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Magnetic structure of Gd, GdH₂ and NdH₂ single crystal films

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Abstract. Single crystal films of Gd and Nd were grown by MBE techniques using the LaMBE facility in Oxford. The thickness of the layers was 5000 Å and the mosaic spread about 0.2–0.3°. Some of the layers were hydrogenated by KTH in Stockholm to obtain the dihydride. The magnetic structures were determined using the TAS1 triple axis spectrometer at the Risø National Laboratory in Denmark. The magnetic structure of the Gd film was a ferromagnet, similar to that of bulk Gd. In detail, however, there were differences and the spin direction differed from that of the bulk material while the phase with the moments aligned along the *c*-axis was absent in the film. The magnetic structure of GdH₂ was antiferromagnetic with a wavevector of $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and a transition temperature of 22 ± 0.5 K, much lower than that of bulk Gd, 290 K. In contrast, the magnetic structure of NdH₂ is incommensurate with a wavevector of $(0.532, 0.532, 1.532)$ and a magnetic ordering temperature of 34 ± 1 K.

1. Introduction

The properties of bulk samples of hydrogenated rare-earths have been reviewed by Vajda [1]. More recently, Huiberts *et al* [2] discovered that a metal–insulator transition occurred in an yttrium hydride thin polycrystalline film when the hydrogen to yttrium ratio changed from 1.8 to 2.9. In the trihydride phase, the formerly shiny metallic film became a transparent semiconductor with a band-gap of 1.8 eV. Furthermore, the hydrogen loading between YH₂ and YH₃ is completely reversible [3] and a single crystal Y film undergoes structural transitions from the face centred cubic dihydride phase to the hexagonal trihydride phase while maintaining a single crystal structure.

Gd has the hcp crystallographic structure and the simplest magnetic structure of the rare earths because the $(4f)^7$ electrons have an isotropic $L = 0$ ground state, $^8S_{7/2}$. The magnetic structure of bulk Gd has been extensively studied by neutron diffraction experiments [4] and by torque magnetometry [5] as reviewed by Jensen and Mackintosh [6]. It is ferromagnetic with a Curie temperature of 290 K and the residual magnetic anisotropy causes the moment to align preferentially along the *c*-axis just below T_C . At lower temperature, the magnetic moments rotate towards the basal plane, reaching a maximum tilt angle of 60° at 180 K before decreasing to just below 30° at 4.2 K. Arons and Schweizer [7] have studied the magnetic properties of GdD_{2+x} samples by susceptibility measurements and neutron diffraction. GdD_{1.93} is face centred cubic and antiferromagnetic with a Néel temperature of 20 K although for $x = 0$,

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a helical structure with a modulation wavevector along the $[111]$ direction is observed. The angle between the moments in the successive $\langle 111 \rangle$ planes is 163.8° and T_N is 15.5 K.

Neodymium is a light rare earth and its crystallographic structure is dhcp. Its magnetic structure displays an extraordinary complexity. Bulk neodymium orders incommensurately below 19.9 K and as the temperature is reduced further, Nd passes through a series of multi- q incommensurate structures [8, 9]. Finally, a polycrystalline sample of face centred cubic neodymium dihydride was found to be ferromagnetic, from susceptibility measurements, with T_C between 5.8 K [10] and 6.5 K [11].

In this paper, we report on the magnetic structure of single crystal films of Gd, GdH₂ and NdH₂ and the paper is organized as follows. In section 2, we describe the experiments. Section 3 is devoted to the results of the neutron and x-ray diffraction studies of Gd, GdH₂ and NdH₂ films. Finally, we close by discussing the results in section 4.

2. Experimental procedure

Thin film samples of Nb/Gd/Nb (or Nb/Nd/Nb) were grown by MBE techniques using the Balzers UMS630 facility in Oxford [12]. The sapphire substrates were of dimension $12 \times 10 \times 1 \text{ mm}^3$ and were polished to an epitaxial finish on the major surface, which was cut within $\pm 0.5^\circ$ of the $(11\bar{2}0)$ plane. Substrate preparation consisted of a solvent degreasing treatment prior to loading, and subsequent annealing under ultra-high vacuum conditions at 1000°C in the growth chamber. Successive films of Nb, Gd (or Nd) and Nb were evaporated from electron beam sources (Gd and Nb) or a K cell (Nd). Four samples were grown, two corresponding to 75 \AA Nb/ 5000 \AA Gd/ 50 \AA Nb and two corresponding to 75 \AA Nb/ 5000 \AA Nd/ 50 \AA Nb. In each case the Nb buffer was grown at a substrate temperature of 1070 K and the rare earths at 770 K (Gd) or 670 K (Nd). The Nb capping layer was deposited after the sample was cooled in order to promote complete coverage of the rare-earth surface (Nb grows in a 3D mode at elevated temperature).

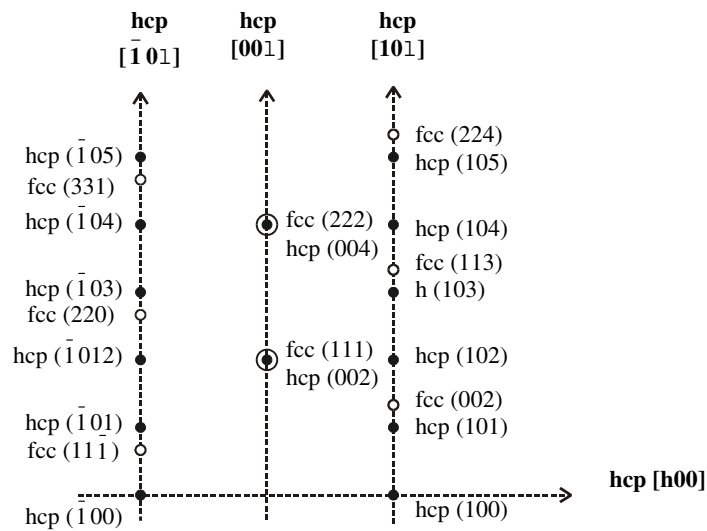


Figure 1. Diagram of reciprocal space showing the reciprocal lattice points of the face-centred cubic structure and of the hexagonal close-packed structure obtained by sliding of the close-packed planes.

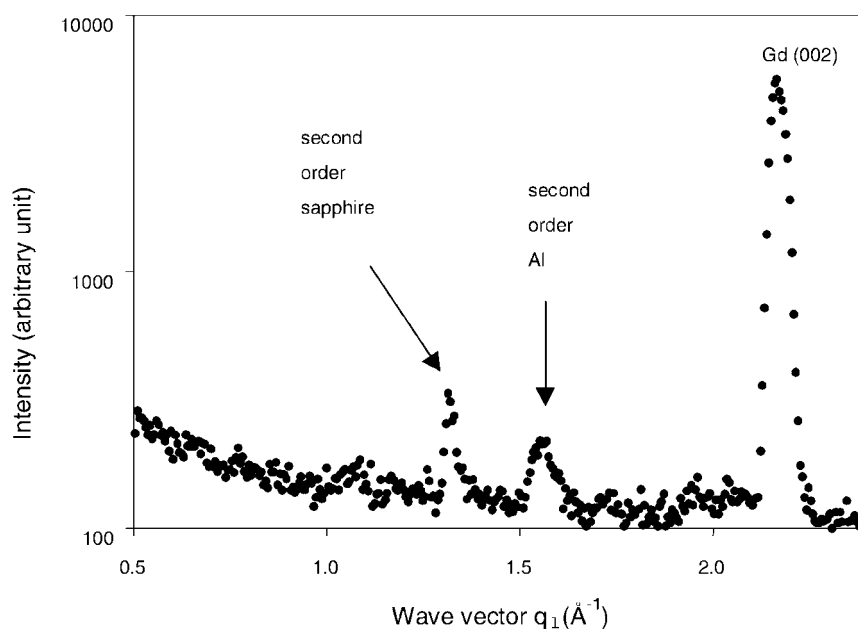


Figure 2. The intensity observed when the wave-vector transfer was scanned along the $[00q_1]$ direction for the Gd sample at 2.1 K. The peak at 1.3 \AA^{-1} arises from second order scattering from the sapphire substrate and at 1.55 \AA^{-1} from second order scattering from the Al sample mount and radiation shields.

The hydrogenation was performed at the Royal Institute of Technology in Stockholm. The first step of the process is the hydrogenation of the thin film at 543 K and at 1 bar pressure of hydrogen, until the trihydride form is reached. Then, pumping at high temperature allows some of the hydrogen to be removed and to obtain the dihydride form. Finally, the sample is cooled down slowly to room temperature.

The crystal structures of the films were determined using a triple-axis diffractometer on a rotating anode x-ray generator at the Clarendon Laboratory, Oxford.

The magnetic structures of the thin films, as grown, and before the application of a magnetic field were determined by neutron diffraction. The experiments were performed at the DR3 reactor at the Risø Laboratory in Denmark, using the triple axis spectrometer TAS1. The collimation from reactor to detector was open- 30° - 60° -open and neutrons of energy 20.3 meV were selected by reflection from the (004) planes of a pyrolytic-graphite monochromator. The (002) planes of a pyrolytic-graphite analyser were used to ensure that only 20.3 meV neutrons entered the detector. The samples were mounted in a variable temperature 'orange' cryostat, with the $(h0l)$ hexagonal plane in the scattering plane. Temperatures between 1.5 and 300 K could be obtained and the temperature controlled to 0.5 K.

The hcp and fcc structures were distinguished by scanning the wave-vector transfer through the hcp $(10l)$ and $(\bar{1}0l)$ reflections. The two structures have peaks in identical positions along the hcp $[00l]$ direction, but the hcp diffraction pattern shows peaks at different wavevectors from those of the fcc phase along the $[10l]$ and $[\bar{1}0l]$ directions. Figure 1 shows the positions of the peaks if there is a single fcc domain. In practice however there are usually both possible domains in approximately equal proportions and the scatterings observed along the $[10l]$ and $[\bar{1}0l]$ directions are the same.

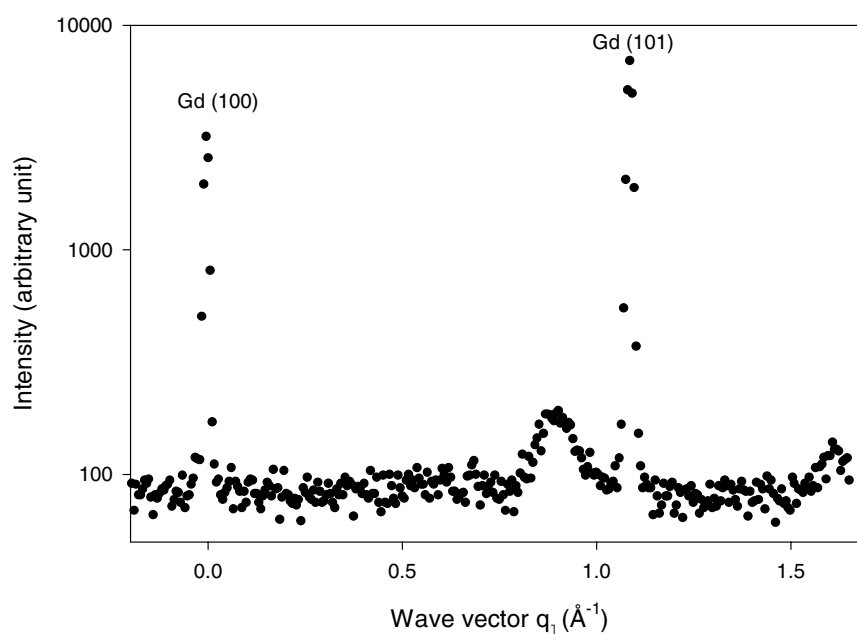


Figure 3. The intensity observed when the wave-vector transfer was scanned along the $[10q_1]$ direction for the Gd sample at 2.1 K. The origin of the broad peak at 0.89 \AA^{-1} is unknown.

3. Results of neutron diffraction and x-ray diffraction

3.1. Gd film

The monocrystalline thin film sample has a mosaic spread of 0.20° . The scattering measured at 2.1 K using neutron diffraction is shown for a wave-vector transfer Q along the $[00l]$ direction in figure 2 and the $[10l]$ direction in figure 3. For the Gd structure, the three peaks (002), (100) and (101) are characteristic of the hexagonal close-packed structure with $a = 3.595 \text{ \AA}$ and $c = 5.785 \text{ \AA}$. We have studied the intensity of these three peaks as a function of the temperature. The results are shown in figure 4 and show: (i) the Gd film is ferromagnetic because there are no new Bragg reflections in the magnetic phase, (ii) the Curie temperature is $300 \pm 5 \text{ K}$ and (iii) when the temperature increases (from 1.5 to 180 K), the intensity of the (002) peak increases whereas the intensities of the two other peaks decrease. The intensity of the (002) peak is proportional to the square of the magnetic moment in the basal plane and the intensities of the two other peaks depend also on the component of the magnetic moment along the c -axis. If we assume a random arrangement of the magnetic domains in the basal plane, we can calculate the angle α between the c -axis and the total magnetic moment of the Gd thin film. This angle increases when the temperature increases from 1.5 to 180 K and, then, as the temperature increases further, the intensity of the (002) peak decreases faster than that of the (100) and (101) peaks and the angle α decreases. Figure 5 shows the total magnetic moment and figure 6 the angle α . At low temperature, the magnetic moment, $6.3 \pm 1.1 \mu_B$, is consistent with the Gd atomic moment, $7 \mu_B$. Figure 6 also shows the values of the angle α for bulk Gd [4]. Below 200 K, the magnetic structure of the film is very similar to that of the bulk sample. Above 200 K, the behaviour differs: in the case of the bulk Gd, the magnetic moment aligns along the c -axis whereas for the film, the moment direction is constant at 30° to the c -axis.

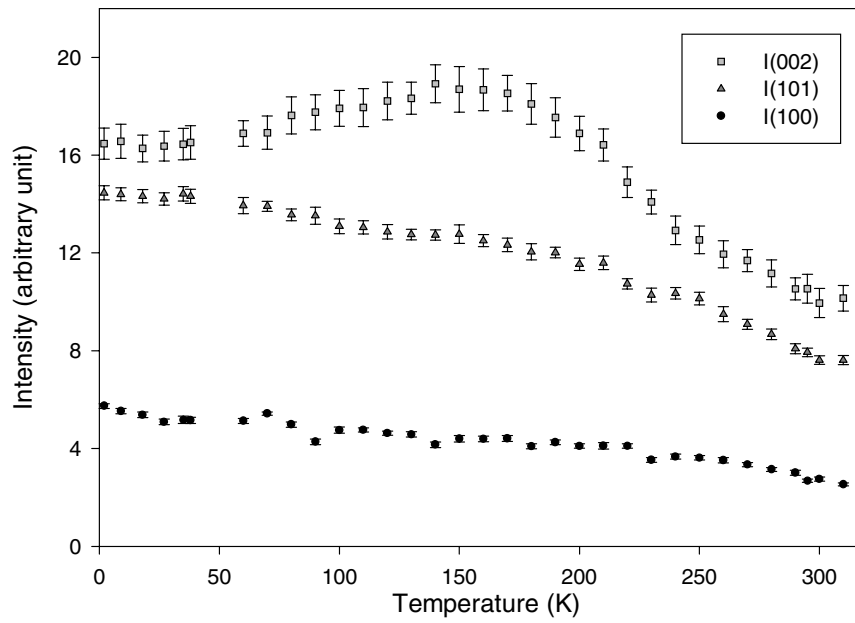


Figure 4. Temperature dependence of the intensity of the (002) (squares), (101) (triangles) and (100) (circles) scattering from the hcp Gd film.

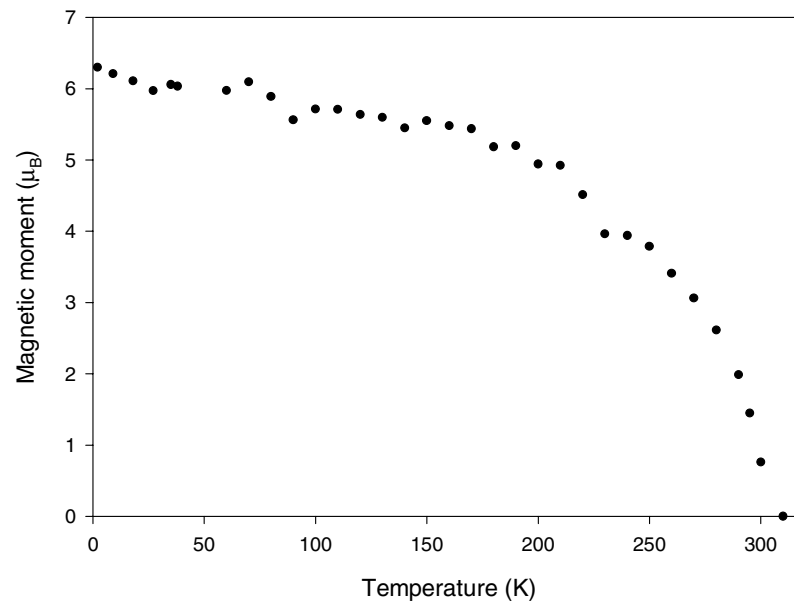


Figure 5. Temperature dependence of the magnitude of the magnetic moment of the Gd film.

3.2. GdH₂ film

After loading hydrogen the mosaic spread of the GdH₂ film is 0.93° and it has the face centred cubic crystal structure. Initially, we measured the scattered intensity using neutron diffraction

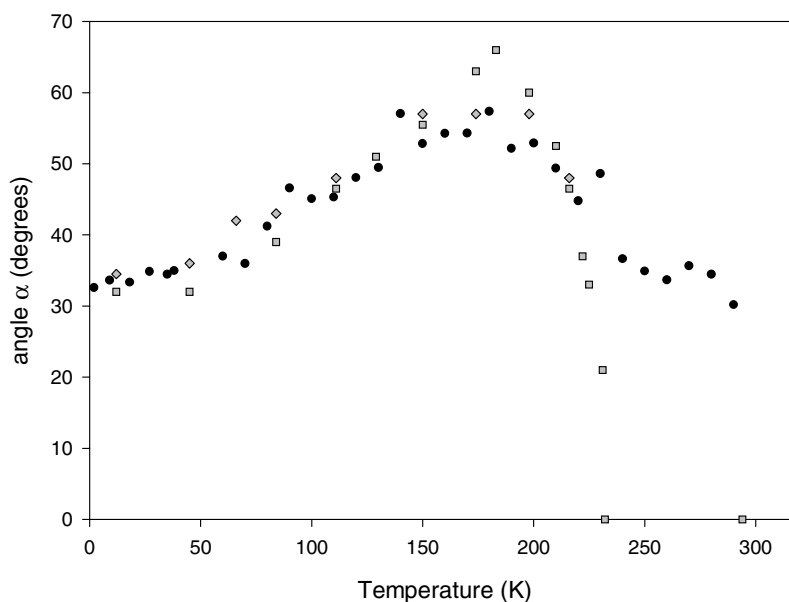


Figure 6. Dependence of the angle α (angle between the c -axis and the direction of the magnetic moment of the Gd sample) measured for the thin film (black circles) and for a bulk sample (grey squares) [4] on the temperature.

when the wave-vector transfer Q is along the hcp $[00l]$ direction (figure 7). The peak labelled (111) is independent of the temperature and is the (111) Bragg reflection from the face centred cubic structure of the GdH_2 and that labelled $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ arises from the magnetic ordering. A second scan along the hcp $[10l]$ direction is shown in figure 8. The presence of the fcc $(11\bar{1})$ and of the (002) reflections shows that the structure of the film is fcc and consists of both crystallographic domains, corresponding to the two possible orientations of the fcc structure with respect to the Gd lattice (cf figure 1). The (111) reflection arises from scattering by both domains. At 1.5 K, we observed several magnetic Bragg reflections. The $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, $(-\frac{1}{2}-\frac{1}{2}\frac{3}{2})$, $(\frac{1}{2}\frac{1}{2}-\frac{3}{2})$ and $(\frac{3}{2}\frac{3}{2}-\frac{1}{2})$ reflections correspond to a wavevector for the magnetic structure along the $[111]$ direction, which is the growth direction of the film. Their relative intensities (3.29, 0.81, 0.75 and 0.51 respectively) are roughly consistent with the magnetic moment being aligned in the basal plane. By comparing these intensities with that of the (111) nuclear scattering Bragg reflection, the magnetic moment per Gd atom is found to be $3.2 \pm 0.6 \mu_B$, much smaller than the magnetic moment of the isolated Gd^{3+} ion. Three other magnetic reflections were also observed: the $(-\frac{1}{2}-\frac{1}{2}\frac{1}{2})$, $(\frac{1}{2}\frac{1}{2}-\frac{1}{2})$ and $(\frac{1}{2}\frac{1}{2}\frac{3}{2})$ reflections arise from a wavevector for the magnetic scattering along the $[111]$ direction which is at 70.5° to the growth direction. These reflections have relative intensities of 1.09, 0.71 and 0.21 respectively. These intensities are much smaller than for $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. This is partly because both fcc domains contribute to the $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ group of magnetic reflections whereas only one contributes to the latter reflections. If the magnetic structure is a multi- q structure, the results suggest that there is a smaller moment associated with the $(-\frac{1}{2}-\frac{1}{2}\frac{1}{2})$ wavevectors than the $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ wavevector. If, however, the structure is a single q structure the populations of the different magnetic domains are unequal. We are unable to distinguish between these different models for the structure because the second order (001) reflections that are expected for a multi- q structure but not for a single q structure are likely to be too small to be observed in scattering from thin films.

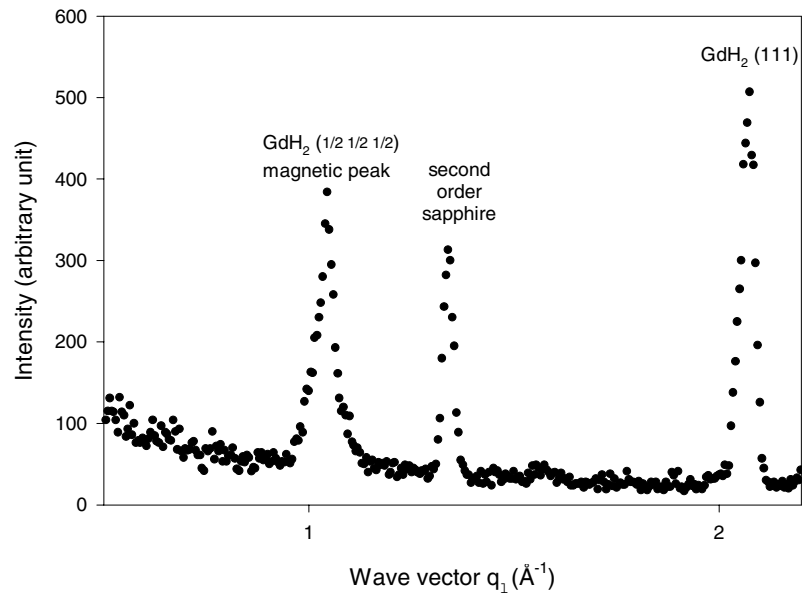


Figure 7. The intensity observed when the wave-vector transfer was scanned along the $[00q_1]$ direction in the GdH₂ sample at $T = 1.5$ K. The second order sapphire peak arises from scattering by the sapphire substrate.

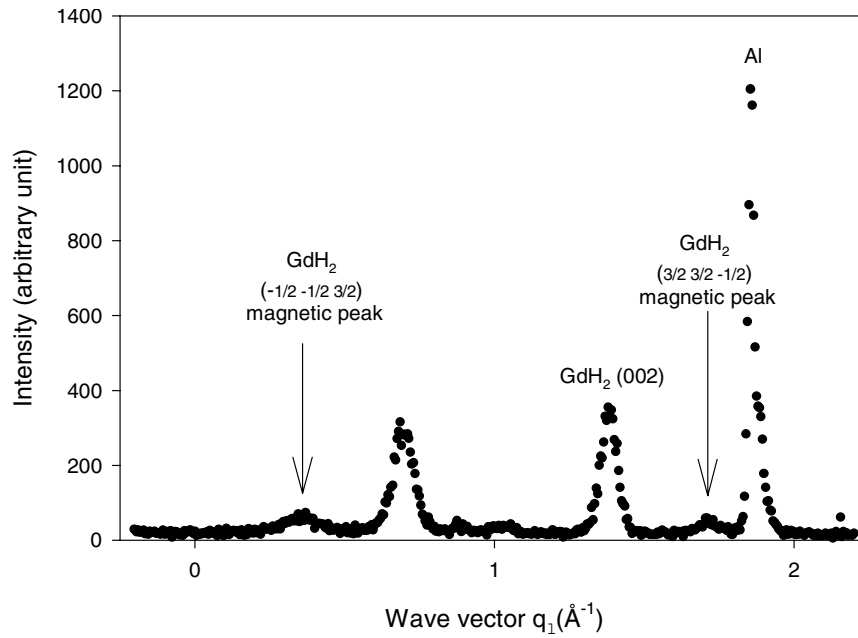


Figure 8. The intensity observed when the wave-vector transfer was scanned along the $[10q_1]$ direction in the GdH₂ sample at $T = 1.5$ K. The results show structural and magnetic peaks as well as scattering from an Al powder peak from the sample mounting.

The temperature dependence of the magnetic ordering of the GdH₂ thin film was determined by the intensity of the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ peak when the temperature increased. The results are shown in figure 9 and the ordering temperature, T_N , is 22 ± 0.5 K.

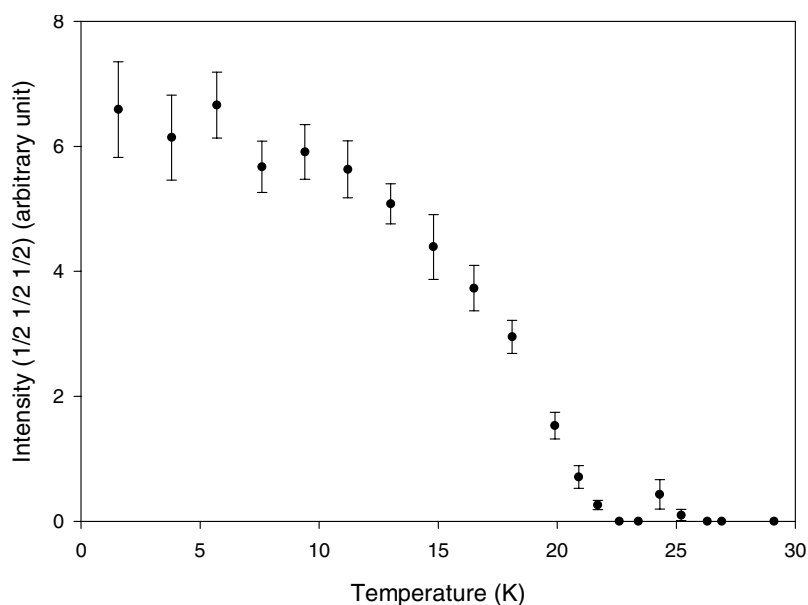


Figure 9. Temperature dependence of the intensity of the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ magnetic scattering from the fcc GdH_2 film.

3.3. Preliminary results concerning a light rare earth: the case of NdH_2

The mosaic spread of the NdH_2 film was found to be 2.75° whereas it was 0.31° for the pure Nd film. After loading with hydrogen, the heavy rare earths have a good crystalline structure but the behaviour of the light rare earths is different and the crystal structure of the dihydride Nd film is not so well maintained. It is not known whether this is characteristic of all hydrides of dhcp rare earths. From the results of the scans of the wave-vector transfer along the hcp $[00l]$ and $[10l]$ directions we deduce that the crystallographic structure of NdH_2 is the same as that of GdH_2 . The NdH_2 film is fcc and has roughly equal amounts of the both fcc domains. It was difficult in this case to determine the magnetic structure of the sample because of the large value of the mosaic spread. Nevertheless, we observed no evidence for ferromagnetism since the intensities of the (111) and $(1\bar{1}\bar{1})$ peaks are within error the same at 1.5 and at 40 K. We have found a broad incommensurate magnetic peak at the position $(0.532 \ 0.532 \ 1.532)$. The dependence of the intensity of this peak on the temperature is shown in figure 10 and the ordering temperature is 34 ± 1 K. It is surprising that the ordering temperature of NdH_2 is higher than that of pure Nd and of the heavy rare earths. Clearly these results are very different from previous measurement on NdH_2 [10, 11] and further experiments on better samples are needed to clarify the magnetic properties.

4. Discussion

Fujiki *et al* [13] have shown that the easy direction of the magnetization of a ferromagnet can be changed from the c -axis to the basal plane by varying the c/a -ratio for any lattice type which can be decomposed into orthorhombic sub-lattices, such as hexagonal lattices and close-packed hexagonal ones. In the case of the hcp lattices, they have studied the dipole interaction versus c/a -ratio and predicted the variation of the direction of the magnetization.

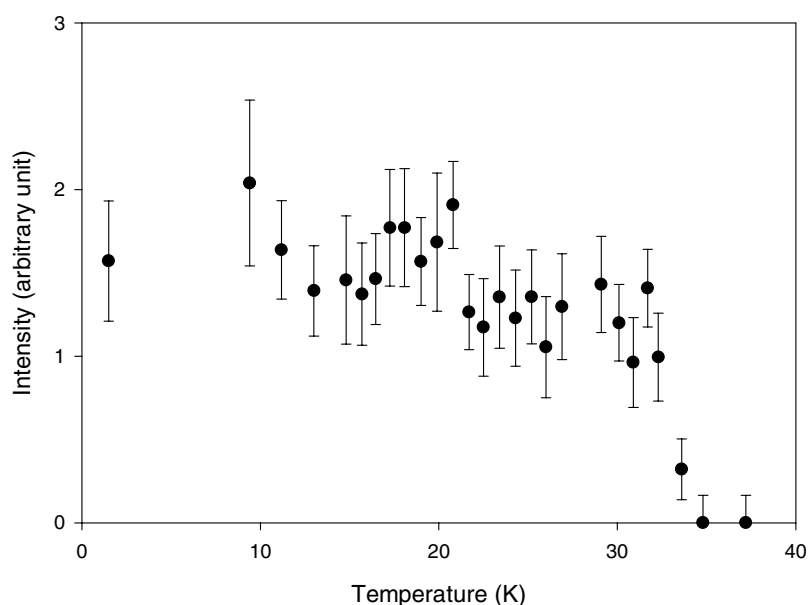


Figure 10. Temperature dependence of the intensity of the incommensurate (0.532 0.532 1.532) scattering from the fcc NdH₂ film.

If the c/a -ratio is smaller than the hcp ideal value of $c/a = 1.63$, the dipolar interaction favours the c -axis while for a c/a -ratio bigger than 1.63, the dipolar interaction favours the basal plane. For gadolinium $c/a = 1.59$ and the dipolar interaction favours the c -axis as the easy direction of the magnetization. This is the structure just below T_C . At lower temperatures, the higher order crystal field terms become larger and the moments tilt away from the c -axis. For the thin film sample the c/a -ratio is 1.61 and so the dipolar interaction might be expected to favour the moment along the c -axis. The film is different from the bulk material and the shape anisotropy makes the c -axis unfavourable. The compromise is apparently 30° from the c -axis. At lower temperatures, the behaviour of the moment is similar to that of the bulk showing that the crystal field effects are similar to those of bulk Gd and dominate over the dipolar interactions.

Finally we have shown that the hydrogen loading induces important changes to the magnetic structure of a Gd film. While the Gd film is ferromagnetic with a Curie temperature of 300 K and a magnetic moment equal to $6.3 \pm 1.1 \mu_B$, the GdH₂ thin film is antiferromagnetic and its Néel temperature is only 22 K. The ordering temperature of the Gd thin film is more than an order of magnitude larger than that of the GdH₂ thin film and this difference between the two ordering temperatures must be due to the decrease of the exchange interactions in the film after loading with hydrogen. For pure gadolinium, while both film and bulk sample are ferromagnets, the spin direction of the film differed from that of the bulk material in that the phase with the moments aligned along the c -axis was absent in the film. The magnetic properties of the GdH₂ thin film are the same as those of a GdD_{1.93} bulk sample since they are both antiferromagnetic with a wavevector along the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ direction. They have similar Néel temperatures (22 K for the film and 20 K for the bulk) and are different from those of bulk GdD₂, which has a helical structure along the [111] direction.

Acknowledgments

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