Investigation of the magnetic hyperfine field at the In site of the rare earth intermetallic Tb_2In

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Abstract. The magnetic and electric hyperfine interaction at the In site of the rare earth intermetallic compound Tb$_2$In has been investigated as a function of temperature by perturbed angular correlation measurements using ^{111}Cd as a nuclear probe. The saturation value of the magnetic hyperfine field of ^{111}Cd in Tb$_2$In H_{hf} (9 K) = −24.5(2) T is about 10% smaller than the hyperfine field of ^{111}Cd in Tb metal. An anomalous temperature dependence is found: with increasing temperature H_{hf} decreases much faster towards the Curie point T_c = 168 K than the Brillouin curve for the Tb spin $S = 3$. The perturbed angular correlation spectra reflect a temperature dependence of the orientation of the 4f spins, which changes from about 65° at 8 K to 90° at 170 K, relative to the hexagonal c axis. These results differ greatly from those obtained with the nucleus ^{119}Sn in the same compound, suggesting a pronounced influence of the nuclear probe on the local rare earth magnetization.

1. Introduction

The large magnetic moments of the rare earth (R) elements are produced by the unclosed 4f shell. As the 4f electrons are strongly localized inside the ion cores, spontaneous magnetic ordering of 4f moments requires a mechanism of indirect f–f coupling. In the RKKY theory (the first theory which successfully described many features of rare earth magnetism) it was assumed that this coupling is provided by the s conduction electrons, which are spin polarized by exchange with the 4f spins.

However, theoretical calculations (Campbell 1972, Harmon and Freeman 1974, Troper *et al* 1979), the systematics of impurity hyperfine fields in Gd (Forker 1985) and experimental data for rare earth intermetallics (Delyagin *et al* 1984, 1989) increasingly suggest that it is not so much s–f exchange, but the exchange of the 4f spins with the 5d electrons of the same atom and d–d interaction which lead to the indirect f–f coupling that is typical for rare earth magnetism.

For a detailed understanding of the coupling mechanism, experimental data on the spin polarization in magnetically ordered rare earth systems are important. Such data can be gained by investigation of the magnetic hyperfine fields experienced by the nuclei of non-magnetic atoms in 4f magnets, since these are produced by the

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Fermi contact interaction and are therefore a direct measure of the electronic spin polarization at the nuclear site. The hyperfine field at the rare earth nucleus itself is of less use in this context: its main contribution comes from the unquenched orbital angular momentum of the 4f shell (except for Gd) and is at least one order of magnitude larger than the contact contribution.

For information on the spin polarization, measurements of the magnetic hyperfine field at the A site of intermetallic compounds $R_x A_{1-x}$ between non-magnetic metals A and the rare earth elements R are of particular interest. By varying the constituents R and A and investigating different compositions x of the two elements, the effect of important parameters such as the average magnetic moments, the interatomic distances and the conduction electron density on the exchange interaction may become visible and help to distinguish between the long-range s–f exchange and the more localized d–d interaction.

We report here the first results of such a programme for the intermetallic compounds $R_{1-x} In_x$, which is being carried out using the perturbed angular correlation (PAC) technique. The choice of this particular series is suggested by the fact that ^{111}In is the mother isotope of ^{111}Cd, which is one of the most favourable PAC nuclei, so that one can be sure that the measurement is in fact carried out on the A site. The compound discussed here is Tb_2In.

2. Properties of Tb_2In

The crystallographic structure of the R_2In compounds has been determined by Palenzona (1968) and Franceschi (1974). The structure is isomorphic with the hexagonal Ni_2In lattice. The lattice parameters of Tb_2In are $a = 5.367$ Å and $c = 6.707$ Å. There are two structurally different R sites, but only one In site. The 11 nearest neighbours of the In site are Tb atoms at different distances d_n: there are six Tb atoms with $d_1 = 3.542$ Å, two Tb with $d_2 = 3.354$ Å and three Tb with $d_3 = 3.099$ Å.

The information presently available on the magnetic properties of Tb_2In is not very detailed. The magnetization and susceptibility measurements of Kawano *et al* (1974) for $T \geqslant 95$ K give an ordering temperature of $T_c = 183$ K and are compatible with ferromagnetic ordering of the 4f moments. A neutron diffraction study by Umezaki *et al* (1974) shows that, at $T = 50$ K, Tb_2In is ferromagnetic, with the 4f moments perpendicular to the hexagonal c axis. Measurements of the magnetic susceptibility extended to 4.2 K by Gamari-Seale and Anagnostopoulos (1979) give an ordering temperature of $T_c = 170$ K and indicate that at very low temperatures the compound is ordered antiferromagnetically. The magnetic structure of the antiferromagnetic phase is still unknown.

3. Experimental details

The PAC measurements were carried out using the 172–247 keV cascade of ^{111}Cd, which is populated in the electron capture (EC) decay of ^{111}In ($T_{1/2} = 2.8$ days). This radioactive source is commercially available as an aqueous solution of ^{111}InCl$_3$.

To dope Tb_2In with trace amounts of ^{111}In, radioactive InCl$_3$ was dropped on a thin In foil and then reduced to the metallic state by melting the foil in a hydrogen atmosphere. The metallic state was verified by taking the PAC spectrum of the molten

foil. In the next step, to the doped molten In was added a corresponding quantity of Tb in an arc furnace under argon atmosphere. As shown by the PAC spectra, this procedure resulted in a well ordered compound and no further heat treatment was necessary. Equivalent results were obtained when, rather than first reducing the In^{3+} by hydrogen, $InCl_3$ was directly added to the In metal before arc melting. The compound was found to react very sensitively when exposed to the atmosphere, visibly oxidizing on the surface within minutes after melting. The samples in the form of small metal spheres (about 30 mg) were therefore immediately transferred to the vacuum of a closed cycle He refrigerator.
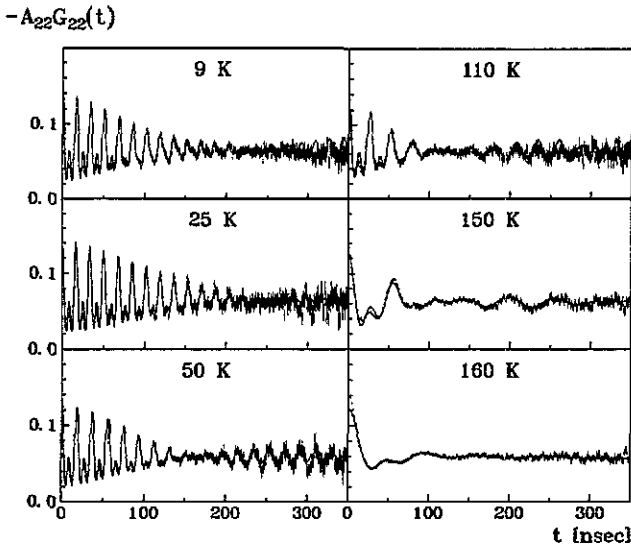

Figure 1. PAC spectra of ^{111}Cd in the magnetically ordered phase of Tb_2In.

The PAC spectra were recorded between 8 and 290 K with a four-detector arrangement, equipped with fast BaF_2 detectors. Two samples were investigated, one covering the temperature range $8\ K \leqslant T \leqslant 290\ K$ in 13 steps of 20 K or more, the other covering the range $8\ K \leqslant T \leqslant 40\ K$ in 9 small steps. The temperature stability was of the order of 0.2 K. Figure 1 shows spectra taken with the first sample for $T \leqslant 160\ K$, figure 2 shows spectra of the same sample for $T \geqslant 170\ K$.

4. Data analysis and results

The perturbation of an angular correlation by hyperfine interactions in polycrystalline samples can be described by a perturbation factor $G_{kk}(t)$, which has the general form (Frauenfelder and Steffen 1965):

$$G_{kk}(t) = \sum_{a,b} S_{ab}^k \exp\left[-i/\hbar(E_a - E_b)t\right] \tag{1}$$

where E_a and E_b are the eigenvalues of the interaction Hamiltonian and the amplitudes S_{ab}^k depend on the multipole character and symmetry of the interaction and on the spin of the intermediate state of the cascade.
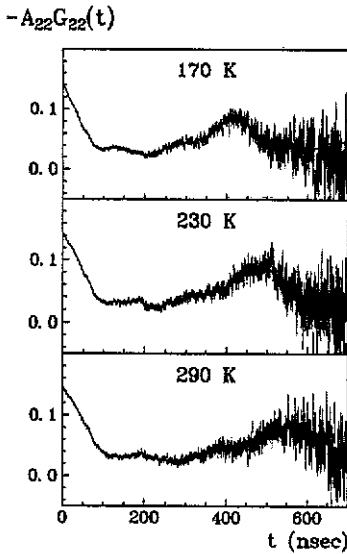
Figure 2. PAC spectra of ^{111}Cd in the paramagnetic phase of Tb$_2$In.

In the magnetically ordered phases of Tb$_2$In we are dealing with a combined magnetic and electric hyperfine interaction. In addition to the magnetic dipole interaction between the nuclear magnetic moment and the magnetic hyperfine field there is an electric quadrupole interaction (QI) between the nuclear quadrupole moment Q and the tensor of the electric field gradient caused by the non-cubic charge distribution at the In site of Tb$_2$In.

For combined interactions, the perturbation factor has to be calculated by numerical diagonalization of the interaction Hamiltonian (Boström et al 1970), which in the case of axial symmetry of the field gradient depends on the magnetic interaction frequency $\omega_M = -g\mu_N H_{hf}/\hbar$, the electric quadrupole frequency $\nu_q = eQV_{zz}/h$ and the angle Θ between the direction of the magnetic hyperfine field H_{hf} and the V_{zz} component of the field gradient, which in a hexagonal lattice is parallel to the c axis.

For the case $\nu_q \ll \omega_M$, the eigenvalues can be calculated in first-order perturbation theory:

$$E_m = m\hbar\omega_M + \left\{ [3m^2 - I(I+1)]/8I(2I-1) \right\} h\nu_q(3\cos^2\Theta - 1). \tag{2}$$

Consequently, for $\nu_q \ll \omega_M$, the quadrupole frequency ν_q and the angle Θ cannot be determined independently from a measurement of the interaction energies.

The measurements in the magnetically ordered phase were analysed by fitting the theoretical perturbation function for combined interaction, calculated by numerical diagonalization of the Hamiltonian, to the PAC spectra. As the samples were not powdered, in order to avoid degradation in air, they showed some texture, clearly visible in the PAC spectra of the paramagnetic phase (figure 2). Nevertheless, the spectra of the magnetic phase were analysed assuming fully polycrystalline samples in order to keep calculation times at a reasonable level. As a consequence there are slight deviations in the amplitudes of the measured spectra and of the fit functions in figure 1. However, a slight texture of the sample affects only the amplitudes and not the frequencies of a PAC spectrum. Therefore neglect of texture effects in the analysis can be justified, as long as the frequencies are the quantities of interest.

At low temperatures, the spectra show many rapid oscillations with a slow decay of the amplitude which is caused by the QI. The quadrupole frequency at 170 K (see figure 2) is $\nu_q = 15.7(2)$ MHz, the rapid oscillation at 8 K corresponds to a magnetic frequency $\omega_M = 374.4(3)$ Mrad s^{-1}. Clearly, one has $\nu_q \ll \omega_M$ in the present case. A series of fits, where for a given temperature ν_q was adjusted for different fixed values of the angle Θ, confirmed that Θ and ν_q could not be determined independently: practically identical fits were obtained for almost all angles $0 \leqslant \Theta \leqslant 90°$, with ν_q adjusting such that the quantity $\nu_q(3\cos^2\Theta - 1)$ was constant, independent of the assumed angle Θ. The upper part of figure 3 shows the temperature dependence of $\nu_q(3\cos^2\Theta - 1)$, determined in this way, for the two samples investigated.
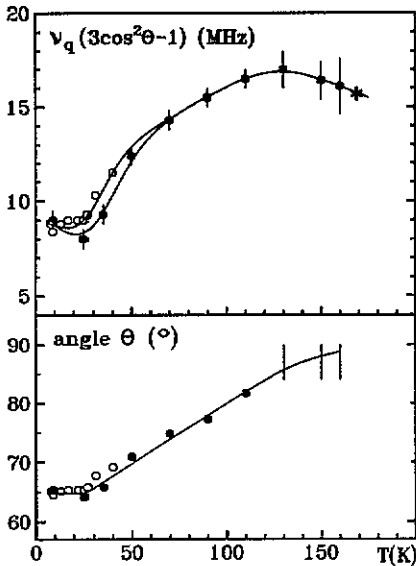

Figure 3. The temperature dependence of the quantity $\nu_q(3\cos^2\Theta - 1)$ for ^{111}Cd in Tb₂In (upper part) and the angle Θ of the 4f moment relative to the c axis, derived from $\nu_q(3\cos^2\Theta)$ with the assumption of a $T^{3/2}$ temperature dependence of ν_q (lower part). The full and open points represent two different samples. The asterisk denotes the quadrupole frequency ν_q measured in the paramagnetic phase.
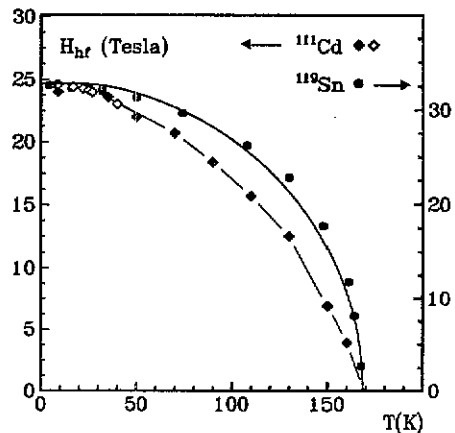
Figure 4. The temperature dependence of the magnetic hyperfine field of ^{111}Cd (this work) and ^{119}Sn (Delyagin *et al* 1989) on the In site of Tb₂In. The full line represents the Brillouin curve $S = 3$, the broken line connects the ^{111}Cd data points.

The fits to the low-temperature spectra suggest the existence of two slightly different magnetic hyperfine fields. This can be seen for example in the 9 K spectrum (figure 1) from the width of the oscillation peaks, which increases with increasing time, reflecting the increasing phase difference between the two sites. The difference is of the order of 3–4% at all temperatures, with nearly equal relative intensity of both fields. In figure 4 we have plotted the average field value versus temperature.

The sign of the magnetic hyperfine field is negative. It has been determined in an integral perturbed angular correlation (IPAC) measurement by observing with a time window of a few nanoseconds the rotation of the angular correlation in an external

magnetic field of 4 T at 4.2 K.

The analysis of the spectra in the paramagnetic phase, based on the perturbation factor for pure QI (Frauenfelder and Steffen 1965) gave the following frequencies ν_q = 15.7(2), 13.7(2) and 11.7(2) MHz at 170, 230 and 290 K, respectively. In all cases, a slight Gaussian frequency distribution ($\delta \sim 0.08$–0.10) was observed which gives rise (Forker 1973) to a small asymmetry $\eta \simeq 0.2$ of the electric field gradient.

Furthermore, the spectra show the presence of another phase, characterized by a strong, axially symmetric QI (ν_q = 107.6(4) MHz at 170 K) with a relative intensity of about 5%. The nature of this contamination is not clear. The quadrupole parameters correspond neither to those of In_2O_3 (Bibiloni *et al* 1985) nor to those of metallic In (Bodenstedt *et al* 1972). Most probably it represents a small fraction of some other phase of the R–In system.

5. Discussion

The observation of two magnetically different sites is unexpected, at least for $T \geqslant$ 50 K, since at these temperatures the compound orders ferromagnetically and all In sites are structurally equivalent. Discussing the appearance of several impurity hyperfine fields in some ferromagnetic rare earth metals, Irkhin and Rozenfel'd (1988) have shown that because of the different effective charges the substitution of a R ion by the impurity may cause a strong local magnetic anisotropy, which, depending on the easy magnetization direction, can lead to several magnetically non-equivalent environments. Such an effect cannot be excluded here, since, although we do not substitute a R ion, the effective charge of the impurity [111]Cd probably differs from the In charge. In the following we shall discuss the average hyperfine field.

The magnetic frequency $\omega_M(8\ K) = 374.4(3)$ Mrad s^{-1} corresponds to a saturation value of the magnetic hyperfine field of $H_{hf} = -24.56$ T. The negative sign of H_{hf} implies that the hyperfine field at the In site is antiparallel to the direction of the Tb spin S, since according to Hund's rule for Tb the spin S is antiparallel to the total angular momentum J.

The magnetic hyperfine field of [111]Cd in Tb metal at 4 K, previously determined by Forker and Hammesfahr (1973) ($|H_{hf}| = 27.5(5)$ T) and Jonsson *et al* (1974) ($H_{hf} = -26.4(6)$ T), is about 10% stronger than H_{hf} in Tb_2In. This is quite surprising, since with the nucleus [119]Sn the opposite trend has been found: $|H_{hf}([119]Sn : Tb)|$ = 23.5(1) T (Bogdanov *et al* 1977) and $H_{hf}([119]Sn : Tb_2In) = -32.8(1)$ T (Delyagin *et al* 1989).

The condition $|H_{hf}([119]Sn : R_2In)| > |H_{hf}([119]Sn : R)|$ holds for all heavy rare earth elements R with the possible exception of Tm, for which the data are rather unprecise (Kuchma and Shnipel' 1972, Delyagin *et al* 1984, 1989). From this trend, Delyagin *et al* (1984) have concluded that only nearest R neighbours contribute to the hyperfine field. A nuclear probe such as [119]Sn on a R site in the pure metals has 12 R nearest neighbours (NN), the In site in Tb_2In has 11 R NN. In this picture, which would point towards f–d exchange and d–d overlap rather than f–s exchange as the dominant coupling mechanism, the smaller field in the pure metals is the result of the larger distance from the R neighbours to the probe site.

Clearly, our result for [111]Cd : Tb_2In is not compatible with this interpretation, since the interatomic distances in Tb metal ($d_1 = 3.6055$ Å, $d_2 = 3.5279$ Å) are also larger than those in Tb_2In (see section 2). The same Curie point was obtained in

the ^{119}Sn : Tb$_2$In and ^{111}Cd : Tb$_2$In measurements, which gives confidence in the sample preparation of both investigations. If we exclude the possibility that, contrary to the normal expectation, ^{119}Sn occupies the R site rather than the In site, then we must conclude from the different trends between Tb metal and Tb$_2$In for ^{111}Cd and ^{119}Sn that the non-magnetic probe itself can strongly affect the local magnetization in Tb$_2$In. This must be related to the fact that in both cases we are dealing with an impurity at the In site.

^{111}Cd : Tb$_2$In and ^{119}Sn : Tb$_2$In also differ with respect to the temperature dependence of the magnetic hyperfine field which is shown in figure 4. While, in the case of ^{119}Sn, H_{hf} closely follows the Brillouin curve for the Tb spin $S = 3$ (solid line in figure 4), the hyperfine field of ^{111}Cd decreases much faster towards the Curie point. Shnipel' (1989) has pointed out that anomalies as observed here for ^{111}Cd easily arise if the local density of states has a complex structure with sharp peaks and sudden dips. Crystal field effects which are known to be strong in rare earth metals and intermetallics (Purwins and Leson 1990) can also lead to deviations from a simple Brillouin behaviour. Both effects can apply hear, since the different effective charge of the impurity can certainly have a strong influence both on the local density of states and the local crystal field. Clearly, further investigations of this aspect with other probes and in other systems are of interest.

The electric field gradient in metallic systems is known to decrease with increasing temperature, frequently following a $T^{3/2}$ or (as in some rare earth metals) a linear relation (Forker 1985). Consequently the increase of the quantity $\nu_q(3\cos^2\Theta - 1)$ with increasing temperature (see figure 3) reflects a change of the angle Θ between H_{hf} and the hexagonal c axis and thus of the orientation of the 4f moment. From the fact that, at 160 K, $\nu_q(3\cos^2\Theta - 1)$ has almost the same value as ν_q at a slightly higher temperature (170 K, asterisk in figure 3) in the paramagnetic phase, where ν_q can be determined with high precision, it follows unambiguously that close to the Curie point the 4f moment is perpendicular to the c axis.

To determine $\Theta(T)$ from $\nu_q(3\cos^2\Theta - 1)(T)$, the temperature dependence of ν_q in the ordered phase must be known, which is not the case. However, the low-temperature values of ν_q can be estimated by extrapolating the three values of ν_q measured in the paramagnetic phase to low temperatures. The variation of the angle Θ shown in the lower part of figure 3 was calculated in this way, assuming a $T^{3/2}$ temperature dependence of ν_q. A linear relation $\nu_q(T)$ gives practically the same result.

In principle, there are two solutions Θ for a given $(3\cos^2\Theta - 1)$, one larger, the other one smaller than $\Theta = 54.7°$, where $(3\cos^2\Theta - 1) = 0$. As shown above, close to T_c the angle Θ can be determined unambiguously as $\Theta \sim 90°$. Consequently one would have to pass through $\Theta = 54.7°$, if at some temperature $T < T_c$ the smaller angle would be the true solution. This point is easily recognized, since the effect of the QI on the PAC spectrum would vanish; the latter would then consist of an unattenuated magnetic oscillation.

In the first sample investigated the decay of the oscillation amplitudes at 25 K was clearly slower than at 8 and 50 K (see figure 1) and it appeared possible that somewhere in this range $\Theta = 54.7°$. Therefore this range was carefully scanned in small steps with a second sample, but disappearance of quadrupole effects was not observed. We are therefore confident that at all temperatures the larger angle is the true solution and we conclude that between 8 K and T_c the orientation of the Tb moment in Tb$_2$In changes continuously from about 65° to 90°, relative to the c axis.

Again, ^{119}Sn in Tb$_2$In behaves differently: here changes of the orientation have not been found.

In summary, PAC measurements with ^{111}Cd in magnetically ordered Tb$_2$In gave a magnetic hyperfine field about 10% smaller than in Tb metal, an anomalous temperature dependence of the hyperfine field and a change of the orientation of the Tb moment with temperature. In all these aspects ^{111}Cd : Tb$_2$In differs strongly from ^{119}Sn : Tb$_2$In, indicating a pronounced influence of the nuclear probe occupying the non-magnetic A site in R$_2$A compounds on the local rare earth magnetization. Clearly, further investigations of this influence are necessary before conclusions on the exchange mechanism can be drawn from measurements of the magnetic hyperfine fields.

Acknowledgments

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