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

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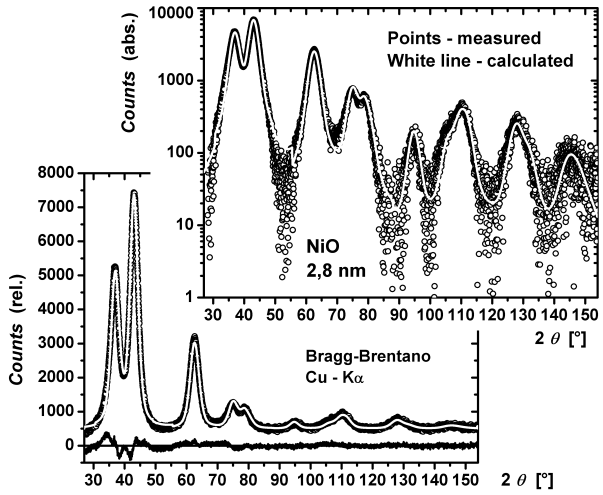
Nickel oxide NiO is a robust room-temperature antiferromagnet, distinguished by strong super-exchange interactions (Néel temperature T_N = 523 K) and a simple magnetic (*fcc*-based type II) and atomic (NaCl-type above T_N) structure. This has made NiO the model antiferromagnet of choice for over half a century. In the last two decades, renewed interest arose in the marked ferrimagnetism observed in nanocrystalline (*nc*-) NiO (Richardson's phenomenon).[1] Recently, we demonstrated that this anomalous nanomagnetism may be explained by a Néel-type random spin-sublattice occupation.[2] The next step is to find an explanation for the unusual size-dependent magnetic anisotropy modulation in *nc*-NiO.[3] To this end, the lattice distortions in NiO nanocrystals have been re-examined by high-sensitivity x-ray powder diffraction, employing a latest-generation semiconductor array detector. Powder patterns of nanocrystals from 1,8 nm through the whole mesoscopic range up to 50 nm have been consistently refined using a basic set of Rietveld parameters (including overall *B* isotropic).



The quality of the fits even at high 2θ (note the semi-logarithmic scale in the upper figure) indicates that, unlike other ultrafine nanoparticles (e.g. CdSe), NiO remains structurally intact, without faulting or major surface reconstruction, even on the ultra-nanoscale. However, two remarkable changes emerge at the lower end of the mesoscale (viz. for 2 to 8 nm NiO crystallites): the Rietveld refinements indicate (1) a significantly enhanced antiferromagnetic exchange striction (rhombohedral contraction),[3] up to 20 times larger than in the bulk, and (2) below 5 nm, a surplus random atomic displacement of up to 2,3(3) Å^2 (static, non-thermal, as evidenced by the unaltered Debye temperature calculated from IR spectra). These phenomena correlate with the above mentioned anomalous modulation – as a function of size – of the magnetocrystalline anisotropy (obtained for the first time[3] from Néel-Wohlfarth and Langevin plots of DC magnetisation data) and point towards an explanation for this novel finite-size effect.

[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] M. Petrik, B. Harbrecht, *Z. Anorg. Allg. Chem.* 2010, *636*, (9), in press.

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