Experimental Report

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Title: Spin Orientation in NiO Nanoparticles

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Researh Area: Physics

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Samples: NiO

Instrument	Req. Days	All. Days	From	To
D1B	2	2	12/03/2013	14/03/2013
D7	4	4	15/03/2013	19/03/2013

Abstract:

NiO was one of the earliest materials to be investigated with neutron scattering in the pioneering work of Shull et al. [1]. While the bulk system is quite well understood, the magnetic structure of NiO nanoparticles is still unresolved. The magnetic properties of nano structured materials can differ considerably from those of bulk systems. The large relative surface area can give rise to considerable surface anisotropies that can result in different spin orientations than in the corresponding bulk systems. In thin films of other materials, a spin direction perpendicular to the film plane has been found for films below a certain critical thickness, whereas the spin direction is within the plane for larger film thickness (see e.g. [2,3]). We wish to perform magnetic powder diffraction on plate-shaped NiO nanoparticles of different sizes to determine the spin orientation in the particles. [1] C. G. Shull et al., Phys. Rev. 83 (1951), 222. [2] P. J. Jensen and K. H. Bennemann, Surf. Sci. Reports 61 (2006), 129. [3] D. S. Deng et al., Phys. Rev. B 69 (2004), 172403.

Spin orientation in NiO nanoparticles

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Four samples of plate shaped NiO nanoparticles and one sample of bulk NiO powder were studied with unpolarised neutrons at D1B and with XYZ-polarisation analysis at D7. The aim of the study was to investigate the magnetic structure, and in particular the spin orientation in the platelets, as function of particle size. Previous experiments on similar particles have suggested that the direction of antiferromagnetic modulation is perpendicular to the particle plane[1], enabeling us to determine the spin orientation with respect to the particle shape from the intensity of the antiferromagnetic $\left\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\right\}$peak.

1 Unpolarised powder diffraction experiment on D1B

For the unpolarised experiment on D1B the samples, each with a mass of approximately 2 g, were loaded in vanadium cans in a helium atmosphere to ensure thermal contact between the nanoparticles at low temperatures. All measurements were performed at a temperature of 1.5 K using a cryo-furnace with an oscillationg collimator. A neutron wavelength of 2.52 Å was selected by the PG002 monochromator. For the bulk sample good statistics were obtained within a few minutes but for the nanoparticles measurements of several hours were necessary because of the very high spin incoherent background from water adsorbed on the particle surfaces and because of the low peak amplitudes because of finite size broadening. The diffraction patterns from the four nanoparticle samples and the bulk sample are shown in Figure 1. The patterns show considerable finite size broadening and a very large background for the nanoparticles as expected. There is a very destinct periodic modulation of the background signal which we ascribe to a shadowing effect of the oscillating collimator. A similar signal was seen in control measurements of vanadium and polyethylen. It was attempted to remove this oscillatory contribution by subtraction of the control measurements and by smoothing procedures, but the results were not satisfactory. This makes it very difficult to accurately obtain the intensity of the $\left\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\right\}$peak (at $q \approx 1.3$ Å^{-1}), which is necessary to determine the spin orientation. The large signal at low q, which we ascribe to small angle scattering from the particle surfaces, needs to be deconvoluted from the magnetic peak, and this further complicates the process of extracting the magnetic intensity. Determining the intensity of one of the nuclear peaks (at $q \approx 2.6$ Å^{-1}, $q \approx 3.0$ Å^{-1}, or $q \approx 4.3$ Å^{-1}), which is needed for normalisation purposes, is difficult for the smaller particles because of a significant peak overlap.

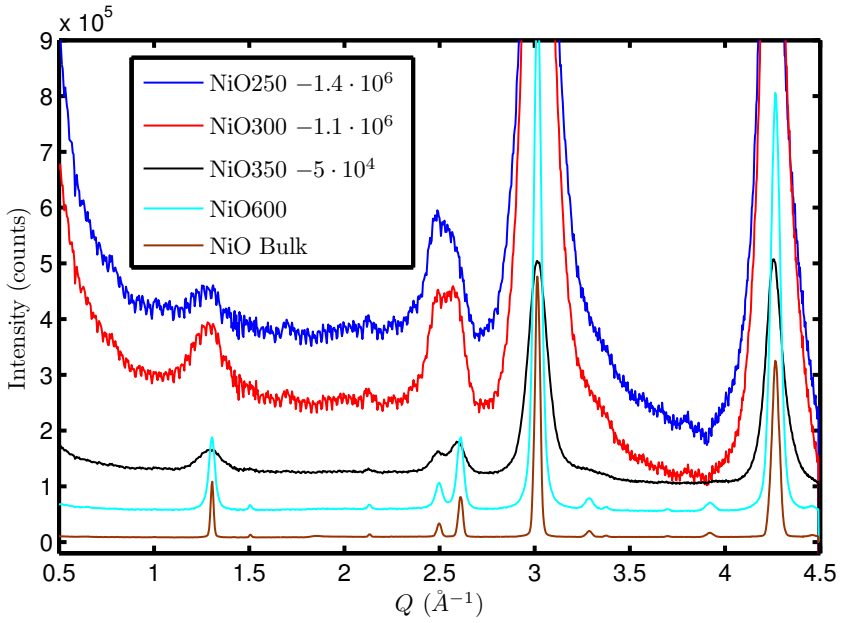

Figure 1: Diffraction patterns of the four samples of NiO nanoaprticles and one sample of bulk NiO obtained at D1B at a temperatures of 1.5 K and a neutron wavelength of 2.52 Å. The samples names correspond to annealing temperatures in °C and NiO250 is the sample with the smallest particle size. A constant have been subtracted from the indicated patterns to make all patterns fit in one figure.

2 XYZ-polarisation analysis experiment on D7

For the polarised experiment at D7 the samples were loaded in hollow cylinder aluminium cans with outer diameters of 20 mm and inner diameters of either 18 mm or 19 mm depending on the amount of sample. The nanoparticle samples were the same as in the D1B experiment and again they were loaded in a helium atmosphere. All measurements were performed with a neutron wavelength of 3.11 Å and at a temperature of 1.5 K provided by a standard orange cryostat. The first day of the experiment was used for callibration measurements (empty can, amorphous silica, vanadium, cadmium). A flipping ratio of about 30 was measured in all channels. The nuclear- magnetic- and spin-incoherent cross sections were separated by the XYZ-polarisation analysis method as described in [2]. Despite the large spin-incoherent signal in the smallest particles the separation of these scattering contributions works well. The ability to issolate the magnetic signal from the other contributions is a significant improvement over the D1B data as well as earlier data from unpolarised experiments. The separated cross sections are shown in Figure 2 for the four nanoparticle samples. The magnetic correlation length determined from the width of the $\left\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\right\}$peak corresponds roughly to the particle thickness measured with transmission electron microscope, confirming that the direction of antiferromagnetic modulation is normal to the particle plane. From the realtive intensities of the $\left\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\right\}$and $\left\{\frac{1}{2}\frac{1}{2}\frac{\overline{3}}{2}\right\}$ peaks the direction of the spins in the antiferromangetic sublattices are found to be oriented close to the particle plane, which is the (111) plane, in which the spins are expected to be in bulk NiO. For the smallest particles, with a thickness of about 2 nm (NiO250), the spin is found to be reoiriented with an out of plane angle of 30°

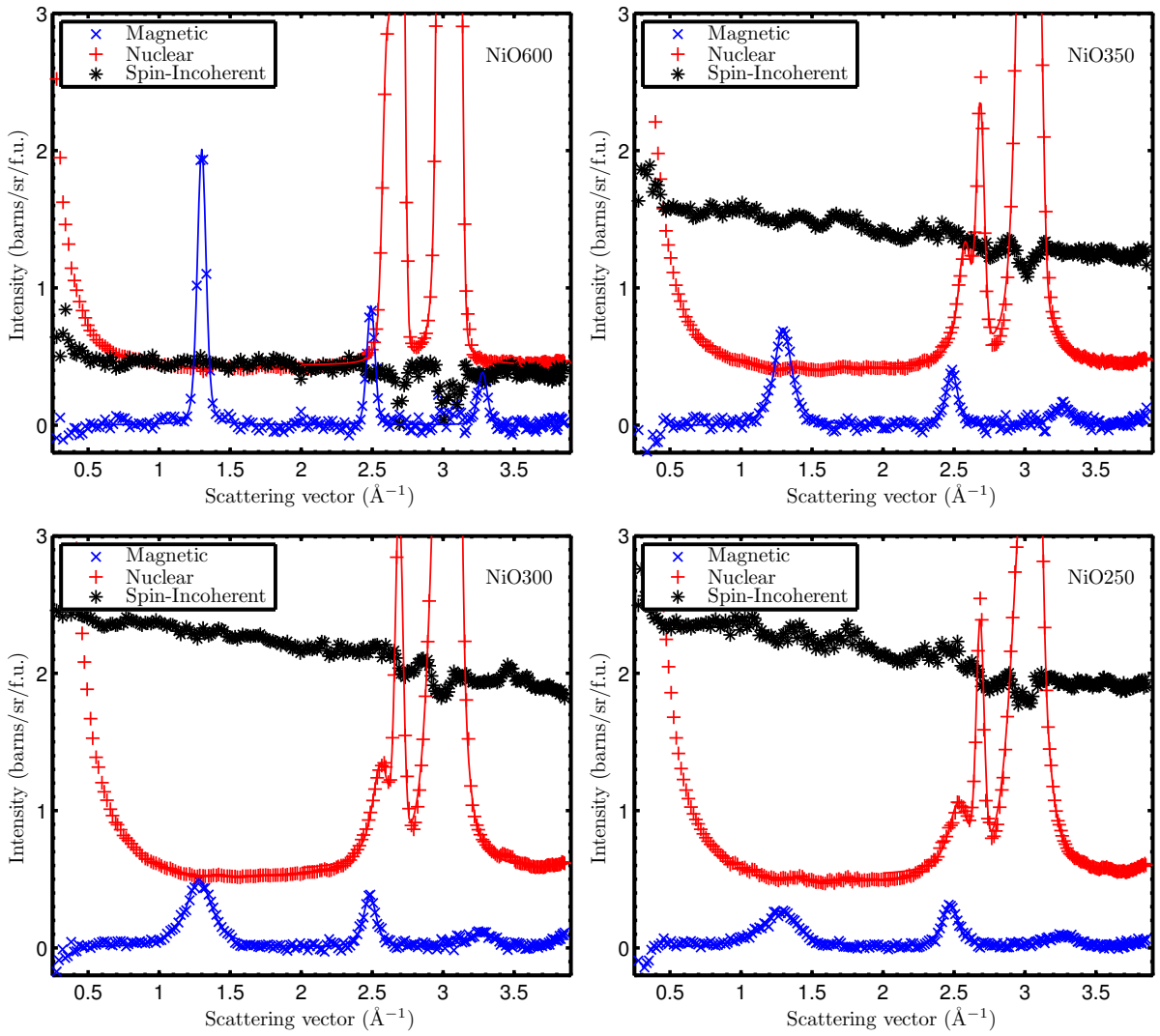

Figure 2: Polarisation analysed neutron powder diffraction patterns on the four samples of plate shaped NiO nanoparticles. The separation of the data into the magnetic, nuclear and spin-incoherent cross-sections have been performed.

References

[1] Bahl, Christian Robert Haffenden, *PhD thesis*, Technical University of Denmark (2006)

[2] Stewart, J. R., Deen, P. P., Andersen, K. H., Schober, H., Barthélémy, J.-F., Hillier, J. M., Murani, A. P., Hayes, T., and Lindenau, B., *Journal of Applied Crystallography*, 42 (2008)