Structure-Magnetism Correlation in Ultrafine Mesoscale NiO: Progressive Exchange Striction and Magnetic Anisotropy

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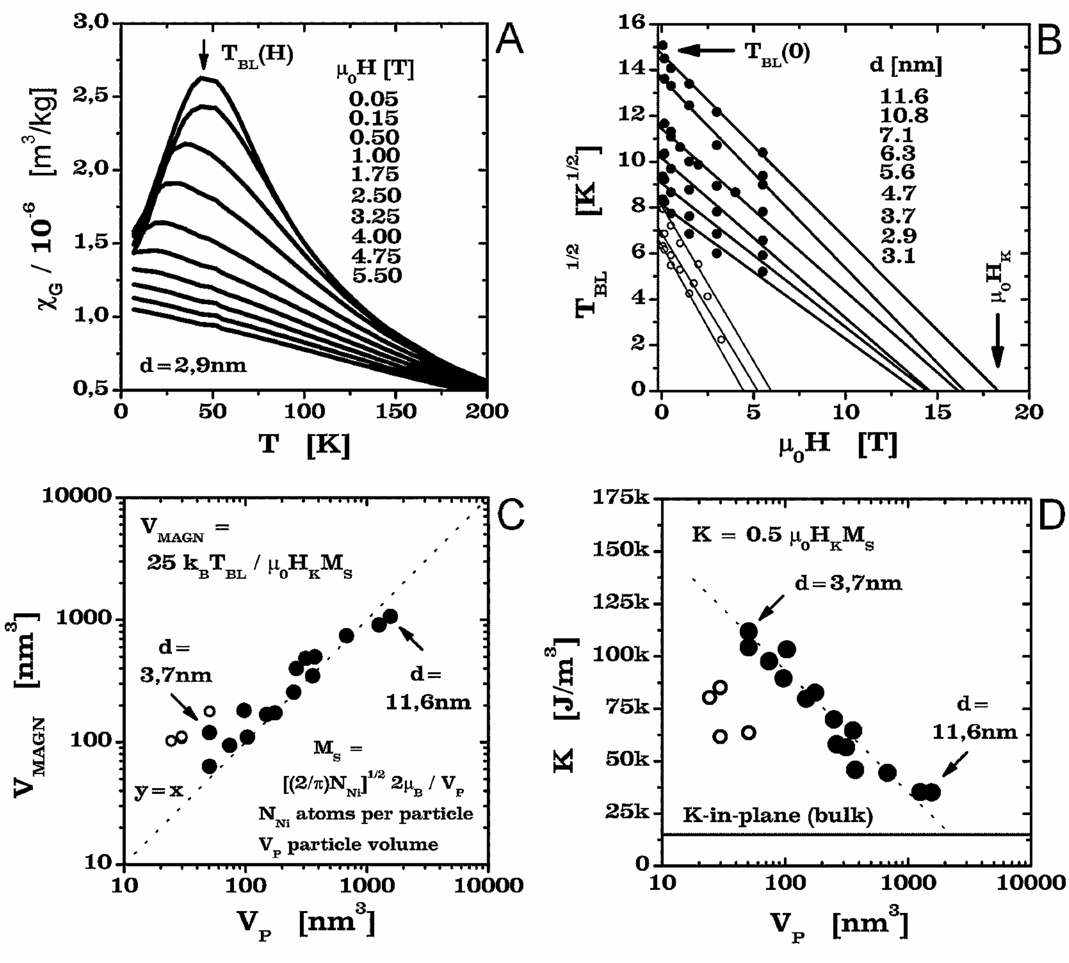
In the course of an ongoing investigation [1] of the size-dependent properties of nanocrystalline (nc) nickel oxide NiO, we have detected a substantial and progressive increase in the antiferromagnetic exchange striction for average particle sizes below about 8 nm. Our results indicate that in these ultrafine NiO nanocrystals, the well known rhombohedral contraction, caused by superexchange-coupling and antiferromagnetic ordering of the Ni^{2+}-spins, attains unusually large values of up to 1.7 % (decrease in c/a ratio) for particle sizes down to 3 nm, as compared to the bulk value of 0.15 %. The progressive distortion is accompanied by, and is probably the cause of, a rise in the principal magneto-crystalline anisotropy which presumably governs the super-paramagnetic blocking of the uncompensated spins in nc-NiO.

Nanocrystalline (nc) NiO of programmable size spanning the full mesoscopic range (2-50 nm according to IUPAC) is currently synthesized at our laboratory in two steps: 1. sub-decomposition-point pyrolysis (SDPP) of Ni-aryl-carboxylates or dehydration of Ni-hydroxide $Ni(OH)_2$, and 2. isothermal grain growth. The ability to adjust the particle size (step 2.) is of prime importance [2] since it puts us in a position to probe the uncompensated spins in nc-NiO indirectly by monitoring the size-dependent changes in magnetic properties.

Our DC-magnetisation studies [1] so far indicate a normal distribution of uncompensated spins within each NiO nanocrystal, in keeping with one of the models originally proposed by Néel. The alternative statistical surface-spin model (cf. Mørup et al. [3]) appears, therefore, to be less likely. Still, it remains an open question why the superparamagnetic blocking temperature T_{BL} apparently scales with the particle diameter d [4] and not, as predicted by Néel-Arrhenius theory, the particle volume V_P ($\sim d^3$). Surface anisotropy was recently put forward as an explanation by Seehra et al. [5]. However, according to our new results, a rise in magneto-crystalline anisotropy K may be the main factor.

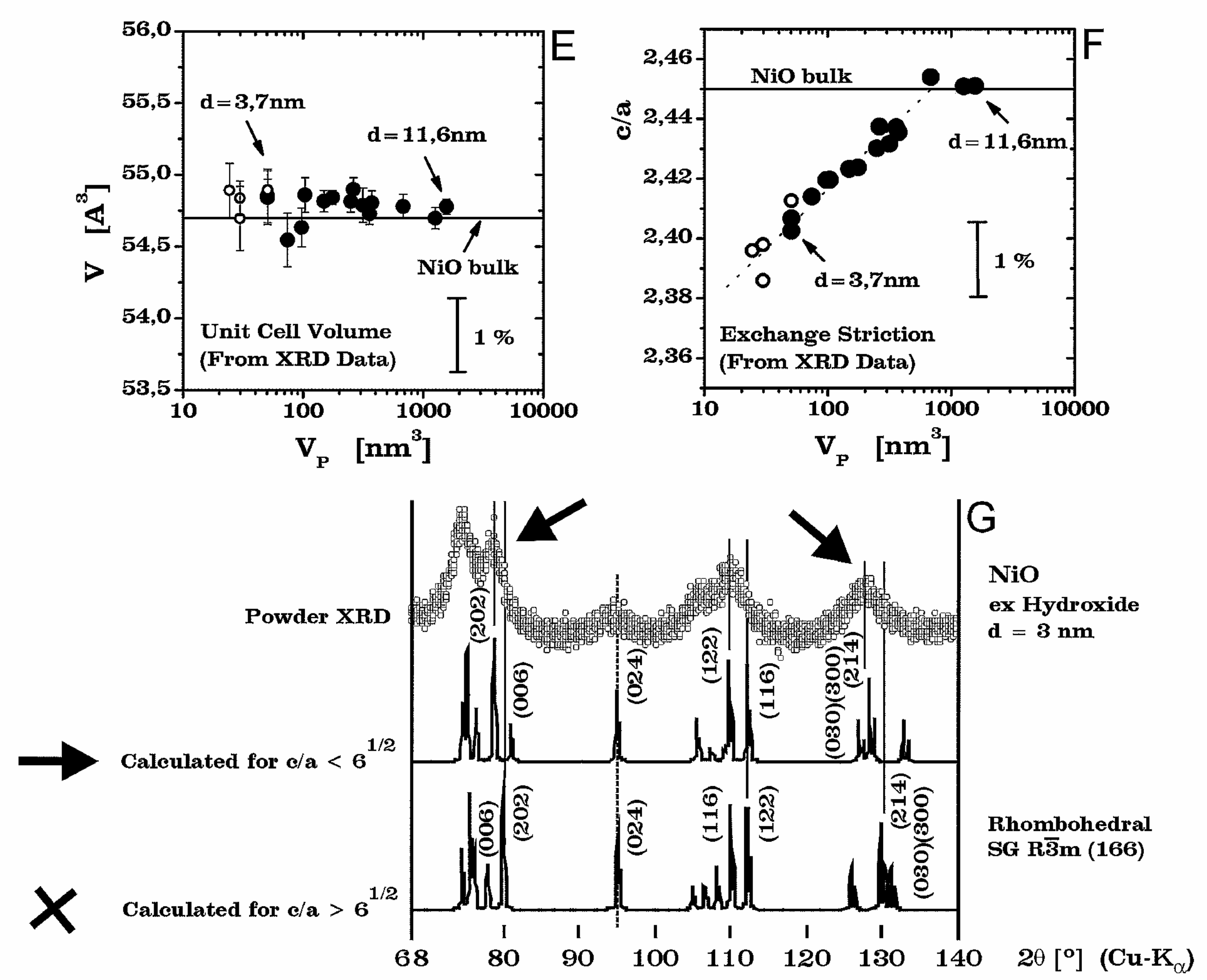
We have determined (fig. A) the superparamagnetic blocking temperature T_{BL} both as a function of the field $B=\mu_0 H$ and the particle size d. From Néel-Wohlfarth plots (fig. B), i.e.

$T_{BL}(H)/T_{BL}(0)= (1-H/H_K)^2$, the anisotropy field $\mu_0 H_K$ is obtained. Since the uncompensated spin density M_S is available from our previous measurements [1], we can calculate, from the magnetisation data alone, the thermally activated volume V_{MAGN} and compare the values with the actual particle volume V_P (~d^3), as calculated from X-ray line-broadening and checked from TEM micrographs. The two correspond quite closely (fig. C). More importantly, we can also calculate the anisotropy constant K as a function of V_P (fig. D). A steady increase of K is observed on going from d= 8 nm down to 4 nm. Below 4 nm, an anomalous behaviour sets in (open symbols in figs. B-D). For the large particles, K approaches the bulk value of the in-plane anisotropy of antiferromagnetically ordered NiO.



A careful analysis of the Bragg positions of massively size-broadened X-ray diffraction lines at high two-theta angles (fig. G) reveals that the increase in magneto-crystalline anisotropy (fig. D) is matched by an anisotropic lattice contraction (fig. F) at practically constant volume (fig. E). We were led by the non-regular relative line intensities and Bragg positions to refine the structure of nc-NiO in a rhombohedral setting instead of the more usual pseudo-cubic one. The progressive lattice distortion below d= 8 nm is quite obvious (fig. F) but, due to the excessive line broadening, it is not clear from conventional

Rietveld analysis whether c/a increases or decreases. Only from the particular positions and intensities of lines especially at high angles (up to 140 degrees in two-theta, fig. G) does it become clear that a considerable contraction (not relaxation) along [001] in excess of the bulk value takes place in very small NiO nanocrystals.



To conclude this brief outline, we observe in ultrafine nc-NiO an unusually pronounced antiferromagnetic exchange striction (fig. F), matched by a correspondingly enhanced magneto-crystalline anisotropy (fig. D) which is presumably responsible for the strong superparamagnetic blocking of the uncompensated spins.

[1] M. Petrik, B. Harbrecht, *Z. Anorg. Allg. Chem.*, 2008, *634*, 2069.

[2] For details cf. M. Petrik, B. Harbrecht, *6th Int. Conf. on Inorg. Mat.*, Dresden, Germany, Sept. 28-30, 2008, Delegate Manual, p. 3-146.

[3] C. R. H. Bahl et al., *J. Phys.: Condens. Matter*, 2006, *18*, 4161.

[4] M. Petrik, B. Harbrecht, unpublished; cf. also ref. [5].

[5] H. Shim et al., *Solid State Comm.*, 2008, *145*, 192.