

Ultrafine Mesoscale NiO

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Exchange Striction and Magnetic Anisotropy

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Nano-crystalline (nc) nickel oxide NiO in the mesoscopic range (2-50 nm, IUPAC) is currently synthesized at our laboratory in two steps: 1. sub-decomposition-point pyrolysis (SDPP) of Ni-aryl-carboxylates or Ni(OH)_x , and 2. isothermal grain growth [1]. The ability to adjust the particle size d is crucial in order to probe the uncompensated spins in nc-NiO by monitoring the accompanying changes in magnetic properties.

Our DC-magnetisation studies [2] indicate a statistical distribution of uncompensated spins in the nanocrystals, as originally proposed by Neel. The alternative surface-spin model (cf. Morup et al. [3]) appears therefore less likely.

An open question has been why the blocking temperature T_{BL} scales with the particle diameter d and not the particle volume V_p . Surface anisotropy was recently suggested as an explanation by Seehra et al. [4]. From our results, a rise in magneto-crystalline anisotropy may be the main factor.

We have determined the blocking temperature T_{BL} both as a function of the field $B = \mu_0 H$ and the particle size d . From Néel-Wohlfarth plots, the anisotropy field $\mu_0 H_K$ is obtained. Since the uncompensated spin density M_s is available from our previous measurements [2], we can calculate the thermally activated volume d_{MAGN} from the magnetisation data and compare the values with the particle diameter d . The two correspond quite closely. More importantly, we can also calculate the anisotropy constant K as a function of d . A steady

increase of K is observed from about 8 nm down to 4 nm. Below 4 nm, an anomalous behaviour sets in. For the large particles, K approaches the bulk value of the in-plane anisotropy of antiferromagnetically ordered NiO.

Whatever the cause may be of the observed increase of the anisotropy energy, it is coupled to a major lattice distortion of the nanocrystals as well.

We were led by unusual relative intensities and positions of powder pattern lines to refine the structure of nc-NiO in a rhombohedral setting instead of a pseudo-cubic one. A progressive lattice distortion sets in below about $d = 8$ nm but, due to excessive line broadening, it is not clear from the Rietveld analysis whether c/a increases or decreases. Only from the particular positions and intensities of lines especially at high angles does it become clear that a considerable contraction along [001] takes place in NiO nanocrystals below about 8 nm.

To conclude this brief outline, we observe in ultrafine nc-NiO a markedly enhanced antiferromagnetic exchange striction coupled with a corresponding rise of the anisotropy.

- [1] For details cf. M. Petrik, B. Harbrecht, 6th Int. Conf. on Inorg. Mat., Dresden, Germany, Sept. 28-30, 2008, book of abstracts, p. p.
- [2] M. Petrik, B. Harbrecht, Z. Anorg. Allg. Chem. 2008, 634, p. 2069.
- [3] C. R. H. Bahl et al., J. Phys.: Condens. Matter 2006, 18, p. 4161.
- [4] H. Shim et al., Solid State Comm. 2008, 145, p. 192.

