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The field dependence of the hyperfine splitting of terbium in TbNi₅

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Abstract. The hyperfine splitting of the ground state of terbium in a single crystal of TbNi₅ has been studied using ¹⁵⁹Tb spin-echo NMR at 1.3 K and in fields up to 8 T. The measurements are in perfect agreement with computations including corrections for the effect of *J*-mixing. From the field dependence of the quadrupolar splitting we have derived the electric field gradient at the terbium nucleus: $V_{cc}'' = (9.77 \pm 0.2) \times 10^{21} \text{ V m}^{-2}$ and the ratio of antishielding factors: $\gamma_N/\gamma_E = 174 \pm 6$. The value obtained for γ_N/γ_E is significantly different from that measured for the insulating compound Tb(OH)₃. The contributions of the spin- and orbitally polarized conduction electrons to the total hyperfine field: $B_{ce} = 3.17 \text{ T}$ and $B_{orb} = 0.63 \text{ T}$ are obtained from the field dependence of the dipolar splitting.

1. Introduction

The intermetallic compounds containing 4f and 3d transition elements can be divided into two categories, those in which the 3d element has a permanent magnetic moment and those in which the 3d element behaves as a Pauli paramagnet. There are however a number of compounds, of which the RNi₅ series is a typical example, where the behaviour of the 3d moment is strongly influenced by the environment.

In the RNi₅ the 3d electrons in the conduction band can be polarized by an applied field and by the 4f moments when the rare earth is magnetic. The resulting induced magnetization is then enhanced by exchange with the surrounding spins. The compounds LaNi₅ and YNi₅, in which the rare earth is non-magnetic, are strongly exchange-enhanced Pauli paramagnets; the magnetic susceptibility per formula unit at 4.2 K is of the order of $40 \times 10^{-4} \mu_B \text{ T}^{-1}$, about five times that of metallic nickel (Gignoux *et al* 1976). Apart from PrNi₅ which displays Van Vleck paramagnet behaviour down to the lowest temperatures, all of the compounds with a magnetic rare earth order ferromagnetically at low temperatures. The gadolinium compound has the highest ordering temperature in the series (32 K).

The RNi₅ series has been extensively studied: see for example the review by Franse and Radwanski (1993) and the references therein. All of the compounds in the series crystallize in the simple hexagonal CaCu₅ structure (space group *P6/mmm*). There is one rare-earth site per unit cell with symmetry D_{6h} (Wernick and Geller 1959). In spite of the continuing research activity (Kim-Ngan *et al* 1995, Novak and Kuriplach 1994, Herrmannsdorfer *et al* 1994, Zhang *et al* 1994, Radwanski *et al* 1992), there have been only few hyperfine studies on the series. The hyperfine splitting of the lanthanide ion in GdNi₅, ErNi₅, DyNi₅

and TmNi_5 has been studied by Mössbauer spectroscopy by Nowik and Wernick (1965), van Steenwijk *et al* (1977) and Gubbens *et al* (1985, 1989). Besides our recent ^{159}Tb NMR measurements of the hyperfine splitting in TbNi_5 (Carboni *et al* 1995), the only NMR study in the RNi_5 that we are aware of is the early work by Kaplan and co-workers on ^{141}Pr in PrNi_5 (Levin *et al* 1979, Kaplan *et al* 1980).

The present paper is a detailed ^{159}Tb NMR study of the field dependence of the hyperfine splitting of Tb^{3+} in a single crystal of TbNi_5 . A summary of the magnetic properties of TbNi_5 is given in appendix A. TbNi_5 orders at 23 K with the spontaneous magnetization along the a axis of the hexagonal structure. The magnetic properties are highly anisotropic, the basal plane being the much preferred orientation for the magnetization. Within the basal plane, the anisotropy is small (Gignoux *et al* 1979).

2. Theory

The interpretation of our NMR data is based on the conventional approach where it is assumed that the interactions experienced by the rare-earth ion in the solid are small perturbations on the free-ion states. To first order, the magnetic behaviour of the ion in the compound is described by an effective Hamiltonian representing only the lowest J -manifold. However, the small admixture of the J -manifolds by the crystal field (J -mixing) may have a significant effect on the hyperfine splitting. Details of the theory for the hyperfine interaction including J -mixing will be given in a different publication. In the present work the effect of J -mixing on the hyperfine splitting is included in the computation of the dipolar hyperfine parameter by a correction term (Bunbury *et al* 1995).

The theory for the hyperfine interaction of rare-earth ions in solids is described in detail by McCausland and Mackenzie (1979). See also Dormann (1991) and Bunbury *et al* (1989, 1995). In sections 2.2 and 2.3 below, we review the main points of the theory which are relevant to the present work. Following McCausland and Mackenzie (1979) we shall use the crystallographic axes (a , b , c) as the reference frame for the electronic Hamiltonian and a Cartesian coordinate system (x , y , z) with the z axis anti-parallel to the rare-earth moment for the nuclear Hamiltonian. The c axis is the quantization axis for the electronic Hamiltonian. In the next section, we give an outline of the theory for the exchange interaction in the RNi_5 compounds. Our approach follows that of Barthem *et al* (1988).

2.1. The exchange interaction

The exchange interaction in the RNi_5 compounds is formally described by three molecular-field coefficients: n_{NiNi} , n_{RNi} and n_{RR} representing, respectively, the nickel–nickel, the nickel–rare-earth and the rare-earth–rare-earth interactions. The molecular-field coefficients are defined by the following expressions for the magnetization of the nickel and the rare-earth sublattices in the paramagnetic phase:

$$M_{\text{Ni}} = \chi_{\text{Ni}}^0 (\mathbf{H}_i + n_{\text{NiNi}} M_{\text{Ni}} + n_{\text{RNi}} M_{\text{R}}) \quad (1)$$

$$M_{\text{R}} = \chi_{\text{R}} \mathbf{H}_{\text{tot}} = \chi_{\text{R}} (\mathbf{H}_i + n_{\text{RR}} M_{\text{R}} + n_{\text{RNi}} M_{\text{Ni}}). \quad (2)$$

\mathbf{H}_{tot} is the total field acting on the rare-earth ion; \mathbf{H}_i , the internal field at the site of interest, is the applied field corrected for demagnetizing effects. χ_{Ni}^0 is the intrinsic susceptibility of nickel—that is, the susceptibility in the absence of any exchange interaction.

It is convenient to define the exchange-enhanced susceptibility for nickel as

$$\chi_{Ni} = \frac{\chi_{Ni}^0}{1 - n_{NiNi} \chi_{Ni}^0} \quad (3)$$

and to rewrite equation (1) as

$$\mathbf{M}_{Ni} = \chi_{Ni}(\mathbf{H}_i + n_{RNi} \mathbf{M}_R). \quad (4)$$

Inserting equation (4) into equation (2) one obtains the total field at the lanthanide site:

$$\mathbf{H}_{tot} = (1 + \alpha)\mathbf{H}_i + n\mathbf{M}_R \quad (5)$$

where $\alpha = \chi_{Ni} n_{RNi}$, $n = n_{RR} + \alpha n_{RNi}$.

In the microscopic single-ion approach which we follow in the remainder of the paper we write the total field in the form

$$\mathbf{B}_{tot} = \mu_0 \mathbf{H}_{tot} = (1 + \alpha)\mu_0 \mathbf{H}_i + n\boldsymbol{\mu} \quad (6)$$

where the units for n are teslas per Bohr magneton; $\boldsymbol{\mu} = g_J \mu_B \langle \mathbf{J} \rangle$ is the localized rare-earth moment; g_J and $\langle \mathbf{J} \rangle$ are respectively the Landé g -factor and the thermal average of the total electronic angular momentum of the rare earth. This change of units is desirable in order to be consistent with the notation of McCausland and Mackenzie (1979).

2.2. The electronic Hamiltonian

The splitting of the ground manifold of the rare-earth ion is described by the effective electronic Hamiltonian

$$\mathcal{H}_{el} = \mathcal{H}_{cf} + \mathcal{H}_z \quad (7)$$

where \mathcal{H}_{cf} is the crystal-field interaction and

$$\mathcal{H}_z = -\mathbf{B}_{tot} \cdot \boldsymbol{\mu} \quad (8)$$

represents, in the molecular-field approximation, the effective Zeeman interaction of the ionic moment $\boldsymbol{\mu}$ with the total field \mathbf{B}_{tot} at the lanthanide site. The relation between the applied and the total fields is given by equation (6). In the notation of Abragam and Bleaney (1969) the crystal-field interaction at a site with D_{6h} symmetry is

$$\mathcal{H}_{cf} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^6 O_6^6. \quad (9)$$

The electronic Hamiltonian \mathcal{H}_{el} is therefore characterized by six parameters: the four crystal-field parameters, α and n . Numerical values of the parameters for Tb³⁺ in TbNi₅ are given in table 1.

Table 1. The crystal-field parameters B_n^m in kelvin, the dimensionless enhancement factor α and the exchange coefficient n in T μ_B^{-1} for Tb³⁺ in TbNi₅. The crystal-field parameters are weighted means of the parameters obtained by several authors (see Carboni *et al* 1995). α and n are from Nait-Saada (1980).

B_2^0	B_4^0	B_6^0	B_6^6	α	n
3.84	-0.15×10^{-2}	-0.19×10^{-4}	-4.78×10^{-4}	-0.06	0.81

In figure 1 we show, as a function of $B_{tot} = |\mathbf{B}_{tot}|$ with \mathbf{B}_{tot} parallel to the \mathbf{a} axis, the behaviour of the five lowest levels of \mathcal{H}_{el} . The data in the figure were obtained by diagonalizing \mathcal{H}_{el} for various values of B_{tot} using the set of crystal-field parameters given

in table 1. In table 2 we give the ground and first excited state of \mathcal{H}_{el} at $B_{tot} = 0$ and $B_{tot} = 6.34$ T, and the magnitude of the molecular field in TbNi₅ at 1.3 K (see section 3 below). In zero total field, the ground state is a Γ_1 singlet and is almost pure $|M_J = 0\rangle$; the first excited state at 5.8 K is a Γ_6 doublet and is almost pure $|M_J = \pm 1\rangle$.

Table 2. The ground and first excited states of Tb³⁺ in the crystal field of TbNi₅. The first line gives the states in the absence of any field and the second the states in the molecular field of TbNi₅ in the ordered phase.

B_{tot} (T)	$ E_0\rangle$	$ E_1\rangle$
0	$0.0129(6\rangle + -6\rangle) + 0.9998 0\rangle$	$-0.0333 \pm 5\rangle - 0.9994 \pm 1\rangle$
6.34	$0.009 \pm 6\rangle + 0.015 \pm 5\rangle + 0.011 \pm 4\rangle$ $+0.025 \pm 3\rangle + 0.142 \pm 2\rangle + 0.471 \pm 1\rangle$ $+0.014 0\rangle$	$\pm 0.006 \pm 6\rangle \pm 0.021 \pm 5\rangle \pm 0.019 \pm 4\rangle$ $+0.048 \pm 3\rangle + 0.316 \pm 2\rangle + 0.630 \pm 1\rangle$ $+0.0 0\rangle$

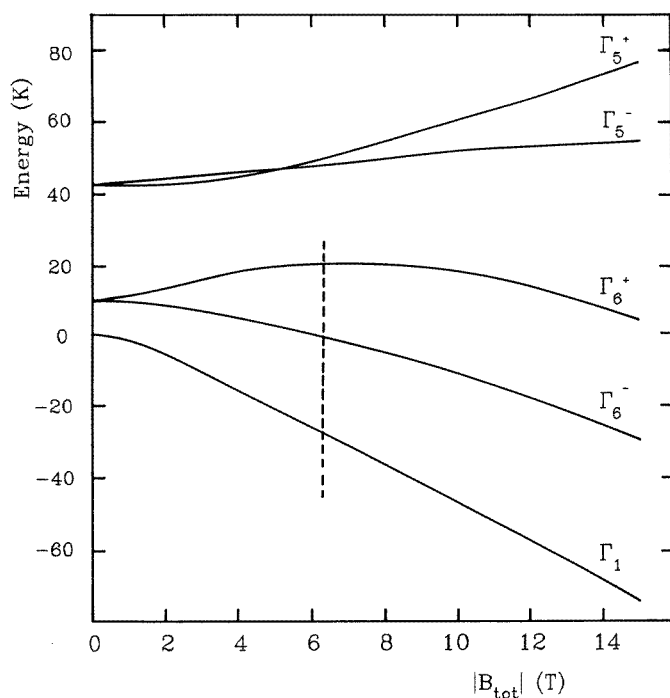


Figure 1. The five lowest electronic energy levels of the terbium ion in the crystal field of TbNi₅ as a function of the total field parallel to the α axis. The vertical broken line represents the molecular field in the ordered phase of TbNi₅ in zero applied field.

2.3. The hyperfine splitting

The hyperfine splitting of the electronic ground state is described, to second order, by the effective nuclear Hamiltonian

$$\mathcal{H}_N = h \left[a_t I_z + P_t \left(I_z^2 - \frac{1}{3} \mathbf{I}^2 \right) + w I_z^3 \right] \quad (10)$$

where \mathbf{I} is the nuclear spin operator. The parameters a_t , P_t and w are respectively the dipolar, quadrupolar and pseudo-octupolar parameters.

The intra-ionic contributions a' and P' to the dipolar and quadrupolar parameters are given by

$$a' = a_0 \frac{\langle J_z \rangle}{J} + \text{second-order term} \quad (11a)$$

$$P' = P_0 \frac{\langle 3J_z^2 - \mathbf{J}^2 \rangle}{J(2J-1)} + \text{second-order term.} \quad (11b)$$

The free-ion hyperfine coupling constants a_0 and P_0 , together with other relevant constants pertaining to the Tb³⁺ ion and the ¹⁵⁹Tb nucleus, are given in appendix A. Explicit expressions for the second-order terms can be found in Bunbury *et al* (1989). The term in I_z^3 in \mathcal{H}_N arises not from the octupolar moment of the nucleus, which is negligible, but from cross-terms between the dipolar and quadrupolar terms in second-order perturbation theory. w is therefore wholly intra-ionic.

Whereas a' , P' and w can be calculated *a priori* using the relevant expectation values for the ground state of \mathcal{H}_{el} , the calculation of a'' and P'' , the extra-ionic contributions to a_t and P_t , is not in general straightforward. However, in the present case the extra-ionic contributions are at least one order of magnitude smaller than the intra-ionic ones so some simplifying approximations may be made without any significant loss of accuracy.

The extra-ionic hyperfine field at the lanthanide's nucleus is written as

$$\mathbf{B}'' = \mathbf{B}_a + \mathbf{B}_{dip} + \mathbf{B}_{ce} + \mathbf{B}_{orb} \quad (12)$$

where \mathbf{B}_{dip} and \mathbf{B}_a are respectively the dipolar field and the applied field. \mathbf{B}_{ce} and \mathbf{B}_{orb} respectively denote the contributions of spin- and orbitally polarized conduction electrons. In the present context we may assume that \mathbf{B}_{ce} and \mathbf{B}_{orb} are collinear with $\langle \mathbf{J} \rangle$ and write

$$\mathbf{B}_{ce} + \mathbf{B}_{orb} = -\kappa \langle J_z \rangle \quad (13)$$

where κ is a phenomenological constant ($\kappa = (K_p + K_n)(g_J - 1) + (2 - g_J)K_{orb}$ in the notation of McCausland and Mackenzie (1979)).

The dipolar field \mathbf{B}_{dip} is the sum of the demagnetizing field \mathbf{B}_{dm} , the field from the dipoles within the Lorentz sphere and the Lorentz field $\mathbf{B}_L = (\mu_0 \mu_B g_J / 3v_0) \langle \mathbf{J} \rangle$ where v_0 is the volume per rare-earth ion. We assume that \mathbf{B}_{dip} is collinear to the rare-earth moment and write

$$\mathbf{B}_{dip} = \mathbf{B}_{dm} + \kappa_{dip} \langle J_z \rangle. \quad (14)$$

When, as in the present case, the external field is also collinear with the rare-earth moment, the extra-ionic contribution to the dipolar hyperfine splitting is

$$a'' = \frac{\gamma}{2\pi} \mathbf{B}'' = \frac{\gamma}{2\pi} \left[\mathbf{B}_a + \mathbf{B}_{dm} + (\kappa_{dip} - \kappa) \langle J_z \rangle \right]. \quad (15)$$

At a site of axial symmetry, P'' , the extra-ionic contribution to the quadrupole parameter, is given by

$$hP'' = \frac{3eQ_n}{4I(2I-1)} \left[\frac{1}{2} (3 \cos^2 \theta - 1) V''_{cc} \right] \quad (16)$$

where V_{cc}'' is the axial component of the extra-ionic electric field gradient tensor seen by the nucleus and θ is the angle between the ionic moment and the axis of the electric field gradient tensor. Q_n is the nuclear quadrupole moment.

It is customary to relate V_{cc}'' and the second-order (quadrupolar) crystal-field parameter B_2^0 to the bare lattice electric field gradient V_{cc} via the proportionality relations

$$V_{cc}'' = \gamma_N V_{cc} \quad (17)$$

and

$$B_2^0 = -\frac{e}{4} \langle J \| \alpha_2 \| J \rangle \langle r^2 \rangle \gamma_E V_{cc} \quad (18)$$

where γ_N and γ_E are respectively the nuclear and the electronic antishielding factors ($\gamma_E = 1 - \sigma$ and $\gamma_N = 1 - \gamma_\infty$ in the notation of Blok and Shirley 1966) and $\langle J \| \alpha_2 \| J \rangle$ is the second-order operator-equivalent coefficient. One can then write equation (15) as

$$P'' = -\frac{3Q_n}{hI(2I-1)\langle J \| \alpha_2 \| J \rangle \langle r^2 \rangle} \frac{\gamma_N}{\gamma_E} \left[\frac{1}{2} (3 \cos^2 \theta - 1) \right] B_2^0. \quad (19)$$

However, recent band-structure calculations by Coehoorn and Buschow (1991) have shown that in metallic compounds the contribution to B_2^0 from the valence-electron charge density may dominate that from the lattice charges. Under such circumstances, the ratio γ_N/γ_E becomes host dependent and the physical meaning of the antishielding factors is not at all obvious. The factors γ_N and γ_E may still be defined formally by equations (17) and (18) but, because of the host dependence of the ratio γ_N/γ_E , there is no simple general proportionality relation between P'' and B_2^0 . In the present work we shall treat P'' as a free parameter which is independent of the applied field.

3. Computation

The computation of the hyperfine parameters as a function of the applied field is carried out as follows. For each value of the applied field a first estimate of the total field (equation (6)) is obtained by assuming that the terbium ion is fully polarized. \mathcal{H}_{el} is then diagonalized and a new value for $\langle J_z \rangle$ and hence for the total field is found. The calculation is iterated until self-consistency is achieved. Finally, the intra-ionic contributions to the hyperfine parameters and the extra-ionic contribution a'' are computed using the ground state of the self-consistent electronic Hamiltonian. In zero applied field, the value thus obtained for B_{tot} is 6.34 T in agreement with the magnetization measurements of Nait-Saada (1980). Numerical values of the various contributions to the internal field B_i are given in table 3. The demagnetizing field was estimated by approximating the specimen to a cylinder of the same cross-section and length. The contribution to the dipolar field from the dipoles within the Lorentz sphere was calculated using the lattice parameters of Haszko (1960). The dipole sum converges (better than 10^{-8} T) within a sphere of radius 81 nm containing 27×10^6 ions. The parameter κ was obtained from a fit to the experimental data. In table 4 we give a breakdown of the contributions to the hyperfine parameters in zero applied field.

4. Experiment

The single crystal used for the measurements is a parallelepiped of dimensions 1.8 mm \times 1.8 mm \times 5.3 mm. The long dimension coincides with the crystal's a axis. The specimen was incorporated as the central conductor of a tunable coaxial microwave cavity

Table 3. The demagnetizing field B_{dm} , the Lorentz field B_L , the field due to the dipoles within the Lorentz sphere B_{LS} and the total field B_{tot} at the terbium site in TbNi₅. All of the figures quoted pertain to the ferromagnetic phase with no applied field. The units are teslas. The coefficient κ was obtained from a fit to the experimental data.

B_{dm}	B_L	B_{LS}	B_{tot}	κ_{dip}	κ
-0.08	0.36	-0.1	6.34	0.032	-0.729

Table 4. The contributions to the hyperfine parameters for the ground state of Tb³⁺ in TbNi₅ in zero applied field. The units are MHz. The superscripts (1) and (2) denote respectively the first- and second-order intra-ionic contributions. a_{J-mix} is the correction for J -mixing.

Dipolar					Quadrupolar				
$a^{(1)}$	$a^{(2)}$	a''	a_{J-mix}	a_t	$P^{(1)}$	$P^{(2)}$	P''	P_t	w
2785.8	-0.12	40.67	-13	2812.4	262.7	2.9	-42.2	223.4	0.58

and immersed in liquid helium at the centre of a superconducting magnet. Details of the cavity and the spin-echo NMR spectrometer are given by Carboni *et al* (1989).

The α axis of the crystal was parallel to within one degree to the magnet's axis. Our computations show that a few degrees of misalignment between the applied field and the α axis do not significantly affect the hyperfine splitting. In a field of 8 T, the estimated shift in the NMR frequencies caused by a three-degree misalignment is less than 0.5 MHz, which is small compared to the experimental uncertainty (3 MHz).

Strong spin-echo signals were detected at 1.3 K from each of the three ¹⁵⁹Tb ($I = \frac{3}{2}$) NMR transitions. The NMR spectra were obtained by stepping the frequency at fixed fields. The spectrum in 8 T is shown in figure 2. At low fields (less than 3 T), the spectrum is partly obscured by signals from domain walls and closure domains. The uncertainty in the measured NMR frequencies, ± 3 MHz in high fields, increases progressively to ± 10 MHz as the field is reduced below 3 T. We were not able to perform a reliable deconvolution of the spectrum in zero applied field; therefore we do not include the zero-field data in our analysis.

5. Results and discussion

5.1. The quadrupolar parameter

Comparison between the value of P_t measured from a single NMR spectrum and computation is not straightforward because the sign of P_t cannot be obtained from the spectrum (Abragam 1961) and also because P'' , the extra-ionic contribution, is not known. However, given an accurate set of crystal-field parameters, P'' and the sign of P_t can be obtained from the field dependence of $|P_t|$ and P' (Bunbury *et al* 1989) provided that the changes in $|P_t|$ with the applied field are large compared to the experimental uncertainties. Since $P'' = P_t - P'$ is independent of the applied field one expects the graph of $|P_t| - P'$ against field to be horizontal if $P_t > 0$ and, conversely, the graph of $-|P_t| - P'$ against field to be horizontal if $P_t < 0$. Both graphs for Tb³⁺ in TbNi₅ are shown in figure 3. It is clear that P_t is positive. The constant value of $P_t - P' = P''$ is -42.2 ± 0.7 MHz. The uncertainty that we quote is based on the experimental errors only. Because the error matrix for the crystal-field

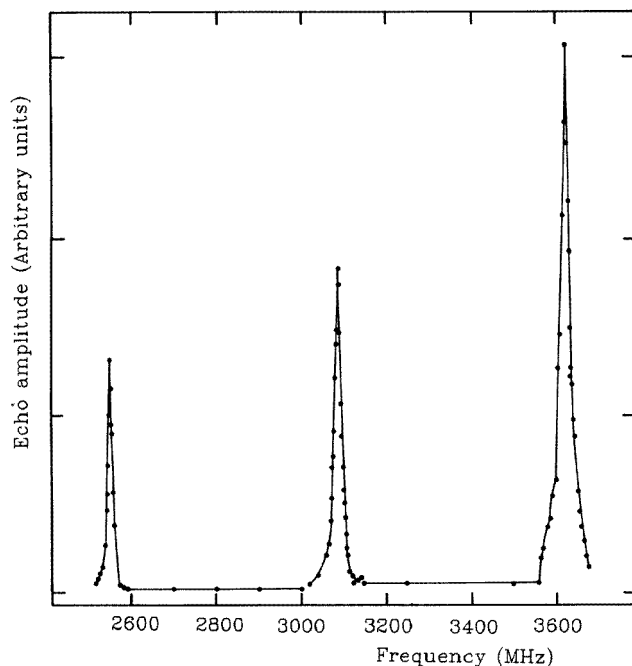


Figure 2. The ^{159}Tb NMR spectrum of Tb^{3+} in TbNi_5 at 1.3 K with a field of 8 T applied along the a axis.

parameters is not known, the uncertainty arising from the inaccuracy in these parameters cannot be quantified.

The constancy of $P_t - P'$ provides a useful test for the accuracy of the crystal-field parameters. By varying independently each of the crystal-field parameters and using the field dependence of $P_t - P'$ as a test, we have estimated upper bounds for the unknown uncertainties on the crystal-field parameters, 4% for B_2^0 and B_6^0 and 8% for B_4^0 and B_6^0 .

Substituting the value of P'' into equation (16) we obtain the electric field gradient at the terbium nucleus, $V''_{cc} = (9.77 \pm 0.2) \times 10^{21} \text{ V m}^{-2}$, in good agreement with the corresponding figure, $V''_{cc} = (10.3 \pm 0.6) \times 10^{21} \text{ V m}^{-2}$, derived from the Mössbauer measurements of van Steenwijk *et al* (1977) on ^{155}Gd in GdNi_5 . From ^{161}Dy , ^{166}Er and ^{169}Tm Mössbauer spectroscopy Gubbens *et al* (1985, 1989) found $V''_{cc} = 6.5 \times 10^{21} \text{ V m}^{-2}$, $14.8 \times 10^{21} \text{ V m}^{-2}$ and $17.7 \times 10^{21} \text{ V m}^{-2}$ at the rare-earth nucleus in DyNi_5 , ErNi_5 and TmNi_5 respectively. Small differences in V''_{cc} for different rare earths in the same series are expected because of the small differences in the lattice parameters and also because of the different shielding.

We may now use equation (19) to estimate the antishielding ratio γ_N/γ_E for Tb^{3+} in TbNi_5 . From the value of B_2^0 given in table 1 and the measured value of P'' we find $\gamma_N/\gamma_E = 174 \pm 6$. This figure may be compared to the much smaller value $\gamma_N/\gamma_E = 104 \pm 20$ obtained by Bunbury *et al* (1992) for the insulating compound $\text{Tb}(\text{OH})_3$. The large discrepancy between the two values for the antishielding factor strongly reinforces the point made in section 2.3 that the relation between B_2^0 and the electric field gradient at the nucleus is not an intrinsic property of the ion but depends strongly on the host material.

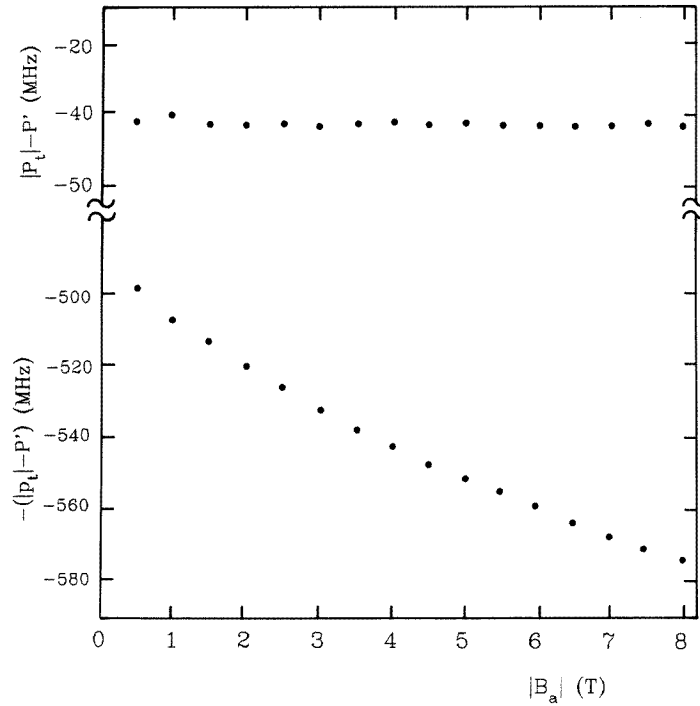


Figure 3. The field dependence of $|P_t| - P'$ and $-(|P_t| + P')$ where $|P_t|$ is measured and P' is computed.

5.2. The dipolar parameter

The measured and computed field dependence of a_t are shown in figure 4. The computed values include corrections for J -mixing (ranging from -13 MHz in zero field to -15 MHz at 8 T). The coefficient κ was treated as a free parameter, independent of the applied field. Its value was derived from the field dependence of a_t using a procedure similar to that used in section 5.1 to find P'' . The value obtained for κ is -0.729 ± 0.005 T, which gives $B_{ce} + B_{orb} = 3.80 \pm 0.03$ T in zero applied field. In the notation of McCausland and Mackenzie (1979) the contributions from the spin- and orbitally polarized conduction electrons to the hyperfine field are separated by writing

$$\kappa = (K_p + K_n)(g_J - 1) + (2 - g_J)K_{orb} \quad (20)$$

where the coefficients $K_p + K_n$ and K_{orb} are considered constant for a given isomorphous rare-earth series. Using the value for $B_{ce} + B_{orb} = 8.6$ T measured by van Steenwijk *et al* (1977) for GdNi₅ and the value that we obtained for TbNi₅ we find $K_p + K_n = -1.23$ T and $K_{orb} = -0.24$ T for the RNi₅ series. This gives $B_{ce} = 3.17$ T and $B_{orb} = 0.63$ T for the contributions from respectively, the spin- and orbitally polarized conduction electrons to the hyperfine field at the terbium nucleus in TbNi₅.

5.3. The pseudo-octupole parameter

The parameter w is a purely second-order effect. Apart from in some special cases (see Bunbury *et al* 1995), w is at least four orders of magnitude smaller than the dipolar

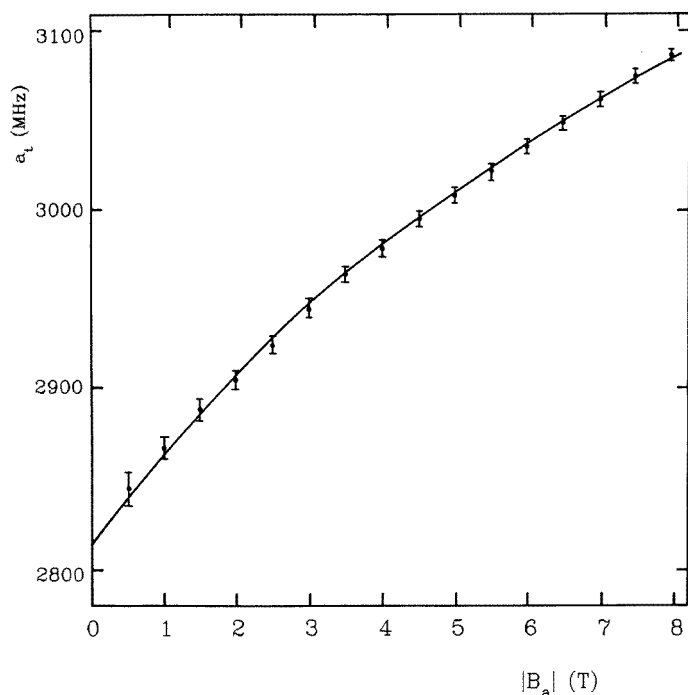


Figure 4. The computed and measured field dependences of the dipolar hyperfine parameter.

parameter. The computed value of w for TbNi₅ in fields between 0 and 8 T varies from 0.4 to 0.5 MHz. For all of the fields in our experiment, we find w of the order of 0.4 ± 0.5 MHz, in broad agreement with the computation. Because of the large relative uncertainty of the measurement, no extra information can be obtained from the field dependence of w .

6. Summary and conclusions

We have made a detailed study of the field dependence of the hyperfine splitting of terbium in a single crystal of TbNi₅. The measured field dependence of the dipolar hyperfine parameters a_t is in perfect agreement with our computation which involves only one field-independent free parameter: κ . As the contribution of κ to a_t is less than 1.5% of the total we conclude that the crystal-field and exchange parameters in table 1 give a very accurate description of the ground state of terbium in TbNi₅. We have measured the electric field gradient at the terbium nucleus and obtained with unprecedented precision the ratio of antishielding factors γ_N/γ_E . The value we obtain for γ_N/γ_E is significantly different from that measured in an insulating compound. This difference is attributed to the contribution $V_{cc}^{(val)}$ of the valence electrons to V_{cc}'' in the metallic host. If, as suggested by Coehoorn and Buschow (1991), the lattice contribution to V_{cc}'' can be estimated using the value of γ_N/γ_E measured in the insulator then the value of $V_{cc}^{(val)}$ derived from our measurements is $V_{cc}^{(val)} = 15.7 \times 10^{21} \text{ V m}^{-2}$ in agreement with the value of $16 \times 10^{21} \text{ V m}^{-2}$ computed by Coehoorn and Buschow (1991) for gadolinium in GdNi₅.

Acknowledgments

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Appendix A**The Tb³⁺ ion for intermediate coupling:**

$$J = 6$$

ground manifold:

$$0.9786 {}^7F_6 + 0.0617 {}^5G_6 + 0.1329 {}^5G'_6 - 0.1401 {}^5G''_6 + 0.0113 {}^5H_6 + 0.0157 {}^5H'_6 \text{ (a)}$$

Landé g -factor: $g_J = 1.493$ (a)

operator-equivalent coefficients (b):

$$\langle J \| \alpha_2 \| J \rangle = -1.0253 \times 10^{-2}$$

$$\langle J \| \alpha_4 \| J \rangle = 1.1988 \times 10^{-4}$$

$$\langle J \| \alpha_6 \| J \rangle = -1.0560 \times 10^{-6}.$$

The mean square radius of the 4f shell:

$$\langle r^2 \rangle = 2.302 \times 10^{-21} \text{ m}^2 \text{ (c).}$$

The ¹⁵⁹Tb nucleus:

$$I = \frac{3}{2}$$

hyperfine coupling constants:

$$\text{dipolar: } a_0 = 3168 \pm 18 \text{ MHz (d)}$$

$$\text{quadrupolar: } P_0 = 360 \pm 8 \text{ MHz (d)}$$

gyromagnetic ratio: $\gamma/2\pi = 10.13 \text{ MHz T}^{-1}$ (e)

quadrupole moment: $Q_n = 1.432 \text{ b (f).}$

TbNi₅:

lattice parameters (g):

$$a = 0.4895 \text{ nm}$$

$$c = 0.3959 \text{ nm}$$

ordering temperature (h):

$$T_c = 23 \pm 1 \text{ K}$$

spontaneous magnetization (h):

a axis

$$7.60 \mu_B \text{ per formula unit}$$

$$\mu_{Ni} = -0.1 \mu_B/\text{Ni}$$

molecular-field coefficients (h):

$$n_{RNi} = -0.65 (\mu_B \text{ T}^{-1})^{-1}$$

$$n_{RR} = 0.41 (\mu_B \text{ T}^{-1})^{-1}$$

nickel susceptibility (h):

$$\chi_{Ni} = 90.0 \times 10^{-4} \mu_B \text{ T}^{-1}.$$

Key to references: (a) Ofelt (1963), (b) Scott (1970), (c) Freeman and Desclaux (1979), (d) Pelletier-Allard and Pelletier (1985), (e) Bleaney (1988), (f) Tanaka *et al* (1983), (g) Haszko (1960), (h) Nait-Saada (1980).

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