Neutron diffraction and magnetism of CoO antiferromagnetic nanoparticles

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Abstract. We report a study on neutron diffraction and magnetic properties of cobalt oxide CoO antiferromagnetic nanoparticles with different sizes. The nanoparticles are composed by a structurally and magnetically ordered core and a structurally ordered and magnetically disordered shell with a thickness of about 2 nm. The ordered core has cell parameters, moments direction and modulus similar to those of bulk CoO. Small differences found are attributed to an increase of the oxidation of the nanoparticles with the decrease of size. A remanent moment $M_r$ can be induced in CoO nanoparticles by crossing the transition temperature in the presence of a magnetic field, while the magnetic structure of the antiferromagnetically ordered moments of the nanoparticles core remains unchanged after field cooling within the experimental precision, suggesting that $M_r$ arises in the magnetically disordered shell.

1. Introduction
Bulk antiferromagnetic (AF) materials, as for instance 3d random-field AF [1] and compounds where magnetic sites are diluted with non magnetic impurities,[2] may exhibit remanent magnetization $M_r$. The origin of $M_r$ in bulk AF is associated to domain walls. With the decrease of size, domain walls are no longer formed and surface is often invoked as the origin of $M_r$, arising from an odd number of AF planes, generation of vacancies and oxidation of surface atoms.[3] In the studies where surface effects are highlighted (most of them performed in ferrimagnetic materials), the nanoparticles (NPs) are modelled as having a magnetic ordered core surrounded by a magnetically disordered shell whose thickness is estimated as about 1 nm.[4, 5] However, $M_r$ associated to in-volume effects is also plausible, as found in other studies.[6]

This report focus on the thermal dependence of powder neutron diffraction (PND) patterns and its relation to a thermal $M_r$ induced by field-cooling across $T_N$ of two samples composed of CoO AF NPs with different average sizes, following another study focused on $M_r$ of CoO AF NPs.[7]
2. Experimental
The CoO NPs were prepared by adaptation of the method of Sun et al.[8] using cobalt acetate as the source of cobalt instead of cobalt formate. The size of the particles was adjusted by changing the cobalt to oleylamine ratio and the heating rate. X-ray diffraction (XRD) measurements were performed in a Philips X-Pert - MPD diffractometer using monochromated CuKα radiation (λ = 1.541 Å). PND was performed in the powder diffractometers D20 (using a monochromatic beam of 1.87 Å) and D1A (monochromatic beam of 1.90 Å) of the Institute Laue Langevin. The analysis of XRD and PND patterns was performed by Rietveld refinement using the FullProf package.[9] The contribution of the finite size of the NPs crystallites to the peaks broadening was taken into account by an isotropic model yielding an apparent size, proportional to the mean size of the structurally ordered region of the NPs ⟨τ⟩XRD.[9] Magnetization was measured as a function of temperature from 2 K to 300 K under a magnetic field of 100 Oe with a superconducting quantum interference device (SQUID) magnetometer (MPMS-XL, Quantum Design). Two cooling procedures were used i) zero field cooling (zfc) and ii) field cooling (fc) across T_N, from 300 K to 210 K and zfc from 210 K to 2 K. M_r was calculated from the difference between the magnetization obtained in ii) and i).

3. Results and discussion
Rietveld analysis to room-temperature XRD patterns [Fig. 1(a)] confirms the existence of cubic face centered CoO NPs (space group Fm3m) with mean structural coherence size ⟨τ⟩XRD of 40 and 68 nm. Any possible amount of Co3O4 present in the samples is below the detection limits.

As temperature decreases bellow T_N the nuclear peaks of the PND patterns become broader due to a monoclinic deformation and tetragonal distortion (space group C2/m).[10] and peaks associated to AF magnetic ordering appear. At 5 K, the PND pattern can be well fit by a monoclinic nuclear cell [Fig. 1(b)] and by a propagation vector k=[1/2,1/2,1/2] refereed to a cubic cell, in accordance with Ref.[10]. The temperature dependence of structural parameters (Fig. 2) is similar to that expected,[10] and cooling the sample across T_N in the presence a field has no apparent influence in the cell parameters. Cell parameters of the NPs are similar to those of bulk. However, there are small differences and, despite the fact that just two samples were studied, the trend is a decrease of a, b and c with the decrease of size. This trend is consistent with an increase of the oxidation state with the decrease of size, as found in the case of Fe_xO, where x was found to increase linearly with the increase of x.[11] At the same time, both the monoclinic deformation and tetragonal distortion of the NPs at low temperature are smaller than those of bulk. The magnetic moment per Co ion at 5 K in samples with ⟨τ⟩XRD = 40 and 68 nm is 3.41(7) and 3.40(4) μ_B, respectively, close to those reported in Ref.[12] (3.4 ±0.1 μ_B) and slightly smaller than that reported in Ref.[10] [3.98(6) μ_B]. All these values are higher than the spin-only moment of 3 μ_B, indicating an important orbital contribution. In the sample with smaller size, where the contribution to the PND peaks broadening due to the sample is more relevant, the difference between the structural and magnetic sizes is 5.4 and 4.4 nm in D20 and D1A instruments, respectively. Therefore, the CoO NPs of sample ⟨τ⟩XRD = 40 nm can be described by a core-shell model, where the core is structural and magnetically ordered and the shell is structurally ordered and magnetically disordered, with a thickness of about 2 nm.

The low field magnetization is severely affected by fc across T_N and thermal irreversibility up to T_N arises due to pinning of the uncompensated/canted moments of the AF NPs in the field direction after fc [Fig. 1(d)]. The peak seen at low temperature in sample ⟨τ⟩XRD = 40 nm at around 5 K is not affected by fc and thus is associated to spins which are not pinned at T_N. The reduced remanent magnetization M_r/M_r(0) (with M_r(0) taken as the M_r at 2 K) induced by cooling in the presence of a magnetic field saturates at low temperature and decreases almost linearly with the temperature up to temperatures near T_N [Fig. 1(c)]. This contrasts with the behavior of the sublattice moment μ which is not affected by fc[Fig. 1(c)].
bulk. The absence of changes in the AF core by the application of a moderate magnetic field deformation and tetragonal distortion of the NPs at low temperature are smaller than those of Fe.

A decrease of size leads to an increase of the relative oxygen content, in accordance to that with size can be associated to a change in the stoichiometry of the NPs with size, such that transition temperature in the presence of a magnetic field. The decrease of the cell parameters in this report we show that a remanent moment

4. Conclusions
In this report we show that a remanent moment \( M_r \) can be induced in CoO NPs by crossing the transition temperature in the presence of a magnetic field. The decrease of the cell parameters with size can be associated to a change in the stoichiometry of the NPs with size, such that a decrease of size leads to an increase of the relative oxygen content, in accordance to that found in Fe,CO systems. At the same time, the sublattice magnetic moment, the monoclinic deformation and tetragonal distortion of the NPs at low temperature are smaller than those of bulk. The absence of changes in the AF core by the application of a moderate magnetic field and the linear dependence of \( M_r \) with temperature support the argument that \( M_r \) arises from pinned uncompensated/canted moments located at the shell.

\[ \langle \tau \rangle_{XRD} = 40 \text{ nm at 300 K. Vertical lines represent the position of the allowed Bragg peaks. Inset shows a zoom over the most intense peak.} \]

\[ \text{At the magnetically disordered surface. The surface origin of } M_r \text{ arises most probably from magnetic moments located } r \text{ with temperature support the argument that } M_r \text{ is not affected by } fc \text{ and that the integral breadth of the} \]

\[ \text{is also supported by the linear behavior of } M_r(T) \text{ at intermediate temperatures.} \]

\[ \text{At the same time } \mu \text{ decreases similarly to that reported for bulk, [12] being described by spin-waves at lower temperatures } (T/T_N < 0.5) \text{ and by a Brillouin law close to } T_N. \text{ The fact that } \mu \text{ is not affected by } fc \text{ and that the integral breadth of the magnetic peaks remains unchanged by } fc \text{ indicate that the size of the magnetically ordered core also remains unchanged. In this view, } M_r \text{ arises most probably from magnetic moments located at the magnetically disordered surface. The surface origin of } M_r \text{ is also supported by the linear behavior of } M_r(T) \text{ at intermediate temperatures.} \]
Figure 2. Temperature dependence of (a) the cell parameter $a$, (b) the cell parameters $b$ and $c$, (c) the monoclinic deformation angle $\Delta \beta$ and (d) tetragonal distortion of the pseudocubic cell $1 - c/a$ corresponding to diffractograms obtained after zfc and fc procedures in samples $\langle \tau \rangle_{XRD} = 40$ nm and $\langle \tau \rangle_{XRD} = 68$ nm. The bulk values at 10 K given in Ref.[10] are also plotted.

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