Magnetic Proximity Effect Features in Antiferromagnetic/Ferrimagnetic Core-Shell Nanoparticles

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A study of “inverted” core-shell, MnO/γ-Mn2O3, nanoparticles is presented. Crystal and magnetic structures and characteristic sizes have been determined by neutron diffraction for the antiferromagnetic core (MnO) and the ferrimagnetic shell (γ-Mn2O3). Remarkably, while the MnO core is found to have a \( T_N \) not far from its bulk value, the magnetic order of the γ-Mn2O3 shell is stable far above \( T_C \), exhibiting two characteristic temperatures, at \( T \approx 40 \text{ K} \) \([T_C(\gamma-\text{Mn}_2\text{O}_3)]\) and at \( T \approx 120 \text{ K} \) \([-T_N(\text{MnO})]\). Magnetization measurements are consistent with these results. The stabilization of the shell moment up to \( T_N \) of the core can be tentatively attributed to core-shell exchange interactions, hinting at a possible magnetic proximity effect.

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Magnetic nanoparticles are currently being extensively studied [1]. Among them, bimagnetic core-shell systems, where both the core and the shell are magnetic, are gaining increased interest due to appealing novel properties and promising applications, such as enhanced superparamagnetic blocking temperatures or tunable coercivities [2–10]. Most of the conventional bimagnetic core-shell nanoparticles have been obtained from the oxidation of transition metal nanoparticles, leading to a ferromagnetic (FM) core and the corresponding antiferromagnetic (AFM) or ferrimagnetic (FIM) shell [2,3]. In this case, the exchange coupling between the core and the shell gives rise to diverse effects such as loop shifts (“exchange bias”) and coercivity enhancement [2,3].

Recently so-called “inverted” core-shell systems with an AFM core and a FIM shell, e.g., MnO/Mn3O4, have come into focus [11–14]. In this particular system the Curie temperature \( T_C \) is below the Néel temperature \( T_N \), in contrast to most of the exchange biased thin film and core-shell systems [2]. This doubly inverted (i.e., AFM core, not FM, and \( T_N > T_C \)) structure gives rise to a number of interesting effects, such as a nonmonotonic dependence of the loop shift on the core diameter and the existence of loop shifts above \( T_C \) [11–13]. Importantly, the latter effect is different from the known enhancement of the blocking temperature in usual core-shell systems, which arises from the increase of the effective anisotropy of the FM core induced by the coupling to the AFM shell [15].

In thin film systems consisting of two different magnetic materials the enhancement of \( T_N \) or \( T_C \) of one of the layers due to exchange interactions (i.e., a magnetic proximity effect) has been reported [16–22]. However, this effect has never been reported in nanoparticles.

In this Letter we present the study of inverted core-shell nanoparticles consisting of a \( \approx 5 \text{ nm} \) (sample 5) or \( \approx 17 \text{ nm} \) (sample L) antiferromagnetic MnO core and a \( \approx 5 \text{ nm}-\text{thick ferrimagnetic } \gamma-\text{Mn}_2\text{O}_3 \) shell [23]. It is found that the ordered magnetic moment of the \( \gamma-\text{Mn}_2\text{O}_3 \) shell remains finite \emph{far above} \( T_C \) of the \( \gamma-\text{Mn}_2\text{O}_3 \) shell and \( T_N \) of the MnO core.

Neutron diffraction measurements were carried out at the diffractometer D20 of the Institute Laue-Langevin with a neutron wavelength of 1.305 \( \text{Å} \) [24]. All diffraction patterns were analyzed using the FULLPROF program [25] based on the known crystal structures of the core and the shell. This method, in contrast to the so-called “matching mode,” provides more stable refinement in the present case due to the strong overlapping of the principal peaks and the presence of small parasitic reflections. Magnetization measurements were carried out using a SQUID magnetometer.

The MnO core exhibits the expected NaCl structure. However, refinement of the occupancy factors shows that sample 5 has defects in the Mn sites, with an occupancy factor of only 0.74(2). Sample L exhibits the stoichiometric structure. Since the detected defects are only observed in the samples with smaller cores (i.e., with a large surface to
MnO are smaller than the expected 5-refined. The values of the saturated magnetic moment of \( \text{MnO} \) core were into account the trigonal distortion due to magnetostriction deviation. Correspond to the error defined as the estimated standard

The shell of the smaller particles has a spinel-type tetragonal structure with two types of voids: tetrahedral (eightfold A position) and octahedral (16-fold B position). From the profile analysis it follows that the shell has the structure formulas \( \text{Mn}_3^+ \square \text{Mn}^{3+}_2 \), which, in fact, corresponds to the defect structure, known as \( \gamma\)-\( \text{Mn}_2\text{O}_3 \) [27,28], not the expected hausmannite \( \text{Mn}_2^+ \square \text{Mn}^{3+}_2 \) (or \( \text{Mn}_3\text{O}_4 \)). Here, the parentheses and square brackets refer to the tetrahedral and octahedral voids, respectively, and the symbol \( \square \) corresponds to vacancies. Note that for the larger particles the structure of the shell cannot be univocally established due to the relatively small diffraction signal.

The temperature dependence of the lattice parameter of the \( \text{MnO} \) cores is consistent with a well structured core [23,29–33]. Similarly, the lattice parameters of \( \gamma\)-\( \text{Mn}_2\text{O}_3 \) are also close to bulk values [23,27,28].

The diffraction lines are broadened with respect to the instrumental resolution, indicating that the correlation length is finite. However, from the neutron diffraction patterns the expected stresses appeared to be negligible within the experimental error. Thus, from the peak broadening the characteristic sizes of the nanoparticles were evaluated. The volume average diameter of the core and the characteristic size of the ferrimagnetic shell are 4.9(3)/4.7(3) and 17.0(5)/5(1) nm, at 170 K, for samples \( S \) and \( L \), respectively. Note that the values in the brackets correspond to the error defined as the estimated standard deviation.

Using the known AFM order in bulk \( \text{MnO} \) and taking into account the trigonal distortion due to magnetostriction [34], the ordered magnetic moments in the \( \text{MnO} \) core were refined. The values of the saturated magnetic moment of \( \text{MnO} \) are smaller than the expected 5\( \mu_B \) for the free \( \text{Mn}^{2+} \) ion [Fig. 1(a)], which can be explained partly due to the lower occupancy of the \( \text{Mn}^{2+} \) sites, that increases the effective valence state and consequently decreases the averaged magnetic moment, and partly by surface spin disordering [30]. The temperature dependence of the magnetic moment shows a continuous transition, in contrast with the first order transition in bulk, due to size effects [30]. Interestingly, \( T_N \sim 130(9) \) K (for sample \( S \)) and 120.9(2) (for sample \( L \)) are enhanced with respect to the bulk value of 117 K [29], similar to what was observed in \( \text{MnO} \) nanoparticles with different shapes and sizes confined within diverse porous media [30,32].

\( \gamma\)-\( \text{Mn}_2\text{O}_3 \) nanoparticles are known to be ferrimagnetic with a \( T_C \) of about 40 K with large coercivities at low temperatures [35]. However, the magnetic structure of \( \gamma\)-\( \text{Mn}_2\text{O}_3 \) is unknown. For the related hausmannite \( \text{Mn}_3\text{O}_4 \) structure, a complex magnetic order with a doubled nuclear cell has been reported [36]. However, we did not observe any superstructure magnetic reflections at low temperatures, implying that the magnetic cell coincides with the chemical one. Therefore we worked in the frame of the two-sublattice collinear ferrimagnetic model of Néel [37], similar to \( \gamma\)-\( \text{Fe}_2\text{O}_3 \). Any small distortions of such structure were beyond our statistic accuracy. The temperature dependence of the magnetic moment in the tetrahedral (\( A \)) and the octahedral (\( B \)) sites for sample \( S \) (Fig. 1) exhibits two remarkable features. First, there is a large difference between the magnetic moments in \( A \) and \( B \) sites, and second, the moments are noticeably reduced with respect to the 4\( \mu_B \) expected for the free \( \text{Mn}^{3+} \) ion. Although the orbital moment of the \( \text{Mn}^{3+} \) ion and the crystalline field (which is different for the \( A \) and \( B \) voids) could affect the value of the magnetic moment, similar effects have been observed in \( \gamma\)-\( \text{Fe}_2\text{O}_3 \), where \( \text{Fe}^{3+} \) does not possess orbital moment. In Néel-type order the effective exchange magnetic field in position \( B \) from the surrounding magnetic moments is about twice weaker than those in position \( A \). The spins which are more weakly coupled should be more disordered due to the breaking of local symmetry, and, consequently, their mean value should be smaller [38]. Hence, we attribute the observed
difference of magnetic moments in the $\gamma$-Mn$_2$O$_3$ shell to this mechanism. Moreover, spin canting in the $\gamma$-Mn$_2$O$_3$ structure (similar to what is observed in $\gamma$-Fe$_2$O$_3$ shells [39]) could also contribute to the reduced moment, although due to high anisotropy of $\gamma$-Mn$_2$O$_3$ the canting is expected to be smaller than in $\gamma$-Fe$_2$O$_3$ and probably confined in the interface layers. Taking into account the number of tetrahedral and octahedral sites the net moment confined in the interface layers. Taking into account the resonance linewidth observed in $T_C$ from the profile analysis. Note that the presence of magnetic signal above $T_C$ in concordance with the magnetic moments obtained from the shell have a sizable intensity even above $T_N$ of MnO and persists far above. Certainly, a weak peak at the position of the $\gamma$-Mn$_2$O$_3$ (1, 0, 1) reflection is clearly seen up to 300 K (inset in Fig. 2). A comprehensive x-ray inspection at these angles does not show any coherent reflections. The peak broadening corresponds to the size of the nanoparticles composing the shell. Hence, we attribute this peak to the coherent magnetic scattering from the shell. The profile analysis renders a magnetic moment of about 1.3(3)$\mu_B$. Within the experimental accuracy, neither intensity nor line shape appear to vary with temperature. Nevertheless, a structural contribution to the peak at ca. 15$^\circ$, due to a possible ordering of vacancies, cannot be completely ruled out, although x-ray diffraction does not show any clear coherent reflections.

To search for further evidence of the presence of potential proximity effects magnetization measurements were also carried out. However, due to the small core size of sample S and the long characteristic measuring time of SQUID ($\tau_{m} \sim 100$ s) no proximity effects are observable using magnetometry (see Fig. 3 and [23]). Interestingly, for sample L, both the temperature dependence of $M_{\text{FC}}(T) - M_{\text{ZFC}}(T)$ (field cooled–zero field cooled) magnetization curves at 5 T (Fig. 3) and the saturation magnetization $M_s(T)$ [23] exhibit a considerable signal well above $T_C$ and up to about $T_N$ (in agreement with Berkowitz et al. [12]), which is consistent with a proximity effect. It should be taken into account that magnetization measurements are not equally as distinctive as neutron diffraction measurements (where the signal comes solely from the $\gamma$-Mn$_2$O$_3$ shell), since in this case uncompensated spins in the MnO could also contribute to the magnetic signal.

FIG. 2. Temperature dependence of the intensity of the magnetic peak at 15.4$^\circ$ ($\bullet$) for sample S. There are contributions from the MnO core: reflections (1/2, 1/2, 1/2), (1/2, 1/2, 1/2), and from the $\gamma$-Mn$_2$O$_3$ shell: reflections (1, 0, 1) and (−1, 0, 1). The contribution from the MnO calculated from the profile analysis is shown by $\blacksquare$. Shown in the inset is the observed magnetic peak at $T = 250$ K.

FIG. 3. Temperature dependence of the difference between the FC and ZFC magnetizations, $M_{\text{FC}} - M_{\text{ZFC}}$, for samples S ($\bullet$) and L ($\bigcirc$). Shown in the inset is an enlargement of the high temperature region. The error bars are smaller than the size of the symbol, and the solid lines are guides for the eye.
Interestingly, in contrast to thin film AFM/FM systems, where magnetic proximity effects are observed in the AFM (since \( T_C > T_N \)), in the MnO/\( \gamma \)-Mn\(_2\)O\(_3\) system induced moments are observed in the FM shell. We attribute the observed stable magnetic moment in the \( \gamma \)-Mn\(_2\)O\(_3\) shell well above \( T_C \) to the interface exchange coupling between the MnO core and the shell, as has been experimentally and theoretically observed in film systems [16–22,41,42], that can tentatively be considered as a magnetic proximity effect. Namely, although uncompensated spins may play a role in the proximity effect [12], the exchange field of each sublattice of the AFM core, which penetrates a few atomic layers, stabilizes the magnetic structure of the sublattices of the FIM shell [41,42]. These results are in agreement with the theoretical results in bilayer thin films from Jensen et al. who predicted an increase of the temperature range of stable moments to above \( T_C \) in AFM/FM systems with \( T_N > T_C \) [41]. Probably both the moderately strong core-shell interface exchange coupling (evidenced by the large exchange bias observed in these systems [11–13]) and the small shell thickness contribute to make the effect more evident. The possible persistence of a magnetic moment in \( \gamma \)-Mn\(_2\)O\(_3\) above \( T_{C,shell} \) and \( T_{N,core} \) is not clear at present, although it could be related to oxygen vacancies in \( \gamma \)-Mn\(_2\)O\(_3\), as has been proposed [43] for other transition metal oxides exhibiting persisting magnetic signal well above their corresponding transition temperatures [43–45].

In conclusion, the magnetic order and temperature dependence of the magnetic moments in the doubly inverted “core-shell” MnO/\( \gamma \)-Mn\(_2\)O\(_3\) system were determined. It is found that an induced moment in the \( \gamma \)-Mn\(_2\)O\(_3\) shell persists above its \( T_C \) due to the exchange coupling with the MnO core (i.e., a likely magnetic proximity effect).

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[23] See EPAPS Document No. E-PRLTAO-103-004927 for the details of the synthesis of the nanoparticles, supplementary figures that show the temperature dependence of the MnO and \( \gamma \)-Mn\(_2\)O\(_3\) lattice parameters, the total moment of \( \gamma \)-Mn\(_2\)O\(_3\) for sample \( S \), the magnetic measurements and the temperature dependence of \( M_S \) for samples \( L \) and \( S \). For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
Magnetic proximity effect features in antiferromagnetic/ferrimagnetic core/shell nanoparticles.


SYNTHESIS

The nanoparticle synthesis has been described elsewhere [1]. In brief, MnO nanoparticles were obtained by dissolving 7.5 mmol of manganese (II) acetylacetonate with 5 mmol of 1,2-hexadecanediol and a given amount of oleylamine (50 mL: small particles - sample S and 12.5 mL: large particles - sample L) in 150 mL of benzylether followed by heating to 200 °C or 290 °C for 30 min for sample S or sample L, respectively. After exposure to air, the passivation of the MnO takes place leading to a defect Mn₃O₄ shell.

LATTICE PARAMETERS

The temperature dependence of the unit cell parameter for MnO displays a distinct feature around 120 K (Fig. 1a), i.e., close to \(T_N(\text{MnO})\), similar to what is observed in bulk [2], implying a well structured MnO core. Such feature has been already observed for isotropic nanoparticles of MnO embedded within porous glass [3], but not in highly anisotropic “ribbon” shaped nanoparticles [4–6]. The smaller lattice parameter of MnO with respect to the bulk could be explained by the presence of the large number of defects and/or the effect of inner pressure due to the covering shell. However, the defects should strongly reduce the effect of the interface stresses. The lattice parameters for \(\gamma\)-Mn₂O₃ exhibit a more monotonic temperature dependence and while the \(a\) is smaller than the corresponding bulk value [7, 8], \(c\) is larger (Fig. 1b). This is probably induced by the growth of a thin layer of the tetragonal \(\gamma\)-Mn₂O₃ on the cubic MnO.

MAGNETIC MOMENT

In order to make more evident the anomaly at \(T_N\), the total moment of \(\gamma\)-Mn₂O₃ is shown in Fig. 2, rather than the moment of each sub-lattice.

MAGNETIC MEASUREMENTS

Given the very small size of the core for sample S and the weak anisotropy of MnO, the blocking temperature, \(T_B\), of the core is below the \(T_C\) of the shell when measured using magnetometry. Namely, \(T_B\) depends of the “characteristic measuring time”, \(\tau_m\), of the technique used to determine it.

FIG. 1: Temperature dependence of the unit cell parameters for (a) MnO core (•) and bulk MnO [2] (○) and (b) \(\gamma\)-Mn₂O₃ (shell), parameters \(a\) (△) and \(c\) (▲). The bulk values for \(a\) and \(c\) are also indicated. Solid lines are guides for the eye.

FIG. 2: Temperature dependence of the total magnetic moment of the \(\gamma\)-Mn₂O₃ shell for sample S. Solid lines are guides for the eye.
FIG. 3: Temperature dependence of the saturation magnetization, $M_S$, for samples S (•) and L (○). Solid lines are guides for the eye.

$T_B = KV/k_B \ln(\tau_m/\tau_0)$,

where $K$ is the anisotropy, $V$ the volume, $k_B$ is the Boltzmann constant and $\tau_0$ is a time constant characteristic of the material (i.e., the reversal attempt time, usually in the $10^{-9} - 10^{-12}$ s range). For SQUID measurements $\tau_m$ is usually taken of the order of $\tau_m$(SQUID) $\sim 100$ s, while neutron diffraction is $\tau_m$(Neutron) $\sim 10^{-11} - 10^{-12}$ s [10]. Using the core size of sample S ($d = 4.7$ nm), the measured effective anisotropy of MnO nanoparticles, $K$(MnO) = $3.5 \times 10^4$ J/m$^3$ [11] and $\tau_0 = 10^{-9}$ s we obtain $T_B = 5$ K!! Thus, since $T_B$(MnO) $<< T_C(\gamma$-Mn$_2$O$_3$) no proximity effect should be observable using SQUID. Contrarily, since $\tau_m$(Neutron) is of the order of the attempt time, $\tau_0$, this implies that the material will be stable up to its bulk $T_N$ when measured using neutron diffraction. This fact allows us to observe the proximity effects using neutron diffraction but not using magnetometry.

In the case of sample L ($d = 17$ nm) the estimated SQUID $T_B$ ($\sim 200$ K) is larger than $T_N = 117$ K, thus for this size the core should be stable up to $T_N$, therefore, proximity effects should be observable using magnetometry.

To further confirm the existence of magnetic moment in the $\gamma$-Mn$_2$O$_3$ the temperature dependence of the saturation magnetization, $M_S(T)$, of the samples was also measured. It can be clearly seen in Fig. 3 that for the sample with the small core (Sample S) $M_S$ virtually vanishes at about 60 K, while for the large core (Sample L) it remains finite up to over 100 K, as expected from a proximity effect.