

● Coalescent Grain Growth ● Invariant Surface Stoichiometry ● Classical Random Ferrimagnetism of nc-NiO, as Revealed by Empirical Scaling Laws

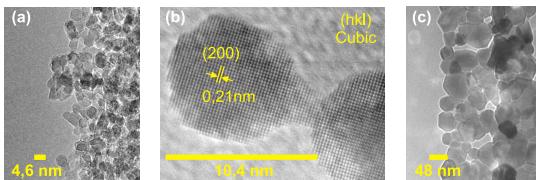
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Introduction

At the nano-scale, properties of materials usually change markedly with size. This is important for practical applications. However, apart from potential applications, the size-dependent changes -- expressed by empirical scaling laws -- may also serve as probes for topochemical and microstructural details which are not accessible by other means. For example, the spin arrangement in antiferromagnets may be investigated (Richardson's phenomenon), and this is one reason why we are searching for empirical scaling laws for nanocrystalline (nc) NiO.

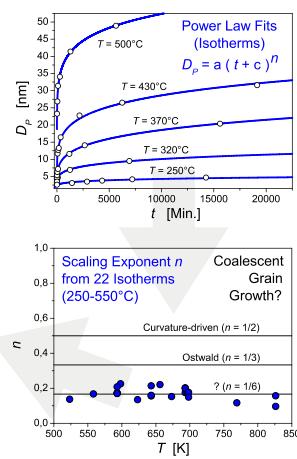
● Grain Growth



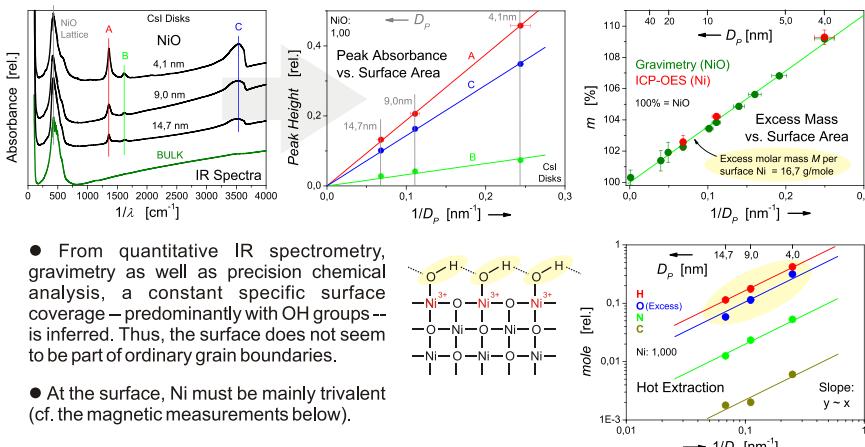
Out of hundreds of TEM micrographs, only one (Figure b) reveals a sintering neck. The two grains are already colinearly oriented (along [002]), indicating 'orientated attachment' with subsequent rapid coalescence. This is corroborated by the anomalous growth exponent ($n=1/6$).

| $n = 1$ | $n = 1/2$ | $n = 1/3$ | $n = 1/6$ |
|--|---|---|--|
| $dV_p / dt \sim A_p$ Surface reaction-rate-limited growth | $dR_p / dt \sim 1/R_p$ Curvature-driven growth | $dV_p / dt \sim \text{Constant}$ Solvent-mediated mass transport (diffusion) ("Ostwald ripening") | $dV_p / dt \sim 1/V_p$ Coalescent grain growth? |

V_p : Volume A_p : Surface Area R_p : Radius



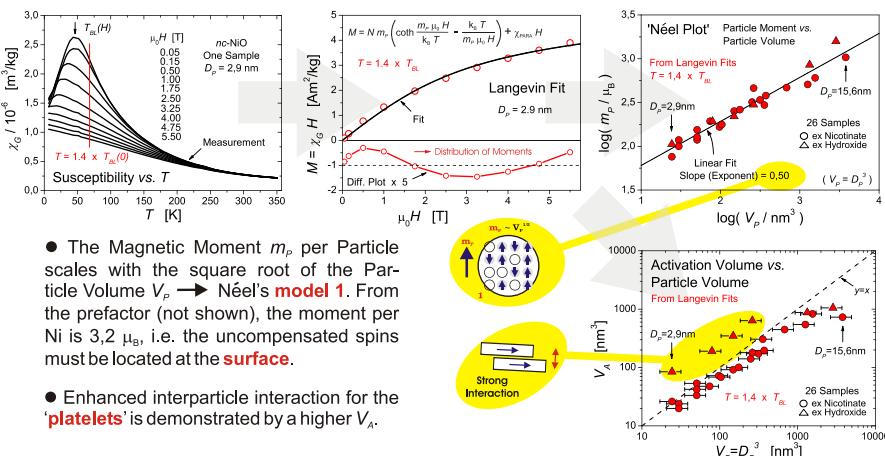
● Surface Stoichiometry



From quantitative IR spectrometry, gravimetry as well as precision chemical analysis, a constant specific surface coverage -- predominantly with OH groups -- is inferred. Thus, the surface does not seem to be part of ordinary grain boundaries.

At the surface, Ni must be mainly trivalent (cf. the magnetic measurements below).

● Random Ferrimagnetism



The Magnetic Moment m_p per Particle scales with the square root of the Particle Volume V_p → Néel's model 1. From the prefactor (not shown), the moment per Ni is $3.2 \mu_B$, i.e. the uncompensated spins must be located at the surface.

Enhanced interparticle interaction for the 'platelets' is demonstrated by a higher V_A .

Acknowledgments

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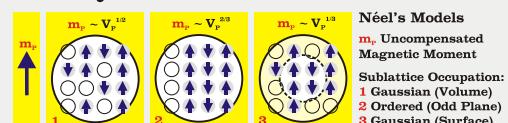
Richardson's Phenomenon

Motivation

Ultrafine (nano) NiO is noticeably attracted by magnets, while bulk NiO is not. In fact, the former is superparamagnetic (Richardson and Milligan, 1956), but the latter, like all antiferromagnets (AFs), is only weakly paramagnetic. Both are antiferromagnetically ordered at room temperature, yet a significant number of spins apparently remain uncompensated in ultrafine NiO. The uncompensated moment per Ni atom on average may surpass 10% of that of metallic Ni. Thus, Richardson's phenomenon is far from being an 'impurity effect'. It might be due to confinement or to the large surface area, or it might be a scalable intrinsic property common to all antiferromagnets. Néel (1961, 1962) favoured the last possibility.



Theory

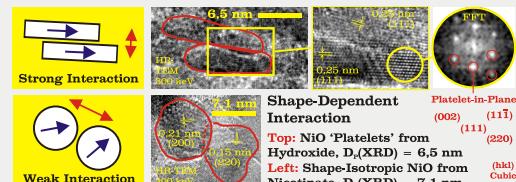


To explain Richardson's phenomenon, Néel (1961) proposed three models based on simple spin counting statistics. Each model predicts a characteristic scaling law for the particle moment m_p (vs. the particle volume $V_p \sim D_p^3$) and may be tested by experiment. **Model 1** implies a random (Gaussian) distribution of Ni atoms on the two sublattices. If it is the right model (Néel, 1962), then the saturation magnetisation M_s will scale with D_p^{-1} to a moderate power (exponent 3/2). For **model 2**, M_s will even scale linearly with D_p^{-1} . If, however, **model 3** applied (Richardson et al., 1991, Bahl et al., 2006), then M_s should scale with D_p^{-2} , meaning a huge (quadratic in D_p^{-1}) rise in M_s for small particles.

Goal

The identification of the pertaining model is of prime interest. If it turns out to be Néel's **model 1**, one can further calculate (from the measured average moment) the oxidation state of the nickel atoms bearing the uncompensated spins. This will indicate whether the surplus spins are located on the **surface** (Ni^{3+}) or in the **volume** (Ni^{2+}) of each particle. Thus, the topological details of the random sublattice occupation will emerge from the volume-averaged magnetisation data.

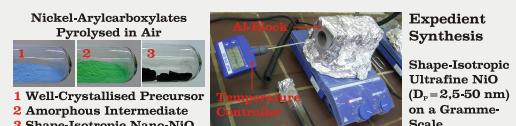
Limitations & Pitfalls



In order to draw the right conclusions from the observed magnetic properties, the shape of the particles must be taken into account. For half a century, **platelet-like** particles have been used in almost all investigations (suspected already by Milligan and Richardson, 1955, demonstrated by Bahl et al., 2006, and others). Other shapes of well-defined NiO have not been accessible by conventional synthesis at the lower limit of the mesoscale.

Since the 'platelets' align themselves easily face-to-face, they are subject to pronounced interparticle interaction (Bahl and Mørup, 2006). This complicates the interpretation of magnetisation data and has misled previous researchers into choosing the wrong theoretical model. Therefore, it is desirable to minimise interaction, but without chemically (i.e. potentially magnetically) modifying the surface. This is achieved by using **shape-isotropic** particles.

Solution



Recently, we found a solid state route (via amorphous intermediates) to **shape-isotropic** NiO. Size is controlled by isothermal grain growth, as with platelet-like NiO. The size- and shape-dependent magnetisation data indicate that not only does Néel's **model 1** apply to NiO at the lower end of the mesoscale (2.9–15 nm), it even does so irrespective of the particle shape (Petrik and Harbrecht, 2008).