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Monodispersed MnO nanoparticles with epitaxial Mn$_3$O$_4$ shells

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Abstract
We report the microstructural and magnetic properties of monodispersed nanoparticles (NPs) of antiferromagnetic MnO ($T_N = 118$ K), with epitaxial ferrimagnetic Mn$_3$O$_4$ ($T_C = 43$ K) shells. Above $T_C$, an unusually large magnetization is present, produced by the uncompensated spins (UCSs) on the surface of the MnO particles. These spins impart a net anisotropy to the MnO particles that is approximately three orders of magnitude larger than the bulk value. As a result, an anomalously high blocking temperature is exhibited by the MnO particles, and finite coercivity and exchange bias are present above $T_C$. When field cooled below $T_C$, a strong exchange bias was established in the Mn$_3$O$_4$ shells as a result of high net anisotropy of the MnO particles. A large coercivity was also observed. Models of several aspects of the behaviour of this unusual system emphasized the essential role of the UCSs on the surfaces of the MnO NPs.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

One of the most interesting features of antiferromagnetic (AFM) nanoparticles (NPs) is that their magnetization in large applied fields is much higher than that expected from the susceptibility of the corresponding bulk AFM materials [1]. There is a general acceptance of Néel’s explanation that this is due to unequal numbers of occupied sites in the antiparallel AFM sublattices of the NPs, i.e. uncompensated spins (UCSs) [2]. It is not generally recognized that when Meiklejohn and Bean reported their discovery of exchange anisotropy in NPs of Co with an AFM CoO coating, they suggested that CoO interfacial UCSs were involved in the most novel manifestation of the interaction, namely, the exchange-bias field ($H_{EB}$), the shift of the hysteresis loop along the field axis when the NPs were field cooled below the CoO AFM ordering temperature [3]. More recently, it was shown that $H_{EB}$ in polycrystalline bilayers of CoO and permalloy could be quantitatively predicted from the calculated density of UCSs derived from the size and orientation of the interfacial CoO crystallites [4]. The significance of the UCSs in AFM NPs and crystallites is associated with the 2007 award of the Nobel Prize in Physics to Albert Fert and Peter Grünfeld for the discovery of giant magnetoresistance (GMR) [5]. The prominence of GMR is due to the enormous technological importance of GMR sensors in every modern computer, which is enabled by the $H_{EB}$ provided by AFM films [6].

The most comprehensive investigations of AFM NPs have been on oxides, principally $\alpha$-Fe$_2$O$_3$, NiO, CoO and MnO [1]. With rare exceptions, these AFM NPs have not been particularly monodispersed, nor have they had regular, well-defined morphology. The papers on MnO NP [7–13] have generally reported significant magnetization well below the bulk value of $T_N = 118$ K [14]. The properties of arc-evaporated Mn NPs oxidized in air were associated with the presence of MnO and Mn$_3$O$_4$ [15]. A very recent paper discussed the properties of a series of spheroidal particles ranging from the smallest Mn$_3$O$_4$ NPs to larger particles with MnO cores and Mn$_3$O$_4$ shells [16].
This paper discusses the behaviour of monodispersed rhomboidal MnO NPs with epitaxial Mn$_3$O$_4$ shells. Microstructural and magnetic properties of these NPs were presented in a previous paper [17]. In this paper, the pivotal role of the UCSs on the surface of the MnO NPs in establishing the unusual properties of this system is examined in detail. The unique atomic microstructure and magnetic features of these NPs facilitate modeling their properties. $T_C$ of the ferrimagnetic Mn$_3$O$_4$ shell is 43 K [18], which is much lower than $T_N$ (= 118 K) of the AFM MnO core. This permits determining the properties of the MnO UCSs with measurements above $T_C$ (Mn$_3$O$_4$). Since the MnO–Mn$_3$O$_4$ interface is epitaxial, the location and nature of the cations providing the UCSs can be specified. From the spontaneous magnetization exhibited by the UCSs above $T_C$ (Mn$_3$O$_4$), a value for the average number of Bohr magnetons on each uncompensated spin can be calculated and compared with the moments of the surface cations. Since the emphasis is on the UCSs in the following sections, some features of the particles are only briefly described. More detailed discussions on these issues are found in [17] and references therein.

2. Sample preparation and microstructure

The NPs were prepared by thermal decomposition of an Mn-oleate complex in a high boiling-point organic solvent [19]. The Mn$_3$O$_4$ shells on the MnO cores may have been present in the initial preparation, or they may have developed from washing in various solvents, or during storage in hexane. Samples of washed particles were dried and mounted for SQUID measurements in Ag cups which were compressed to provide the UCSs can be specified. From the spontaneous magnetization exhibited by the UCSs above $T_C$ (Mn$_3$O$_4$), a value for the average number of Bohr magnetons on each uncompensated spin can be calculated and compared with the moments of the surface cations. Since the emphasis is on the UCSs in the following sections, some features of the particles are only briefly described. More detailed discussions on these issues are found in [17] and references therein.

![Image](331x473 to 522x650)

Figure 1. (a) Low magnification electron micrograph showing MnO/Mn$_3$O$_4$ NPs dispersed on thin carbon support film and (b) high resolution electron micrograph showing MnO/Mn$_3$O$_4$ NPs with excellent alignment of the [1 1 1] lattice planes of each phase.

![Image](523x772)

Figure 2. Model of epitaxial interfacial sites, and some of these sites are vacant.

The morphology and microstructure of the particles are shown in figure 1. The particles generally have rhomboidal shapes with average sizes of 26–28 nm, as seen in figure 1(a). Figure 1(b), at a higher resolution, shows that the NPs have an MnO core with an Mn$_3$O$_4$ shell that has an average thickness of $\sim$4 nm. The [1 1 1] lattice planes of the phases are clearly well aligned, and the [1 1 1] spacings are indicated. The NPs exhibited broad and shallow x-ray diffraction peaks at the [2 1 1], [1 0 3] and [2 2 0] Mn$_3$O$_4$ positions and broad electron diffraction rings with diameters consistent with the large Mn$_3$O$_4$ unit cell.

Mn$_3$O$_4$ is a native oxide of MnO, as reported for bulk [20] and np [21]. Thus an epitaxial relationship is not surprising. As discussed in detail in [17], the MnO/Mn$_3$O$_4$ epitaxy can be modelled as depicted in figure 2. Cation vacancies are the most common defect in MnO; this requires the presence of Mn$^{3+}$ for charge balance. This combination of vacancies and Mn$^{3+}$ cations creates the normal spinel structure and occupancy of Mn$_3$O$_4$. Consequently, both Mn$^{2+}$ and Mn$^{3+}$ cations occupy epitaxial interfacial sites, and some of these sites are vacant.

3. Magnetic properties

Figure 3 shows the temperature dependence of the spontaneous magnetization $\sigma_0$, the coercivity, $H_C$, and the exchange-bias field, $H_{EB}$. $\sigma_0$ was measured by extrapolating the high field magnetization back to $H = 0$. $H_C$ and $H_{EB}$ were measured from hysteresis loops recorded after field cooling (FC) in 50 kOe to 5 K. $H_C$ and $H_{EB}$ decrease rapidly with increasing temperature from large values at 5 K. $\sigma_0$ has a less precipitous temperature dependence. Remarkably, all three magnetic properties exhibit finite values above $T_C$ (Mn$_3$O$_4$) and do not vanish until much higher temperatures. In particular, $\sigma_0$ has a value at 43 K that is 20% of the value at 5 K.

Thermoremanent magnetization (TRM) was measured by cooling the NPs in 50 kOe to 10 K, reducing the field to zero and recording the remanence as the sample warmed (figure 4). TRM below 43 K was dominated by the remanence of the Mn$_3$O$_4$; above $T_C$(Mn$_3$O$_4$), the UCS provided the TRM, and thereby monitored the superparamagnetic relaxation of the MnO NPs. The blocking temperature, $T_B$, of the MnO NPs was determined to be 95 K, as shown in the inset, from the nominal vanishing of the TRM.

For most magnetic NP systems, the susceptibility is measured in low fields, $\ll 100$ Oe, after FC in these fields or cooling in the zero field (ZFC), and the blocking temperature, $T_B$, is associated with the peak temperature of the ZFC data. With the present MnO/Mn$_3$O$_4$, this measurement was overwhelmed by the Mn$_3$O$_4$ signal. Therefore, the temperature dependence of the magnetization was measured in 50 kOe after cooling in 50 kOe, and after ZFC, with the results shown in figure 5. Measuring in such a high field ensures that the FC magnetization is saturated and that the ZFC values are
Figure 2. Site occupancy on (1 1 1) planes of MnO and Mn$_3$O$_4$. Mn$_3$O$_4$ cations are Mn$^{3+}$ in octahedral ‘B’ sites with normal spinel occupancy. With no vacancies, MnO sites are occupied by Mn$^{2+}$ cations. Cation vacancies produce Mn$^{3+}$ on Mn (1 1 1).

Figure 3. Temperature dependence of the spontaneous magnetization, $\sigma_0$, the coercivity, $H_C$, and the exchange-bias, $H_{EB}$, after cooling in 50 kOe.

The spontaneous magnetization at 43 K ($T_C$) of (Mn$_3$O$_4$), the magnetic behaviour exhibited in figures 3–5 is attributed to the UCSs on the MnO NPs.

Figure 4. TMR after cooling in 50 kOe. Inset shows measurement of the temperature at which TMR vanishes.

Figure 5. Temperature dependence of magnetization in 50 kOe after cooling in 50 kOe (FC) and after cooling in the zero field (ZFC). The enlarged view in the inset shows the temperature at which magnetization vanishes.

An alternative view is that the magnetization in this region is induced in the nominally paramagnetic Mn$_3$O$_4$ by the ordered MnO. This latter view does not clearly differ from a UCS model, since the surfaces of the MnO cores, where the UCS magnetization originates, can be specified to consist of epitaxial monolayers of Mn$^{2+}$ and Mn$^{3+}$ cations with some vacant sites. It is shown below that treating the magnetization at temperatures above 43 K as that of MnO UCSs, provides a consistent model for the unusual properties in this temperature region, as well as at lower temperatures.

Above 43 K $T_C$ of (Mn$_3$O$_4$), the magnetic behaviour exhibited in figures 3–5 is attributed to the UCSs on the MnO NPs.
compute the average moment of each uncompensated spin, an
average particle is assumed to be a cube with 27 nm edges, an
MnO cube core and a 4 nm Mn$_3$O$_4$ shell. Using the densities of
the two phases and the MnO lattice spacing, a straightforward
calculation yields the number of cation sites on the surfaces of
the MnO cubes, per gram of sample. Dividing $\sigma_0$ by this
number gives the result that, to two significant figures, the
average number of Bohr magnetons on each uncompensated
spin is 2.0$\mu_B$. Aside from the amusing coincidence that the
result of a computation involving $\sim 10^{13}$ particles resulted in
a single digit number of Bohr magnetons, 2.0$\mu_B$/UCS can be
compared with the moments expected from the cations
occupying the epitaxial interfaces, i.e. principally Mn$^{2+}$
and some Mn$^{3+}$. Mn$^{2+}$ has 5$\mu_B$ and 1$\mu_B$ in the high and low
spin states, respectively; Mn$^{3+}$ has 1$\mu_B$ less in each state. While it
is likely that deviations from cubic crystal fields at the surfaces of
the MnO cores would promote low spin states, no reliable
estimate of the accuracy of the calculated average UCS moment
can be inferred from the present data. However, it is clear that
the calculated 2.0$\mu_B$/UCS is comfortably within the range of
possible values. The 2.0$\mu_B$/UCS estimate is made on the basis
that all interfacial cation sites are occupied. Even allowing for
the fact that some sites are vacant (figure 2), this would be an
unusually high occupancy for UCSs on AFM NPs. Generally,
only a few per cent of the potential UCS sites are estimated to
be occupied, e.g. CoO polycrystalline films [4]. The reason for
the high occupancy in this case is that the FM/AFM interface
is epitaxial, and the UCSs constitute a surface monolayer of
the NPs. In turn, this latter fact supports the model of complete
epitaxy, even though only {1 1 1} plane alignment is visible in
figure 1(a).

The blocking temperature, $T_B$, was determined to be 95 K
from both the vanishing of TRM (inset, figure 4), and the
disappearance of irreversibility in 50 kOe FC and ZFC
magnetization measurements (inset, figure 5). When this
value is compared with that obtained from superparamagnetic
relaxation considerations, it becomes clear that the MnO NPs
have anomalously high anisotropies as compared with bulk
values. For $T \rightarrow 0$ K, the anisotropy in the easy (1 1 1) plane
of an MnO single crystal is $K_2 = 276$ erg cm$^{-3}$ [22]. It is
generally accepted that for SQUID measurements that require
about 1 min per point, the expression $KV/kT$, where $K$ is the
anisotropy constant of NPs with volume $V$, should be about 25
for magnetic thermal stability. For the MnO NPs, $K V/kT = 3.4$ at 4 K, i.e. a vanishing blocking temperature. For stability
at 95 K, the MnO NPs would require $K = 4.9 \times 10^4$ erg cm$^{-3}$
at 95 K, which implies that $K > 10^5$ erg cm$^{-3}$ at 4 K, three
orders of magnitude higher than the bulk value. The low coordination
of surface cations, surface cation vacancies and the presence of
other surface defects have been shown to produce anomalously
high values of anisotropy and disorder in various magnetic
oxide NPs [23, 24]. Morales et al [11] have comprehensively
examined the issue of surface-induced high anisotropy in
MnO NPs and arrived at expressions for the ground state net
anisotropy, $K_{\text{eff}}$, of MnO particles with $N$ total Mn atoms
and $N_S$ surface Mn atoms. With no anisotropy correlations
among the surface atoms, i.e. complete disorder, $K_{\text{eff}} = N_S^{1/2}K_0/N$; for no disorder, $K_{\text{eff}} = N_SK_0/N$. Here $K_0$ is
the specific anisotropy energy per atomic volume contributing
to the energy barrier. For the MnO NPs, $K_0$ is taken to be
$2 \times 10^7$ erg cm$^{-3}$. For the present MnO NPs, these expressions
yield: for complete disorder, $K_{\text{eff}} = 2.7 \times 10^5$ erg cm$^{-3}$; for
no disorder, $K_{\text{eff}} = 2.8 \times 10^6$ erg cm$^3$. Since the measured $T_B$
implies a value of $K > 10^5$, a significant amount of surface
disorder is suggested by these calculated boundary values.

A plausible model for $H_C$ above 43 K after FC is that the
UCSs are polarized by the applied fields and, assisted by
thermal excitation, exert sufficient torque on their respective
single domain MnO NPs to switch the Néel axis reversibly as
the field is cycled. Thermal excitation reduces $H_C$, which
remains finite until $T_B$ is reached. The origin of the apparent
finite $H_{\text{EB}}$ above 43 K is more difficult to visualize. It does not
seem reasonable to attribute the $H_{\text{EB}}$ above 43 K to the
switching of exchange-biased UCSs, since it is these same
UCSs that induce a large enough anisotropy in the MnO NPs
to permit a finite $H_{\text{EB}}$. The apparent $H_{\text{EB}}$ could result from a
vertical shift of $\sim 1\%$ of the saturated magnetization of the
hysteresis loops in that temperature region. Our measurements
could not resolve a shift of that magnitude. However, the very
large anisotropies of some UCSs, present as discussed above,
could readily produce a strong enough moment, polarized by
FC, to provide an upward shift of the hysteresis loops on the
order of 1%.

Below 43 K, the Mn$_3$O$_4$ magnetization dominates. The
Mn$_3$O$_4$ particles are essentially hollow rhomboids with a shell
thickness of $\sim 40\AA$. The $H_C$ values are quite large, although
smaller than those of equi-axed Mn$_3$O$_4$ NPs with an average
size of 15 nm [25], and they decrease more steeply with
temperature. The large surface/volume ratios of these particles
emphasize the role of surface anisotropy. Spin disorder on
the outer surfaces is likely present and contributes to the net
anisotropy. The large anisotropies on the inner surfaces were
discussed above. Certainly the very high $c$-axis anisotropy of
Mn$_3$O$_4$ is an important energy barrier, since it is likely
to be involved in any magnetization reversal in these hollow
rhomboids. The magnetic switching processes of hollow
rhomboidal Mn$_3$O$_4$ particles are clearly a separate complex
issue that needs attention, possibly along the lines of the recent
work on hollow spheres [26].

$H_{\text{EB}}$ is also large at 5 K and decreases rapidly with
temperature. Its significant magnitude is a strong support
of the model that the MnO NPs can be regarded as having a
net effective anisotropy much larger than the bulk due to
the contributions of the surface cations, thereby supporting
a large $H_{\text{EB}}$ in the Mn$_3$O$_4$ shell. The MnO UCSs are also
responsible for establishing $H_{\text{EB}}$, as well as supporting it.
Field-cooled from above $T_N$, the polarized UCSs polarize the
Mn$_3$O$_4$, induce a high net anisotropy in the MnO NPs, and
provide the interfacial Mn$_3$O$_4$-MnO exchange link.

5. Summary

Due to their unique magnetic and atomic microstructures,
these AFM MnO NPs with their native-oxide, epitaxial,
ferrimagnetic Mn$_3$O$_4$ shells present a number of magnetic
properties that are quite unusual for AFM NPs. Since

\[ K_{\text{eff}} = \frac{N_S^{1/2} K_0}{N} \text{ for complete disorder,} \]

\[ K_{\text{eff}} = \frac{N_S K_0}{N} \text{ for no disorder.} \]
$T_N(MnO)$ is much greater than $T_C(Mn_3O_4)$, measurements above $T_C(Mn_3O_4)$ permit the investigation of the properties of a sample of relatively monodispersed AFM NPs. Since the MnO–Mn3O4 interface is epitaxial, the interfacial cation occupancy can be specified with some confidence. A large moment per interfacial cation site is found, which implies an unusually high UCS surface-site occupancy. These features are due to the epitaxial nature of the MnO–Mn3O4 interface. The UCSs on the MnO NP surfaces induce an effective anisotropy in the MnO NPs that is approximately three orders of magnitude greater than the bulk MnO value. This effective MnO anisotropy is responsible for the large exchange bias below $T_N(MnO)$, and contributes to the coercivity. Above $T_C(Mn_3O_4)$ results from the irreversible switching of the spin lattices of the MnO NPs by the torque exerted by the UCSs as the applied field is cycled. $H_EB$ at high temperatures could be due to a 1% upward shift of the hysteresis loops by polarized, high anisotropy UCSs after FC. Thus, virtually all of the anomalous behaviour in this NP system can be ascribed to the properties of the interfacial UCSs.

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References

[38] Masala O and Seshadri R 2005 J. Am. Chem. Soc. 127 9354