Thermoinduced Magnetization in Nanoparticles of Antiferromagnetic Materials

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(Received 7 November 2003; published 26 May 2004)

We show that there is a thermoinduced contribution to the magnetic moment of nanoparticles of antiferromagnetic materials. It arises from thermal excitations of the uniform spin-precession mode, and it has the unusual property that its magnitude increases with increasing temperature. This has the consequence that antiferromagnetism is nonexistent in nanoparticles at finite temperatures and it explains magnetic anomalies, which recently have been reported in a number of studies of nanoparticles of antiferromagnetic materials.

DOI: 10.1103/PhysRevLett.92.217201 PACS numbers: 75.50.Ee, 75.75.+a, 76.50.+g

Currently, there is a rapid development in fabrication and applications of nanostructured magnetic devices such as spin valves and magnetic random access memories. In this context, an understanding of the size-dependent magnetic properties of ferro-, ferri-, and antiferromagnetic materials is crucial. The magnetic properties of most ferro- and ferrimagnetic nanostructured materials, including thin film structures and nanoparticles, seem on the whole to be well understood. However, several authors have reported that nanoparticles of antiferromagnetic materials show anomalies, which have not yet been explained.

The magnetization of nanoparticles of antiferromagnetic materials is often significantly larger than the bulk value [1–6]. Néel [7] suggested that the finite magnetic moment of nanoparticles of antiferromagnetic materials is due to uncompensated spins at the surface or in the interior of the particles. Still, the dependence of the magnetization on particle size and temperature has shown features that are not fully understood. Several studies have revealed that the temperature dependence is not in accordance with the Langevin behavior, i.e., the magnetization does not decrease with increasing temperature in the expected way [8–15]. These results have been observed in several synthetic samples, in the iron storage protein ferritin, and in ferrihydrite, which can be found in sediments in nature. Some examples are given below.

Seehra *et al.* [8] reported that the magnetic moment of 4 nm particles of ferrihydrite increases consistently with increasing temperature such that the room temperature value is about twice the low-temperature value. Their data are shown in Fig. 1. Harris *et al.* [9] found in a study of ferritin samples with different particle sizes that the magnetic moment of the particles increases with temperature, and the authors remarked that "the reason for this temperature dependence is not clear." In another study of ferritin particles with about 4000 iron atoms, Kilcoyne and Cywinski [10] noted that "above 120 K, μ is surprisingly found to increase slowly with increasing temperature." Makhlouf *et al.* [11] found that the magnetic moment of ferritin particles at finite temperatures was considerably larger than expected from the low-temperature value. Vollath *et al.* [12] observed a substantial increase with increasing temperature of the magnetic moment of Cr_2O_3 particles with diameters below 4 nm. A qualitatively similar temperature dependence of the magnetic moment was found in a study of 21 nm Cr_2O_3 nanoparticles [13]. In a study of NiO nanoparticles Makhlouf *et al.* [4] found that "the magnetizations do not scale with H/T as found for very small ferri- and ferromagnetic particles."

In this Letter we show that there is a thermoinduced contribution to the magnetic moment of nanoparticles of antiferromagnetic materials, which can explain such anomalies. We find that for particles of antiferromagnetic materials with a size below a few nm, the thermoinduced moment may be predominant at room temperature. We also point out that relaxation of the thermoinduced moment in some cases may be difficult to distinguish from macroscopic quantum tunneling.

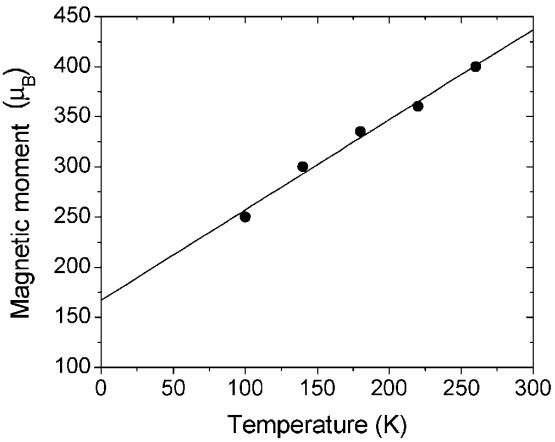

FIG. 1. The magnetic moment of 4 nm ferrihydrite particles as a function of temperature. The experimental data, shown by bold circles, are those obtained by Seehra *et al.* [8] from magnetization measurements. The solid line is a linear fit to the data in accordance with Eq. (4).

The magnetic energy of a nanoparticle with uniaxial anisotropy may be written

$$E(\theta) = KV\sin^2\theta, \tag{1}$$

where K is the magnetic anisotropy energy constant, V is the particle volume, and θ is the angle between the magnetization direction and the easy direction of magnetization. At finite temperatures, the (sublattice) magnetization direction fluctuates, because the magnetic anisotropy energy is comparable to the thermal energy. At high temperatures, the magnetic properties are commonly dominated by superparamagnetic relaxation, i.e., reversals of the (sublattice) magnetization directions. At lower temperatures, the thermal energy may be insufficient to result in frequent magnetization reversals, but still the (sublattice) magnetization direction may fluctuate in directions close to an energy minimum. These fluctuations, termed collective magnetic excitations, can be described as a uniform precession of the magnetization vector around an easy direction of magnetization in combination with transitions between these precession states [16,17]. In nanoparticles, the uniform precession mode, which can be described as a spin wave with wave vector $q = 0$, is predominant compared to other spin wave excitations with $q \neq 0$ [17]. In Mössbauer spectroscopy, these magnetic fluctuations result in a reduction of the magnetic hyperfine splitting because they can be considered fast compared to the time scale of the experimental technique [16,17]. In inelastic neutron scattering experiments, transitions between the $q = 0$ precession states can be studied [18,19].

In ferromagnetic nanoparticles, the excitations can be considered as uniform precessions with all ionic spins parallel. Similarly, in ferrimagnetic nanoparticles, the dynamics can be described in terms of precession of two antiparallel sublattices. However, in antiferromagnetic materials, the excited states are more complex. Both classical and quantum mechanical calculations [20] show that the two sublattices are not strictly antiparallel, but precess in such a way that they make slightly different angles, θ_A and θ_B, with the easy direction of magnetization. This leads to precession frequencies, which are much higher than the typical frequencies of ferro- and ferrimagnetic resonances. The theoretical results have been confirmed in numerous experimental studies of antiferromagnetic resonance; see, for example, [21,22]. The relationship between the two angles can be written [20,21]

$$\frac{\sin\theta_A}{\sin\theta_B} \approx 1 \pm \delta, \tag{2}$$

where $\delta \approx (2B_a/B_E)^{1/2}$. Here, $B_a = K/M_s$ is the anisotropy field, where M_s is the sublattice magnetization, and B_E is the exchange field. Equation (2) is a good approximation for $\delta \ll 1$. Because $\theta_A \neq \theta_B$, the crystal has a nonzero magnetic moment when the uniform mode is excited by an external ac field. Similarly, a nanoparticle of an antiferromagnetic material will have a net magnetic moment when the uniform mode is thermally excited. When averaging over the precession motion, the absolute value of the magnetic moment of a particle is given by $|\mu| = M_s V|\cos\theta_B - \cos\theta_A|$. This is illustrated schematically in Fig. 2. By use of Eq. (2) one finds for $\delta \ll 1$

$$|\mu| \approx M_s V\delta\frac{\sin^2\theta_B}{\cos\theta_B}. \tag{3}$$

Using Boltzmann statistics one can calculate the thermal average of $|\mu|$. Because $\theta_A \approx \theta_B$, the magnetic energy is to a good approximation given by Eq. (1) with $\theta \approx \theta_A \approx \theta_B$. Neglecting the quantization of the precession states, we obtain for $k_BT \ll KV$ (corresponding to $\theta \ll 1$)

$$\langle|\mu|\rangle_T \approx M_s V\delta\frac{k_BT}{KV} \approx 2g\mu_B\frac{k_BT}{\hbar\omega_0}, \tag{4}$$

where g is the Landé factor, μ_B is the Bohr magneton, k_B is Boltzmann's constant, T is the temperature, and we have introduced the angular frequency of the precession [20,21] $\omega_0 \approx \hbar^{-1}g\mu_B(2B_aB_E)^{1/2}$. The angular frequency ω_0 of the uniform mode of antiferromagnetic materials is typically of the order of 10^{12} s^{-1} [22], which gives a size-independent moment $\langle|\mu|\rangle_T \sim 200\mu_B$ at room temperature. This is the same order of magnitude as the expected magnetic moment due to uncompensated spins in a typical antiferromagnetic particle with diameter of the order of 5 nm. For smaller particles, the thermoinduced magnetic moment may be predominant at room temperature. As opposed to the behavior of normal bulk magnetic

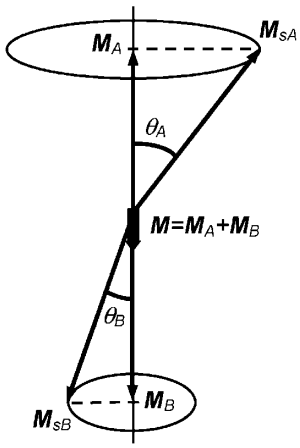

FIG. 2. Schematic illustration of thermoinduced magnetization in nanoparticles of antiferromagnetic materials. $\boldsymbol{M}_{sA}$ and $\boldsymbol{M}_{sB}$ are the instantaneous sublattice magnetization vectors. $\boldsymbol{M}_A$and $\boldsymbol{M}_B$ are the sublattice magnetization vectors after averaging over the precession in a state with precession angles θ_A and θ_B. $\boldsymbol{M} = \boldsymbol{M}_A + \boldsymbol{M}_B$ is the net magnetization. For clarity, the difference between θ_A and θ_B is exaggerated.

materials, the magnitude of the thermoinduced magnetic moment increases with increasing temperature until it starts to decrease when the Néel temperature is approached.

Because the thermal average of the absolute value of the thermoinduced magnetization, $\langle |M| \rangle = \langle |\mu| \rangle_T / V$, is inversely proportional to the volume, it is significant only in nanoparticles. In bulk antiferromagnets, a large number of other spin wave excitation modes with $q \neq 0$ are populated at finite temperatures. For each of these modes, the probabilities for $\theta_A > \theta_B$ and $\theta_A < \theta_B$ are equal. Since a large number of positive and negative contributions are added together the resulting net magnetization will be vanishingly small in bulk. In a nanoparticle the population of modes with $q \neq 0$ may be negligible at low temperatures because of the energy gap between the $q = 0$ state and the $q \neq 0$ states [23]. The $q = 0$ modes with $\theta_A > \theta_B$ and $\theta_A < \theta_B$ have equal probabilities, but, at a given instant of time, only one precession state exists in a given particle. Therefore the particle will have a nonzero magnetic moment.

In practice, there can be several contributions to the magnetic moment of nanoparticles of antiferromagnetic materials. Apart from the contributions from uncompensated spins, even a tiny amount of strongly magnetic impurity phases can have a decisive influence on the magnetization because of the small susceptibility of perfect antiferromagnetic materials [3]. Furthermore, the magnetic structure of nanoparticles may differ from that of bulk materials [6]. The Néel temperature of nanoparticles may differ from the bulk value [23,24], and this must also be taken into account when analyzing magnetization data. The thermoinduced magnetization in nanoparticles may be distinguished from other contributions, because its magnitude increases with temperature. Moreover, it is proportional to d^{-3}, where d is the particle diameter, whereas the size dependence due to uncompensated spins is expected to be smaller [3], e.g., approximately proportional to d^{-1}.

We have fitted the data of Seehra *et al.* [8], shown in Fig. 1, to the linear relation of Eq. (4). In the fit we have neglected other possible contributions to the temperature dependence of the magnetic moment, and we have not taken into account the random orientation of easy axes of the particles in the sample. From the slope of the linear fit we find an angular frequency, $\omega_0 \approx 0.52 \times 10^{12}\ \mathrm{s}^{-1}$, which is the expected order of magnitude for the uniform mode. The intercept at $\mu \approx 167 \mu_B$ can be attributed to the magnetic moment due to uncompensated spins. The thermoinduced moment at room temperature is of the order of $250 \mu_B$ in accordance with Eq. (4). The increase in magnetic moment with temperature in ferritin particles with nominally 1000, 2000, and 3000 iron atoms, found by Harris *et al.* [9], also shows a linear temperature dependence with a slope corresponding to $\omega_0 \approx 0.4 \times 10^{12}\ \mathrm{s}^{-1}$. For smaller particles a larger slope was found. Although other explanations for the anomalous behavior of antiferromagnetic nanoparticles have been suggested [9,12,14,15], the experimental data and the fit, shown in Fig. 1, together with a number of similar experimental observations, give experimental evidence for a temperature dependent magnetic moment that is in accordance with the model for thermoinduced magnetization. Thus the thermoinduced magnetization can explain anomalous magnetic properties of nanoparticles of antiferromagnetic materials, which have been discussed in the literature [4,8–15].

The magnitude and direction of the thermoinduced magnetic moment fluctuates because of rapid relaxation between the precession states with different precession angles. In zero applied field, the time average of the magnetic moment will be zero. However, in an applied field, the thermoinduced moments will to some extent be aligned as is the case for the magnetic moments of superparamagnetic particles of ferro- or ferrimagnetic materials. The magnetization, induced by a small magnetic field applied parallel to the easy direction of magnetization, can be calculated by using Boltzmann statistics, and one finds that the contribution to the initial susceptibility from the thermoinduced magnetic moment is given by

$$\chi_i \approx \frac{8 k_B T}{V} \left(\frac{g \mu_B}{\hbar \omega_0} \right)^2. \tag{5}$$

We see that χ_i like $\langle |\mu| \rangle_T$ increases with temperature. This is in accordance with experimental studies of, for example, Cr_2O_3 nanoparticles [12].

It is noteworthy that fluctuations between precession states with net magnetization "up" and "down" can take place without surmounting any energy barrier. Therefore, the thermoinduced magnetization may respond quickly to variations of an applied field, and the high-frequency susceptibility of nanoparticles of antiferromagnetic materials can thus be expected to be significant. Further, because magnetic relaxation between all populated $q = 0$ precession states can take place without thermal activation, the relaxation may be independent of temperature. Macroscopic quantum tunneling is also characterized by a temperature-independent magnetic relaxation at low temperatures. In antiferromagnetic nanoparticles, macroscopic quantum tunneling is expected to be more pronounced than in ferro- or ferrimagnetic particles [25,26]. Temperature-independent relaxation at very low temperatures has been observed in, for example, nanoparticles of antiferromagnetic ferritin [27,28] and α-Fe_2O_3 [29], but in experimental studies it may be difficult to distinguish between macroscopic quantum tunneling and classical magnetic relaxation, such as the relaxation of the thermoinduced moment.

In the case where nanoparticles of antiferromagnetic materials are exposed to a dc magnetic field, the thermoinduced magnetic moment will be aligned with the

field. This will partially suppress the superparamagnetic relaxation, which otherwise may take place at high temperatures. Similarly, if a nanoparticle of an antiferromagnetic material is in close contact with another magnetic material, the exchange coupling between surface atoms of neighboring particles can also have a significant influence on the relaxation behavior [30]. Such an exchange coupling may also result in a preferred direction of the thermoinduced magnetic moment, which then contributes to the permanent magnetization.

In conclusion, we have shown that there is a thermoinduced contribution to the magnetic moment of nanoparticles of antiferromagnetic materials, which explains a number of recently reported anomalies. Because nanostructured magnetic materials are produced at a growing rate due to their important technological applications we anticipate that thermoinduced magnetization will be encountered more frequently in the future and that it will play a role in future applications of magnetic nanoparticles in nanotechnology.

The work was supported by the Danish Technical Research Council and the Danish Natural Science Research Council. We thank P. J. van der Zaag and J. Nygård for valuable comments.

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