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# On the exchange bias effect in NiO nanoparticles with a core(antiferromagnetic)/shell (spin glass) morphology

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**Abstract.** The unexpected appearance of magnetic hysteresis and exchange bias effects in nominally antiferromagnetic NiO nanoparticles is usually explained in terms of a core/shell morphology, where a spin glass-like shell is exchange coupled to an antiferromagnetic core. However, recent studies have challenged the validity of this assumption for small enough NiO nanoparticles. In this work we present proof of the core/shell model for NiO nanoparticles with sizes below 10 nm by combining neutron powder diffraction and magnetic measurements. In addition, we have verified that the exchange bias effect persists even when the particle size is reduced down to 4 nm.

## 1. Introduction

In the recent years, magnetic nanoparticles (NPs) have attracted an intense research effort because they appear to play by a different set of rules compared to those governing bulk materials [1]. As size reduction down to nanometric scale usually changes the magnetic properties of the system, NPs emerge as promising candidates in different applications such as catalysis, solar cells, supercapacitors and biomedicine [2]. In order to optimize the performance and efficiency of the NPs, a deep understanding of their physicochemical properties is needed. A feature common to all the NPs is that their magnetic behavior is strongly influenced by finite size effects. Many studies point out the importance of surface anisotropy as the main cause for the surface spins to become non-magnetic or orientated in a different direction from the core spins [3]. In particular, NPs made up of materials which are antiferromagnetic (AFM) in their bulk form constitute suitable systems for studying finite size magnetism. As AFM materials need a



high degree of symmetry in order to maintain a compensated magnetic structure, their magnetic behavior experiences noticeable changes when reducing size.

Bulk NiO is a paradigmatic AFM material with a Néel temperature ( $T_N$ ) of approximately 523 K. However, the anomalous appearance of a ferromagnetic (FM) moment in nominally AFM NPs was first predicted by Néel in the early 1960s [4] and later confirmed by numerous experimental works [5, 6]. The most widely accepted theory explains this feature as arising from a core/shell model, where the core spins are antiferromagnetically aligned and the outer shell spins are in a disordered spin glass (SG)-like state [6, 7]. One of the most remarkable consequences of this core/shell morphology is the occurrence of the exchange bias (EB) effect. EB emerges as a consequence of the exchange interaction at the interface between two magnetic phases with different anisotropy energies. It manifests as a shift of the magnetic hysteresis loop along the field axis when the system is cooled down in an external magnetic field through the ordering temperature of the most anisotropic phase. However, a recent study has reported that NiO NPs with an average diameter of 7 nm present a core(AFM)/shell(SG) structure without any trace of EB effects [8]. Hence, the assumption that the occurrence of the EB effect is a direct consequence of the core/shell model could be no longer appropriate for small enough NP sizes.

In this work we have performed a neutron powder diffraction and magnetometry joint investigation in order to check the correlation between the core/shell morphology and the occurrence of the EB effect in NiO NPs with sizes below 10 nm.

## 2. Experiment

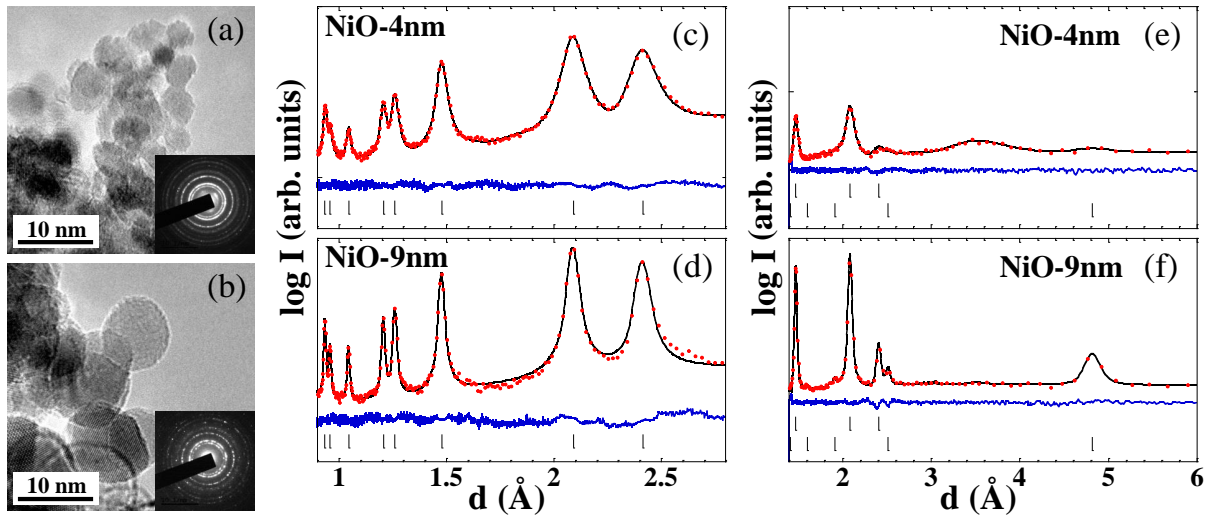
Two samples of NiO NPs assemblies (NiO-4nm and NiO-9nm) were synthesized via the pyrolysis of a nickel nitrate taking place under  $N_2$  within the restricted volume formed by the porosity of a commercial activated carbon. The average size of the NPs was controlled by means of the heating temperature. NiO-4nm and NiO-9nm were prepared at 300 °C and 400 °C, respectively. High-resolution transmission electron microscopy (HRTEM) images of each sample were obtained under a JEOL-JEM-2100F microscope aiming to determine the size, shape and aggregation state of the NPs. The crystalline structure of the samples was investigated by powder x-ray diffraction (XRD) using a Philips X'Pert PRO MPD diffractometer with Cu  $K\alpha_1$  radiation ( $\lambda = 1.5406$  Å). Room temperature powder neutron diffraction (ND) patterns were recorded at the Institut Laue-Langevin (D1B instrument) using a wavelength of  $\lambda = 2.52$  Å. Magnetization data were measured on a Quantum Design PPMS-9T magnetometer.

## 3. Results and Discussion

Figures 1(a)-1(b) display representative HRTEM images of the samples showing the monodispersity, crystallinity and quasi-spheroidal shape of the NPs. The fit of size histograms to lognormal distributions provides values for average NP diameter and standard deviation,  $D(\sigma)$ , of 4(1) nm and 9(1) nm for samples NiO-4nm and NiO-9nm, respectively.

Rietveld refinement of the XRD patterns [see Figures 1(c)-1(d)] was performed using FullProf package. XRD data were fitted according to a rocksalt  $Fm\bar{3}m$  crystal structure. The average NP diameters obtained for NiO-4nm and NiO-9nm coincide with those estimated from HRTEM histograms. The value of the cell parameter obtained for both samples is 4.18(1) Å, very close to that reported for bulk NiO ( $a_{NiO}^{bulk} = 4.178$  Å).

ND patterns in Figures 1(e)-1(f) were modelled according to a  $Fm\bar{3}m$  crystal structure and a propagation vector  $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  referred to a cubic cell [9]. During the fitting process, the unit cell parameters and the scale factors were constrained so as to have the same values in the nuclear and magnetic phases. The obtained values for the magnetic moment per Ni ion ( $\mu$ ) are 1.4(1) $\mu_B$  and 1.7(1) $\mu_B$  for samples NiO-4nm and NiO-9nm, respectively, thus smaller than the value reported for bulk NiO ( $2\mu_B$ ) [9]. As the number of Ni atoms was fixed to be the same in

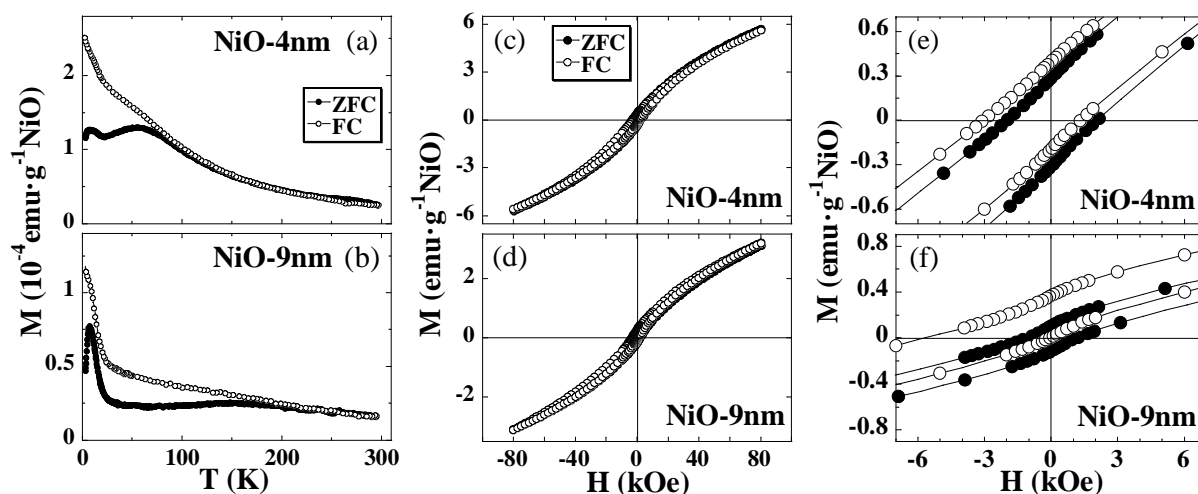


**Figure 1.** (Color online) (a-b) HRTEM images of samples NiO-4nm (top) and NiO-9nm (bottom). Insets display selected area electron diffraction (SAED) patterns. (c-d) XRD and (e-f) ND patterns in logarithmic vertical scale measured at room temperature. Red dots and black solid line represent the experimental data and the Rietveld fit, respectively. Blue lines correspond to the difference between experimental and calculated patterns. For ND patterns, vertical markers indicate the position of nuclear (upper row) and magnetic (lower row) Bragg reflections, while for XRD patterns only vertical markers corresponding to nuclear reflections are shown.

both the nuclear and magnetic phases, the effective reduction in the expected magnetic moment per Ni atom can be linked to the presence of a magnetically disordered shell at the surface of the NPs [10].

Figures 2(a)-2(b) show the temperature dependence of the dc magnetization measured under zero-field-cooling (ZFC) and field-cooling (FC) conditions between 2 K and 300 K. The  $M_{ZFC}(T)$  and  $M_{FC}(T)$  curves of both samples reveal identical features, so that three characteristic temperatures of the system can be identified: (i) a sharp peak at low temperature ( $T \sim 9$  K); (ii) a broad maximum centred at  $T \sim 58$  K (155 K) for NiO-4nm (NiO-9nm); and (iii) a splitting temperature between  $M_{ZFC}(T)$  and  $M_{FC}(T)$  curves at  $T \sim 97$  K (300 K) for NiO-4nm (NiO-9nm). This phenomenology in NiO NPs can be well-explained in the frame of the core/shell model. Then, each NP would be formed by: (i) an AFM ordered core with uncompensated magnetic sublattices (giving rise to a net magnetic moment) due to the reduction in the number of exchange coupled moments caused by finite size effects; and (ii) a magnetically disordered shell, which thermally fluctuates like a SG system [6, 7].

Finally, the magnetic hysteresis loops measured at  $T = 5$  K under ZFC and FC ( $H_{cool} = 80$  kOe) conditions are depicted in Figures 2(c)-2(d). The shift of the loops toward both the negative field (the EB field,  $H_{EB}$ , increases from 0.90 kOe for NiO-4nm to 2.75 kOe for NiO-9nm) and the positive magnetization axis, together with an enhanced coercive field constitute strong evidence of the existence of an EB effect [see Figures 2(e)-2(f)]. The EB origin can be understood starting out from the core(AFM)/shell(SG) morphology derived from ND and dc magnetization measurements. Therefore, the exchange coupling at the interface between the AFM core and the SG shell arises as the most likely mechanism for the occurrence of the EB effect.



**Figure 2.** (a-b) Temperature dependence of the magnetization measured under ZFC and FC conditions for samples NiO-4 nm (top) and NiO-9nm (bottom) under an applied magnetic field of 100 Oe. (c-d) Magnetic hysteresis loops measured at  $T = 5$  K after cooling the samples under ZFC and FC ( $H_{cool} = 80$  kOe) conditions. (e-f) Enlarged view of the central part of the hysteresis loops evidencing the characteristic features of the exchange bias effect.

#### 4. Conclusions

We have shown that the exchange bias effect in NiO nanoparticles with average diameters below 10 nm arises as a consequence of the core(antiferromagnetic)/shell(spin glass) morphology. The magnitude of the exchange bias effect decreases when reducing particle size due to the smaller core-to-shell volume ratio, but still persists for diameter values as small as 4 nm.

#### Acknowledgments

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#### References

- [1] Dormann J L and Fiorani D 1992 *Magnetic Properties of Fine Particles* Edited by North Holland, Amsterdam.
- [2] Teja A S and Koh P Y 2009 *Prog. Cryst. Growth Charact. Mater.* **55** 22
- [3] Iglesias O and Labarta A 2001 *Phys. Rev. B* **63** 184416
- [4] Néel 1949 *Physica* **15** 225
- [5] Kodama R H, Makhlof S A and Berkowitz A E 1997 *Phys. Rev. Lett.* **79** 1393
- [6] Winkler E, Zysler R D, Mansilla M V, Fiorani D, Rinaldi D, Vasilakaki M and Trohidou K N 2008 *Nanotechnology* **19** 185702
- [7] Rinaldi-Montes N, Gorria P, Martinez-Blanco D, Fuertes A B, Barquin L F, Fernandez J R, de Pedro I, Gubieda M L F, Alonso J, Olivi L, Aquilanti G and Blanco J A 2014 *Nanoscale* **6** 457
- [8] Cooper J F K, Ionescu A, Langford R M, Ziebeck K R A, Barnes C H W, Gruar R, Tighe C, Darr J A, Thanh N T K and Ouladdiaf B 2013 *J. Appl. Phys.* **114** 083906
- [9] Roth W 1958 *Phys. Rev.* **110** 1333
- [10] Martinez B, Obradors X, Balcells L, Rouanet A and Monty C 1998 *Phys. Rev. Lett.* **80** 181