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Thermoinduced magnetization and uncompensated spins in antiferromagnetic nanoparticles

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We have investigated the combined effect of an uncompensated moment and the thermoinduced magnetization on the initial susceptibility of nanoparticles of antiferromagnetic materials. We find that for nanoparticles with small values of the anisotropy and exchange fields, the thermoinduced magnetization may be predominant at finite temperatures. In other cases the uncompensated moment may be predominant.

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I. INTRODUCTION

The magnetic properties of antiferromagnetic nanoparticles have in recent years received much attention. Unlike their bulk counterparts, such nanoparticles possess a finite, albeit small, magnetic moment, originally attributed by Néel¹ to the uncompensated spins present in nanoparticles due to their finite size.

Recently, the existence of another contribution to the magnetic moment of nanoparticles has been suggested.^{2,3} This so-called thermoinduced magnetic moment is due to thermally induced spin wave excitations in the form of a uniform precession mode. When this mode is excited, the two sublattices are not strictly antiparallel, and the angle between them increases with increasing excitation energy, leading to a magnetic moment that increases with increasing temperature. Subsequent Monte Carlo simulations of the magnetization of antiferromagnetic nanoparticles support this model.⁴

In several experimental studies of antiferromagnetic nanoparticles, an anomalous increase of the magnetic moment with increasing temperature has in fact been reported and this seems to give experimental support for the existence of thermoinduced magnetization.² However, Silva *et al.*^{5,6} have pointed out that if the distribution of magnetic moments due to uncompensated spins is disregarded in the analysis of magnetization curves of samples of antiferromagnetic nanoparticles, one may observe an apparent increase of the magnetic moment with temperature, and this may explain the experimental data. It has also been pointed out that the magnetic anisotropy can have a significant influence on magnetization curves of samples of antiferromagnetic nanoparticles.^{7,8} Both the moment distribution and the magnetic anisotropy have been neglected in most studies of the magnetization of antiferromagnetic nanoparticles, and therefore, there is not yet unambiguous experimental evidence for thermoinduced magnetization in antiferromagnetic nanoparticles.

In the first derivation of thermoinduced magnetization,^{2,3} only perfect antiferromagnetic nanoparticles were considered, i.e., nanoparticles without uncompensated magnetic moments. It has since been debated^{9,10} whether the uncompensated magnetic moments in typical antiferromagnetic nanoparticles may be predominant. This would result in a net magnetic moment that decreases with increasing temperature. In order to clarify this, we have extended the previous model for thermoinduced magnetization and calculated the

initial susceptibility of antiferromagnetic nanoparticles with a finite uncompensated magnetic moment. We show that the thermoinduced magnetization can be predominant at finite temperatures in particles with relatively small exchange and anisotropy fields and a moderate uncompensated magnetic moment.

II. MODEL

When considering magnetic nanoparticles, a uniaxial anisotropy is often assumed and the magnetic energy is written as

$$E(\theta) = KV \sin^2 \theta \quad (1)$$

where K is the magnetic anisotropy constant, V is the volume of the particle, and θ is the angle between the anisotropy axis and the (sublattice) magnetization. At low temperatures, the (sublattice) magnetization will fluctuate around the local energy minima, a process termed collective magnetic excitations.¹¹ As the temperature is increased, magnetization reversals (i.e., jumps between the two minima at $\theta=0$ and $\theta=\pi$) also take place. This superparamagnetic relaxation can be observed above a critical temperature, known as the blocking temperature (T_B), where the time between successive magnetization reversals becomes comparable to the timescale of the experimental method.

The collective magnetic excitations may be thought of as a uniform precession of the spins combined with transitions between precession states with different precession angles. As pointed out previously³ the uniform precession, which can be considered as a spin wave with wave vector $q=0$, is particularly prominent in nanoparticles. Furthermore, in the antiferromagnetic case it has been shown^{12,13} that the two sublattices are not exactly antiparallel during the precession.

In the following we consider a two-sublattice antiferromagnetic nanoparticle, with sublattice magnetic moments $\vec{\mu}_1$ and $\vec{\mu}_2$ (the magnitudes of which are slightly different from the average value μ_S because of uncompensated spins) as shown in Fig. 1. We here assume that the uncompensated spins are coupled through the ordinary exchange interaction to the other spins, such that their presence is expressed as a difference between $|\vec{\mu}_1|$ and $|\vec{\mu}_2|$, i.e. we write the magnetic moment due to the uncompensated spins, μ_u , as $|\mu_u| = |\mu_1| - |\mu_2|$. For simplicity, we further assume that μ_1 and μ_2 do not depend on temperature, as we are only considering temperatures well below the Néel temperature, i.e., we neglect the

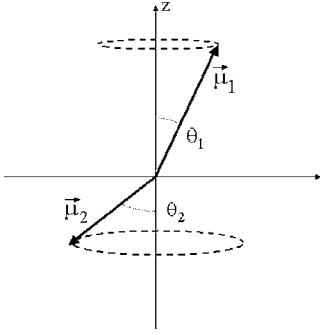


FIG. 1. Coordinate system used in the calculations. The differences in angles and lengths are exaggerated.

influence of spin waves with $q \neq 0$. The precession of the two sublattice magnetic moments around the z -axis is described by the angles θ_1 and θ_2 , differing slightly from the average value θ . The difference between the two angles is denoted $\theta_\delta = \theta_2 - \theta_1$ such that the resulting magnetic moment in the z -direction may be written as

$$\mu_r^z = \mu_1 \cos \theta_1 - \mu_2 \cos \theta_2 \approx \mu_u \cos \theta - \mu_1 \sin \theta \sin \theta_\delta \quad (2)$$

where we have assumed that θ_δ is small.

A. The modes of uniform precession

In order to proceed, one must analyze in some detail the precession modes of such a system. In a perfect antiferromagnetic material the relationship between the precession angles of the two sublattices can be written as^{12,13}

$$\frac{\sin \theta_1}{\sin \theta_2} = 1 \pm \delta. \quad (3)$$

Here $\delta \approx \sqrt{2B_a/B_E}$, where $B_E = \mu_0 \lambda_{12} \mu_S / V$ is the exchange field, λ_{12} is the exchange constant, and $B_a = KV / \mu_S$ is the anisotropy field.

In order to extend the calculation to a particle with a small uncompensated moment, we treat the system as that of a ferrimagnet, but in the limit where the difference between the sublattice magnetic moments is very small. In such a case, following the derivation by Wangness^{14,15} where the magnetic moments are treated as classical vectors, one may write the equations of motion for each of the two sublattice magnetic moments as

$$\frac{\partial \vec{\mu}_i}{\partial t} = \gamma (\vec{\mu}_i \times \vec{B}_{m,i}), \quad (4)$$

where $i \in (1, 2)$, γ is the gyromagnetic ratio, and $\vec{B}_{m,i}$ is the field acting on each sublattice. The contributions to this field include the anisotropy field \vec{B}_a , the exchange field \vec{B}_E , and an applied field, \vec{B}_{app} . The anisotropy is assumed to be uniaxial following Eq. (1), the easy axis coinciding with the z -axis, along which the external magnetic field is also applied. Further, the particles considered here have a very small net magnetization such that the demagnetization field may be ne-

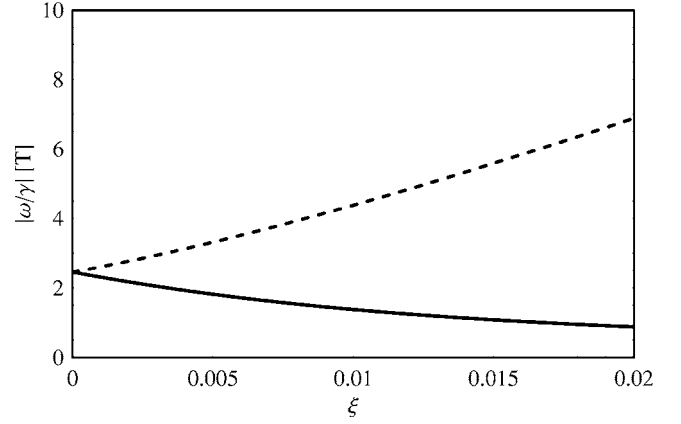


FIG. 2. $|\omega_\pm/\gamma|$ as a function of ξ , calculated using Eq. (7), with $B_{app}=0$ T, $B_a=0.01$ T, and $B_E=300$ T. Full line: $-$ mode, dashed line: $+$ mode.

glected, and in this case the field can be expressed as

$$\vec{B}_{m,1} = \vec{B}_{app} - \mu_0 \lambda_{12} \frac{\vec{\mu}_2}{V} + \vec{B}_a, \quad (5)$$

$$\vec{B}_{m,2} = \vec{B}_{app} - \mu_0 \lambda_{12} \frac{\vec{\mu}_1}{V} - \vec{B}_a. \quad (6)$$

In the calculation it is assumed that the precession angles are small, i.e., $\cos \theta \approx 1$. Four different modes are found with frequencies pairwise of equal magnitude, i.e., two distinct modes exist (in the following denoted by $+$ and $-$), and are given by¹²

$$\frac{\omega_\pm}{\gamma} = B_{app} - \frac{\xi B_E}{2} \pm B_E \sqrt{\frac{\delta^4}{4} + \delta^2 \left(1 + \frac{\xi}{2}\right) + \frac{\xi^2}{4}}, \quad (7)$$

where $\xi = \mu_r^z / \mu_2^z$. The dependence of ω_\pm on ξ is illustrated in Fig. 2.

For the precession angles we find in the limit where $\xi \ll \delta$

$$\frac{\mu_1}{\mu_2} \frac{\sin \theta_1}{\sin \theta_2} \approx 1 + \frac{\xi}{2} \pm \delta \quad (8)$$

which, when compared with Eq. (3), shows that the uncompensated moment itself will have an effect on the relative precession angles.

By expressing the angles θ_1 and θ_2 in terms of θ and θ_δ one finds

$$\frac{\sin \theta_1}{\sin \theta_2} \approx 1 + \cot \theta \sin \theta_\delta. \quad (9)$$

When inserting this into Eq. (8) and solving for $\sin \theta_\delta$ one obtains

$$\sin \theta_{\delta(\pm)} \approx \left(\frac{1}{2} \frac{\mu_r^z}{\mu_1 \cos \theta} - \frac{\mu_u}{\mu_1} \pm \delta \frac{\mu_2}{\mu_1} \right) \tan \theta. \quad (10)$$

Inserting this in Eq. (2) gives

$$\mu_{r(\pm)}^z \approx \mu_u \left[\frac{2 \cos \theta}{2 - \sin^2 \theta} \right] \pm 2 \delta \mu_2 \left[\frac{\cos \theta}{2 \cot^2 \theta + 1} \right] \quad (11)$$

after averaging over the fast precessional motion.

B. The initial susceptibility

Two precession states have been found, and with two possible orientations with respect to B_{app} one is left with four possible combinations. Hence, using Boltzmann statistics one obtains for a particle in thermal equilibrium, i.e., for $T > T_B$

$$\langle \mu \rangle_T = \frac{1}{Z} \sum_{\theta} P(\theta) \times (\mu_{r+} [e^{-\mu_{r+} B/k_B T} - e^{\mu_{r+} B/k_B T}] + \mu_{r-} [e^{-\mu_{r-} B/k_B T} - e^{\mu_{r-} B/k_B T}]), \quad (12)$$

where Z is the partition function

$$Z = e^{-\mu_{r+} B/k_B T} + e^{\mu_{r+} B/k_B T} + e^{-\mu_{r-} B/k_B T} + e^{\mu_{r-} B/k_B T} \quad (13)$$

and $P(\theta)$ is the probability of finding a precession state with angle θ . In the following we consider the initial susceptibility χ_i for a single particle, i.e., the limit where $\mu_{\pm} B_{\text{app}} \ll k_B T$. In this case $Z \approx 4$, and we find from Eq. (12)

$$\chi_i = \frac{1}{2} \frac{\mu_0}{V k_B T} \sum_{\theta} P(\theta) (\mu_{r+}^2 + \mu_{r-}^2), \quad (14)$$

When inserting Eq. (11) in Eq. (14) we obtain

$$\chi_i = \frac{\mu_0}{V k_B T} \sum_{\theta} P(\theta) \times \left(\frac{4 \mu_u^2 \cos^2 \theta}{(2 - \sin^2 \theta)^2} + \frac{4 \delta^2 \mu_2^2 \cos \theta}{(2 \cot^2 \theta + 1)^2} \right). \quad (15)$$

Using that $\theta_1 \approx \theta_2 \approx \theta$ we obtain by use of Eq. (1)

$$P(\theta) = \frac{e^{-\alpha \sin^2 \theta}}{\sum_{\theta} e^{-\alpha \sin^2 \theta}}, \quad (16)$$

where $\alpha = KV/k_B T$. Inserting this into (15) and assuming that the precession states are close-lying, such that the sums may be turned into integrals, we finally obtain

$$\chi_i = \frac{\mu_0}{V} \left[\frac{\frac{\mu_u^2}{k_B T} \int_0^{\pi/2} e^{-\alpha \sin^2 \theta} [4 \cos^2 \theta \sin \theta / (2 - \sin^2 \theta)^2] d\theta}{\int_0^{\pi/2} \sin \theta e^{-\alpha \sin^2 \theta} d\theta} + \frac{4 \delta^2 \mu_2^2}{k_B T} \frac{\int_0^{\pi/2} e^{-\alpha \sin^2 \theta} [\cos \theta \sin \theta / (2 \cot^2 \theta + 1)^2] d\theta}{\int_0^{\pi/2} \sin \theta e^{-\alpha \sin^2 \theta} d\theta} \right]. \quad (17)$$

If we assume, as in the previous derivations^{2,3} that the temperature is low such that only the lowest precession states are occupied, we may write

$$\chi_i \approx \frac{\mu_0}{V} \left[\frac{\mu_u^2}{k_B T} + \frac{\delta^2 \mu_2^2}{k_B T} \frac{\int_0^{\infty} x^5 e^{-\alpha x^2} dx}{\int_0^{\infty} x e^{-\alpha x^2} dx} \right] = \frac{\mu_0}{V} \left[\frac{\mu_u^2}{k_B T} + \frac{2 \delta^2 \mu_2^2}{(KV)^2 k_B T} \right], \quad (18)$$

where the first term is what we would expect from the uncompensated magnetic moment alone, and the second term is due to the thermoinduced moment for a pure antiferromagnet obtained previously.^{2,3} Hence, in this approximation, the uncompensated moment simply results in an extra term for the initial susceptibility. By using that $\mu_2 \approx \mu_s$, this may be expressed as

$$\chi_i \approx \frac{\mu_0}{V} \left(\frac{\mu_u^2}{k_B T} + \frac{4 k_B T}{B_a B_E} \right). \quad (19)$$

According to Eq. (19) the contribution due to the thermoinduced magnetization will be predominant for $T > \mu_u \sqrt{B_a B_E} / 2 k_B$. Thus a particle in which the thermoinduced contribution is measurable must have small exchange and anisotropy fields and the uncompensated moment should not be too large. We have simulated the initial susceptibility of nanoparticles by use of Eq. (19). We have used $V = 10^{-24} \text{ m}^3$, $B_a = 0.01 \text{ T}$, and $B_E = 300 \text{ T}$. These values are of the same order of magnitude as those of, for example, ferritin and typical NiO nanoparticles. Magnetization curves for three different values of the uncompensated moment, $\mu_u = 50, 100, \text{ and } 200 \mu_B$ are shown in Fig. 3. For simplicity, we have assumed that the blocking temperature is a sharp transition. Thus, the contributions from the uncompensated moment are only included at temperatures above the blocking temperature, which here is assumed to be 25 K. Below T_B the contribution from the uncompensated moment to χ_i is negligible, when the applied field is parallel to the easy axis, but because there is no energy barrier between states with opposite directions of the thermoinduced moment,² one should expect it to contribute to the susceptibility even at very low temperatures. At higher temperatures, the assumptions concerning small values of the angles θ_1 and θ_2 may not be fulfilled, and Eqs. (18) and (19) may not be good approximations to the susceptibility. The value of $\langle \cos \theta \rangle$ depends linearly of temperature and is given by^{3,11}

$$\langle \cos \theta \rangle \approx 1 - \frac{k_B T}{2KV}. \quad (20)$$

For a particle with sublattice magnetization $M_s = \mu_s / V \approx 10^6 \text{ A m}^{-1}$ one finds that $K = B_a M_s \approx 10^4 \text{ J m}^{-3}$. At 100 K we then find that $\langle \cos \theta \rangle \approx 0.93$, i.e., the condition $\langle \cos \theta \rangle \approx 1$ is reasonably well fulfilled at temperatures up to around 100 K. In Fig. 3, we have therefore only shown data up to 100 K.

III. DISCUSSION

Most of the previously published magnetization data for antiferromagnetic nanoparticles have been analyzed using a

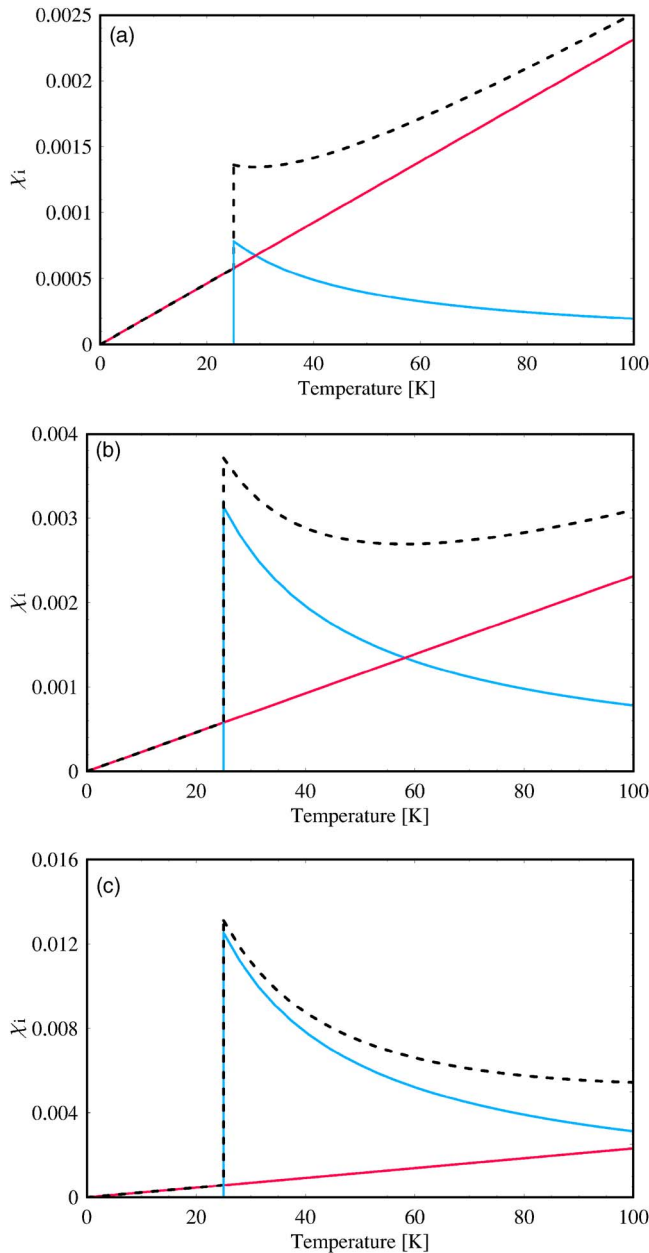


FIG. 3. (Color online) Simulated χ_i vs temperature curves, with $V=10^{-24}$ m³, $B_a=0.01$ T, $B_E=300$ T, and $\mu_u=(a) 50\mu_B$, (b) $100\mu_B$, and (c) $200\mu_B$. The dashed line shows the total susceptibility, the increasing full line shows the thermally induced contribution, while the decreasing full line shows the contribution from the uncompensated spins.

model in which it is assumed that the magnetization is given by the sum of a Langevin function and a linear term. However, as it has been pointed out by Silva *et al.*,^{5,6} the inevitable distributions in particle size and particle moments may result in erroneous values of the magnetic moment when this simple model is used. Furthermore, because of the relatively small values of the magnetic moments of antiferromagnetic nanoparticles the magnetic anisotropy plays a relatively larger role in magnetization measurements than in nanoparticles of ferro- and ferrimagnetic nanoparticles, and this can also result in erroneous results when a simple data analysis is

used.^{7,8} It has been suggested^{8,16} that one should focus on the initial susceptibility when analyzing magnetization data for antiferromagnetic nanoparticles, because χ_i for a sample of randomly oriented nanoparticles does not depend on the anisotropy and the detailed form of the size distribution.

In practice, the distribution in the values of the magnetic moments of the particles will smear the features around 25 K in Fig. 3, and it may not be possible to conclude whether an initial susceptibility, which increases with temperature, is due to the distribution of blocking temperatures or if it is due to thermally induced magnetization. Furthermore, in a sample of randomly oriented particles at temperatures below T_B , the uncompensated magnetic moments give rise to a nonzero, temperature-independent contribution to the susceptibility given by¹⁷

$$\chi = a \frac{\mu_0 \mu_u^2}{|K|V^2}, \quad (21)$$

where $a = \frac{1}{2} \langle \sin^2 \beta \rangle$ and β is the angle between the applied field and the easy axis. The average is over all particles. In an analysis of the initial susceptibility of antiferromagnetic nanoparticles, it is also necessary to take into account that the antiferromagnetic susceptibility χ_{AF} , which is due to the canting of the sublattice moments in response to the applied field, also contributes to the total susceptibility. This contribution increases with temperature like the contribution from the thermally induced moment. The value of χ_{AF} is about $1/\lambda_{12}$ at the Néel temperature.

It should also be realized that surface effects and defects in the interior of a nanoparticle with antiferromagnetic exchange coupling constants can result in localized, non-collinear spin structures, which can contribute to the net magnetic moment.^{18,19} The magnitude of this contribution will depend on the particle size, the surface structure, and the concentration of defects. However, normally this contribution to the magnetic moment is expected to be small compared to those discussed above, because only a limited number of spins contribute, and the magnetic moments due to the localized noncollinear spin structures may to a large extent cancel out due to more or less random orientations.

IV. SUMMARY

We have extended the previous model for thermally induced magnetization in antiferromagnetic nanoparticles with the effect of an uncompensated moment. We find that the uncompensated moment may contribute significantly, as compared to the thermally induced moment, to the initial susceptibility of such particles. However, for nanoparticles with values of the exchange field and the anisotropy field that are not too large, the thermally induced magnetization may give a predominant contribution to the initial susceptibility at finite temperatures.

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