

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

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For five decades, ever since the pioneering paper by Richardson and Milligan of 1956,^[1] nanocrystalline (nc) NiO has remained a scientific riddle not only in terms of magnetism - the uncompensated moment per Ni atom of this highly dispersed antiferromagnet (AF) may exceed 10% of that of metallic Ni - but also with respect to chemical composition. This is epitomised by recurrent textbook references to dubious black 'higher oxides' of nickel, e.g. 'Ni₃O₄' or 'Ni₂O₃'. A panoply of experimental methods, including neutron scattering,^[2] dc magnetisation measurements,^[3-5] FT-IR spectroscopy^[6] and x-ray absorption spectroscopy XAS,^[7] have been applied in order to elucidate the magnetic structure and chemical composition of nc-NiO. Mean-field calculations of the spontaneous magnetisation^[2] and numerical modeling of the AF spin arrangement^[8] have also been performed. Yet, the efforts have remained inconclusive, partly because of the inherently low reproducibility of sample properties which makes quantitative data unreliable, but mainly because synthetic routes to nc-NiO, offering proper control over size and shape, have been lacking. Thus, most measurements are available for only a single type of NiO nanoparticle - nanoplatelets of pronounced shape-anisotropy, studied for a limited number of average sizes from 5 nm upwards. The shape-anisotropy of the particles complicates the assessment of the magnetisation data, while the small number of sizes does not allow for a proper statistics. In view of this, we have developed a new size-selective solid state synthesis of equiaxed nc-NiO, covering the whole mesoscopic range of 2.5-50 nm. From a systematic investigation of the dependence of its properties on the particle size, we derive empirical scaling laws for nc-NiO. The properties studied as a function of size include dc magnetisation, isothermal growth rate, IR absorption and chemical composition. Owing to the large number of samples analysed - especially by magnetic and kinetic measurements - the inherently limited reproducibility is outweighed by statistical averaging. In this way, the following empirical scaling exponents, applying to the particle volume, are obtained: 1/2 for the magnetic moment, -1 for the growth rate and 2/3 for the concentration of excess chemical species. The first - hitherto unrecognized - is characteristic of a classical random ferrimagnet (Néel, 1961),^[9] the second indicates a type of coalescent grain growth in 3-D, similar to known 2-D types, and the third reveals a well defined surface stoichiometry which is size-invariant. Thus, the empirical scaling laws provide insights not only into the magnetic and chemical nature of nc-NiO, but also into the mesoscopic growth dynamics exploited in the size-controlled synthesis of nc-NiO.

Literature:

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