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Hyperfine splitting of terbium in $\text{Tb}_2\text{Fe}_{17}\text{C}_x$

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Abstract. We have studied the zero-field hyperfine splitting of ^{159}Tb in ferrimagnetic $\text{Tb}_2\text{Fe}_{17}\text{C}_x$ ($x = 1, 1.5, 2$) using spin-echo NMR at 4.2 K. Distinct spectra arising from the different sites characterized by the numbers of carbon nearest neighbours ($\text{NN} = 0, 1, 2, 3$) are observed. The measured hyperfine parameters a_i and P_i for all four spectra are given for $x = 1.5$ and 2. Analysis of the quadrupolar splitting indicates that in $\text{Tb}_2\text{Fe}_{17}\text{C}_{1.5}$ the dominant contribution to the magnetocrystalline anisotropy arises from the $\text{NN} = 3$ sites.

1. Introduction

The rare-earth (R) compounds of general formula R_2Fe_{17} can accommodate appreciable amounts of interstitial carbon (de Mooij and Buschow 1988). Maximum occupancy of the 9e interstitial sites corresponds to the formula $\text{R}_2\text{Fe}_{17}\text{C}_3$, in which structure each rare-earth ion is surrounded by three nearest-neighbour (NN) carbon atoms. Like their parent compounds the carbides may crystallize in either the hexagonal $\text{Th}_2\text{Ni}_{17}$ or the rhombohedral $\text{Th}_2\text{Zn}_{17}$ structure; the rhombohedral structure predominates in the lighter rare-earth, Gd and Tb ternary compounds while the hexagonal structure predominates from $\text{Ho}_2\text{Fe}_{17}\text{C}_x$ to $\text{Lu}_2\text{Fe}_{17}\text{C}_x$. The two structures coexist in the Dy ternary compound. In the hexagonal structure there are two inequivalent rare-earth sites (2b and 2d in Wyckoff's notation) which occur in equal abundance; in the rhombohedral structure there is a single rare-earth site. In some compounds there is a carbon-induced structural transformation from the hexagonal phase (low carbon concentration) to the rhombohedral phase (high carbon concentration) (Coene *et al* 1990, Sun *et al* 1990, Haije *et al* 1990).

Carbon uptake causes a considerable lattice expansion and an increase in Curie temperature (Li and Coey 1991). The carbon-induced changes in the crystal-field anisotropy of the rare-earth sublattice have been observed in the magnetization measurements on $\text{Sm}_2\text{Fe}_{17}\text{C}_{0.5}$ of Grössinger *et al* (1991), and of Ding and Rosenberg (1991). Previous hyperfine studies at the lanthanide sites include Mössbauer spectroscopy of ^{169}Tm in $\text{Tm}_2\text{Fe}_{17}\text{C}_x$ (Gubbens *et al* 1989) and of ^{155}Gd in $\text{Gd}_2\text{Fe}_{17}\text{C}_x$ (Dirken *et al* 1989) and NMR of ^{89}Y in $\text{Y}_2\text{Fe}_{17}\text{C}_x$ (Kapusta *et al* 1991). In the present paper we report the extension of our previous hyperfine study of $\text{Tb}_2\text{Fe}_{17}$ (Li *et al* 1995) to $\text{Tb}_2\text{Fe}_{17}\text{C}_x$ ($x = 1, 1.5, 2$).

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2. Theory

The high Curie temperatures (~ 600 K) in $\text{Tb}_2\text{Fe}_{17}\text{C}_x$ ($x = 1, 1.5, 2$) (Cao *et al* 1993) indicate that the exchange interaction is greater than the crystal-field interaction. So far as we are aware, no crystal-field parameters have been published for the rhombohedral $\text{Tb}_2\text{Fe}_{17}\text{C}_x$. We shall therefore assume that, as is the case for $\text{Tb}_2\text{Co}_{17}$ (Li *et al* 1993), the crystal-field quenching of the terbium moment is dominated by the crystal-field parameter term B_2^0 . In the $\text{Tb}_2\text{Fe}_{17}\text{C}_x$ compounds the direction of easy magnetization is perpendicular to the c -axis. The first-order ionic ground state is then given in terms of the eigenstates $|J, M\rangle$ of J_z by

$$|E_0\rangle = |J, J\rangle + \varepsilon|J, J-2\rangle \quad (1)$$

where

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

The exchange parameter α used here is related to the commonly used exchange field H_{exch} by $\alpha = -2\mu_B(g_J-1)H_{exch}$. A straightforward calculation then gives, to second order in ε ,

$$\langle J_z \rangle = J - 2\varepsilon^2 \quad (3)$$

and

$$\langle J_z^2 \rangle = J^2 - 4(J-1)\varepsilon^2. \quad (4)$$

Following the notation of McCausland and Mackenzie (1979) we express the total hyperfine field as

$$B_t = \frac{2\pi}{\gamma}a_t = B' + B'' = \frac{2\pi}{\gamma}A\langle J_z \rangle + B'' \quad (5)$$

where γ is the gyromagnetic ratio of the Tb nucleus and A is the free-ion dipolar coupling constant, which is related to the constant a'_0 by $A = a'_0/J$ (see, for example, McCausland and Mackenzie 1979). The principal contributions to the extra-ionic hyperfine field B'' are the transferred hyperfine fields B_n^K and B_n^{Fe} from R and Fe neighbours, and the field B_p due to conduction electrons polarized by the spin of the parent Tb ion. The hyperfine parameter P_t may be expressed as

$$P_t = P' + P'' = C[3\langle J_z^2 \rangle - J(J+1)] + P'' \quad (6)$$

where C is the free-ion quadrupolar coupling constant which is related to the constant P'_0 by $C = P'_0/J(2J-1)$ (see, for example, McCausland and Mackenzie 1979). The extra-ionic quadrupole parameter P'' is related to the crystalline-electric-field gradient (EFG) by

$$P'' = -\frac{3eQ_N}{8hI(2I-1)}\gamma_N V_{cc} \quad (7)$$

where Q_N is the nuclear quadrupole moment, 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) and V_{cc} is the component of the EFG along the principal symmetry axis.

3. Experimental details

The samples under study are $\text{Tb}_2\text{Fe}_{17}\text{C}_x$ ($x = 1, 1.5, 2$) which were prepared by the melt-spinning method. The details of this melt-spinning method can be found elsewhere (Cao *et al* 1993). The samples were examined by x-ray diffraction and have the rhombohedral $\text{Th}_2\text{Zn}_{17}$ -type structure. The samples were powdered and then 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.

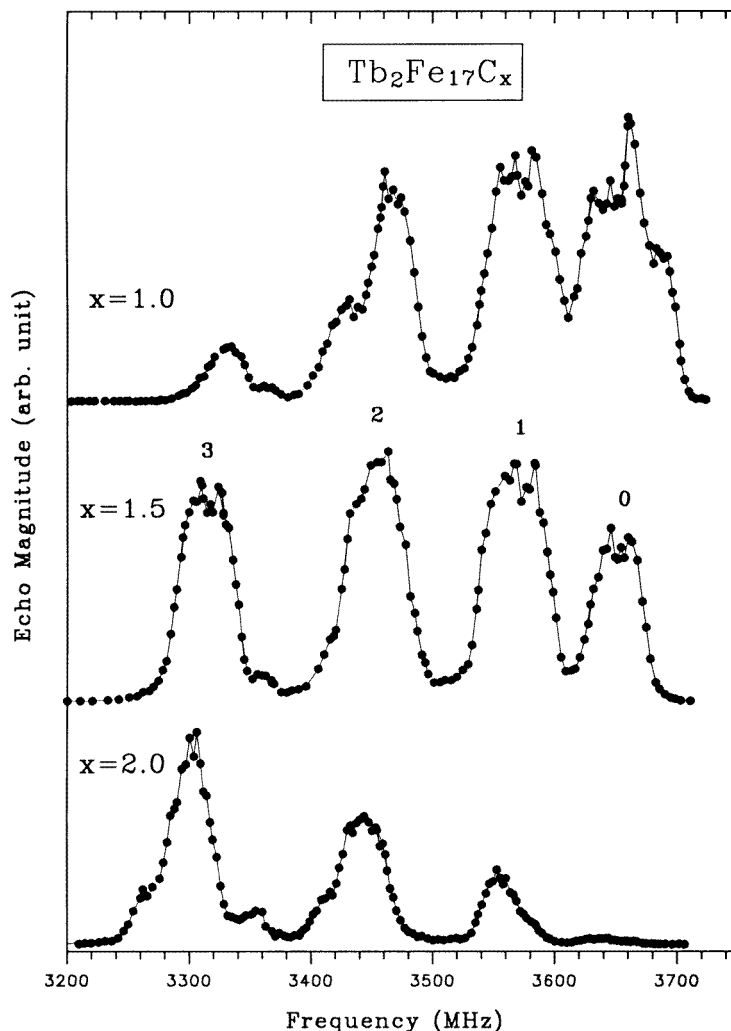


Figure 1. The zero-field NMR spectra for the central lines of ^{159}Tb in $\text{Tb}_2\text{Fe}_{17}\text{C}_x$ ($x = 1, 1.5, 2$) at 4.2 K. The peak labels are identified as the different sites characterized by the numbers of nearest carbon neighbours $NN = 0, 1, 2, 3$.

4. Results and discussion

The zero-field NMR spectra for the central lines of ^{159}Tb in $\text{Tb}_2\text{Fe}_{17}\text{C}_x$ ($x = 1, 1.5, 2$) are shown in figure 1. Four distinct resonant frequencies, corresponding to the four possible occupancies of the NN interstitial sites by carbon atoms, are clearly evident. The frequency separations of neighbouring peaks $\Delta\nu_{01}^{(x)}$, $\Delta\nu_{12}^{(x)}$ and $\Delta\nu_{23}^{(x)}$ are independent of carbon concentration within experimental error (see table 1). The full quadrupole-split spectra of ^{159}Tb in $\text{Tb}_2\text{Fe}_{17}\text{C}_x$ ($x = 1.5, 2$) are shown in figure 2. The hyperfine parameters a_i and P_i deduced from those spectra are listed in table 2 together with those determined previously for $\text{Tb}_2\text{Fe}_{17}$ (Li *et al* 1995).

The principal aim of our analysis is to estimate the extra-ionic quadrupolar parameter

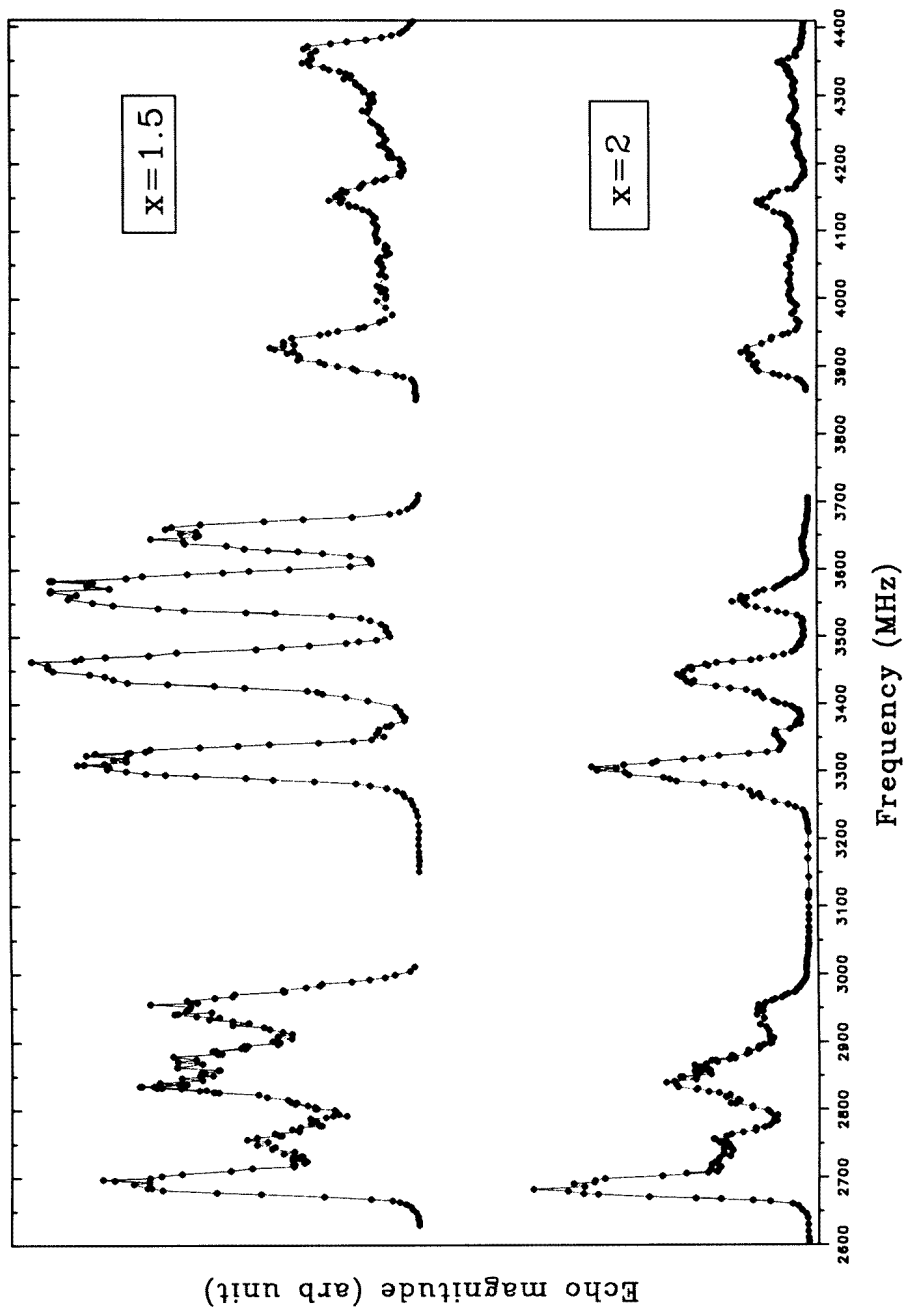


Figure 2. The zero-field NMR quadrupole-split spectra of ^{159}Tb in $\text{Tb}_2\text{Fe}_{17}\text{C}_x$ ($x = 1.5, 2$) at 4.2 K.

Table 1. Hyperfine parameters for the central-line spectra of ¹⁵⁹Tb in Tb₂Fe₁₇C_x ($x = 1, 1.5, 2$) at different sites (NN = 0, 1, 2, 3).

Carbon content x	a_i (MHz)				$\Delta\nu_{01}^{(x)\dagger}$ (MHz)	$\Delta\nu_{12}^{(x)\dagger}$ (MHz)	$\Delta\nu_{23}^{(x)\dagger}$ (MHz)
	Different sites (NN)						
	0	1	2	3			
1	3660(3)	3575(3)	3468(3)	3330(3)	85(4)	107(4)	138(4)
1.5	3650(3)	3570(3)	3455(3)	3315(3)	80(4)	115(4)	140(4)
2	3642(3)	3557(3)	3443(3)	3301(3)	85(4)	114(4)	142(4)

$\dagger \Delta\nu_{mn}^{(x)}$ denotes frequency differences between the neighbouring peak positions, x the carbon concentration, and m and n the neighbouring peak labels in figure 1.

Table 2. Measured hyperfine parameters for Tb₂Fe₁₇C_x ($x = 0, 1.5, 2$).

Compound	Hyperfine parameter	Site \dagger (NN = 0)	Site \dagger (NN = 1)	Site \dagger (NN = 2)	Site \dagger (NN = 3)
Tb ₂ Fe ₁₇ \ddagger	a_i (MHz)	3653(3)			
	B_i \S (T)	360.6(3)			
	P_i (MHz)	348(3)			
Tb ₂ Fe ₁₇ C _{1.5}	a_i (MHz)	3650(3)	3570(3)	3455(3)	3315(3)
	B_i \S (T)	360.3(3)	352.4(3)	341.1(3)	327.2(3)
	P_i (MHz)	350(3)	354(3)	349(3)	307(3)
Tb ₂ Fe ₁₇ C ₂	a_i (MHz)	3642(3)	3557(3)	3443(3)	3300(3)
	B_i \S (T)	359.5(3)	351.1(3)	339.9(3)	325.8(3)
	P_i (MHz)	350(3)	353(3)	350(3)	308(3)

\dagger The different sites are characterized by the numbers of nearest carbon neighbours, NN.

\ddagger Li *et al* (1995).

\S $B_i = 2\pi a_i/\gamma$ where $\gamma/2\pi = 10.13$ MHz T⁻¹ (after Bleaney 1988).

P'' , and hence $\gamma_N V_{cc}$, at the four terbium sites. We begin by assuming that, as is the case for Tb₂Fe₁₇ (Li *et al* 1995), the contribution of the rare-earth sublattice to the extra-ionic dipolar field B'' is negligible in comparison to that of the iron sublattice. The latter quantity may be estimated by multiplying the corresponding value for Y₂Fe₁₇C_{1.5} (Kapusta *et al* 1991) by the ratio $\mathcal{A}(\text{Tb})/\mathcal{A}(\text{Y})$ (see Campbell 1969). For the four terbium sites in Tb₂Fe₁₇C_{1.5}, using equation (5) we may then estimate B' and $\langle J_z \rangle$ and hence, from equations (3) and (4), $\langle J_z^2 \rangle$ and P' . Finally, we obtain P'' and $\gamma_N V_{cc}$ from equations (6) and (7), respectively. The values so derived are listed in table 3, taking $Q_N = 1.43 \times 10^{-28}$ m² (Tanaka *et al* 1983), $A = 528 \pm 3$ MHz and $C = 5.45 \pm 0.10$ MHz (after Pelletier-Allard and Pelletier 1985).

Our primary concern is with the values of V_{cc} in the last row of table 3. Within experimental error, V_{cc} is independent of the number of carbon nearest neighbours up to NN = 2, but increases sharply for NN = 3. Because the rare-earth contribution to the magnetocrystalline anisotropy is directly related to the EFG at the rare-earth site, we conclude that the dominant contribution to that anisotropy arises from sites with NN = 3.

It should be noted that Dirken *et al* (1989) arrived at a rather different conclusion on the basis of their ¹⁵⁵Gd Mössbauer study of the Gd₂Fe₁₇C_x ($x = 0.6, 1.2$) systems; they found that the largest contribution to the anisotropy arose from sites with NN = 1. However, their analysis of the Mössbauer data rests on the assumption that the carbon atoms are randomly

Table 3. Values of B' , $\langle J_z \rangle$ and $\gamma_N V_{cc}$, and hyperfine parameters for Tb^{3+} in $\text{Tb}_2\text{Fe}_{17}\text{C}_{1.5}$.

Compound	Parameter	Site (NN=0)	Site (NN=1)	Site (NN=2)	Site (NN=3)
$\text{Y}_2\text{Fe}_{17}\text{C}_{1.5}$	$B_t^\dagger = B_n^{Fe}$ (T)	20.1	17.3	13.2	8.0
$\text{Tb}_2\text{Fe}_{17}\text{C}_{1.5}$	$B_n^{Fe\ddagger}$ (T)	48.1	41.4	31.6	19.2
	B' (T)	312.2(2.0)	311.0(2.0)	309.5(2.0)	308.0(2.0)
	$\langle J_z \rangle$	5.99(0.05)	5.96(0.05)	5.95(0.05)	5.91(0.05)
	P' (MHz)	358(8)	353(8)	350(8)	345(8)
	P_t (MHz)	350(3)	354(3)	349(3)	307(3)
	P'' (MHz)	-8(9)	1(9)	-1(9)	-38(9)
	$\gamma_N V_{cc}$ (10^{21} V m $^{-2}$)	1.6(2.1)	-0.2(2.1)	0.2(2.1)	8.8(2.1)

\dagger For $\text{Y}_2\text{Fe}_{17}\text{C}_{1.5}$, $B_n^{Fe} = B_t$ where the values of B_t are from Kapusta *et al* (1991).

\ddagger For $\text{Tb}_2\text{Fe}_{17}\text{C}_{1.5}$, the values of B_n^{Fe} are scaled from those for $\text{Y}_2\text{Fe}_{17}\text{C}_{1.5}$ by the ratio $\mathcal{A}(\text{Tb})/\mathcal{A}(\text{Y})$.

distributed among the available interstitial sites, and that the distribution of carbon atoms conforms to the statistical expectation. There is good reason to doubt the validity of that assumption. The work of Kapusta *et al* (1991) on $\text{Y}_2\text{Fe}_{17}\text{C}_x$ shows that, for that system at least, a large difference between the experimental line intensities and the theoretical statistical expectations of the random occupation of carbon sites exists for $x \geq 1$. In the present work, we have estimated the relative abundance of the four sites by measuring the areas of the NMR lines. Our results shown in table 4 are not consistent with random occupation of the possible carbon sites. We suggest that this tendency may also exist in the Gd compounds, and that it might account for the discrepancy between the present work and that of Dirken *et al* (1989).

Table 4. The calculated probability ratios for different numbers of NN, $\mathcal{P}(\text{NN}, x)$, and the corresponding resonance line area ratios, $\mathcal{S}(\text{NN}, x)$, in $\text{Tb}_2\text{Fe}_{17}\text{C}_x$.

Carbon content x	Calculated probability ratios	Resonance line area ratios
	$\mathcal{P}(0, x): \mathcal{P}(1, x): \mathcal{P}(2, x): \mathcal{P}(3, x)$	$\mathcal{S}(0, x): \mathcal{S}(1, x): \mathcal{S}(2, x): \mathcal{S}(3, x)$
1	1:1.5:0.7:0.2	1:0.9:0.8:0.2
1.5	1:3.0:3.0:1.0	1:1.5:1.5:1.3
2	1:6.0:12.0:8.0	1:7.2:13.0:16.0

5. Conclusions

We have measured the dipolar and quadrupolar hyperfine splittings of ^{159}Tb at the different sites which are characterized by the numbers of nearest carbon neighbours in rhombohedral $\text{Tb}_2\text{Fe}_{17}\text{C}_x$ ($x = 1.5, 2$) at 4.2 K. We have estimated the crystal-field quenching of the terbium moment and the EFGs at the terbium nucleus at the different sites for $\text{Tb}_2\text{Fe}_{17}\text{C}_{1.5}$. We have found that the site $\text{NN} = 3$ has a dominant contribution to the EFG and crystal field. We conclude that the crystal-field-induced anisotropy of the R sublattice is mainly contributed by the $\text{NN} = 3$ site at which the three nearest interstitial positions around a rare-earth ion are fully occupied by carbon atoms.

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