Neutron diffraction and magnetism of CoO antiferromagnetic nanoparticles

N. J. O. Silva[1], I. Puente-Orench[2], M. Martins[3], T. Trindade[3], A. Millán[4], J. Campo[2], F. Palacio[4]

[1] CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal

E-mail: `nunojoao@ua.pt`
[2] Instituto de Ciencia de Materiales de Aragón CSIC - Universidad de Zaragoza and Institut Laue-Langevin, BP 156, F-38042 Grenoble Cedex 9, France
[3] Departamento de Química and CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal
[4] Instituto de Ciencia de Materiales de Aragón, CSIC - Universidad de Zaragoza.
Departamento de Física de la Materia Condensada, Facultad de Ciencias, 50009 Zaragoza, Spain.

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, 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 (NP) 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 M_r induced by field-cooling across T_N of two samples composed of CoO AF NP with different average sizes, following another study focused on M_r of CoO AF NP.[7]

2. Experimental

The CoO nanoparticles 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 CuK_{α} radiation ($\lambda = 1.541$ 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 nanoparticles 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 nanoparticles $\langle\tau\rangle_{XRD}$.[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 nanoparticles (space group $Fm\bar{3}m$) with mean structural coherence size $\langle\tau\rangle_{XRD}$ of 40 and 68 nm. Any possible amount of Co_3O_4 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 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 $\mathbf{k}=[1/2,1/2,1/2]$ 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 NP 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 a was found to increase linearly with the increase of x.[11] At the same time, both the monoclinic deformation and tetragonal distortion of the NP at low temperature are smaller than those of bulk. The magnetic moment per Co ion at 5 K in samples with $\langle\tau\rangle_{XRD} = 40$ 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 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 nanoparticles of sample $\langle\tau\rangle_{XRD} = 40$ 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 the uncompensated/canted moments of the AF NP are pinned in the field direction after fc. The reduced remanent magnetization $M_r/M_r(0)$ 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(d)]. At the same time μ decreases similarly to that reported for bulk,[12] being described by spin-waves at lower temperatures ($T/T_N < 0.5$) and by a Brillouin law close
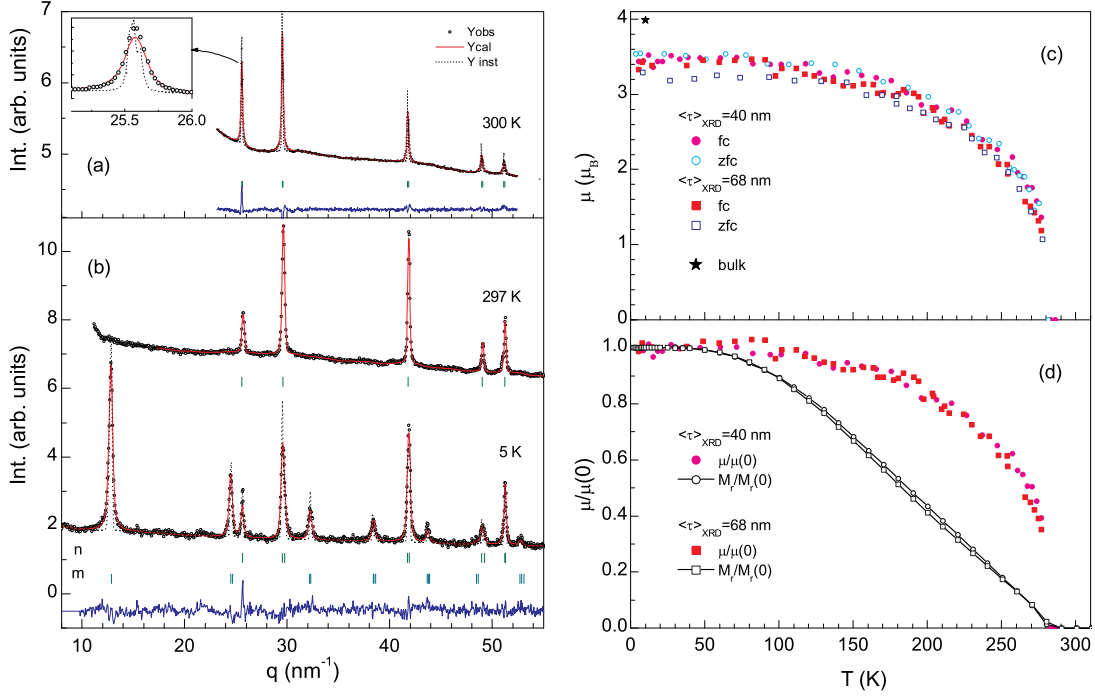
Figure 1. (a) XRD pattern of the CoO nanoparticles with $\langle\tau\rangle_{XRD} = 40$ nm at 300 K. Vertical lines represent the position of the allowed Bragg preaks. Inset shows a zoom over the most intense peak. (b) PND pattern of the same sample at 297 K and at 5 K. Vertical lines represent the position of the allowed Bragg peaks of nuclear (n) and magnetic (m) origin. In panels (a) and (b), the instrument contribution to the peaks shape is shown in dotted lines and Rietveld refinement considering the finite size effect of the nanoparticles to the peaks shape is shown in continuous (red) lines. Temperature dependence of (c) the sublattice magnetic moments μ and (d) of the reduced remanent magnetization $M_r/M_r(0)$ compared to the reduced sublattice magnetic moment $\mu/\mu(0)$, of samples $\langle\tau\rangle_{XRD} = 40$ nm and $\langle\tau\rangle_{XRD} = 68$ nm, corresponding to diffractograms obtained after zfc and fc procedures. The bulk value of μ at 10 K given in Ref.[10] is also plotted in pannel (c).

to T_N. The fact that μ is not affected by fc and that the integral breadth of the magnetic peaks remains unchanged by fc indicate that the size of the magnetically ordered core also remains unchanged. In this view, M_r arises most probably from magnetic moments located at the magnetically disordered surface. The surface origin of M_r is also supported by the linear behavior of $M_r(T)$ at intermediate temperatures.[13]

4. Conclusions

In this report we show that a remanent moment M_r can be induced in CoO nanoparticles by crossing the transition temperature in the presence of a magnetic field. As size decreases, the NP become more oxidized, as deduced by the decrease of the cell parameters a, b and c. At the same time, the sublattice magnetic moment, the monoclinic deformation and tetragonal distortion of the NP 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.
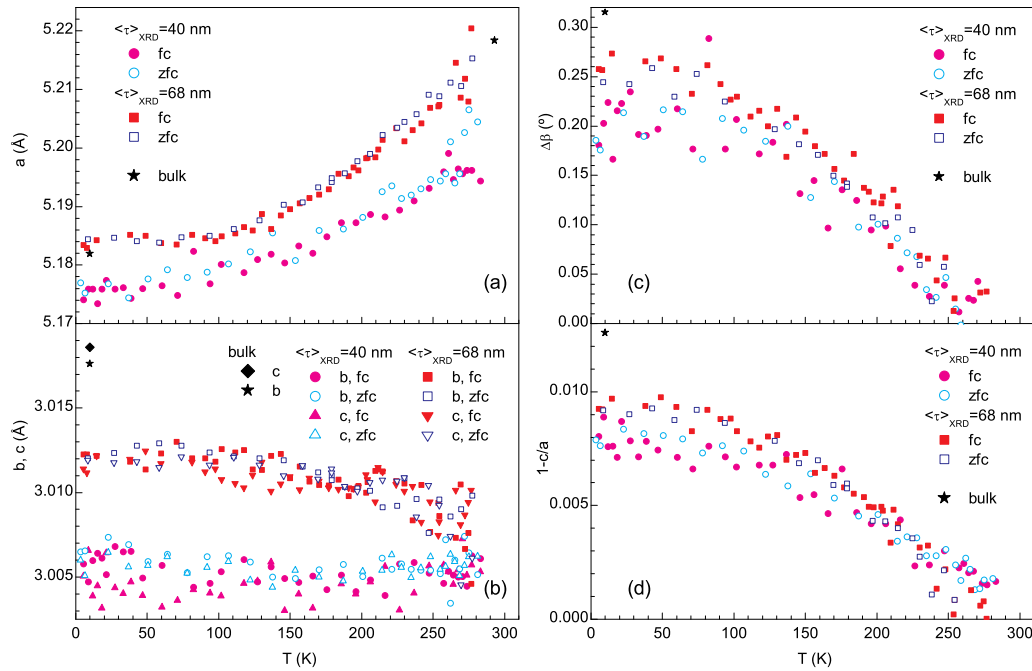
Figure 2. Temperature dependence of (*a*) the cell parameter *a*, (*b*) the cell parameters *b* and *c*, (*c*) the monoclinic deformation angle $\Delta\beta$ and (*d*) tetragonal distortion of the pseudocubic cell $(1 - c/a)$ corresponding to diffractograms obtained after zfc and fc procedures in samples $\langle\tau\rangle_{XRD} = 40$ 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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