A ^{159}Tb NMR study of the hexagonal and rhombohedral phases of Tb$_2$Co$_{17}$

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Abstract. The zero-field hyperfine splitting of ^{159}Tb in ferrimagnetic Tb$_2$Co$_{17}$ has been studied by NMR at 4.2 K. Distinct domain and wall spectra are obtained from the dominant rhombohedral phase; weaker spectra from the two inequivalent lanthanide sites in the hexagonal phase have also been observed. The data are interpreted in terms of the single-ion mean-field model. Estimates of the extra-ionic hyperfine fields and the electric-field gradients, and the antishielding ratios at the rhombohedral and hexagonal sites have been made using exchange and crystal-field parameters derived from magnetization and anisotropy measurements. Results are discussed in the light of complementary data obtained from other sources.

1. Introduction

The discovery of the powerful permanent magnet material Nd$_2$Fe$_{14}$B by Sagawa *et al* (1984) and by Croat *et al* (1984) has stimulated renewed interest in the intermetallic compounds of rare earths (R) and transition metals (T), especially when T is iron or cobalt. The R$_2$T$_{17}$ compounds are of interest for technical applications because of their high Curie temperatures (~ 1100 K), high room-temperature saturation moments and, in some cases, unusally large magnetocrystalline anisotropies.

The R$_2$Co$_{17}$ compounds crystallize in the hexagonal Th$_2$Ni$_{17}$ or the rhombohedral Th$_2$Zn$_{17}$ structure. Both structures are derivatives of CaCu$_5$-type RCo$_5$ and can be obtained by replacing one-third of all R atoms by dumb-bell pairs of Co atoms. This can lead to either structure, depending on the stacking sequence. Most members of the series, especially the Tb, Dy and Ho compounds, can exist in either form, depending on the preparative procedure. However, the rhombohedral structure predominates in the lighter rare-earth compounds (including Y$_2$Co$_{17}$) up to Tb$_2$Co$_{17}$, while the hexagonal structure predominates from Ho$_2$Co$_{17}$ to Lu$_2$Co$_{17}$ (Wallace 1973, Figiel *et al* 1977, Kou *et al* 1992). In the hexagonal structure there are two inequivalent R sites (2b and 2d in Wyckoff's notation) which occur in equal abundance; in the rhombohedral structure there is a single R site. Further crystallographic details can be found in the paper by Khan (1973).

In the light rare-earth compounds the rare-earth and cobalt sublattices couple ferromagnetically; in the heavy rare earths the coupling is antiferromagnetic, leading to an overall ferrimagnetic structure. The holmium compound (probably the best documented of the heavy lanthanide compounds) has been studied by inelastic neutron scattering (Clausen and Lebech 1982) and by high-field magnetization measurements (Radwański *et al* 1985, Radwański and Franse 1989), but there are marked differences between the crystal-field parameters obtained by different workers. A summary of high-field magnetization studies of other members of the series is given by Franse *et al* (1992). Previous hyperfine studies

at the lanthanide sites include Mössbauer spectroscopy of ^{155}Gd in Gd_2Co_{17} (van Steenwijk *et al* 1977) and of ^{169}Tm in Tm_2Co_{17} (Gubbens *et al* 1987), NMR of ^{89}Y in Y_2Co_{17} (Figiel *et al* 1976, 1977) and of ^{147,149}Sm in Sm_2Co_{17} (Figiel *et al* 1991) and a perturbed angular correlation study of ^{177}Hf in Lu_2Co_{17} (Hollander 1981).

2. Theory

2.1. The electronic Hamiltonian

The interaction of the R ion with its environment may be expressed, within the mean-field approximation, by the effective electronic Hamiltonian

$$\mathcal{H}_{\text{el}} = \mathcal{H}_{\text{cf}} - \boldsymbol{\alpha} \cdot \boldsymbol{J} \tag{1}$$

where $\mathcal{H}_{\text{cf}}$ represents the crystal-field interaction. In general, the vector $\boldsymbol{\alpha}$ includes contributions from the exchange, dipolar and applied fields (McMorrow *et al* 1989). In the system under consideration the dipolar field is negligible in comparison with the large exchange field which arises mainly from the cobalt sublattice; moreover, the measurements to be described were carried out in zero applied field, so we may write

$$\boldsymbol{\alpha} = \boldsymbol{\alpha}_{\text{ex}} = (g_J - 1)\boldsymbol{X} \tag{2}$$

where X represents the exchange field acting on the projected spin $\sigma = (g_J - 1)J$ of the lanthanide ion (McCausland and Mackenzie 1979). α_{ex} is related to the effective molecular field B_m notionally acting on the lanthanide moment $\mu = -g_J\mu_B J$ by $\alpha_{\text{ex}} = -g_J\mu_B B_m$; the exchange field X used here is related to a commonly used 'exchange field' H_{exch} (see, for example, Radwański *et al* (1985)) by $X = -2\mu_B H_{\text{exch}}$. X, like H_{exch}, varies only slowly across a given (isostructural) R-Fe or R-Co intermetallic series (Belorizky *et al* 1987, Brooks *et al* 1991).

In the rhombohedral structure the point symmetry at the unique R site is C_{3v} and $\mathcal{H}_{\text{cf}}$ can be written, in the notation of Abragam and Bleaney (1970),

$$\mathcal{H}_{\text{cf}}^{\text{rhom}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^3 O_4^3 + B_6^0 O_6^0 + B_6^3 O_6^3 + B_6^6 O_6^6. \tag{3}$$

In the hexagonal structure the point symmetry at both Tb sites is D_{3h} and

$$\mathcal{H}_{\text{cf}}^{\text{hex}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^6 O_6^6. \tag{4}$$

The two inequivalent sites are distinguished by different sets of crystal field parameters.

To avoid confusion with the magnetic coordinate system (x, y, z) to be used in the analysis of the hyperfine interaction we express the operator equivalents O_n^m in terms of the components of J along the mutually orthogonal crystallographic axes a ($\equiv [10\bar{1}0]$), b ($\equiv [\bar{1}2\bar{1}0]$) and c ($\equiv [0001]$). Thus, for example, $O_2^0 = 3J_c^2 - J^2$; $O_6^6 = \frac{1}{2}(J_+^6 + J_-^6)$ where $J_\pm = J_a \pm iJ_b$.

In the notation of Bunbury *et al* (1989), the B_n^m may be expressed in the form

$$B_n^m = \langle J||\alpha_n||J\rangle \langle r^n\rangle A_n^m \tag{5}$$

where the $\langle J||\alpha_n||J\rangle$ are operator-equivalent coefficients and the $\langle r^n\rangle$ are radial averages for the 4f electrons. The A_n^m are proportional to the nth derivatives of the crystalline potential

and may therefore be expected to be approximately constant for an isostuctural intermetallic series. In particular,

$$A_2^0 = -\tfrac{1}{4}e\gamma_E V_{cc} \tag{6}$$

where V_{cc} is the component of the electric-field gradient tensor (EFG) along the principal symmetry axis and γ_E is the electronic antishielding factor in the notation of Edmonds (1963) ($\gamma_E = 1 - \sigma_2$ in the notation of Blok and Shirley (1966)).

The magnetocrystalline anisotropy is usually dominated by the term in B_2^0. In that case, if B_2^0 is negative the easy direction of magnetization is parallel to c; if it is positive, as in Tb$_2$Co$_{17}$, the easy direction lies in the basal plane. In the rhombohedral phase the easy direction within the basal plane is determined by the signs and relative magnitudes of the coefficients B_4^3, B_6^3 and B_6^6; in the hexagonal phase it is determined solely by the sign of B_6^6. In the latter case, if B_6^6 is positive (as in the hexagonal phase of Tb$_2$Co$_{17}$) then b is the preferred axis.

At this point we remark that the point-charge calculations of Greedan and Rao (1973) for the hexagonal R$_2$Co$_{17}$ compounds indicate that the sign of V_{cc} (and hence of A_2^0 and of B_2^0) is different at the 2b and 2d sites. That this is contradicted by the available experimental evidence (Clausen and Lebech 1982, Radwański and Franse 1989), which requires positive values of V_{cc} at both sites, is not surprising in view of the notorious unreliability of point-charge calculations. However, the disagreement might alternatively be explained by the fact that Greedan and Rao included only nearest and next-nearest neighbours in their calculation and, moreover, assumed the effective charge on the cobalt ions to be zero. In order to obtain a better test of the point-charge model we have computed lattice sums for both R and Co sites over a region large enough to ensure that the sums are close to convergence and have allowed Z_{Co}, the effective charge on the Co sites, to vary from -1 to $+2$ (in units of the electronic charge). Our results are shown in figure 1. It will be seen that positive values of V_{cc} at both sites are obtained only for $Z_{Co} < -0.2$.
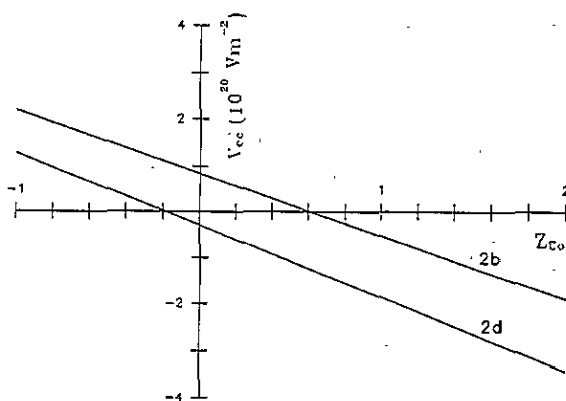

Figure 1. Electric-field gradients at the lanthanide sites in hexagonal Tb$_2$Co$_{17}$ according to the point-charge model, expressed as functions of the effective charge on the cobalt site. The relevant lattice sums have been evaluated over a sphere of radius 20 nm and are close to their asymptotic values.

2.2. *The hyperfine interaction*

The hyperfine interaction may be described by the effective nuclear Hamiltonian

$$\mathcal{H} = h[a_t I_z + P_t(I_z^2 - \tfrac{1}{3}\boldsymbol{I}^2) + P_{1t}(I_x^2 - I_y^2) + wI_z^3] \tag{7}$$

where $\boldsymbol{I}$ is the nuclear spin operator and the z axis is along the direction of $\langle \boldsymbol{J} \rangle$. (See, for example, McCausland and Mackenzie (1979) or Bunbury *et al* (1989).) In the present context, the z axis coincides with the crystallographic b axis; we take the x and y axes parallel to c and a, respectively. The off-diagonal term in P_{1t} arises from the fact that the magnetic quantization axis (z) is orthogonal to the crystallographic symmetry axis (c). Its effect on the hyperfine splitting is of order P_{1t}^2/a_t and is expected to be small. Like the term in w, its qualitative effect is to make the quadrupole splitting asymmetrical. We note in passing that the term in P_{1t} is experimentally indistinguishable from that in w unless $I > \tfrac{3}{2}$.

The hyperfine parameters a_t, P_t and P_{1t} are sums of intra- and extra-ionic contributions:

$$a_t = a' + a'' \tag{8}$$

$$P_t = P' + P'' \tag{9}$$

$$P_{1t} = P_1' + P_1'' \tag{10}$$

where the single and double primes denote the intra- and extra-ionic terms, respectively (McCausland and Mackenzie 1979). The intra-ionic parameters are dominated by the first-order contributions

$$a'^{(1)} = A\langle J_z \rangle \tag{11}$$

$$P'^{(1)} = C\langle 3J_z^2 - \boldsymbol{J}^2 \rangle \tag{12}$$

$$P_1'^{(1)} = C\langle J_x^2 - J_y^2 \rangle \tag{13}$$

in the notation of Bunbury *et al* (1989). The free-ion hyperfine coupling constants A and C are related to the constants a_0' and P_0' (see, for example, McCausland and Mackenzie (1979)) by $A = a_0'/J$ and $C = P_0'/J(2J - 1)$. The octupolar term in w is a purely intra-ionic second-order effect; expressions for w and for the second-order contributions to a' and P' are given by Bunbury *et al* (1989).

The extra-ionic dipolar parameter a'' is related to the extra-ionic hyperfine field B'' by

$$a'' = \gamma B''/2\pi \tag{14}$$

where γ is the gyromagnetic ratio of the R nucleus. The principal contributions to B'' are the transferred hyperfine fields B_n^R and B_n^{Co} from R and Co neighbours, and the field B_p due to conduction electrons polarized by the spin of the parent ion. The extra-ionic quadrupole parameters are related to the crystalline EFG by

$$P'' = \frac{3eQ_N}{4hI(2I - 1)}\gamma_N V_{zz} \tag{15}$$

and

$$P_1'' = \frac{eQ_N}{4hI(2I - 1)}\gamma_N(V_{xx} - V_{yy}) \tag{16}$$

where Q_N is the nuclear quadrupole moment and γ_N is the nuclear antishielding factor in the notation of Edmonds (1963) ($\gamma_N = 1 - \gamma_\infty$ in the notation of Blok and Shirley (1966)). In the case under discussion the EFG is axially symmetrical about the c axis so $V_{xx} - V_{yy} \equiv V_{cc} - V_{aa} = \frac{3}{2}V_{cc}$ and $V_{zz} \equiv V_{bb} = -\frac{1}{2}V_{cc}$. Thus equations (15) and (16) reduce to

$$P_1'' = -P'' = \frac{3e\,Q_N}{8hI(2I-1)}\gamma_N V_{cc}. \tag{17}$$

3. Experimental

The sample was prepared by melting together the 99.99% pure starting materials in an argon-arc furnace. In order to suppress the formation of TbCo₅ the proportion of cobalt used was approximately 10% by weight above that required for stoichiometry (Buschow and den Broeder 1973). The ingot was annealed under argon for fourteen days at 1100 °C, then quenched in oil. X-ray diffraction revealed weak lines characteristic of the hexagonal Th₂Ni₁₇ phase in addition to the dominant rhombohedral Th₂Zn₁₇ phase. The annealed material was powdered and embedded in epoxy resin prior to mounting in the coaxial resonator of a 2–8 GHz pulsed NMR spectrometer (Carboni *et al* 1989). The spin-echo measurements were performed in zero applied field at 4.2 K.

4. Results

The zero-field NMR spectrum is shown in figure 2. It consists of three distinct quadrupole-split spectra, each of which is characteristic of ¹⁵⁹Tb ($I = \frac{3}{2}$). We assign the strongest spectrum to nuclei in the dominant rhombohedral phase and the two weaker spectra, of approximately equal intensity, to nuclei at the two equally abundant sites in the hexagonal phase.

The rhombohedral spectrum shows marginally resolved features on the high-frequency side of each line. These features (labelled RW) are attributed to nuclei within domain walls because they persist when the microwave power is reduced to a level at which the main spectrum disappears (see inset). The main rhombohedral spectrum (RD) is attributed to nuclei within domains.

We have no means of determining which of the hexagonal spectra (H1, H2) is associated with the 2b site and which with the 2d site. The individual lines belonging to H1 and H2 have been identified by assuming that any asymmetry in each spectrum is small compared to the line separations.

The values of the hyperfine parameters a_t and P_t for all four spectra are given in table 1. We have provisionally assumed that the 'asymmetry' terms (P_{1t} and w) in equation (7) are negligible. This assumption will be re-examined in §5.

Transverse relaxation times T_2 measured at the peak positions of the RD spectrum are approximately 10, 5 and 4 μs for the low-frequency, central and high-frequency lines, respectively.
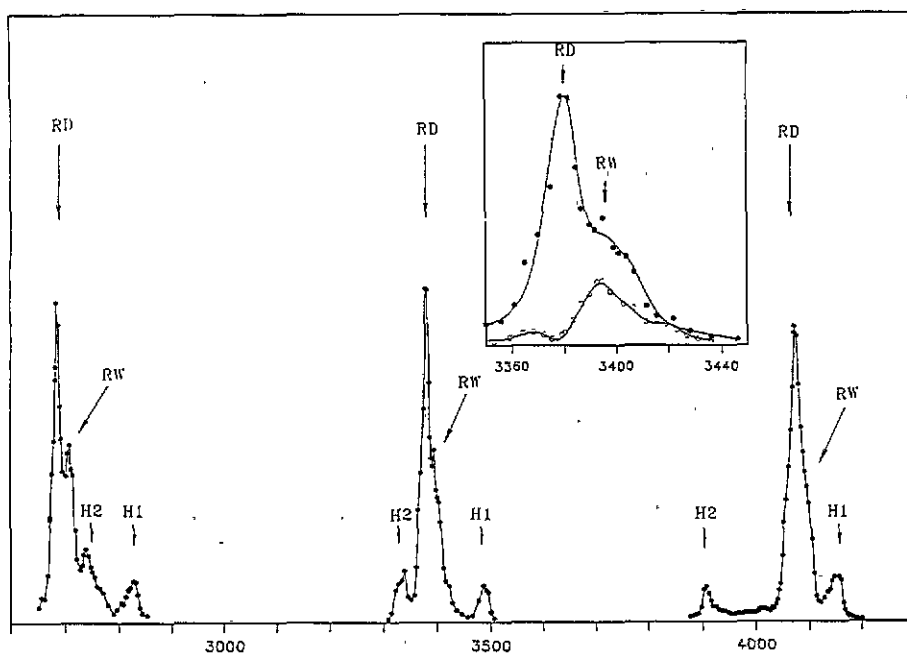
Figure 2. The zero-field NMR spectrum of ^{159}Tb in Tb$_2$Co$_{17}$ at 4.2 K. The main splitting (~ 600 MHz) is due to the quadrupole interaction; the smaller splittings of the central line and of the quadrupole satellites are associated with Tb^{3+} ions in different environments. The symbols RD and RW respectively identify lines belonging to the spectra from nuclei in domains and in walls in the dominant rhombohedral phase; H1 and H2 identify lines belonging to the spectra from the two different crystallographic sites in the hexagonal phase. Inset: power dependence of the central RD and RW lines. Full circles: high power; open circles: low power.

Table 1. Measured hyperfine parameters (MHz).

Phase	Spectrum	a_t	P_t
Rhombohedral	RD	3383 ± 3	347 ± 3
	RW	3387 ± 3	343 ± 3
Hexagonal	H1	3494 ± 6	332 ± 6
	H2	3326 ± 6	292 ± 6

5. Discussion

The analysis of our results may be outlined as follows. We first consider the hexagonal phase of Tb$_2$Co$_{17}$, for which the exchange and crystal-field parameters can be estimated from the corresponding values for Ho$_2$Co$_{17}$. From these we can compute the intra-ionic contributions to the the measured hyperfine parameters and deduce the extra-ionic hyperfine field and the electric-field gradient at each site. A similar procedure is followed for the rhombohedral phase, except that a complete set of parameters is not available. We are therefore obliged to base our calculations on a truncated Hamiltonian which includes only the dominant crystal-field term in B_2^0 and to assume that the exchange field is similar to that in the hexagonal phase.

5.1. The hexagonal phase

Since there are no direct measurements of exchange or crystal-field parameters for Tb_2Co_{17}, we have estimated them by scaling from isostructural Ho_2Co_{17}. The basis of our scaling procedure is to assume the constancy of the exchange field X and of the crystal-field parameters A_n^m. (See equations (2) and (5).) Our NMR results show that the 2b and 2d sites are not magnetically identical; we therefore make use of the data on Ho_2Co_{17} given by Radwański and Franse (1989), the only work so far published which differentiates between the two sites. However, we do not make use of their site assignments, as they are based on an appeal to the point-charge calculations of Greedan and Rao (1973), notwithstanding the conflict of signs referred to in §2.1. We have therefore relabelled the two sets of parameters by the non-committal symbols I and II in table 2. We also note that the common value of α assigned to both sites by Radwański and Franse (1989) is an artefact of their fitting procedure, which is based on a macroscopic molecular-field coupling between the total magnetization of the lanthanide sublattice and that of the cobalt sublattice. (See also Franse et al (1992).) The quoted value of α, therefore, is presumably an average value for the two sites.

Table 2. Exchange and crystal-field parameters for hexagonal R_2Co_{17}. Units: K.

R	Site	α	B_2^0	$10^4 B_4^0$	$10^6 B_6^0$	$10^6 B_6^6$	Ref.
Ho	Both	52 ± 2	0.12 ± 0.6	-9 ± 6	10 ± 6	28 ± 13	a
Ho	Both	54	—	—	—	61	b
Ho	I	53.3	0.2	-8.2	-18.1	137	c
Ho	II	53.3	0.58	6	-13.5	137	c
Tb	I	108	1.1	38	-20	160	d
Tb	II	108	3.2	-28	-15	160	d

[a] Clausen and Lebech (1982).
[b] Radwański et al (1985).
[c] Radwański and Franse (1989).
[d] Scaled from Ho_2Co_{17} (see text).

The scaled parameters for Tb_2Co_{17} are given in the last two rows of table 2. The operator-equivalent coefficients $\langle J||\alpha_n||J\rangle$ and g_J used in the scaling calculations allow for intermediate coupling; the radial averages $\langle r^n\rangle$ are taken from the relativistic calculations of Freeman and Desclaux (1979). Numerical values are given in table 3.

Table 3. Ionic parameters.

Ion	g_J	$10^2\langle J||\alpha_2||J\rangle$	$10^{20}\langle r^2\rangle$ (m²)	$10^4\langle J||\alpha_4||J\rangle$	$10^{40}\langle r^4\rangle$ (m⁴)	$10^6\langle J||\alpha_6||J\rangle$	$10^{60}\langle r^6\rangle$ (m⁶)
Tb^{3+}	1.492	-1.0253	0.2302	1.199	0.1295	-1.056	0.1505
Ho^{3+}	1.242	-0.204	0.2085	-0.3082	0.1081	-1.203	0.1181

Computed quantities for Tb^{3+} are summarized in table 4. In the absence of information to the contrary we have provisionally assumed, with Radwański and Franse (1989), that α has the same value at both sites. Since E_1, the energy of the first excited state of the ion, is over 100 K at both sites, only the ground state needs to be considered in the analysis of our NMR measurements. The moment at site I is almost unquenched; the quenching of the moment at site II is small ($\sim 0.6\%$) but not insignificant. The intra-ionic

parameters a', P' and P'_1 are obtained from equations (11)–(13) with $A = 528 \pm 3$ MHz and $C = 5.45 \pm 0.10$ MHz (after Pelletier-Allard and Pelletier 1985). Second-order corrections, including the octupolar parameter w, have been calculated and found to be insignificant compared to the experimental uncertainties.

Table 4. Excited-state energies, ground-state expectation values and hyperfine parameters for Tb^{3+} in Tb_2Co_{17}.

	Hexagonal		Rhombohedral		
	H1 (site I)	H2 (site II)	RD	RW	Units
E_1	113	162	130		K
$\langle J_z \rangle$	5.9988	5.9636	5.988		—
$\langle J_z^2 \rangle$	35.9898	35.6404	35.88		—
$\langle J_x^2 - J_y^2 \rangle$	0.2	−2.21	−1.23		—
a'	3167 ± 18	3149 ± 18	3162 ± 18		MHz
P'	360 ± 8	354 ± 8	358 ± 8		MHz
P'_1	1.12 ± 0.02	$−13.5 \pm 0.03$	$−5.7 \pm 0.1$		MHz
a_t	3494 ± 6	3326 ± 6	3383 ± 3	3387 ± 3	MHz
P_t	332 ± 6	292 ± 6	347 ± 3	343 ± 3	MHz
a''	327 ± 19	177 ± 19	221 ± 18	225 ± 18	MHz
B''	32 ± 2	17 ± 2	22 ± 2		T
P''	$−28 \pm 10$	$−62 \pm 10$	$−11 \pm 9$	$−15 \pm 9$	MHz
$\gamma_N V_{cc}$	6.5 ± 2.3	14.3 ± 2.3	3 ± 2		10^{21} V m^{-2}
γ_N/γ_E	400 ± 140	300 ± 50	160 ± 100		—
	$[980 \pm 140]$	$[110 \pm 50]$			

Our calculations were made with α parallel to the easy direction b, and therefore apply to spins in the interior of domains. Because of the possiblity that our NMR signals came from domain walls, we have also computed the intra-ionic hyperfine parameters with α parallel to a. The differences between the parameters calculated for the two directions are less than the uncertainties in the measured parameters. We conclude that the analysis of our data for the hexagonal phase does not depend critically on whether the NMR signals come from domains or from walls.

In order to compare the measured hyperfine parameters with the computed data and so to deduce the extra-ionic contributions to the dipolar and quadrupolar splittings, we need to know which spectrum is associated with which site or, more precisely, with which set of crystal-field parameters. We tentatively assign spectrum H1, which has the larger values of a_t and P_t, to the site labelled I, which has the lower quenching and hence the larger values of a' and P'. With that assignment we obtain the extra-ionic parameters a'' and P'' given in table 4. The corresponding values of B'' and $\gamma_N V_{cc}$ are obtained from equations (14) and (17), taking $\gamma/2\pi = 10.13$ MHz T^{-1} (after Bleaney 1988) and $Q_N = 1.43 \times 10^{-28}$ m^2 (Tanaka *et al* 1983).

The uncertainties given in table 4 are dominated by the uncertainties in the free-ion hyperfine coupling constants A and C. No allowance has been made for the unknown uncertainties in the exchange and crystal-field parameters. Fortunately, the intra-ionic hyperfine parameters depend only weakly on these quantities because the quenching of the ionic moment is of second order in the small quantities B_n^m/α. For example, a 40% error in the B_n^m/α would alter B'' and P'' by less than half a standard deviation in the worst case (site II). The only results seriously compromised by the unknown uncertainties in the crystal-field parameters are therefore the antishielding ratios γ_N/γ_E, which depend directly on the B_2^0.

We are now in a position to quantify the term P_{1t} (which we provisionally assumed to be negligible) and the associated asymmetry in the hyperfine spectrum. A straightforward perturbation calculation, allowing for the fact that P_t is small compared to a_t, shows that P_{1t} has negligible effect on the frequencies of the quadrupole satellites; its chief effect is to increase the frequency of the central line by an amount $\delta v \simeq 3P_{1t}^2/a_t$. By equations (10) and (17) $P_{1t} = P_1' - P''$. In the worst case (site II) we obtain $P_{1t} = 49$ MHz, which gives $\delta v \simeq 2.3$ MHz. This is smaller than the uncertainties in the measured hyperfine parameters and we conclude that our provisional neglect of the asymmetry terms was justified.

The values of the antishielding ratio γ_N/γ_E given in table 4 are obtained from equations (5), (6) and (17), using the data in tables 2, 3 and 4. Our provisional site assignments are supported by the fact that the values of γ_N/γ_E for the two hexagonal sites agree within a standard deviation, whereas they differ by about nine standard deviations if the site assignments are interchanged. (See the figures in square brackets in the last row of table 4. We have taken account of the fact that the uncertainties are partly correlated through the common value of C.) It is unlikely that a difference of that order can be explained by the host dependence of the antishielding ratio (cf Carboni *et al* (1988)). Our values for γ_N/γ_E are considerably larger than the theoretical figure of 180 given by Gupta and Sen (1973) for the free Tb^{3+} ion.

Our values for the extra-ionic EFGs at the terbium nucleus in the hexagonal phase of Tb_2Co_{17} may be compared with the values of $\gamma_N V_{cc}(I) = (1.4 \pm 1.0) \times 10^{21}$ V m^{-2} and $\gamma_N V_{cc}(II) = (4.2\pm0.9) \times 10^{21}$ V m^{-2} at the thulium nucleus as deduced from the Mössbauer measurements of Gubbens *et al* (1987) on hexagonal Tm_2Co_{17}. The latter values differ considerably from those in Tb_2Co_{17} (perhaps because of different antishielding factors) but the ratios $V_{cc}(II)/V_{cc}(I)$ (~ 3 for both compounds) are in good agreement. (We have no means of identifying the sites in either compound, but we assume that the larger value of $\gamma_N V_{cc}$ in the Tm compound corresponds to the larger value in the Tb compound, and conversely.) The ratio $V_{cc}(II)/V_{cc}(I) \sim 3$ is also supported by the values of B_2^0 given in table 2. This, together with the fact that all of the available data indicate that V_{cc} is positive at both sites, further confirms the inadequacy of the point-charge model: referring to figure 1 we see that a 3:1 ratio for the electric-field gradients at the two sites would require $Z_{Co} < -0.5$.

Since the exchange field α and the extra-ionic hyperfine field B'' arise mainly from the cobalt sublattice, we would expect B''/α to have roughly similar values at both sites. The provisionally assumed equality of the exchange fields at sites I and II is therefore difficult to reconcile with our finding that the extra-ionic hyperfine field at site I is nearly double that at site II. We have already noted that the fitting procedure of Radwański and Franse (1989) determines only the mean value of α for the two sites and, moreover, that our estimates of the extra-ionic hyperfine parameters are insensitive to the exact values of the exchange and crystal-field parameters. This opens up the possibility of bringing the two values of B''/α into closer agreement by increasing α at site I, with a compensating decrease at site II. If, for example, we leave the crystal-field parameters unaltered, increase $\alpha(I)$ to 134 K (which leaves $B''(I)$ almost unchanged) and reduce $\alpha(II)$ to 82 K (which increases $B''(II)$ to 20 T) we obtain $B''/\alpha \simeq 0.24$ T K^{-1} at both sites. This is a purely illustrative calculation because any readjustment of the individual values of α in the fit to the magnetization data would entail concomitant readjustments of the B_n^m which, in turn, would affect the crystal-field quenching and hence our estimates of the extra-ionic field.

5.2. The rhombohedral phase

As noted above, a complete set of crystal-field parameters is not available for the

Table 5. Extra-ionic hyperfine fields in rhombohedral R_2Co_{17} compounds. Units: tesla.

R	$\sigma(R)$	$\mathcal{A}(R)$	B''	B_n^{Co}	$B_p + B_n^R$	Notes
Y	0	1.7	8.74 ● 0.05	8.74 ± 0.05	0	a
Gd	3.5	3.95	39.2 ± 1	20.3 ± 0.1	18.9 ± 1	b
			25.2 ± 1		4.9 ± 1	b
Tb	3	4.07	37.6 ± 1	20.9 ± 0.1	16.7 ± 1	c
			25.2 ± 1		4.3 ± 1	c

[a] For Y_2Co_{17}, $B_n^{Co} = B'' = B_t$ with $B_t = 2\pi a_t/\gamma = 8.74 \pm 0.05$ T (Figiel *et al* 1976).
[b] For Gd_2Co_{17}, $B'' = B_t - B'$ with $B_t = \pm 7 \pm 1$ T (van Steenwijk *et al* 1977) and $B' = -32.2$ T (after Bleaney 1988). $B_p + B_n^R = B'' - B_n^{Co}$ with B_n^{Co} scaled from Y_2Co_{17} by the factor $\mathcal{A}(Gd)/\mathcal{A}(Y)$ (after Campbell 1969). The upper and lower values for B'' and for $B_p + B_n^R$ correspond to positive and negative values of B_t, respectively (see text).
[c] $B'' = B_n^{Co} + B_p + B_n^R$. B_n^{Co} scaled from Y_2Co_{17} by the factor $\mathcal{A}(Tb)/\mathcal{A}(Y)$; $B_p + B_n^R$ scaled from Gd_2Co_{17} by the factor $\{\sigma(Tb)/\sigma(Gd)\}\{\mathcal{A}(Tb)/\mathcal{A}(Gd)\}$ where $\sigma = (g_J - 1)J$. The upper and lower values for B'' and for $B_p + B_n^R$ respectively correspond to the positive and negative values of B_t for Gd_2Co_{17}.

rhombohedral phase. However, the crystal-field quenching of the terbium moment at site II in the hexagonal phase is dominated by the leading term $B_2^0 O_2^0$ in equation (4) and we may surmise that the same holds good for the rhombohedral phase (equation (3)). Then, in first-order perturbation theory (an adequate approximation when the quenching is small), the ionic ground state is given in terms of the eigenstates $|J, M\rangle$ of J_z by

$$|E_0\rangle = |J, J\rangle + \varepsilon|J, J - 2\rangle \tag{18}$$

where

$$\varepsilon = -\tfrac{3}{4}[J(2J - 1)]^{1/2}(B_2^0/\alpha). \tag{19}$$

A straightforward calculation then gives, to second order in ε,

$$\langle J_z\rangle = J - 2\varepsilon^2 \tag{20}$$

$$\langle J_z^2\rangle = J^2 - 4(J - 1)\varepsilon^2 \tag{21}$$

and

$$\langle J_x^2 - J_y^2\rangle = 2[J(2J - 1)]^{1/2}\varepsilon. \tag{22}$$

Using the value of the anisotropy constant K_1^{Tb} obtained by Franse *et al* (1992) for Tb_2Co_{17} we deduce that $B_2^0 \simeq 1.35$ K; assuming that the exchange field is similar to that in the hexagonal phase (i.e. $\alpha \simeq 108$ K) and setting $J = 6$ in equation (19) we obtain $\varepsilon \simeq -0.076$. The resulting values of $\langle J_z\rangle$, $\langle J_z^2\rangle$ and $\langle J_x^2 - J_y^2\rangle$ are set out in table 4, together with the corresponding hyperfine parameters.

The omission of the terms in B_4^3, B_6^3 and B_6^6 from our calculations means that our computed results do not reflect any anisotropy of the hyperfine parameters in the basal plane; they therefore apply indiscriminately to the domain and wall spectra. The differences between the values of a'' and P'' for domains and walls are in any case comparable to the uncertainties which, as in the case of our results for the hexagonal phase, arise mainly from the uncertainties in the free-ion hyperfine parameters. For that reason we present the extra-ionic field B'', the extra-ionic EFG $\gamma_N V_{cc}$ and the antishielding ratio γ_N/γ_E as averages of domain and wall results.

The value of B'' derived from our NMR spectra in the rhombohedral phase of Tb_2Co_{17} may be compared with that obtained by scaling from NMR and Mössbauer data on the isostructural yttrium and gadolinium compounds (see table 5). Our sign convention is to reckon hyperfine fields positive if they are parallel to the lanthanide moment or, equivalently, antiparallel to the cobalt moment. (The latter definition is required in the case of Y_2Co_{17}.) The sign of B_t ($= 2\pi a_t/\gamma$) for Gd_2Co_{17} was considered to be uncertain by van Steenwijk *et al* (1977) but we believe that a value of 18.9 T for $B_p + B_n^R$ is implausibly large for the lanthanide contribution to the extra-ionic field and therefore think it probable that B_t is negative. If that is correct, the scaled value of 25.2 ± 1 T for the extra-ionic field in rhombohedral Tb_2Co_{17} is in good agreement with the figure obtained from our NMR data.

The uncertainties quoted in table 4, which are dominated by the uncertainties in the hyperfine coupling constants A and C, include no allowance for the unknown errors in the assumed values of α and of B_2^0 or for the error implicit in the neglect of all higher terms in the crystal-field interaction. Assuming, however, that the crystal-field quenching is in fact dominated by B_2^0 (as it is in the hexagonal phase), a 100% error in B_2^0/α would alter B'' and P'' by less than half a standard deviation. As in the hexagonal phase, only the antishielding ratio is seriously affected by the unknown uncertainty in B_2^0.

6. Conclusions

We have measured the dipolar and quadrupolar hyperfine splittings of terbium in the hexagonal and rhombohedral phases of Tb_2Co_{17} at 4.2 K. Using parameters scaled from those obtained from magnetization measurements on hexagonal Ho_2Co_{17} we have estimated the crystal-field quenching of the Tb^{3+} ion at both inequivalent sites in hexagonal Tb_2Co_{17} and thus obtained estimates of the extra-ionic hyperfine fields and electric-field gradients. The extra-ionic hyperfine field at one site is found to be almost twice that at the other, in contrast with the assumed equality of the exchange fields derived from magnetization measurements. It would doubtless be possible to obtain an equally good or better fit to the magnetization data with unequal exchange fields.

The ratio of nuclear to electronic antishielding factors for Tb ions in the hexagonal sites is found to be considerably larger than that calculated theoretically, a finding which may be attributed either to the host dependence of antishielding factors or to the fact that a re-fit of the magnetization data along the lines suggested at the end of §5.1 might yield significantly different values of the crystal-field parameter B_2^0.

A relatively crude estimate of the crystal-field quenching of the Tb^{3+} ion in the rhombohedral phase leads to an antishielding ratio consistent with the theoretical value of Gupta and Sen (1973) and to an extra-ionic hyperfine field which agrees well with the value deduced from NMR and Mössbauer measurements on the isostructural Y_2Co_{17} and Gd_2Co_{17} compounds.

Our results confirm that the electric-field gradient V_{cc} is positive at the unique lanthanide site in the rhombohedral phase and at both lanthanide sites in the hexagonal phase. The latter result, together with our determination of the ratio $V_{cc}(II)/V_{cc}(I)$, provides further evidence for the unreliability of the point-charge model. Unambiguous identification of the two sets of crystal-field parameters with the crystallographic 2b and 2d sites must await a proper band-theoretical calculation of the electric-field gradient.

The uncertainties in our determination of the extra-ionic quantities (a'', P'', B'' and $\gamma_N V_{cc}$) are probably dominated by the uncertainties in the free-ion hyperfine coupling constants A and C; it is unlikely that they are seriously affected by the unknown uncertainties

in the exchange and crystal-field parameters. It would however be desirable to have more complete and reliable values for α and the B_n^m in both phases of Tb_2Co_{17}. Until more accurate values of B_2^0 become available our estimates of antishielding ratios must be regarded as provisional.

Acknowledgments

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