A Random Ferrimagnet in Disguise: Ultrafine Mesoscale NiO

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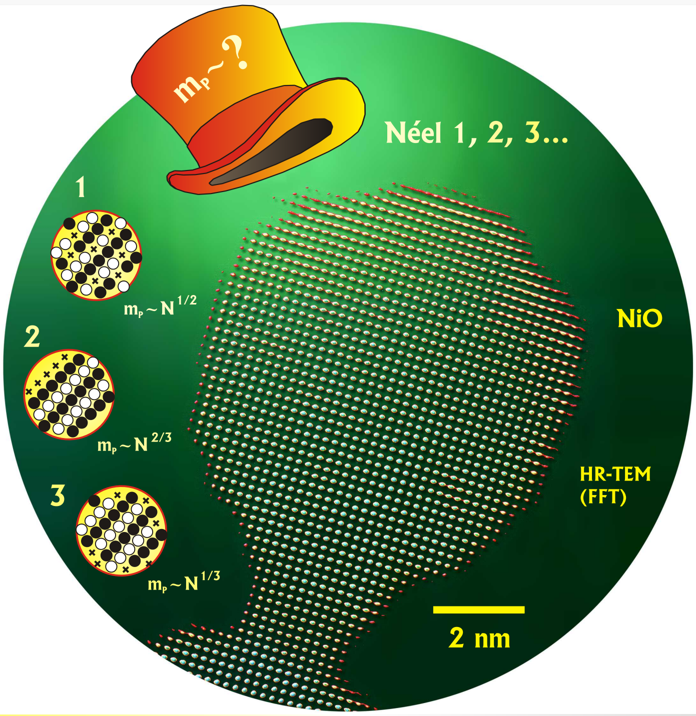
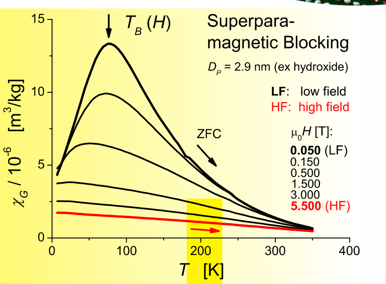
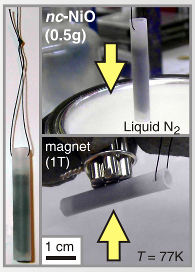
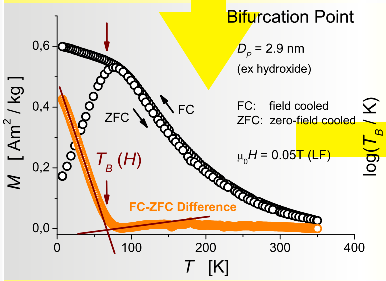
Antiferromagnetic NiO, even if highly crystalline, carries an uncompensated magnetic moment ($\boldsymbol{m_P}$) which, for ultrafine nanoparticles, is only an order of magnitude below that of regular ferrimagnets (Richardson's phenomenon).[1, 2] This reflects an inherent statistical imbalance (symbol **x**) in the number (***N*** per particle) of 'up' and 'down' (**black** and **white**) spins. The underlying mechanism (Néel model) is revealed by the characteristic rational order of the function $\boldsymbol{m_P} = \mathrm{f}(\boldsymbol{N})$.

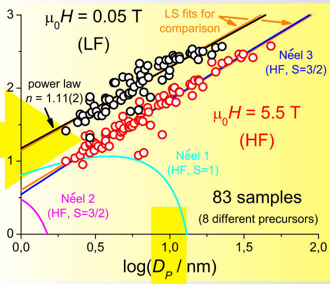


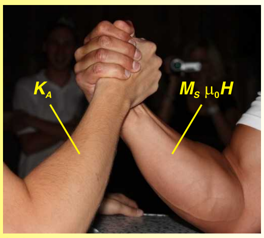


Half a gram of antiferromagnetic ultrafine NiO (average particle size 2.9 nm, prepared by careful dehydration of nickel hydroxide),[3] can be lifted by means of a common rare-earth magnet, after having been dipped in liquid nitrogen for some time. The mass susceptibility χ_G is thus seen to be particularly high in the vicinity of the blocking temperature T_B.









(III.) Anisotropy energy *vs.* Zeeman energy

(I.) $$T_B^{HF} = T_B^{LF}\left(1 - \frac{H}{H_A}\right)^{\alpha}$$

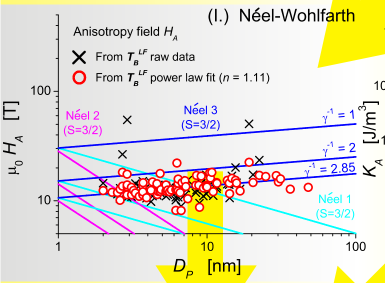
α = 2 (simple anisotropy energy landscape)
$\mu_0 H$ = 5.5 T (high field, HF)
$\mu_0 = 4\pi\ 10^7$ Tm/A (vacuum permeability)

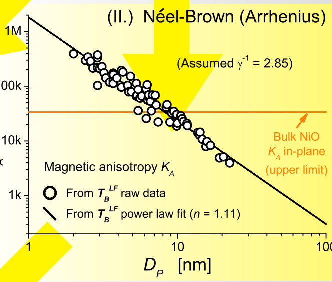
(II.) $$K_A V_P = \beta\ k_B\ \gamma\, T_B^{LF}$$

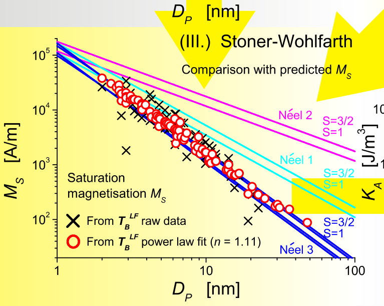
$V_P = D_P^3$ (Scherrer length D_P from XRD)
β = 25 (default Arrhenius parameters)
γ = 1/2.85 (from multivariant refinement)

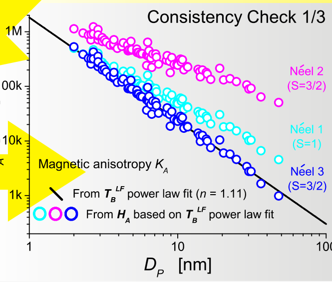
(III.) $$K_A = \delta\ M_S\ \mu_0 H_A$$

δ = 1/0.964 (random orientation Stoner-Wohlfarth)









Aim of this work: To determine the size-dependence of the anomalous uncompensated magnetic moment of antiferromagnetic ultrafine (< 5 nm) mesoscale (2-50 nm) NiO nanoparticles:
-- Qualitatively: How does the particle moment m_P scale with the particle diameter D_P? Does one of Néel's power-laws 1, 2 or 3 apply?
-- Quantitatively: If some scaling law applies, are the measured moments correct or are they too small or too large?

The importance of representative sampling: To prove a scaling law with confidence, the range of the pertinent experimental variable (here: D_P) has to be as large as possible. If the measured property is subject to uncertainty (scatter), the range investigated must be larger in proportion. Nano-science is ridden by uncertainty (large scatter).
Therefore:
-- Investigate the whole mesoscopic range (D_P = 2-50 nm), *i.e.* the volume V_P spans more than four orders.
-- Prepare a large number of samples (83) via various pyrolytic routes (from 8 different precursors) leading to as nearly clean ('naked') nanoparticles as is possible in air. Apply the measurement procedure (D_P from XRD, m_P using the SQUID) to each one of the large number of samples.
-- Secondary factors, *e.g.* particle shape, interparticle interaction, surface chemistry, will average out over the large range studied.

Conventional methods: The saturation magnetisation M_S arising from the anomalous uncompensated moment of nanoantiferromagnets is hardly accessible by conventional magnetisation measurements:
-- The hysteresis loops do not saturate since the anisotropy energy K_A is large while M_S is small.
-- Complete Langevin-type superparamagnetism measurements are rather lengthy and impractical.
-- The paramagnetism due to field-induced spin canting (classical as well as Néel-type superantiferromagnetism) has to be corrected for, even though it cannot be measured.

Micromagnetic armwrestling: In an applied field H, the superparamagnetic blocking temperature T_B is shifted to lower values (Néel-Wohlfarth equation I.). This shift depends crucially on the size of the uncompensated moment m_P (per particle) whose vector direction is pulled by force (Zeeman energy) nearer to the top of the anisotropy energy barrier. The barrier height ($K_A V_P$) determines the low-(zero)-field value of T_B, according to the Néel-Brown expression (equation II.). Referring to a unit volume instead of a particle, M_S replaces m_P and K_A replaces $K_A V_P$. The 'armwrestling' between the magnetic anisotropy and an external field is epitomised by Stoner-Wohlfarth theory (equation III.).

Multivariant refinement: The micromagnetic 'armwrestling' is exploited as follows. Only two blocking temperatures per sample are needed, *viz.* at low-(zero)-field (LF) and high-field (HF). A large number of samples (83) can thus be managed. The bifurcation point, being accessible even at high paramagnetic (Curie-type) background, is preferred to the less well defined ZFC-maximum.

Proceed as follows:
-1- Fit the LF data by a power law (resulting n = 1.15) and extrapolate beyond the upper temperature limit of the SQUID, thus making sizes up to D_P = 50 nm accessible.
-2- Use this, rather than the raw data, together with the HF data to calculate the two variables H_A and K_A (initial value of γ = 1/2), and from them M_S.
-3- Calculate M_S theoretically for each of Néel's models 1, 2 and 3: *Néel3* compares very well with experiment.
-4- Check for consistency by calculating K_A, H_A and T_B^{HF} using the *theoretical* M_S functions.
-5- Adjust γ so that H_A from -4- fits H_A from -2- (the latter does not depend on γ since in equation (I.), γ would apply to both T_B^{LF} and T_B^{HF}).
-6- Repeat -2- and -4- with the new γ.
-7- T_B^{HF} from -4- (*Néel3*) will not yet fit the experimental values well unless n in -1- is lowered (and the power law refitted with n fixed) and steps -1- through -7- followed once more (*recursive procedure*). This yields n = 1.11(2).

Conclusion: Micromagnetic 'armwrestling' is exploited for the indirect determination of the weak saturation magnetisation of a superparamagnet in the presence of strong magnetic anisotropy. The anomalous nanomagnetism of the antiferromagnet NiO is thus shown to be consistent, both qualitatively and quantitatively, with one of Néel's models of a random ferrimagnet. The scaling of the magnetic moment with particle size has been tracked over more than four orders of magnitude in particle volume, covering the whole mesoscopic range.

References: [1] J. T. Richardson, W. O. Milligan, *Phys. Rev.* **1956**, *102*, 1289-1294.
[2] M. Petrik, B. Harbrecht, *Solid State Phenomena* **2011**, *170*, 244-247.
[3] M. Petrik, B. Harbrecht, *Z. Kristallogr. Suppl.* **2011**, 6 pages (accepted).

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