Evidence of low-temperature superparamagnetism in Mn₃O₄ nanoparticle ensembles

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Abstract
Using ac-susceptibility, dc-magnetization, and transmission electron microscopy, we have investigated the magnetic behavior of Mn₃O₄ nanoparticle ensembles at temperatures below the paramagnetic-to-ferrimagnetic transition of the title material (Tₜ ≃ 41 K). Our data show no evidence of the complex magnetic ordering exhibited by bulk Mn₃O₄, or of a magnetic behavior around Tₜ that has a dynamic (relaxation) origin. Instead, we find a low-temperature (at ∼11 K) magnetic anomaly that manifests itself as a peak in the out-of-phase component of the ac-susceptibility. Analysis of the frequency and average-particle-size dependence of the peak temperature demonstrates that this behavior is due to the onset of superparamagnetic relaxation, and not to a previously hinted at spin-glass-like transition. Indeed, the relative peak temperature variation per frequency decade ΔT/TΔ log(f) is 0.11, an order of magnitude larger than the value expected for collective spin freezing, but within the range of values observed for superparamagnetic blocking. Furthermore, attempts to fit the frequency f/observation time τ = 1/2πf dependence of the peak temperature by a power law led to parameter values unexpected for a spin-glass transition. On the other hand, a Vogel–Fulcher law τ = τ₀ exp[E_B/k_B(T − T₀)]—where E_B is the energy barrier to magnetization reversal, k_B is the Boltzmann constant, τ₀ and T₀ are constants related to the attempt frequency and the interparticle interaction strength—correctly describes the peak shift and yields values consistent with the superparamagnetic behavior of a slightly interacting system of nanoparticles. In addition, the peak temperature T is sensitive to minute changes in the average particle size ⟨D⟩, and scales as (T − T₀) ∝ ⟨D⟩³, another signature of superparamagnetic relaxation.

1. Introduction
Investigations of the magnetic behavior exhibited by bulk Mn₃O₄ at temperatures below its paramagnetic-to-ferrimagnetic transition (Tₜ ≃ 41 K) revealed the existence of complex (long-wavelength) ordering induced by two consecutive transitions: one to an incommensurate magnetic state at 39 K, and another to a commensurate state upon further cooling to 33 K [1, 2]. More recent work confirmed these transitions, and also demonstrated that these low-temperature magnetic states exhibit magnetodielectric coupling [3, 4]. Mn₃O₄ nanoparticles, however, seem to show a very different magnetic behavior within the same temperature range. As reported by Regmi et al [5], the above-mentioned magnetic ordering is suppressed in a 20 nm-average-size Mn₃O₄ nanoparticle ensemble. Instead, a single magnetic event is
observed below $T_N$, namely a weak frequency-dependent peak in the out-of-phase component of the ac-susceptibility $\chi''$ at about 31 K. Interestingly, the microscopic origin of this magnetic behavior has not been fully elucidated. The authors of [5] hint at surface-spin-freezing effects, yet, as we argue below, the superparamagnetic relaxation of the nanoparticle ensemble could be a viable alternative explanation.

Due to the similarity of their basic ac-susceptibility signature—a peak in the $\chi''$ versus $T$ dependence—distinguishing between superparamagnetic blocking [6,7] and collective spin-glass-like freezing (of either surface spins [8,9] or superspins [10,11]) is often not straightforward. However, close examination of the frequency and average-particle-size dependence of the peak temperature may be used to differentiate between the two types of magnetic behavior [12]. For example, the relative variation of the peak temperature per frequency decade associated with a spin-glass-like transition is expected to be an order of magnitude smaller than that exhibited by the onset of superparamagnetic blocking [13−15].

In addition, the frequency/observation time dependence of the peak temperature for collective spin freezing follows the conventional dynamic scaling theory [16−17], while its counterpart associated with superparamagnetic blocking is best described by either the Néel–Brown equation [6] (for ideal non-interacting ensembles) or the phenomenological Vogel–Fulcher law [18,19] (for slightly interacting systems). Furthermore, the collective spin freezing temperature does not change significantly with the nanoparticle dimensions, while the superparamagnetic blocking temperature exhibits a pronounced dependence on the ensemble’s average particle size [20]. Finally, it is worth noting that surface spin effects in Mn$_3$O$_4$ nanoparticles have been previously investigated in the context of interparticle interactions [21].

Here we present a study aimed at clarifying the low-temperature magnetic behavior of Mn$_3$O$_4$ nanoparticle ensembles. Our temperature-resolved ac-susceptibility data collected on $\langle D \rangle = 13$ nm (average size) nanoparticles at different frequencies $f$ confirm the suppression of the long-wavelength magnetic ordering exhibited by bulk Mn$_3$O$_4$. The observed $\chi''$ versus $T$ dependence exhibits two peaks: one near $T_N$, and another at about 11 K. Detailed dynamic susceptibility measurements demonstrate that the first peak temperature is frequency-independent. This peak corresponds to the well documented paramagnetic-to-ferrimagnetic transition of Mn$_3$O$_4$ [1−5]. The low-temperature peak, however, is frequency-dependent, and since it represents the sole magnetic anomaly below the transition temperature, we believe it has the same microscopic origin as its counterpart observed in larger nanoparticles ($\langle D \rangle = 20$ nm) at $T \sim 31$ K (in [5]). Yet, such common microscopic origin is not likely to be collective spin freezing, as there is no reason for the freezing temperature to decrease from 31 to 11 K upon the average-nanoparticle-size reduction from 20 to 13 nm. On the other hand, the blocking temperature associated with the superparamagnetic relaxation of a ferromagnetic or ferrimagnetic nanoparticle ensemble, $T_B$, is predicted to depend on $\langle D \rangle$. For an ideal system of magnetic nanoparticles, for example, $T_B \propto K/4k_B$, where $K$ is the magnetic anisotropy and $k_B$ is the Boltzmann constant.

Remarkably, this relationship is consistent with the $\chi''$-peak temperature change between the two ensembles with $\langle D \rangle = 20$ and 13 nm, which strongly suggests that the magnetic behavior observed below $T_N$ stems from the superparamagnetic relaxation of the ferrimagnetic nanoparticle ensemble and not from a collective freezing of surface spins.

To confirm the superparamagnetic origin of the magnetic anomaly observed near 11 K, we carried out a detailed analysis of the frequency and particle-size dependence of this $\chi''$-peak temperature $T$. We found that the relative variation of $T$ per frequency decade $\Delta T/\Delta \log f$ falls within the typical range of values expected for superparamagnetic blocking, which is one order of magnitude greater than that of its spin-glass-transition counterpart. We also observed that a Vogel–Fulcher law $\tau = \tau_0 \exp[E_B/k_B(T−T_0)]$ accurately describes the shift of $T$ with the observation time $\tau = 1/2\pi f$, yielding values of a barrier to magnetization reversal $E_B$, time constant $\tau_0$, and interparticle interaction strength parameter $T_0$ consistent with the superparamagnetic relaxation of a slightly interacting system of nanoparticles. Finally, we demonstrate that even a slight change in the ensemble’s average size leads to a measurable shift in the $\chi''$-peak temperature (recorded at a given frequency), and that the magnitude of the shift is in quantitative agreement with the nanoparticle-size dependence of the superparamagnetic blocking temperature.

2. Experimental details

Mn$_3$O$_4$ nanocrystals were synthesized using a co-precipitation technique whereby sodium hydroxide was added dropwise to a MnCl$_2$-4H$_2$O solution in deionized water. The size of the precipitated nanoparticles was controlled by varying the molarity of the manganese chloride solution. Subsequent to precipitation, the particles were boiled in solution for 90 min, rinsed with deionized water and allowed to air dry for 24 h.

The crystal structure and impurity-free nature of the Mn$_3$O$_4$ ensembles were confirmed via laboratory x-ray powder diffraction measurements carried out using a Siemens D5000 diffractometer (wavelength $\lambda = 1.5406$ Å) equipped with a Braun position sensitive detector. The sample was loaded in a flat-plate holder and diffraction patterns were collected in the reflectivity geometry for $d$-spacing values between 1.5 and 3.5 Å, or, equivalently, over the $20^{\circ}−60^{\circ}$ detector angle ($2\theta$) range. The data collection time for each diffraction pattern was approximately 60 min. The process was repeated several times to ensure the reproducibility of the results. No significant difference was observed between experimental runs. XRD data were also used to estimate the nanoparticle ensemble’s average size using the Scherrer equation [22].

The average size and size distribution of the Mn$_3$O$_4$ nanoparticles were accurately determined from transmission electron microscopy (TEM) measurements conducted using a Hitachi H-9500, high-resolution microscope operating at 300 kV, utilizing a goniometer-tilt stage and fitted with a CCD digital imaging camera. The samples were suspended in a pyridine solution and solution drops deposited onto 3 mm, silicon monoxide coated, 200 mesh copper TEM grids, while a second grid was placed on the dried Mn$_3$O$_4$ particle deposit.
to form a sandwich. The grid sandwich was then placed in the TEM and images recorded in both bright and dark field using direct magnifications ranging from 20,000× to 700,000×; or digitized from 200 k× to 2000 k×. In addition, selected-area electron diffraction patterns were taken to confirm the x-ray diffraction results and to obtain systematic dark-field images and high-resolution lattice images. Nanoparticle sizes were determined using a random grid overlay on enlarged, dark-field images and measured for particles falling upon the grid lines. Finally, particle sizes were plotted in histograms and the average particle diameter \( \langle D \rangle \) determined. The same magnifications (100,000×) and statistical measuring areas were maintained for all particle measurements, with essentially the same sample size (or number of measurements, \( N \)).

Ac-magnetic-susceptibility and dc-magnetization measurements were carried out using a Quantum Design® Physical Properties Measurement System (PPMS). Approximately 25 mg of sample was loaded into a polycarbonate capsule, attached to the sample rod, and lowered into the cryostat of the PPMS. Approximately 25 mg of sample was loaded into a polycarbonate capsule, attached to the sample rod, and lowered into the cryostat of the PPMS. The in-phase and the out-of-phase components of the ac-susceptibility were recorded over the temperature range from 3 to 50 K upon heating at different frequencies between 100 Hz and 10 kHz. For all ac measurements the amplitude of the applied alternating magnetic field was 3 Oe. Dc-magnetization versus applied magnetic field data were collected at temperatures of 3, 25 and 37 K, in applied fields up to 50 kOe.

3. Results and discussion

Figure 1 shows the x-ray diffraction (XRD) pattern from a Mn₃O₄ nanoparticle ensemble. The open symbols represent the observed intensity recorded for different \( d \)-spacings values between 1.5 and 3.5 Å. The solid line is a full-profile (Le Bail) fit [23] to the data, the vertical bars indicate the \( d \)-spacings of the Bragg reflections, and the lower trace is the difference curve between the observed and the calculated intensities. The fit confirms that the sample consists of a single nanocrystalline Mn₃O₄ phase with tetragonal \((I4_1/amd)\) symmetry and lattice constants \( a = 5.76\ \text{Å} \) and \( c = 9.44\ \text{Å} \). Using the full-width at half-maximum of the (112) reflection in Scherrer’s equation, a nanoparticle average size of 17 nm is estimated for this ensemble.

Transmission electron microscopy (TEM) was then used to more accurately determine the average size, and also reveal the size distribution of the nanoparticles in the two ensembles used in this study. Figure 2 shows (a) bright-field and (c) dark-field images of one of the two samples. The dark-field image was obtained by positioning the objective aperture over a region corresponding to combined [011], [112], and [020] diffraction spots (circled area in figure 2(b)), which simultaneously showed differentiated, crystalline nanoparticles whose sizes (diameters) could be measured from random grid line intersections. These measurements were plotted in histograms (figures 3(a) and (b)) and the average nanoparticle diameters \( \langle D \rangle \) for the two ensembles were determined to be 13 and 16 nm. As the XRD data in figure 1 correspond to the smaller average-nanoparticle-size ensemble, we note that there is a difference between the results for \( \langle D \rangle \) obtained from the two techniques. This is not unexpected, however, as several factors (other than the crystallite size) influence the XRD peak width (e.g. shape factors, preferred orientation, anisotropic strain, etc) making the Scherrer method inherently less precise than TEM. Figure 2(d) illustrates (020) lattice plane images for several overlapping Mn₃O₄ particles which create rotation Moiré fringes. The long arrows here indicate traces of (020) planes in two crystals M1 and M2 oriented at an angle of about 15° with respect to one another. The \( d \)-spacings of the (020) planes is \( d_{020} \approx 2.9\ \text{Å} \), while the Moiré fringe spacing is 8.7 Å and 10.4 Å in M1 and M2 nanocrystals, respectively. These crystalline areas are best viewed by sighting along the long arrows or parallel to the Moiré fringes. The short arrows indicate the edges of nanoparticle crystal M2—it can be observed that the fringes extend to the nanoparticle edges.

The temperature dependence of the out-of-phase ac-susceptibility \( \chi'' \) measured within the 3–50 K range on the \( \langle D \rangle = 13\ \text{nm} \) Mn₃O₄ nanoparticle ensemble is shown in figure 4. The five datasets were collected at different frequencies of the driving magnetic field: \( f = 100\ \text{Hz} \) (open circles), \( f = 300\ \text{Hz} \) (filled circles), \( f = 1\ \text{kHz} \) (open triangles), \( f = 3\ \text{kHz} \) (filled triangles), and \( f = 10\ \text{kHz} \) (open squares). The first feature revealed by the \( \chi'' \) versus \( T \) curves is a pronounced peak at about 40 K, which, as we demonstrate below, corresponds to the cooling-induced transition of Mn₃O₄ to its ferrimagnetic Yafet–Kittel phase [1, 2]. Below this temperature, our data do not show any evidence of the complex magnetic ordering previously observed in bulk Mn₃O₄ [1–4]. Instead, we found a weak and relatively broad \( \chi'' \) peak at about 11 K. More detailed measurements of this feature (shown in the inset) revealed a well-defined frequency dependence of the peak temperature, which increases with increasing \( f \).
We now discuss the possible origin of the magnetic behavior shown by our dynamic susceptibility data around 40 K. This is important, as previous studies of Mn$_3$O$_4$ nanosystems using dc-magnetization FC–ZFC protocols (recently summarized by He [24]) revealed a peak in the ZFC branch at about 40 K and attributed this observation to superparamagnetic blocking. To investigate if blocking actually occurs at this temperature in our nanoparticle ensembles, we carried out more detailed frequency-resolved ac-susceptibility measurements within the 30–42 K temperature range using a temperature step of 0.5 K. The $\chi''$ versus $T$ results from these measurements are shown in figure 5, where the five datasets collected at different measuring frequencies have been vertically shifted for clarity. While there is a slight variation of the peak asymmetry with frequency, the data reveal that there is no frequency dependence of the peak temperature, which unambiguously demonstrates that the $\chi''$ peak does not have a superparamagnetic origin. Indeed, due to the dynamic nature of the superspin reorientation over an energy barrier to magnetization reversal, a conclusive signature of superparamagnetism is the variation of the blocking temperature ($\chi''$ versus $T$ peak) with the measuring frequency/observation time in the form of either an Arrhenius dependence [6] or a Vogel–Fulcher law [18, 19]. Thus, we believe that the frequency-independence of the $\chi''$ peak temperature demonstrated in figure 5 indicates that this magnetic behavior does not stem from a dynamic phenomenon, but simply from the paramagnetic-to-ferrimagnetic transition of Mn$_3$O$_4$.

Returning to the frequency-dependent $\chi''$ versus $T$ data shown in the inset of figure 4, we note that a similar magnetic behavior was recently observed below the paramagnetic-to-ferrimagnetic-transition temperature in larger Mn$_3$O$_4$ nanoparticles ($\langle D \rangle = 20$ nm) [5], but its microscopic origin has not been yet clarified. The authors of [5] hint at the possibility that this frequency-dependent magnetic anomaly, observed by them near 31 K, might be due to the collective spin freezing of a surface layer that surrounds the ferrimagnetic core on the nanoparticles. Yet, in view of our above-presented findings, the 20 K difference in the peak position between the two studies (in the context of the increase of the nanoparticle
Figure 3. Histograms of the particle-size distribution for the two Mn₃O₄ nanoparticle ensembles used in this study. The histograms show the ensembles’ polydispersity and yield average diameters of (a) 13 nm and (b) 16 nm.

Figure 4. Temperature dependence of the out-of-phase magnetic susceptibility $\chi''$ measured on the $\langle D \rangle = 13$ nm average-particle-size Mn₃O₄ nanoparticle ensemble at five different frequencies: $f = 100$ Hz (open circles), $f = 300$ Hz (filled circles), $f = 1$ kHz (open triangles), $f = 3$ kHz (filled triangles), and $f = 10$ kHz (open squares). The solid lines in the inset are fits to polynomial functions that allow a precise determination of the $\chi''$ versus $T$ peak position for each frequency.

average size) appears not to support a spin-glass-like transition origin, since the spin freezing temperature is not expected to change significantly with $\langle D \rangle$. Instead, the fact that

Figure 5. $\chi''$ versus $T$ measured on the $\langle D \rangle = 13$ nm average-particle-size Mn₃O₄ nanoparticle ensemble around $T_N$ at different frequencies: $f = 100$ Hz (open circles), $f = 300$ Hz (filled circles), $f = 1$ kHz (open triangles), $f = 3$ kHz (filled triangles), and $f = 10$ kHz (open squares). The five datasets are shifted vertically for clarity.

the peak temperature $T$ roughly changes as $\langle D \rangle^3$ strongly suggests a superparamagnetic relaxation origin, as the blocking temperature $T_B$ of an ideal magnetic nanoparticle ensemble is indeed proportional to the cube of the nanoparticle size according to:

$$T_B \propto \frac{K \langle D \rangle^3}{k_B},$$

where $K$ is the magnetic anisotropy assumed to be uniaxial and $k_B$ is the Boltzmann constant. In this scenario, cooling down Mn₃O₄ nanoparticles below the Néel temperature leads to a ferromagnetic-to-paramagnetic transition in the nanoparticles’ material. However, for small enough nanoparticles, the nanoparticle ensemble still behaves (super)paramagnetically at temperatures below $T_N$. In our $\langle D \rangle = 13$ nm ensemble, for example, all nanoparticles of sizes smaller than 20 nm (i.e. the majority of the ensemble) are in their unblocked (superparamagnetic) state even at 30 K. Upon further cooling, an increasing number of nanoparticles become blocked with the average sized (13 nm) ones blocking at $T_B \sim 11$ K. Even lower temperatures are required for the majority of the ensemble to block. It is also important to mention that, due to the size distribution of the nanoparticles in the ensemble,
dc-magnetization ($M$) versus magnetic field ($H$) hysteresis loops are expected to stay open (i.e. exhibit remanence and coercivity) at temperatures well above the average blocking temperature of the ensemble. This is demonstrated in figure 6, where such hysteresis loops measured on the $\langle D \rangle = 13$ nm ensemble at temperatures of 3 K (filled circles), 25 K (empty circles), and 37 K (filled squares) are shown. We observe that the coercive field $H_c$, which reaches 7 kOe at $T = 3$ K, still exhibits a sizable value (1.5 kOe) at $T = 25$ K, and further heating to 37 K is necessary to obtain an essentially closed loop ($H_c < 50$ Oe). Below, we present ac-susceptibility evidence for the superparamagnetic nature of the behavior of Mn$_3$O$_4$ nanoparticles below $T_N$.

The low-temperature $\chi''$ peak positions $T$ for the $\langle D \rangle = 13$ nm ensemble were accurately determined at each frequency $f$ (or, equivalently, observation time $1/2\pi f$) from polynomial fits to the $\chi''$ versus $T$ data (solid lines in the inset to figure 4). These values were first used to calculate the relative variation of the peak temperature per frequency decade. We found $\frac{\Delta T}{T f} \approx 0.11$, a value that is one order of magnitude larger than that expected for spin freezing [8, 13], but within the range of values commonly observed in superparamagnetic systems [15]. To further test the origin of the system’s low-temperature dynamic behavior, we analyzed the observation time dependence of the peak temperature on the basis of conventional dynamic scaling theory which holds that the relaxation time, $\tau$, of a system diverges as a power law within the correlation length, $\xi$, such that $\tau = \tau_0 \xi^{\nu}$. Here $\tau_0$ is a characteristic time constant (related to the attempt frequency by the relation $\tau_0 = 1/2\pi f_0$) and $\nu$ is a dynamic scaling exponent. In addition, according to the static scaling hypothesis, $\xi = [(T/T_f) - 1]^{\alpha}$, where $T_f$ is the critical freezing temperature and $\alpha$ is a critical exponent. One eventually finds:

$$\tau = \tau_0 \left(\frac{T}{T_f} - 1\right)^{-\nu}$$

where, in our case, $\tau$ is the observation time (as the relaxation time of the system is equal to the observation time at the $\chi''$ peak temperature $T_f$). Figure 7 shows a least-squares fit of equation (2) (solid line) to the observed $\tau$ versus $T$ dependence (solid symbols). The fit converges to low residuals yielding parameters $\tau_0 \sim 10^{-7}$ s, $\nu \approx 4.6$, and $T_f = 9.1$ K. Significantly, however, the values for the time constant $\tau_0$ and for the exponent $\nu$ are outside of the range of values expected for spin-glass-like transitions (i.e. $\tau_0$ between $10^{-11}$ and $10^{-13}$ s and $\nu$ between 8 and 10 [25]). This further indicates that surface spin freezing is not likely to be the microscopic origin of the low-temperature magnetic behavior observed in Mn$_3$O$_4$ nanoparticle ensembles.

The superparamagnetic relaxation of an ideal system of non-interacting, single-domain, and monodisperse magnetic nanoparticles is described by the Néel–Brown equation $\tau = \tau_0 \exp[\frac{E_B}{k_B(T - T_0)}]$, which predicts how rapidly the magnetic moment of a single particle flips along an easy axis by thermal activation [6]. Here $\tau$ is the relaxation time at a given temperature, $E_B$ the energy barrier to superspin reversal, $k_B$ the Boltzmann constant, and $T_0$ a time constant. To investigate if superparamagnetic blocking is indeed responsible for the magnetic behavior of the Mn$_3$O$_4$ nanoparticles below $T_N$, we first made an attempt at fitting the Néel–Brown equation to our observed $\tau$ versus $T$ dependence obtained from frequency-dependent ac-susceptibility measurements. The best fit describes this dependence well, but yields an unphysically short time constant $\tau_0 \approx 10^{-14}$ s (the shortest timescale in magnetism is the spin flip time of a single atom $\tau_s \sim 10^{-13}$ s). As previously demonstrated [12], this indicates that the magnetic nanoparticle system is not ideal, and interparticle interactions play a non-negligible role; in this case in a Vogel–Fulcher law:

$$\tau = \tau_0 \exp\left[\frac{E_B}{k_B(T - T_0)}\right]$$

![Figure 6. $M$ versus $H$ loops on the $\langle D \rangle = 13$ nm average-particle-size Mn$_3$O$_4$ nanoparticle ensemble at three different temperatures: $T = 3$ K (solid circles), $T = 25$ K (empty circles), and $T = 37$ K (solid squares).](image)

![Figure 7. Best fit of equation (2) (solid line) to the observed frequency ($f$) observation time ($\tau$) versus $T$ dependence for the low-temperature $\chi''$ peak (solid symbols).](image)
has been proven to describe the system’s relaxation [18, 19] and to provide information about the strength of the interparticle interactions through the value of the additional parameter $T_0$. Figure 8 shows the $\tau$ versus $T$ dependence for the Mn$_3$O$_4$ nanoparticle ensemble of average size $\langle D \rangle = 13$ nm (solid symbols) and $\langle D \rangle = 16$ nm counterpart (empty symbols). The two datasets were obtained from frequency-resolved $\chi''$ versus $T$ measurements. The solid lines here represent best fits to equation (3). For the $\langle D \rangle = 13$ nm ensemble the fit yields $\tau_0 \sim 10^{-10}$ s, $E_B/k_B = 87$ K, and $T_0 = 4.8$ K, whereas for the $\langle D \rangle = 16$ nm values of $E_B/k_B = 182$ K, and $T_0 = 5.2$ K were obtained. All these values are within the range expected for slightly interacting superparamagnetic systems. They are also consistent with the fact that the interaction strength is not expected to change significantly with the ensemble’s average size $\langle D \rangle$, but the barrier to magnetization reversal does (as $E_B = K \langle D \rangle^3$). Finally, the presence of interparticle interactions is significant in view of recent studies showing that such interactions weaken the contribution from surface spins to the magnetic properties of Mn$_3$O$_4$ nanoparticles [21].

Another signature of superparamagnetic relaxation is that the blocking temperature measured at a given frequency (which, in our case, is determined as the $\chi''$-peak temperature $T$) is sensitive to small changes in the ensemble’s average size $\langle D \rangle$. Moreover, if interactions are present in the system, and the parameter $T_0$ that describes the strength of such interactions is known, a quantitative relationship between $T$ and $\langle D \rangle$ can easily be derived. Indeed, using equation (3) and the fact that the barrier to magnetization reversal is proportional to the magnetic anisotropy constant and the cube of the average nanoparticle size (i.e. $E_B \propto K \langle D \rangle^3$) on finds:

$$T - T_0 \propto \langle D \rangle^3.$$  

(4)

Figure 9 shows the temperature dependence of the out-of-phase susceptibility measured at $f = 100$ Hz on two Mn$_3$O$_4$ nanoparticle ensembles: one with average nanoparticle size $\langle D \rangle = 13$ nm (solid symbols) and another with slightly larger nanoparticles $\langle D \rangle = 16$ nm (open symbols). We first note that the $\chi''$-peak temperature shifts from $T_1 = 10.3$ K to $T_2 = 14.8$ K upon the increase of the nanoparticle average size. This is clearly consistent with a superparamagnetic blocking rather than a spin freezing origin of the observed $\chi''$ versus $T$ behavior. Even more importantly, the magnitude of the above-mentioned temperature shift is in very good quantitative agreement with the behavior of the superparamagnetic blocking temperature upon the nanoparticle-size variation predicted by equation (4). Indeed, using $T_{01} = 4.8$ K and $T_{02} = 5.2$ K we find $\frac{1}{T_{02}} - \frac{1}{T_{01}} \approx \langle D \rangle^3$. This is highly significant, as the 4.8 and 5.2 K values of the interaction strength parameters have been obtained via Volger–Fulcher law fits to data from frequency-resolved $\chi''$ observations, i.e. in a totally independent measurement from the one used to yield the $T$ versus $\langle D \rangle$ dependence. We believe this represents strong evidence for the superparamagnetic nature of the behavior of fine Mn$_3$O$_4$ nanoparticles below the Néel temperature of the title material.

4. Summary

We have investigated the magnetic behavior of Mn$_3$O$_4$ nanoparticle ensembles at temperatures below the paramagnetic-to-ferrimagnetic transition of the title material ($T_N \cong 41$ K) using ac-susceptibility, dc-magnetization, and transmission electron microscopy. Our data confirm the suppression of the low-temperature complex magnetic order exhibited in bulk Mn$_3$O$_4$. We also demonstrate that the magnetic behavior observed around $T_N$ does not stem from a dynamic phenomenon, but simply from the paramagnetic-to-ferrimagnetic transition of Mn$_3$O$_4$. We found a frequency-dependent peak in the out-of-phase component of the ac-
magnetic-susceptibility $\chi''$ at a temperature near 11 K, a type of magnetic anomaly previously observed in [5] and tentatively associated with surface spin effects. Our analysis of the frequency and average-particle-size dependence of the $\chi''$ versus $T$ data demonstrates that, in fact, superparamagnetic blocking is responsible for this low-temperature magnetic behavior. We found that the relative variation of the peak temperature per frequency decade $\Delta T / T \Delta \log(f)$ is one order of magnitude larger than the values typically observed for collective spin freezing, but within the range expected for superparamagnetic systems. In addition, attempts to fit the frequency (observation time) dependence of the $\chi''$ versus $T$ peak by a power law according to the dynamic scaling theory led to parameter values well outside of the predicted range for glassy transitions. Yet, this dependence is very well described by a Vogel–Fulcher law, which is known describe the superparamagnetic relaxation of ensembles of slightly interacting magnetic nanoparticles. Finally we demonstrated that the shift of the $\chi''$ peak temperature upon the modification of the ensemble’s average size is consistent with the expected variation of the superparamagnetic blocking temperature of a nanoparticle system.

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