

Ultrafine Mesoscale NiO

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Exchange Striction and Magnetic Anisotropy

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The size-controlled, precursor-based^{*)} solid state synthesis of shape-isotropic nanocrystalline (nc) NiO -- spanning the entire mesoscopic range from 2.5 nm to 50 nm -- has made possible a systematic study of scaling laws for this prototypical antiferromagnet (AF). DC magnetisation data as a function of size and shape, for example, indicate (after half a century of controversy [1]) that nc-NiO is a Néel-type random ferrimagnet [2].

Herein, we present experimental evidence for a correlation between the in-plane magneto-crystalline anisotropy constant K_2 and the AF exchange striction (i.e. reduction in the crystallographic c/a ratio).

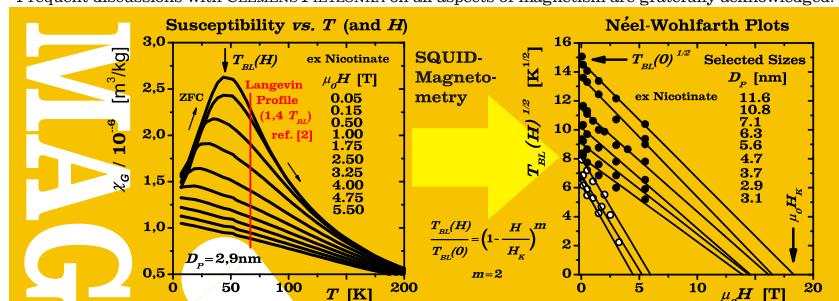
Both $(c/a)^{-1}$ and K_2 (blue symbols in the two linked Figures) increase substantially and progressively for particle sizes D_p below about 8 nm. For the smallest particles ($D_p < 4$ nm), an anomalous behaviour sets in (open symbols in all the Figures). For the largest particles ($D_p > 10$ nm), K_2 comes close to the rather scarce literature data for bulk NiO (cf. ref. [3]), and the results reported herein provide an independent measure of this elusive anisotropy parameter.

Due to the drop in K_2 with increasing D_p , the super-paramagnetic blocking temperature $T_{BL}(0)$ (from Néel-Wohlfarth plots) does no longer scale linearly with the particle volume V_p , but rather with the diameter D_p . Assuming K_2 to be an intrinsic function of c/a , the previously puzzling linear $T_{BL}(0) \cdot D_p$ relationship now follows naturally from the c/a relaxation (finite-size effect).

Finally, the activation volume V_A compares well with previous values based on Langevin fits [2], even though the latter values -- obtained at higher temperatures ($1.4 T_{BL}$) -- are systematically smaller (red symbols in the Activation Volume Figure). Thus, the model of a super-paramagnetic Néel-type random ferrimagnet is self-consistent and quite invariant with regard to different temperature regimes (largely blocked in the present analysis based on $T_{BL}(0)$, but more freely relaxing at $1.4 T_{BL}$ in [2]).

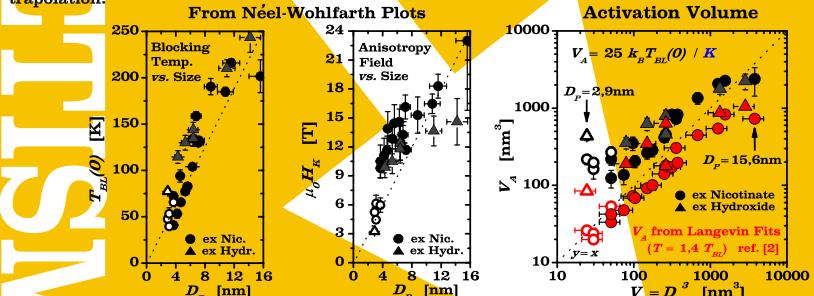
- [1] J. T. Richardson, W. O. Milligan, Phys. Rev. **102** (1956) 1289.
- [2] M. Petrik, B. Harbrecht, Z. Anorg. Allg. Chem. **634** (2008) 2069.
- [3] C. R. H. Bahri et al., S. Merup, Physica B **385/386** (2006) 398.
- [4] H. Shim et al., M. S. Seehra, Solid State Comm. **145** (2008) 192.

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For each particle size D_p (or volume $V_p = D_p^3$), the blocking temperature $T_{BL}(H)$ is determined as a function of the field $B = \mu_0 H$.

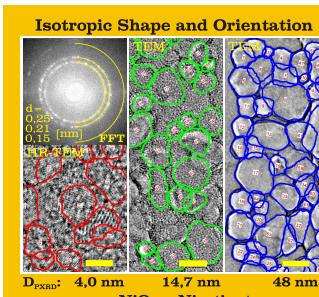
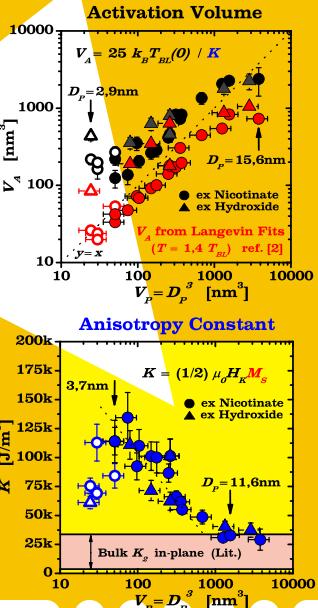
From Néel-Wohlfarth plots (top right), the blocking temperature at zero field $T_{BL}(0)$ and the anisotropy field $\mu_0 H_K$ are obtained by extrapolation:



The anisotropy constant K is calculated from the above experimentally determined anisotropy field $\mu_0 H_K$ and the previously measured [2] spin density M_s , even without knowing the particle volume V_p , i.e. self-consistently with regard to the magnetisation data and hence without possible uncertainties caused by the particle size distribution or the particle shape:

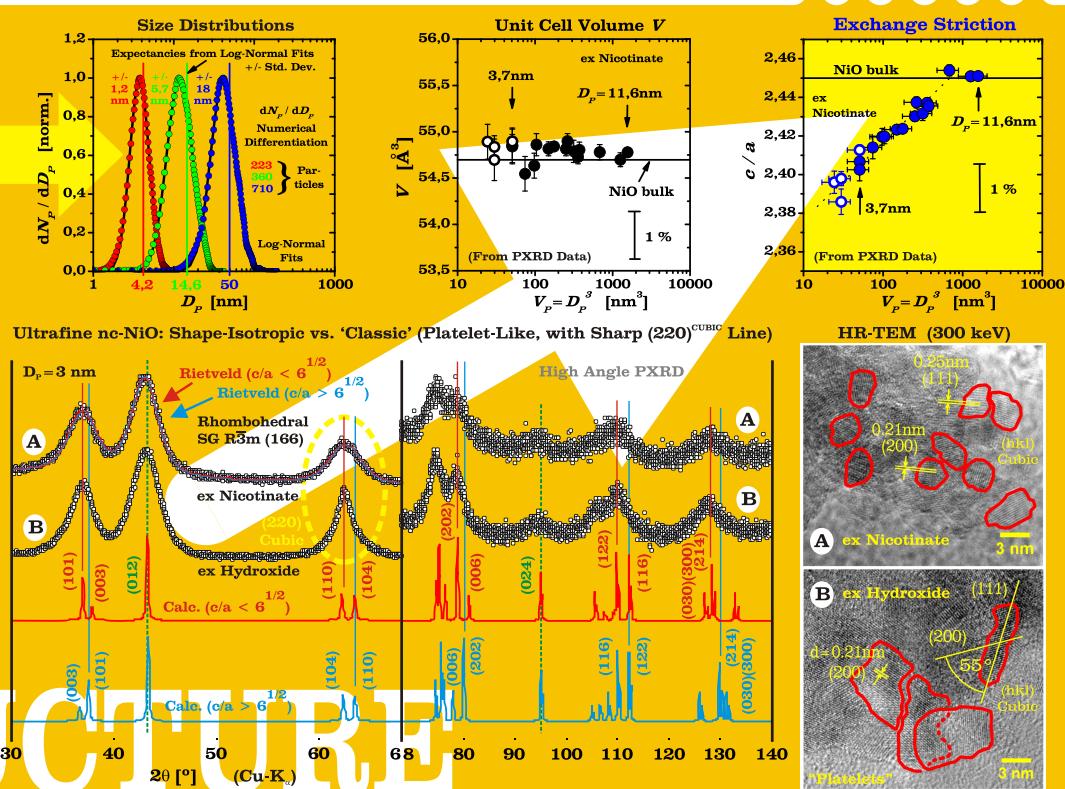
It has been suggested [4] that the rise in K for small NiO particles may be due to surface anisotropy. We believe, however, that, since $(c/a)^{-1}$ and K_2 increase simultaneously starting at about the same particle size ($D_p = \text{ca. } 8$ nm), the rise in K_2 is more likely an intrinsic effect triggered by the uncommonly large exchange striction (a drop in c/a by up to 2.5 %) presented herein.

Since the uncompensated spin density M_s is known from previous measurements [2], the anisotropy constant K (cf. below), and hence the activation volume V_A , are obtained from the magnetisation data. V_A is plotted vs. the particle volume V_p (calculated from PXRD line widths and checked using HR-TEM):



By the unusual relative intensities and positions of powder pattern lines (right), we were led to refine the structure of ultrafine nc-NiO in a rhombohedral setting instead of the commonly used cubic one. However, due to excessive line broadening, it was not clear from the Rietveld analysis whether c/a is larger or smaller than the theoretical (cubic) value of $6^{1/2}$.

Only from the particular positions and intensities of lines especially at high angles (e.g. around 80° and 130°) -- and for the hydroxide-derived 'platelets' B by the expected predominance of low- ℓ reflections (e.g. (122) rather than (116) around 110°) -- did it become clear that for D_p less than ca. 8 nm, a contraction along [001] takes place, by more than an order of magnitude larger (drop in c/a) than the usual bulk AF exchange striction.



^{*)} Starting from Ni-arylcroboxylates, e.g. Ni(Nic)₄H₄O, Nic = Nicotinate. SQUID = Superconducting Quantum Interference Device. PXRD = Powder X-Ray Diffraction. HR-TEM = High Resolution Transmission Electron Microscopy.