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Anomalous transferred hyperfine interactions in bulk and epitaxial Tb:Y alloys: a ^{159}Tb NMR study

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Abstract. We have made an NMR study of the effect of yttrium substitution on the hyperfine splitting of ^{159}Tb in ferromagnetic terbium at 4.2 K. In conventionally prepared polycrystalline samples the average transferred hyperfine field increases linearly with yttrium content, an effect attributed to the reduction of the negative transferred hyperfine fields from the 4f spins on neighbouring Tb ions. The rate of increase, however, is about half of that expected from similar measurements on inter-rare-earth alloys. We have also studied the transferred hyperfine interaction in epitaxially grown laminae of Tb containing 5% and 10% Y, in which resolved satellites associated with individual nearest-neighbour Y atoms are observed. The satellite shift, per unit change in 4f spin, is less than half of that observed in epitaxially grown Ho:Dy and Ho:Gd alloys. We conclude that the nominally non-magnetic Y is not a simple spin diluent, and that it makes a substantial contribution to the transferred hyperfine field.

1. Introduction

It has long been known that polarized conduction electrons make a substantial contribution to hyperfine fields in magnetically ordered rare-earth metals (see, for example, Mackenzie *et al* 1974, Sano *et al* 1975, McCausland and Mackenzie 1979). In conventionally prepared rare-earth alloys it is not possible to resolve the transferred hyperfine fields (THFFs) arising from individual neighbours of a given ion; only their collective contribution to the total hyperfine field can be determined. The advent of exceptionally high-quality alloys grown by molecular-beam epitaxy has made it possible to measure contributions of individual nearest neighbours to the total THFF (Graham *et al* 1993, Li *et al* 1996). The work described here is an NMR investigation of ^{159}Tb in polycrystalline and epitaxially grown Tb:Y alloys. It is a sequel to related studies of ^{165}Ho in polycrystalline alloys (Mackenzie *et al* 1974) and in epitaxial alloys (Graham *et al* 1993, Li *et al* 1996).

2. Experimental procedures and results

Our spin-echo NMR measurements were carried out on polycrystalline and epitaxial Tb:Y alloys at frequencies in the range 2.4 to 4 GHz. All the measurements to be described here were made in zero field and at 4.2 K.

The quadrupole-split NMR spectra which we obtained are characteristic of ^{159}Tb , with three lines centred at ~ 3000 MHz and separated by ~ 600 MHz (see figure 1). The fine structure is characteristic of the epitaxial material, to be discussed in subsection 2.2. None

of the spectra show any measurable asymmetry associated either with the presence of an octupole term or with off-diagonal terms in the quadrupolar interaction (cf Li *et al* 1993). We have therefore fitted each distinct spectrum to a two-parameter nuclear spin Hamiltonian of the form

$$\mathcal{H} = h[a_t I_z + P_t(I_z^2 - \frac{1}{3}I^2)]. \quad (1)$$

Except where stated otherwise, our notation follows that of McMorrow *et al* (1989). The measured dipolar and quadrupolar parameters, a_t and P_t respectively, are given in tables 1 and 2.

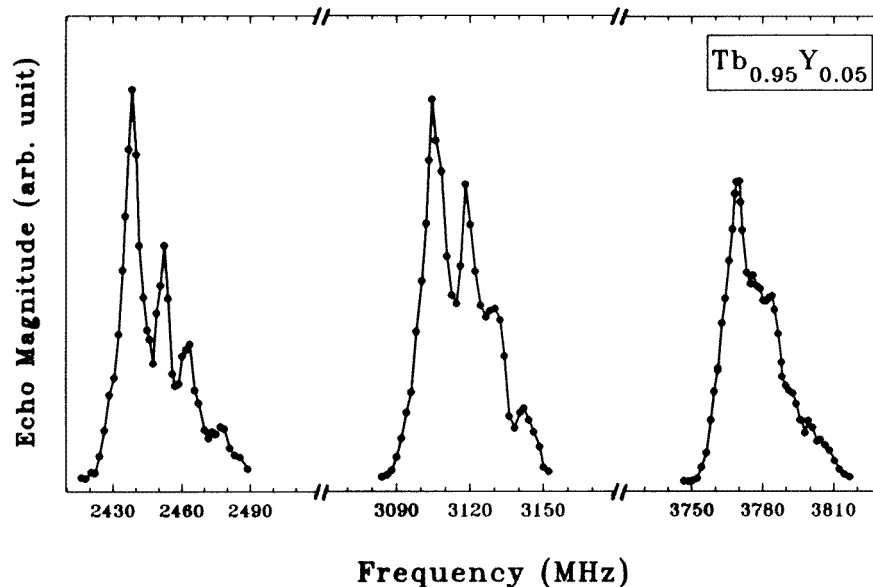


Figure 1. Representative zero-field NMR spectrum of ^{159}Tb in epitaxially grown $\text{Tb}_{0.95}\text{Y}_{0.05}$ at 4.2 K.

Table 1. The measured hyperfine parameters a_t and P_t of ^{159}Tb in polycrystalline $\text{Y}_x\text{Tb}_{1-x}$ alloys in zero applied field and at 4.2 K. The hyperfine parameters for the single crystal of pure Tb metal ($x = 0$) are obtained by Li *et al* (1996). \bar{S} is the mean ionic spin.

Y content	a_t (MHz)	P_t (MHz)	\bar{S}
$x = 0$	3106.5 ± 1.5	332.5 ± 1.0	3
$x = 0.10$	3121.5 ± 2.5	333 ± 2	2.7
$x = 0.20$	3136 ± 3	333 ± 2	2.4
$x = 0.30$	3147 ± 4	331 ± 3	2.1

2.1. The polycrystalline material

$\text{Y}_x\text{Tb}_{1-x}$ alloys with $x = 0.10, 0.20$ and 0.30 were prepared by melting together the 99.99% pure starting materials in an argon-arc furnace. The quadrupole-split NMR spectra from these alloys have been obtained. There are no observed satellites associated with individual

neighbours, see figure 2(a). The measured hyperfine parameters for each alloy are given in table 1.

The extra-ionic contribution to the quadrupole splitting is given by $P'' = P_t - P'$ where P' , the intra-ionic contribution, is (360 ± 8) MHz for a fully polarized Tb ion (Pelletier-Allard and Pelletier 1985). Thus $P'' = -(27 \pm 8)$ MHz. This corresponds to an electric-field gradient of $-(3 \pm 1) \times 10^{21}$ V m⁻² along the crystallographic b axis, the easy direction of magnetization for terbium. The uncertainties are dominated by the uncertainty on P' .

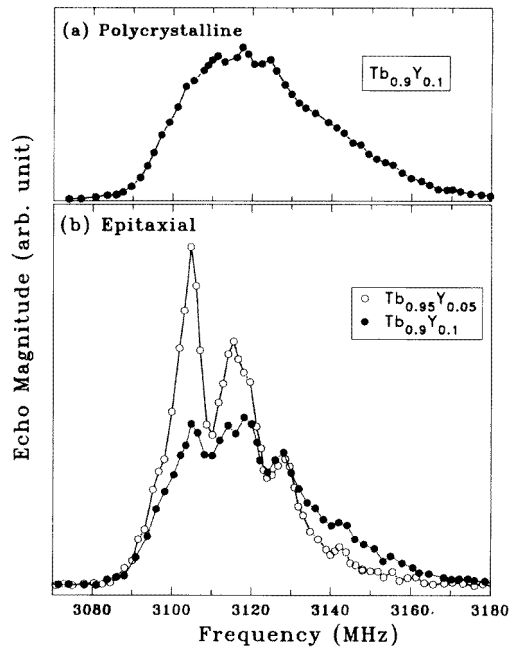


Figure 2. The zero-field NMR spectra for the central lines of ^{159}Tb in (a) polycrystalline $\text{Tb}_{0.9}\text{Y}_{0.1}$, and in (b) epitaxially grown $\text{Tb}_{0.95}\text{Y}_{0.05}$ and $\text{Tb}_{0.9}\text{Y}_{0.1}$. The measurements were made at 4.2 K.

2.2. The epitaxial material

Our NMR measurements were made on ^{159}Tb in epitaxially grown laminae of terbium containing 5% and 10% yttrium as a substitutional impurity. The laminae, approximately 300 nm thick, were grown on sapphire substrates at the Oxford LaMBE facility. Details of the sample preparation are essentially the same as those described by Graham *et al* (1993). The crystallographic c axis is normal to the plane of the lamina and perpendicular to the direction of the RF field. The easy direction of magnetization for terbium is the b axis and the magnetization therefore lies in the plane of the lamina.

The fine structure shown in figure 1 can be seen more clearly in figure 2(b), which shows the central lines of the spectra from the alloys containing 5% and 10% Y. The fine structure is attributed to partially overlapping sub-spectra from terbium ions with $N = 0, 1, 2$ and 3 yttrium ions in the nearest-neighbour shell. The relative intensities of the satellites are consistent with that assignment.

We have fitted each sub-spectrum to the two-parameter Hamiltonian defined by

Table 2. The measured hyperfine parameters (MHz) of terbium in epitaxially grown Tb_{0.95}Y_{0.05} and Tb_{0.9}Y_{0.1} alloys in zero applied field and at 4.2 K.

	Hyperfine parameter	Site ^a (<i>N</i> = 0)	Site ^a (<i>N</i> = 1)	Site ^a (<i>N</i> = 2)	Site ^a (<i>N</i> = 3)
Tb _{0.95} Y _{0.05}	<i>a_i</i>	3105.4 ± 1.0	3118.6 ± 1.0	3130.2 ± 1.0	3142.6 ± 2.0
	<i>P_i</i>	332.7 ± 1.0	332.8 ± 1.5	332.5 ± 1.5	332.2 ± 2.0
Tb _{0.9} Y _{0.1}	<i>a_i</i>	3105.2 ± 1.0	3117.2 ± 1.0	3128.3 ± 1.5	3141.4 ± 2.5
	<i>P_i</i>	332.1 ± 1.0	333.1 ± 1.5	331.8 ± 1.5	332.5 ± 2.5

^a The different sites are characterized by the number of nearest-neighbour Y atoms.

equation (1). The resulting hyperfine parameters for each sub-spectrum are given in table 2. The hyperfine parameters for *N* = 0 are almost identical with those obtained from a recent measurement on a single crystal of pure terbium (Li *et al* 1996). The absence of any systematic variation in the quadrupolar parameter *P_i* with *N* confirms that the terbium moment remains practically unquenched even when it has three adjacent yttrium neighbours. The values of *P_i* given in table 2 are identical, within the experimental uncertainties, with those obtained in the polycrystalline alloys.

3. Extra-ionic contributions to the hyperfine field

We are principally concerned with transferred hyperfine fields driven by the spins on neighbouring ions. For the sake of generality, we express the total extra-ionic hyperfine field in the form

$$\mathbf{B}'' = \mathbf{B}_a + \mathbf{B}_{ce} + \mathbf{B}_{orb} + \mathbf{B}_{dip} \quad (2)$$

where \mathbf{B}_a is the applied field, \mathbf{B}_{ce} is the field due to spin-polarized conduction electrons and \mathbf{B}_{orb} is associated with orbitally polarized conduction electrons in the immediate vicinity of the parent ion. \mathbf{B}_{dip} is the dipolar field arising from all other moments in the sample. Our notation here differs from that of McMorro *et al* (1989) by the replacement of the symbol σ for the spin operator by \mathbf{S} and the introduction of the outer-electron correction factor $\chi(\mathbf{R})$ (see equation (4)).

\mathbf{B}_{ce} may be expressed as a sum of contributions from conduction electrons polarized by the spins on the parent ion (*p*) and by the spins on neighbouring ions (*n*)

$$\mathbf{B}_{ce} = \mathbf{B}_p + \mathbf{B}_n. \quad (3)$$

The available evidence indicates that contributions from individual neighbours to \mathbf{B}_n are additive and proportional to the spins $\langle \mathbf{S}_j \rangle = (g_j - 1)\langle \mathbf{J}_j \rangle$ on each ion. Thus

$$\mathbf{B}_n = \chi(\mathbf{R}) \sum_j f(\mathbf{r}_j) \langle \mathbf{S}_j \rangle \quad (4)$$

where $f(\mathbf{r}_j)$ is a range function characteristic of the alloy system and the factor $\chi(\mathbf{R})$ allows for the fact that the THFF seen by a given probe ion \mathbf{R} varies with the outer s electron hyperfine coupling parameter $\mathcal{A}(\mathbf{R})$ (Campbell 1969). We define $\chi(\mathbf{R})$ in such a way that $\chi(\text{Gd}) = 1$; values of $\chi(\mathbf{R}) = \mathcal{A}(\mathbf{R})/\mathcal{A}(\text{Gd})$ for other ions are obtained by interpolation from the Campbell values for $\mathcal{A}(\text{La})$ and $\mathcal{A}(\text{Lu})$ (table 3).

It follows from equation (4) that the change in \mathbf{B}_n when an ion with spin $\langle \mathbf{S} \rangle$ at position \mathbf{r}_j is replaced by a different ion with spin $\langle \mathbf{S} \rangle + \Delta \langle \mathbf{S} \rangle$ is given by

$$\Delta \mathbf{B}_n = \chi(\mathbf{R}) f(\mathbf{r}_j) \Delta \langle \mathbf{S} \rangle \quad (5)$$

Table 3. Representative values of K_n , correction factors $\chi(\text{R})$ and $\sum_j f(r_j)$ for rare-earth alloys.

Probe ion R	Gd	Tb	Dy	Ho	Lu
Alloyed with	Lu	Gd,Dy,Er	Gd,Tb,Er	Gd,Tb,Dy	Gd
Reference	a	b	b	c	a
K_n (T)	-7.7	~ -6	-8.5	$-(8.3 \pm 0.2)$	-7.7
$\chi(\text{R})$	1.00	1.03	1.06	1.09	1.22
$\sum_j f(r_j)$ (T)	-7.7	~ -5.8	-8.0	-7.6	-6.3

^a Zmora *et al* 1969.

^b Sano *et al* 1975.

^c Mackenzie *et al* 1974.

and that the mean value of B_n at a given nuclear species in a random alloy is

$$\langle B_n \rangle = K_n \bar{S} \quad (6)$$

where the bar denotes the average expectation value for all ions in the alloy and

$$K_n = \chi(\text{R}) \sum_j f(r_j). \quad (7)$$

Following Mackenzie *et al* (1974) we express the ‘parent’ contribution to B_{ce} in the form

$$B_p = K_p \langle S_p \rangle = K_p (g - 1) \langle J \rangle \quad (8)$$

where J and g pertain to the parent ion, and write

$$B_{orb} = K_{orb} \langle L_p \rangle = K_{orb} (2 - g) \langle J \rangle \quad (9)$$

where K_p and K_{orb} , like K_n , are constants for a given probe ion.

4. Discussion

The extra-ionic hyperfine field B'' is derived from the relationship $a'' = (\gamma/2\pi)B''$, where $(\gamma/2\pi) = 10.13 \text{ MHz T}^{-1}$ for ^{159}Tb (after Bleaney 1988), $a'' = a_t - a'$ and a' is the intra-ionic hyperfine parameter. Calculations based on realistic estimates of exchange and crystal-field parameters indicate that the moment on the parent Tb^{3+} is insignificantly quenched and that the second-order contributions to a' are negligible. We may therefore equate a' to $AJ = (3168 \pm 18) \text{ MHz}$ (Pelletier-Allard and Pelletier 1985), which corresponds to an intra-ionic hyperfine field $B' = (313 \pm 2) \text{ T}$.

In the ferromagnetic alloys to be discussed the ionic moments are collinear, and it will be convenient to replace the vectors in equations (2) to (9) by their scalar magnitudes, with due regard for signs. We have already noted that crystal-field quenching of the terbium moment is insignificant, whence $\langle J \rangle \simeq J$. It follows that not only the intra-ionic hyperfine field B' but also the ‘parent’ and ‘orbital’ contributions to the extra-ionic field may be treated as constants: $B_p \simeq K_p (g - 1)J$ ($=3K_p$ for Tb^{3+}) and $B_{orb} \simeq K_{orb} (2 - g)J$ ($=3K_{orb}$ for Tb^{3+}). Any variation in B'' with composition or with nearest neighbours is associated only with B_n and with the dipolar term B_{dip} . In the system under discussion the dipolar field may, to a very good approximation, be equated to the Lorentz field. (The dipole sum within the Lorentz sphere is very small because the c/a ratio approximates closely to its ideal close-packed value; the demagnetizing field is negligible in the epitaxial samples because the demagnetizing factor for a thin lamina magnetized in its own plane is practically zero.)

Thus $\langle B_{dip} \rangle \simeq \frac{1}{3} \mu_0 M$ where M is the intra-domain magnetization. For the $Y_x Tb_{1-x}$ system under discussion, $\langle B_{dip} \rangle \simeq 0.12g\bar{J} = 1.1(1-x)$ T. Since the average ionic spin is given by $\bar{S} = 3(1-x)$, we obtain $\langle B_{dip} \rangle \simeq 0.37\bar{S}$ T.

4.1. The polycrystalline alloys

Figure 3 shows that the magnetic hyperfine parameter a_t of terbium in polycrystalline $Y_x Tb_{1-x}$ varies as a function of \bar{S} , the mean ionic spin (see table 1). The graph is linear to within the experimental uncertainty in a_t . A least-squares analysis of the data gives $d\langle B'' \rangle/d\bar{S} = -(4.63 \pm 0.38)$ T. Since $d\langle B_{dip} \rangle/d\bar{S} \simeq 0.37$ T it follows that $K_n = -(5.00 \pm 0.38)$ T. Setting $\chi(\text{Tb}) = 1.03$ (see table 3) in equation (7) we obtain $\sum_j f(r_j) = -(4.85 \pm 0.37)$ T for the system under discussion. This figure is considerably smaller than the values typically obtained from hyperfine measurements on alloys composed entirely of rare-earth metals.

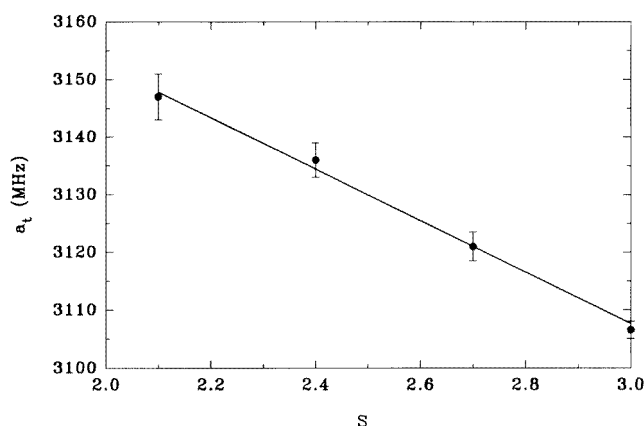


Figure 3. The magnetic hyperfine parameter a_t of terbium in polycrystalline $Y_x Tb_{1-x}$ alloys as a function of \bar{S} , the mean ionic spin. See table 1.

4.2. The epitaxially grown alloys

We have already noted that each of the sub-spectra observed in the epitaxial alloys can be associated with a particular number, N , of Y atoms in the nearest-neighbour shell. The satellite spacings are equal to within the experimental uncertainties, showing that the contributions of individual Y neighbours to the THFF are additive. Bearing in mind that the Y atoms are randomly distributed within the shell, the very existence of resolved satellites also shows that the THFF must be at least approximately isotropic. Close examination of figure 2(b) shows that the widths of the satellites increase with increasing N . The small degree of anisotropy which this implies is largely accounted for by the anisotropy of the dipolar contribution to the transferred hyperfine field. We conclude that the conduction-electron contribution to the THFF is isotropic to within our experimental uncertainties. It follows that the range function $f(r)$ depends only on the distance r between the parent ion and the neighbour of interest: $f(\mathbf{r}) = f(r)$. The additivity and isotropy of the THFF are supported by our observations on epitaxial Ho:Dy (Graham *et al* 1993) and Ho:Gd (Li *et al* 1996).

The average spacing between successive sub-satellites in the NMR spectra shown in figures 1 and 2(b) is (12.1 ± 0.5) MHz, which corresponds to a shift in the THFF of $\Delta B_n = (1.19 \pm 0.05)$ T for each Y atom in the nearest-neighbour shell. Recalling that the change in 4f spin is -3 for each Y substituted for a Tb, we obtain $f(a) = -(0.38 \pm 0.01)$ T, where $a \cong 0.36$ nm is the nearest-neighbour distance. This value of $f(a)$ is less than half of that derived from our NMR measurements on epitaxial Ho:Dy and Ho:Gd alloys, for which $f(a) \cong 0.9$ T and 1.1 T respectively. (The differences between the lattice constants a for the various alloys are $\sim 1\%$ or less and cannot account for a factor of ~ 2 in the THFF.) This result complements our finding, in subsection 4.1, that the value of $\sum_j f(r_j)$ obtained in polycrystalline Tb:Y alloys is considerably smaller than those obtained in true heavy rare-earth alloys.

It has been shown above that the total sum, $\sum_j f(r_j) = -(4.85 \pm 0.37)$ T; of this, the contribution of the nearest neighbours accounts for $12 f(a) = -(4.6 \pm 0.1)$ T. It follows that the contribution of more distant neighbours to the sum $\sum_j^{(r>a)} f(r_j)$ is $-(0.23 \pm 0.38)$ T.

Our data on the epitaxial alloys show a small but systematic dependence of the satellite frequencies on the yttrium content. This provides independent information about any long-range contribution to the THFF. Analysis of the data in table 2, after allowance for the dipolar contribution to the THFF, gives the following result: $\sum_j^{(r>a)} f(r_j) = (0.3 \pm 0.5)$ T. This result is consistent, to within the experimental uncertainties, with the corresponding value derived in the last paragraph. The weighted mean of the two values is $\sum_j^{(r>a)} f(r_j) = -(0.05 \pm 0.30)$ T. This is much smaller than the figure of $\sim +4$ T found in epitaxial Ho:Dy and Ho:Gd alloys (Graham *et al* 1993, Li *et al* 1996).

Our anomalous results for Tb:Y alloys are consistent with the existence of a predominantly orbital, short-range THFF similar to that theoretically predicted by Gasche (1995) for Gd:Y alloys.

5. Summary and conclusions

The quality of the spectra obtained from the epitaxially grown laminae is evidence of the excellent crystallinity of the material. Detailed analysis of the data shows that the THFF arising from individual ions comes predominantly from the nearest-neighbour shell and that it is additive and isotropic to within the experimental uncertainties. We also find that the nature of the THFF in Tb:Y alloys differs markedly from that observed in alloys consisting solely of heavy rare-earth metals. We conclude that yttrium, though nominally non-magnetic, does not behave as a simple 'magnetic hole'. This conclusion is consistent with observations by Foldeaki *et al* (1995) on Gd:Y alloys.

We propose to carry out a similar study of the THFF in Tb:Lu alloys. The replacement of the pseudo-lanthanide Y by a true non-magnetic lanthanide Lu should help us to clarify further the anomalous behaviour of Y.

Acknowledgment

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