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LETTER TO THE EDITOR

# NMR of $^{165}$Ho in an epitaxially grown lamina of dysprosium

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**Abstract.** We have studied the field dependence of the hyperfine splitting of holmium as a dilute substituent in a lamina of dysprosium prepared by molecular-beam epitaxy. The measurements were made by spin-echo NMR at temperatures below 2 K and in fields up to 8 T. In fields above 3 T we obtain sharp seven-line spectra which are characteristic of $^{165}$Ho in fully polarized holmium ions in a ferromagnetically ordered host medium. The resolution is markedly superior to that obtained in bulk rare-earth alloys and has enabled us to resolve features hitherto unmeasurable. The form of the zero-field spectrum suggests that helimagnetic and ferromagnetic phases coexist in the zero-field-cooled material. Magnetization measurements support this interpretation.

The work reported here is part of an exploratory study of hyperfine interactions in epitaxially grown rare-earth laminates†. The samples were prepared at the Oxford LaMBE facility and have been studied by spin-echo NMR, supplemented by VSM measurements, at Manchester. The subject of the present letter is a laminate of form [Y|$Ho_{0.05}Dy_{0.95}$|Y], grown on a 10 mm × 12 mm sapphire substrate with a niobium buffer, following the procedures developed by Kwo *et al* (1985a,b). The thickness of the alloy lamina is approximately 300 nm. Details of the epitaxial relationships between the substrate, buffer and rare-earth laminae are given in the review article of Majkrzak *et al* (1991). The *c* axis of the rare-earth HCP lattice is normal to the substrate; in the specimen under discussion the *a* and *b* axes lie in the plane of the lamina at approximately 5° to the 12 mm and 10 mm edges, respectively.

The sample was mounted in a specially designed $TE_{011}$ resonator, tunable from 3000 MHz to 7000 MHz, immersed in liquid helium and surrounded by a superconducting solenoid. The RF and DC fields were mutually orthogonal and in the plane of the film, parallel to the 12 mm and 10 mm edges of the substrate respectively. The total thickness of the laminate was less than the estimated RF penetration depth (1 $\mu$m). In very low fields both the RF and DC fields are expelled from the superconducting niobium buffer layer, but the geometry is such that the fields within the lanthanide layers are practically unaffected. Flux expulsion is non-existent in DC fields above 0.19 T, the upper critical field of Nb.

In zero field the orientation of the magnetization within the basal plane is dominated by the preference of dysprosium for the *a* axis. (The strong axial anisotropy of dysprosium confines both the holmium and the dysprosium moments to the *ab* plane.) A simple calculation based on the known basal-plane anisotropies of the two metals shows that the

† In the absence of a generally accepted terminology we use 'laminate' to denote the entire range of available epitaxial structures, including alloys, multilayers and superlattices. A laminate consists of two or more *laminae*, each of which is a chemically homogeneous block of atomic *layers*. We reserve the term *superlattice* for a periodic laminate.

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misalignment of the *holmium* moments with the applied field decreases rapidly as the field increases and that its effect on our NMR measurements is insignificant.

Our spin-echo NMR measurements were made at 1.4 K and in fields up to 8 T. A representative high-field spectrum is shown in figure 1(a). The seven-line quadrupole-split spectrum is characteristic of $^{165}$Ho ($I$ = 7/2). The lines are much sharper than those observed by Mackenzie *et al* (1974) in bulk rare-earth alloys and indicate a high degree of crystallinity. The variation of intensity from line to line is due partly to the line dependence of the transition matrix elements and partly to the sensitivity profile of the spectrometer.

Close examination of the individual lines in the spectrum reveals a consistent pattern of unresolved structure. This is illustrated by the expanded views of a central line (figure 1(b)), which can be fitted rather accurately to two Gaussians of relative weights 1 and 0.67, in excellent and probably fortuitous agreement with the relative probabilities (1 and 0.63) for any given ion to have zero or one Ho nearest neighbour in a 5% Ho:Dy alloy. The fact that the width of the satellite is greater than that of the main line may be attributed to the fact that not all twelve possible locations of the Ho neighbour are physically equivalent in the presence of an applied field.

The 4.4 MHz shift of the satellite relative to the main line indicates that the presence of a single Ho ion in the nearest-neighbour shell increases the transferred hyperfine field (THFF) by approximately 0.5 T. Assuming, with Mackenzie *et al* (1974), that the THFF in rare-earth metals is due mainly to conduction electrons polarized by the spins on neighbouring ions and recalling that the spins of Ho and Dy are respectively 2 and 2.5 we conclude that the nearest-neighbour THFF per unit spin and per neighbour is approximately 1 T. It follows that the average THFF from the 12 nearest neighbours in an alloy of mean spin $\bar{S}$ is $-12\bar{S}$ T. Combining this result with the result obtained by Mackenzie *et al* (1974) for *all* neighbours in rare-earth alloys, viz, $B_n = -8.3\bar{S}$ T, we find that the average contribution of the more distant neighbours to the total THFF is about $+4\bar{S}$ T, a result consistent with the oscillatory nature of the RKKY interaction. It will be possible to obtain more precise data on the THFF from alloy systems such as Tb:Y with larger spin differences between host and solute.

Both the main and satellite spectra can be fitted to a nuclear spin Hamiltonian of the form given by Li *et al* (1993). As in that work, the contribution of the off-diagonal quadrupolar term $P_{\mathrm{lt}}$ to the NMR frequencies is insignificant (<30 kHz in the worst case). The remaining hyperfine parameters for the main spectrum, measured at 8 T, are given in table 1, together with $\delta\nu$, the full width of the central line at half height. For comparison, we give the hyperfine parameters obtained by Mackenzie *et al* (1974) for a 1% solution of holmium in a bulk sample of ferromagnetic dysprosium in zero field. (The chemical environment of the Ho nuclei in the alloy should be very similar to that of the nuclei contributing to the main spectrum in the 5% Ho:Dy lamina.)

**Table 1.** Hyperfine parameters of $^{165}$Ho in ferromagnetic Dy (MHz).

| | $a_t$ | $P_t$ | $w$ | $\delta\nu$ | Notes |
|---|---|---|---|---|---|
| Lamina at 8 T (main spectrum) | 6503.6 | 52.6 | 0.09 | 3.4 | a |
| Bulk Ho:Dy alloy ($B$ = 0) | 6431 | 52.4 | — | 15 | b |

(a) Present work.
(b) Mackenzie *et al* (1974).

Taking $\mu_N$ = (4.09 ± 0.05) nuclear magnetons for $^{165}$Ho (Haberstroh *et al* 1972), we expect a shift of (72 ± 1) MHz in the dipolar parameter $a_t$ due to the direct interaction

of the nuclear moment with an 8 T field. This is in excellent agreement with the 73 MHz difference between the two values of $a_t$ given in table 1; we conclude that the holmium ion must be almost fully polarized. The small difference in the quadrupole parameters $P_t$ is tentatively attributed to the fact that the orthorhombic distortion associated with the ferromagnetic phase in bulk dysprosium (Darnell 1963, McEwen 1978) is inhibited in the laminate by the constraint of epitaxy. The pseudo-octupole term, $w$, was unmeasurable in the bulk material because of the relatively poor resolution of the spectrum.

The character of the NMR spectrum changes markedly in fields below 3 T. Transverse relaxation becomes so rapid that only the outer quadrupole satellites (which relax more slowly because of their smaller transition matrix elements) can be measured with any accuracy. The detailed form of the zero-field spectrum depends on whether or not the specimen is cooled in zero field. Figure 2 shows the profile of the highest-frequency quadrupole satellite before and after the application of an external field of 8 T. The spectrum obtained on cooling in zero field consists of two components with maxima near 6738 MHz and 6752 MHz. Application and subsequent removal of the field enhances the former at the expense of the latter. The original spectrum is recovered only on warming and re-cooling the sample in zero field. Our explanation for this behaviour is as follows.

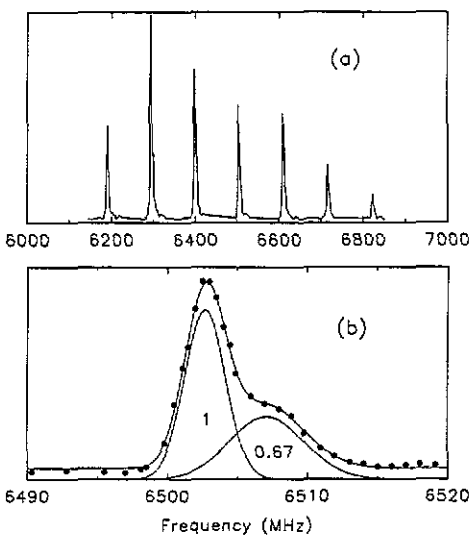


**Figure 1.** (a) NMR spectrum measured at 8 T and 1.4 K. (b) Expanded view of central line. The relative areas of the two Gaussian components are shown beneath the curves.

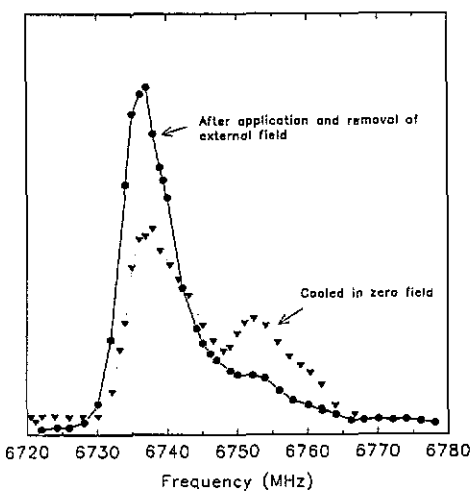


**Figure 2.** Profile of the highest frequency quadrupole satellite measured in zero field before (▼) and after (●) the application of an external field of 8 T.

Bulk dysprosium is helimagnetic between $T_n$ (185 K) and $T_c$ ($\simeq$85 K). At $T_c$ there is a first-order transition to ferromagnetism, accompanied by orthorhombic distortion. The magnetoelastic energy so gained is believed to stabilize the ferromagnetic phase. The behaviour can be markedly different in epitaxially grown material (Erwin *et al* 1987, Rhyne *et al* 1989). In [Dy|Y] laminates with sufficiently thin laminae of dysprosium the ferromagnetic phase is completely suppressed, an effect which may be attributed to the inhibition of orthorhombic distortion by neighbouring yttrium laminae or, perhaps, to the epitaxial constraints imposed by the substrate. At low temperatures the application of a field

of the order to 1 T suffices to induce ferromagnetic order; once induced, this order persists even when the field is removed. A thicker lamina of dysprosium showed behaviour similar to that of the bulk metal, but with $T_c$ lowered by about 5 K, and the hysteresis associated with the first-order ferromagnetic transition increased from 5 K to 15 K (Erwin *et al* 1987). In the present case, the dysprosium lamina is of intermediate thickness and we conjecture that the 6738 MHz signal comes from nuclei in the interior of the film, where epitaxial constraints may be relaxed sufficiently to allow ferromagnetism to be established, while the 6752 MHz signal comes from constrained, helically ordered regions.

The postulated coexistence of helimagnetic and ferromagnetic phases has been confirmed by vibrating-sample magnetometry on the same sample. Details, to be published elsewhere, may be summarized as follows. (i) The temperature dependence of the magnetization in a field of 4 mT shows that ferromagnetism appears at about 30 K on cooling and disappears at about 75 K on warming. The depression of $T_c$ and the hysteresis are qualitatively similar to, but larger than, the effects observed by Erwin *et al* (1987) in a 400 nm dysprosium lamina. (ii) As the field is increased at a constant temperature of 5 K the magnetization makes an abrupt transition almost to saturation at a field of about 0.7 T. The additional magnetization is maintained when the field is reduced towards zero.

Having established the coexistence of helimagnetic and ferromagnetic phases, we want to find the location of the physical boundary between them. We propose to do this by exploiting special features of the NMR and the MBE techniques. The method is as follows. A series of specimens is prepared, each containing a single lamina of pure dysprosium approximately 300 nm thick. Within each lamina, at a preassigned depth $d$, there will be a much thinner region lightly doped with foreign 'probe' nuclei, e.g. $^{159}$Tb or $^{165}$Ho. The character of the NMR signal from the probe nuclei will reveal the magnetic state (helimagnetic or ferromagnetic, as the case may be) at depth $d$. Repetition of the experiment for various values of $d$ will locate the phase boundary with a resolution determined by the thickness of the doped region. The ultimate limit will be set by the sensitivity of the NMR measurement. We have already detected very small concentrations of $^{165}$Ho nuclei close to the inter-laminar junctions in a [Lu|Ho] superlattice and in a [Y|Ho|Y] laminate and are confident that the proposed method, though technically challenging, is viable.

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