Magnetic ordering in nanocrystalline gadolinium

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While the half-filled $4f$−shell ($L = 0$; $J = S = \frac{7}{2}$) should make gadolinium metal one of the simplest of the magnetic rare earth systems, it still continues to attract interest. In bulk gadolinium metal, the c−axis ferromagnetic order that appears at $T_c \sim 293$ K is followed by a reorientation that starts at $T_{sr} \sim 232$ K as the moments cant away from the c−axis by more than 60° at 180 K before returning to about 30° off the c−axis as T→0.[1]

The current interest in nanocrystalline materials and application of the inert-gas condensation technique[4] to rare earths has opened up the influence of a new parameter – grain size – and its impacts on the ordering and anisotropy of gadolinium. As the grains become smaller, a larger fraction of the atoms are located at the surfaces, in grain boundary regions, and by 10 nm, ~30% of the atoms lie on the boundaries, in regions where disorder dominates, as seen in small-angle neutron scattering (SANS) measurements[8–10].

We extend the SANS investigation of nanocrystalline gadolinium (nc-Gd) by looking at one of the simplest local magnetic parameters: the easy axis. Working with two ^{160}Gd samples from a previous study (a coarse-grained "bulk" reference sample and one with a grain size of 21 nm[10]) and a newly prepared 38 nm sample, we have used neutron diffraction to determine the temperature dependence of the magnetic ordering direction. The reference sample closely follows the reorientation behaviour described by Cable and Wollan[1], however the ordering direction in both nc-Gd samples is largely independent of temperature, with the moments canted by 40°–50° from the c−axis from T_c down to 4 K.

The 8 mm diameter, 300 μm thick nc-Gd samples were prepared by inert-gas condensation of 98.6 at.% ^{160}Gd.[10] Measurements were made in $\theta - 2\theta$ mode in a conventional Bragg-Brentano geometry. The first two allowed reflections from gadolinium ((1 0 0) and (0 0 2)) conveniently provide the information needed to determine the magnitude and direction of the magnetic moment, and at the wavelength used here, they are less than 3° apart, so any absorption correction due to the residual 0.2 at.% ^{155}Gd and ^{157}Gd present in the sample, can be neglected. We covered the 2θ range 28°–38° so that we also recorded the (1 0 1) reflection as it is stronger than the first two and partially overlaps the (0 0 2) reflection (see Fig. 1). Peak

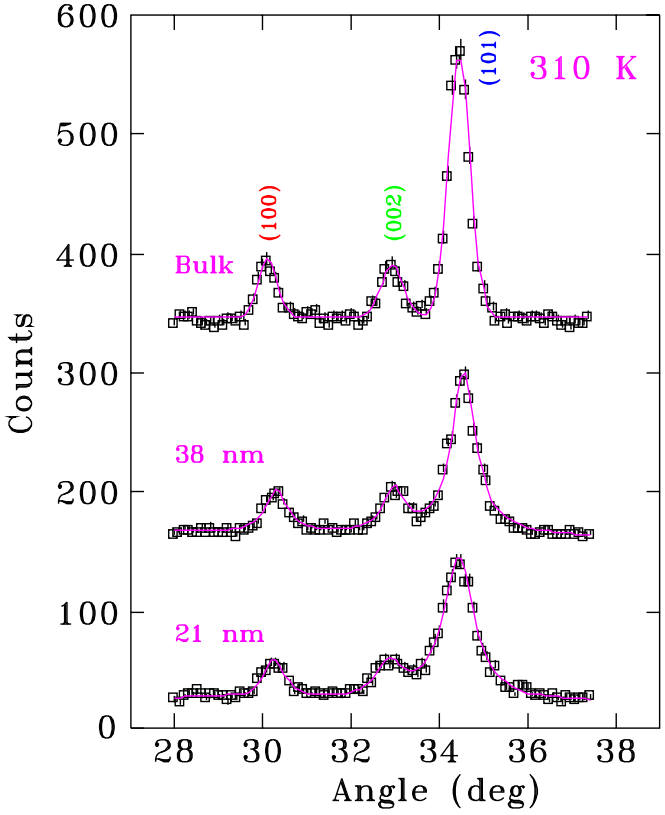

FIG. 1. Neutron diffraction patterns taken at 310 K (above T_c) for the three ^{160}Gd metal samples studied here. The patterns have been offset vertically for clarity. Solid lines show fits to three gaussian peaks.

positions, widths and integrated areas were determined by fitting three gaussians to the observed patterns.

It is clear from Fig. 1 that the diffraction peaks from the two nanocrystalline samples are much broader than those from the reference sample. Taking the width of the (1 0 1) reflection from the reference sample as the instrumental resolution, the additional width of the corresponding peaks for the nc-Gd samples can be used to obtain estimates of the particle sizes, using the simple Scherrer formula. This method yields 21.2±1.4 nm and 46.7±4.5 nm, in agreement with the more com-

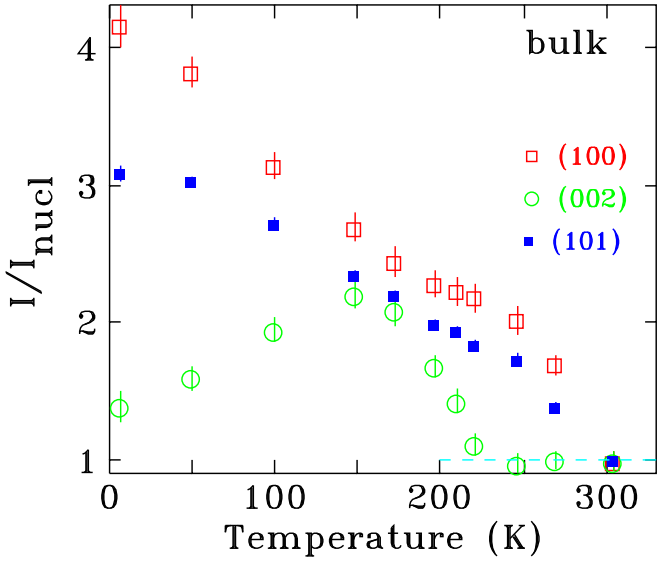

FIG. 2. Temperature dependence of the normalised integrated intensities for the coarse-grained "bulk" reference sample of ^{160}Gd metal showing the onset of order at 290(4) K and the subsequent canting of the moments away from the $c-$axis below T_{sr} =229(2) K.

plete Williamson-Hall x-ray characterisation[11] carried out during the preparation of the samples.

Tracking the integrated intensities as a function of temperature and normalising to the nuclear-only intensity recorded at 310 K (Fig. 2) shows that in the bulk sample, a magnetic contribution to the (1 0 0) and (1 0 1) peaks appears as soon as the sample orders at 290(4) K, but that the (0 0 2) reflection only starts to increase in intensity below T_{sr} =229(2) K as the moments cant away from the $c-$axis. The subsequent increase and then decrease in the (0 0 2) intensity reflects the progressive canting of the moments followed by their rotation back towards the $c-$axis.

Two nc-Gd samples with 21 nm and 38 nm grain sizes were measured and analysed in the same way as the coarse-grained reference sample. The earlier SANS work[8–10] suggested that the magnetic ordering of the nc-Gd grains takes the form of an ordered core surrounded by a ~3 nm thick shell of disordered moments. This core–shell picture implies that the coherent magnetic scattering ordered cores comes from a smaller volume than the crystallographic grains that contribute to the nuclear scattering. This model is supported by the observation that all three peaks for both nc-Gd samples studied here are *broader* at 3 K than they are at 310 K. No such broadening is observed for the reference sample. Analysis yields a magnetic "grain size" 6(2) nm smaller than the crystallographic grain size.

As shown in Fig. 3, bulk gadolinium orders with its moments parallel to the $c-$axis at 293 K and then the moments cant away by up to 50° below 230 K. The behaviour of the nc-Gd magnetic order is quite different. Fig. 3 shows that neither nc-Gd sample exhibits $c-$axis ordering at any temperature, and that the canting angle (ϕ_c) is largely temperature independent at ~ 50° for both samples. There is a weak trend to smaller canting angles on cooling (stronger in the 38 nm sample) but the trends seen in our reference sample (Fig. 2) and single-crystal gadolinium[1] are clearly absent.

A complete description of this work has been published in Phys. Rev. B[12].

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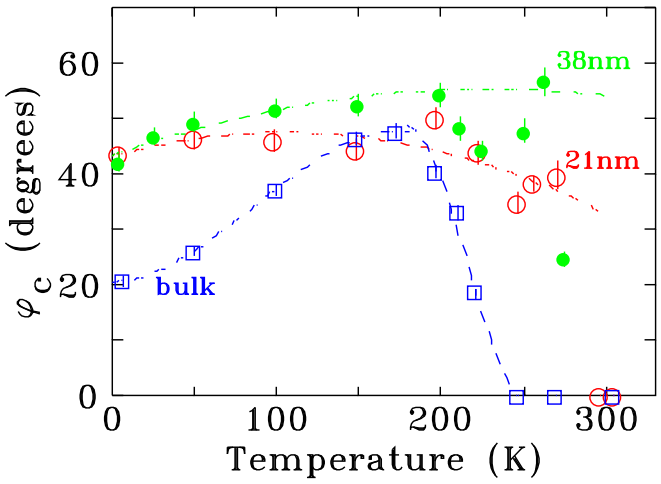

FIG. 3. Temperature dependence of the canting angle (ϕ_c) for the three samples studied here: ● 38 nm, ○ 21 nm, □ bulk reference sample (shown for comparison). Dashed lines are guides to the eye.