanol, 15 mL of H₂O, and 10 mL of ammonia (25%) by ultrasonic wave. The citric acid solutions (1 M) were added to the solution until flocculation was visible. The precipitate was redispersed by increasing the pH value with tetramethylammonium hydroxide. While stirring, 0.2 mL of tetraethyl orthosilicate (TEOS) was slowly added to the ethanol mixture solution, and after 12 h another 0.3 mL of TEOS was added. The precipitate was collected by filtration and washed several times with distilled water and ethanol and finally dried in a vacuum oven at 60 °C for about 6 h.

Magnetization was measured using a Quantum Design vibrating sample magnetometer (VSM). The moment measurement was carried out after the sample chamber reached a high vacuum of better than 9×10⁻⁶ torr. The absolute measurement uncertainty in moment is less than 30 K/min. The precipitate was redispersed by increasing the pH value with tetramethylammonium hydroxide. While stirring, 0.2 mL of tetraethyl orthosilicate (TEOS) was slowly added to the ethanol mixture solution, and after 12 h another 0.3 mL of TEOS was added. The precipitate was collected by filtration and washed several times with distilled water and ethanol and finally dried in a vacuum oven at 60 °C for about 6 h.

FIG. 1: a) X-ray diffraction (XRD) spectrum of hydrothermally synthesized α-Fe₂O₃ nanoparticles. From the width of the (104) peak, the mean diameter of the sample is found to be 59.3 nm.

Magnetization was measured using a Quantum Design vibrating sample magnetometer (VSM). The moment measurement was carried out after the sample chamber reached a high vacuum of better than 9×10⁻⁶ torr. The absolute measurement uncertainty in moment is less than 1×10⁻⁶ emu. The heating and cooling rates for the magnetic measurements are 30 K/min.

Figure 1 shows x-ray diffraction (XRD) spectrum of hydrothermally synthesized α-Fe₂O₃ nanoparticles. It is apparent that the sample is of single phase. We can determine the average diameter from the width of the (104) peak. The full width at half maximum (HWHM) of the (104) peak is found to be 0.150±0.005° from a Gaussian fit. Using the Scherrer equation [13]: \[ d = 0.89\lambda/(\beta \cos \theta) \]
and with \( \beta = 0.137° \) (after correcting for the instrumental broadening), we calculate \( d = 59.3 \) nm.

Figure 2a shows magnetization versus temperature (up to 1000 K) for a virgin sample of α-Fe₂O₃ nanoparticles, which was measured in a magnetic field of 10 kOe. One can clearly that, upon heating the magnetization shows a rapid rise above 650 K, which is the onset temperature of the reduction of the weak-ferromagnetic α-Fe₂O₃ to the ferrimagnetic Fe₃O₄ phase. Upon cooling, the magnetization data show a magnetic transition at about 850 K (see Fig. 2b), which is the same as the Curie temperature of Fe₃O₄.

In order to check whether all α-Fe₂O₃ nanoparticles have been reduced after the magnetic measurement up to 1000 K, we took x-ray diffraction right after the magnetic measurement. The XRD spectrum is shown in Fig. 3a. It is clear that the sample contains about 90% of Fe₃O₄ and about 10% of FeO. There is no trace of the α-Fe₂O₃ phase. Upon cooling, the magnetization data show a magnetic transition at about 850 K (see Fig. 2b), which is the same as the Curie temperature of Fe₃O₄.

FIG. 2: a) Temperature dependence of the magnetization for a virgin sample of α-Fe₂O₃ nanoparticles, which was measured up to 1000 K. b) The derivative of the cooling-down magnetization \((dM/dT)\) versus temperature for the sample. A minimum of \(dM/dT\) at 848 K corresponds to a magnetic transition.
Fe$_3$O$_4$ nanoparticles is in quantitative agreement with the reported value [14].

Figure 4 shows magnetization versus temperature (up to 930 K) for a sample of α-Fe$_2$O$_3$ nanoparticles coated with SiO$_2$. Upon heating, the magnetization starts to rise up above 690 K, indicating reduction of α-Fe$_2$O$_3$ to Fe$_3$O$_4$ nanoparticles. The onset temperature of the reduction for the SiO$_2$-coated α-Fe$_2$O$_3$ nanoparticles is about 40 K higher than that for the bare α-Fe$_2$O$_3$ nanoparticles. Upon cooling, the magnetization data show a magnetic transition at about 850 K which is the same as the Curie temperature of Fe$_3$O$_4$. The difference between Fig. 2 and Fig. 4 is that the saturation magnetization at 330 K for the SiO$_2$-coated α-Fe$_2$O$_3$ nanoparticles is about 20% of that for the bare α-Fe$_2$O$_3$ nanoparticles. This implies that only about 20% of α-Fe$_2$O$_3$ nanoparticles have been reduced to Fe$_3$O$_4$ nanoparticles. Therefore, coating nanoparticles with SiO$_2$ can effectively protect the nanoparticles from oxidation or reduction.

Since about 80% of α-Fe$_2$O$_3$ nanoparticles are not reduced between 850 and 930 K due to the protection of SiO$_2$, we can determine the Néel temperature of the 60-nm α-Fe$_2$O$_3$ nanoparticles by extrapolation of the warm-up magnetization data to higher temperatures. The solid line in Fig. 5 is a fit using the $M(T)$ curve of a bulk α-Fe$_2$O$_3$ sample [10], appropriately scaled to $T_N = 945$ K. The inferred $T_N$ of 945 K for the 60-nm α-Fe$_2$O$_3$ nanoparticles is about 15 K lower than the bulk value of 960 K (Ref. [10]).
The reduction of the Néel temperature $T_N(d)$ of the nanoparticles from the bulk value $T_N(\infty)$ is due to finite-size effects. The finite-size effects lead to a simple scaling relationship \[1\]:

$$T_N(\infty) - T_N(d) = T_N(\infty)(d_0/d)^{1/\nu},$$

where $d_0$ is a microscopic length scale that is in the same order of the lattice constant $a$ (Refs. 1, 2). The exponent $\nu$ is predicted to be 0.7048 for a pure three-dimensional Heisenberg magnet 15 and 0.6417 for the Ising systems 16. For antiferromagnetic thin films of CoO, $d_0 = 2$ nm $\approx 5a$ and $\nu = 0.65$ (Ref. 9). The measured exponent is in better agreement with the theoretical prediction for the Ising systems 15, which is consistent with the fact that CoO behaves more like an Ising than a Heisenberg system 17. If we adopt $\nu = 0.65$ and $d_0 = 5(a^2c)^{1/3} = 3.5$ nm for $\alpha$-Fe$_2$O$_3$ (where the lattice constants $a = 0.50$ nm and $c = 1.38$ nm 11), we calculate the $T_N$ reduction of 60-nm nanoparticles to be 12.0 K. If we use $\nu = 0.70$ and $d_0 = 3.5$ nm, we find the $T_N$ suppression of 16.5 K. Both values are in good agreement with the measured one (15 K).

On the other hand, a $T_N$ reduction of about 100 K was reported for single-crystal $\alpha$-Fe$_2$O$_3$ nanowire arrays with $d = 150$ nm 10. This reduction seems too large to be compatible with Eq. (1) which gives a $T_N$ reduction of about 4.5 K for $d = 150$ nm. Since we have shown that $\alpha$-Fe$_2$O$_3$ nanoparticles are easy to reduce to the Fe$_3$O$_4$ phase in the high-vacuum environment, the argon environment for the magnetic measurement of the $\alpha$-Fe$_2$O$_3$ nanowire arrays 11 should also cause reduction of the $\alpha$-Fe$_2$O$_3$ to Fe$_3$O$_4$ phase. Therefore, the reported $T_N$ of 852 K for the nanowire arrays 10 is very likely to be associated with the ferrimagnetic transition of the converted Fe$_3$O$_4$ phase.

In summary, magnetic measurements up to 1000 K have been performed on hydrothermally synthesized $\alpha$-Fe$_2$O$_3$ nanoparticles using a Quantum Design vibrating sample magnetometer. The high vacuum environment ($1 \times 10^{-5}$ torr) during the magnetic measurement up to 1000 K leads to a complete reduction of $\alpha$-Fe$_2$O$_3$ to Fe$_3$O$_4$. This precludes the determination of the Néel temperature of the $\alpha$-Fe$_2$O$_3$ nanoparticles. In contrast, coating $\alpha$-Fe$_2$O$_3$ nanoparticles with SiO$_2$ can effectively protect the nanoparticles from reduction, which allows us to determine the Néel temperature of the $\alpha$-Fe$_2$O$_3$ nanoparticles for the first time. The Néel temperature of the 60-nm $\alpha$-Fe$_2$O$_3$ nanoparticles is found to be 945 K, about 15 K below the bulk value. The small reduction of the Néel temperature of the $\alpha$-Fe$_2$O$_3$ nanoparticles is consistent with a finite-size scaling theory.

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