

# Structure-Magnetism Correlations in *nc*-NiO: High-Sensitivity Powder Diffraction

**1. Introduction** Although bulk nickel oxide is the canonical type II (fcc) antiferromagnet (AF), nanocrystalline (*nc*) NiO is distinguished by an anomalous size-dependent ferrimagnetism (Richardson's phenomenon [1]). *nc*-NiO may be prepared in two distinct morphologies: as semiregular platelets (aspect ratio ca. 4, figures 1a-b) and nearly spherically shaped (figures 1c-d). In both types, the ferrimagnetism obeys the same scaling law [2]. However, the platelets are subject to pronounced surface-mediated interparticle exchange interaction [3]. As a result, the thermally activated magnetic moment (Langevin-type superparamagnetism) is significantly larger than the average moment per particle (ratio ca. 5) [2].

**2. Motivation** The above-mentioned interparticle exchange interaction presumably couples adjacent NiO nano-platelets via the flat <111> (cubic) surfaces. The intuitive picture (figure 2a) of this scenario is, however, misleading: the spins lying within a <111> (cubic) face are either parallel or antiparallel to the particle's overall moment (50% chance), so that within a stack of platelets the moments should nearly compensate rather than add (figure 2b).

Therefore, a less intuitive, but more realistic, model (figure 2c) for the constructive interparticle exchange is here proposed: an edge-on coupling of the tilted (out-of-plane) <111> (cubic) lattice planes across the interfaces. Elastic coupling would ensure that exchange striction occurs in the same {111} direction in all the platelets of any stack. All particle moments can then align colinearly via thermally activated in-plane rotation (overcoming a small anisotropy energy).

How can the new model (figure 2c) be verified -- or rejected -- experimentally? The direction of the exchange striction (AF ordering vector) is an important indicator. For instance, if the ordering vector proved to be oriented always perpendicularly to the flat faces (figure 2a-b), the new model would obviously have to be rejected.

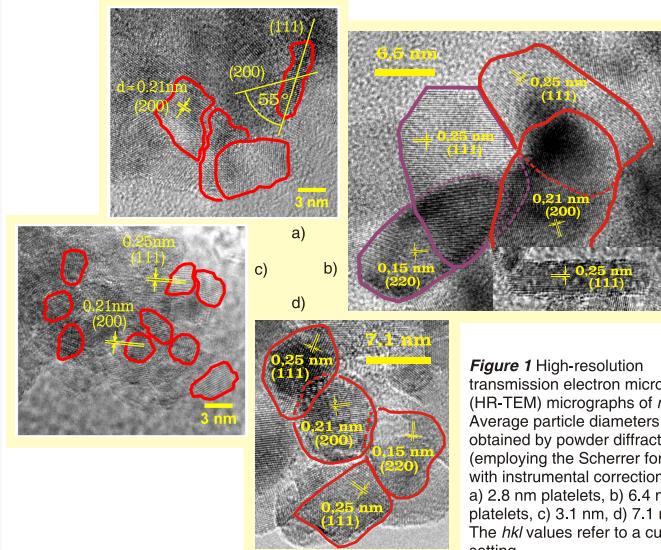
**3. Powder Diffraction** High-sensitivity powder diffraction (figure 3a-b, typical equivalent measuring time for 3 nm particles at 40kV/40mA x-ray power: two months) reveals for the first time a continually increasing AF exchange striction at particle diameters smaller than about 20 nm (figure 3c). For the platelets, the <220> (cubic) reflection apparently splits into sharp (in-plane scattering vector) and broad (out-of-plane scattering vector) lines, so that the Rietveld refinement deviates strongly (inset of figure 3b). Indeed, systematic line broadening is expected (table 1), depending on whether the AF ordering vector is free to take any {111} (cubic) direction within the platelet or not. The (cubic) <220> line is split into (rhombohedral) <110> and <104>. From the multiplicities of table 1, <110> is sharper ('platelet normal'), less sharp ('other') or equal in width ('both') to <104>. For <111> or <200> (cubic), such fine differentiation is not possible (table 1). A simulation of the <110>/<104> doublet (figure 4) -- using the same pseudo-Voigt profile, line positions and intensities as obtained from the Rietveld refinement (figure 3b), and mixing sharp and broad profiles according to table 1 -- shows that the exchange striction has no preferred orientation (i.e. column 'both' in table 1) in platelet-shaped *nc*-NiO. In order to reproduce the measured overall intensity, the FWHM is found iteratively to be 1.3° and 5.6° for the 'sharp' and 'broad' profiles, respectively. Thus, the average aspect ratio of the platelets is 5.6:1.3, in excellent agreement with the value (ca. 4) obtained by high-resolution transmission electron microscopy (HR-TEM).

**4. Conclusion** Inspite of the pronounced shape-anisotropy of ultrafine platelet-shaped *nc*-NiO, the AF ordering vector can take any of the four degenerate {111} (cubic) directions. For one of these (the platelet normal), constructive interaction with adjacent particles via the platelet's faces is unlikely. Consequently, the new model of interparticle exchange interaction (figure 2c) applies to three out of four particles on average. This may explain the mean number (5) of magnetically coupled ultrafine particles, which was previously shown to remain constant in the whole size range up to 7 nm [2]. These insights are obtained by the combination of two techniques: 1. Rietveld refinement of the whole powder pattern (including the high angle region) and 2. deconvolution of the split <220> (cubic) line profile.

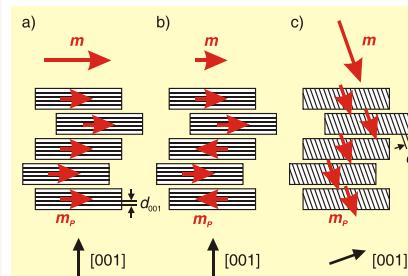
**References** [1] J. T. Richardson, W. O. Milligan, *Phys. Rev.* **1956**, *102*, 1289. [2] M. Petrik, B. Harbrecht, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2069. [3] C. R. H. Bahl, S. Mørup, *Nanotechnology* **2006**, *17*, 2835.

**Table 1** Diffraction line widths (and multiplicities) for rhombohedral, nearly cubic, platelet-shaped nano-crystals.

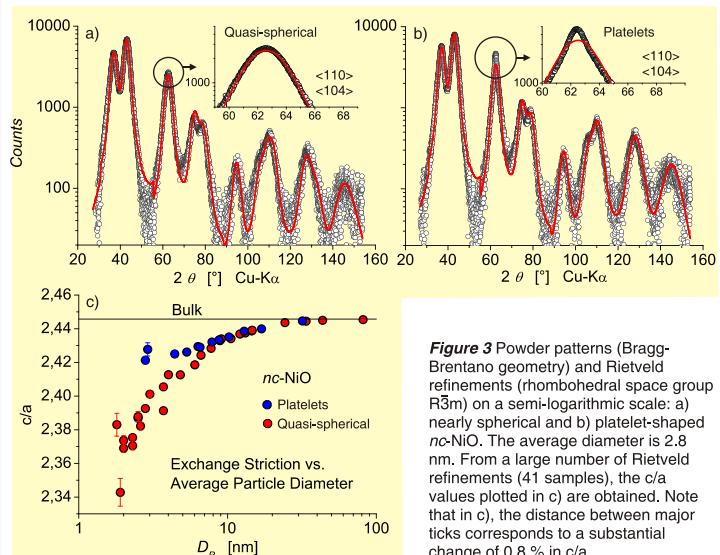
hkl		Rhombohedral contraction axis		
Cubic	Rhomb.	Platelet normal (1)	Other (3)	Both (4)
<111> "	<101> (003)	SHARP (3) BROAD (1)	SHARP (2) SHARP (1) BROAD (1)	SHARP (9) SHARP (3) BROAD (3) BROAD (1)
<200>	<012>	MEDIUM (3)	MEDIUM (3)	MEDIUM (3)
<220> "	<110> <104>	SHARP (3) BROAD (3)	SHARP (1) SHARP (2) BROAD (2) BROAD (1)	SHARP (6) SHARP (6) BROAD (6) BROAD (6)



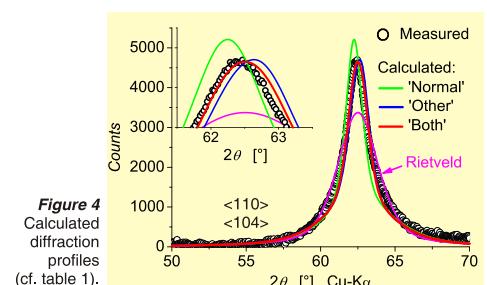
**Figure 1** High-resolution transmission electron microscopy (HR-TEM) micrographs of *nc*-NiO. Average particle diameters obtained by powder diffraction (employing the Scherrer formula with instrumental correction) are: a) 2.8 nm platelets, b) 6.4 nm platelets, c) 3.1 nm, d) 7.1 nm. The *hkl* values refer to a cubic setting.



**Figure 2** The rhombohedral c axis [001] is the antiferromagnetic (AF) ordering vector in NiO. Spins are ferromagnetically ordered within each 001 plane, the spin direction lies in the plane. Adjacent 001 planes are AF ordered. Each nanocrystal's uncompensated moment  $m_p$  contributes to the resulting moment  $m$  of the aggregate. In a) and b) the AF ordering vector is always the platelet normal, but a) is unlikely. Therefore, only c) results in a large moment  $m$ .



**Figure 3** Powder patterns (Bragg-Brentano geometry) and Rietveld refinements (rhombohedral space group  $\bar{R}\bar{3}m$ ) on a semi-logarithmic scale: a) nearly spherical and b) platelet-shaped *nc*-NiO. The average diameter is 2.8 nm. From a large number of Rietveld refinements (41 samples), the  $c/a$  values plotted in c) are obtained. Note that in c), the distance between major ticks corresponds to a substantial change of 0.8 % in  $c/a$ .



**Figure 4** Calculated diffraction profiles (cf. table 1). The plot shows measured (black circles) and calculated (green, blue, red curves) profiles for <110> and <104> reflections. The Rietveld fit is shown as a solid black line.