

# NMR IN HEAVY RARE EARTH METALS AND ALLOYS

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## ABSTRACT

Nuclear magnetic resonance responses of  $^{159}\text{Tb}$ ,  $^{163}\text{Dy}$  and  $^{167}\text{Er}$  in Tb, Dy and Er metals, and of Gd-Tb, Gd-Dy, Gd-Er, Tb-Dy, Tb-Er and Dy-Er alloys have been measured at the liquid helium temperature by the spin echo method. At this temperature all these metals and alloys are in magnetically ordered states, being either ferromagnetic, spiral or conical. Over the entire concentration range the n.m.r. responses were measured systematically, and the changes of magnetic dipole and electric quadrupole hyperfine energies were investigated. These hyperfine interactions arise mainly from the unfilled 4f shell, but there exist some contributions originating from the lattice and conduction electrons. From the results of our measurements we tried to separate the contributions arising from different origins.

All the heavy rare earth metals and their manifold solid solution alloys have crystal structures of simple hexagonal symmetry, in which  $c/a$  values are slightly different from that in the ideal hexagonal close packed structure. In these metals and alloys trivalent rare earth ions are embedded in a sea of conduction electrons. Since the unfilled 4f shell of the ion which is responsible for the magnetism of these materials is shielded by outer closed shells, the magnetic moment of the ion is highly localized at each lattice site and the total angular momentum  $J$  of the ion which is determined by the Hund rule is a good quantum number. The conduction electrons are polarized by the 4f spins through s-f exchange interactions, and this polarization in turn produces exchange interactions between 4f moments. These exchange interactions together with anisotropy energies are the origins of various interesting magnetic structures appearing in heavy rare earth metals and alloys. The magnetic structures of heavy rare earth metals at the liquid helium temperature, at which our present experiments have been done, are as follows: Gd is ferromagnetic in the direction of about  $30^\circ$  from the  $c$ -axis; Tb and Dy are ferromagnetic in the  $c$ -plane; and Ho and Er are conical with the cone axis along the  $c$ -axis<sup>1</sup>.

Both magnetic and electric quadrupole hyperfine interactions in these metals and alloys arise mainly from the 4f shell. Owing to the orbital angular momentum, the hyperfine energies are very large and n.m.r. frequencies in the magnetically ordered phase are expected in the range from a few hundred MHz up to several GHz, except in Gd, which is an s state ion. Because the magnetic hyperfine energy is much larger than the quadrupole energy, the hyperfine energy can be expressed as

$$H_{\text{hf}} = aI_z + P[I_z^2 - I(I+1)/3] \quad (1)$$

where  $a$  is the Zeeman energy,  $P$  is the electric quadrupole energy and  $I_z$  is the component of the nuclear spin  $I$  along the direction of the hyperfine field. Then the n.m.r. spectrum is expected to consist of equally spaced  $2I$  lines. Since the spin values are all odd for nuclei investigated in our present experiments, the frequency of the centre line,  $\nu_z$ , is equal to  $a/h$  and the separation of the neighbouring lines,  $\nu_Q$ , is equal to  $2P/h$ .

We constructed spin echo spectrometers covering the frequency range up to 4GHz, and the signals of Tb, Dy and Er were easily observed in various individual metals and their solid solution alloys. The measurements were done at liquid helium temperatures. As an example of the results for pure metals, the resonances of  $^{163}\text{Dy}$  in Dy metal<sup>2</sup> are shown in Figure 1. Five

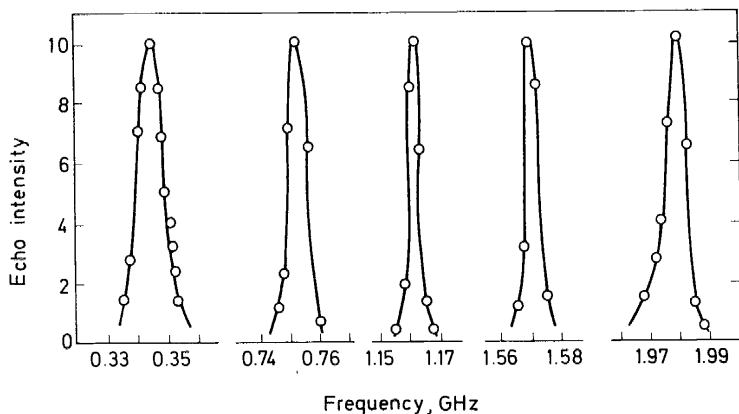


Figure 1. Line shapes of  $^{163}\text{Dy}$  resonances in Dy metal

lines were obtained, corresponding to the spin value of  $5/2$ , as expected. The whole spectrum ranges from about 300 MHz to 2 GHz. All the lines have widths of about 10 MHz. The centre line is the narrowest, while the satellite lines are broader. These broadenings certainly arise from fluctuations of the Zeeman and quadrupole energies due to some crystal imperfections. The peak frequencies and separations of neighbouring lines are shown in Table 1. The separations are all equal within experimental error, as expected. Similar results were obtained in  $\text{Tb}^3$  and  $\text{Er}^4$  metals. On the other hand, Wagg and McCausland observed n.m.r. in Ho metal and obtained a similar result<sup>5</sup>. Thus, up to the present, the only untested one left in the study of n.m.r. in magnetically ordered heavy rare earth metals is Tm. We tried to observe n.m.r. in Tm metal, which has an anti-phase domain structure, but we could not detect the resonance, although strong resonance was observed in Gd-Tm alloys of about 10% Tm concentration, which is simply ferromagnetic. The Tm resonance disappeared when the concentration of Tm was increased to about 50 per cent. The reason why the resonance could not be detected in Tm metal is not clear. It might be the anti-phase domain structure in Tm metal.

Table 1. Resonance frequencies of  $^{163}\text{Dy}$  in Dy metal

Resonance frequency, MHz	345	753	1 162	1 570	1 979
Frequency difference between neighbouring lines	408	409	408	409	

Besides the large contribution of 4f electrons to the hyperfine energies, there exist some minor contributions arising from various origins. It is the aim of our present experiments to separate the contributions arising from different origins by systematic n.m.r. studies of solid solution alloys of heavy rare earth metals. First, we shall consider the contribution of conduction electron polarization to the magnetic energy. If there is a polarization of the conduction electrons at a nuclear site, it will produce a hyperfine field at that nucleus. The polarization of the conduction electrons is the sum of the polarizations induced by 4f spins of all ions through s-f exchange interactions. The polarization induced by one ion which distributes rather widely in space around that ion is proportional to  $(\lambda - 1)J$  of that ion, where  $\lambda$  is the Lande factor.  $(\lambda - 1)J$  is the projection of the spin of the 4f shell along the direction of  $J$ . To sum up, the hyperfine field in the solid solution alloys is expressed as

$$H_{\text{hf}} = 2\pi\nu_z/\gamma = H_{4f} + h(\lambda - 1)J + h'(\overline{\lambda - 1}J) \quad (2)$$

$H_{4f}$  is the contribution from 4f electrons, and the second and third terms are those arising from the conduction electron polarization induced by the parent and surrounding ions, respectively. Because of the long-range nature of the RKKY interactions, the latter can be well approximated to be proportional to the average of  $(\lambda - 1)J$ , which is denoted as  $\overline{(\lambda - 1)J}$  in equation (2). Since the 4f shell is shielded by outer closed shells, the values of  $H_{4f}$  can be considered to be nearly independent of the composition and concentration of the alloys. Also,  $h$  and  $h'$  are nearly constant for all alloys, because the values of s-f exchange integrals are nearly the same in all heavy rare earth metals. Then the only term which changes with the concentration of the alloys is  $\overline{(\lambda - 1)J}$ , and from the observed change of  $H_{\text{hf}}$  with the change of  $\overline{(\lambda - 1)J}$  the value of  $h'$  can be determined. If we assume that  $H_{4f}$  in the alloys is equal to that in the free ion which was given by Bleaney<sup>6</sup> from the analysis of e.s.r. data after correcting crystalline field effects, the value of  $h$  can easily be determined.

Next, the electric quadrupole interaction will be discussed. Also, there exist some contributions other than that from 4f electrons. Because trivalent ions are located at lattice sites and the crystal structure is not exactly equal to the hexagonal close packed one, there arises an electric field gradient produced by these trivalent charges at each nuclear site, which should be multiplied by the Sternheimer coefficient. Also, the distribution of the conduction electron charges has not exact hexagonal close packed symmetry and a field gradient is produced at each nuclear site. These two gradients have axial symmetry about the  $c$ -axis. Because these two gradients cannot be separated by n.m.r. experiments alone, the sum of the quadrupole interactions arising from these two origins will be denoted by  $P_c$ .  $P_c$  is the principal

value about the  $c$ -axis. In magnetically ordered phases it is often the case that the  $4f$  moments make an angle  $\theta$  from the  $c$ -axis. Because the contribution from the  $4f$  electrons,  $P_{4f}$ , is much larger than  $P_c$ , the effective quadrupole energy is given by

$$P = P_{4f} + P_c(3 \cos^2 \theta - 1)/2 \quad (3)$$

As in the discussion of the Zeeman energy,  $P_{4f}$  can be considered to be nearly independent of alloying and is about the same as that in the free ion. Because the deviation from ideal hexagonal close packed symmetry is small, the contribution of lattice charges to  $P$  is well represented by a first order term in  $(c/a - 1.633)$ , where 1.633 is the  $c/a$  value in the ideal hexagonal close packed lattice. Since the contribution from the conduction electron charges arises also from the slight deviation of  $c/a$  from 1.633, this contribution too is well assumed to be proportional to  $(c/a - 1.633)$ . The Sternheimer coefficient may be assumed to be independent of alloying. Then  $P_c$  becomes proportional to the lattice charge contribution, which was calculated by Das and Pomerantz<sup>7</sup> in detail using a point charge model. Thus  $P_c$  will change following the change in  $a$  and  $c$  produced by alloying, and from the observed change in  $P$  due to alloying the value of  $P_c$  will be determined, so long as the value of  $\theta$  does not change by such alloying. If the value of  $P_c$  is known,  $P_{4f}$  is easily obtained from the observed value of  $P$ . In these ways  $P_{4f}$  and  $P_c$  can be determined independently by the analysis of n.m.r. results with solid solution alloys.

We have measured n.m.r. of  $^{159}\text{Tb}$ ,  $^{163}\text{Dy}$  and  $^{167}\text{Er}$  in several solid solution alloys shown in *Table 2* together with their magnetic structures<sup>1</sup> and

*Table 2.* Solid solution alloys investigated in our present experiment

Alloy	Remarks
Gd-Tb}	Ferromagnetic in $c$ -plane. $\theta = 90^\circ$
Gd-Dy}	
Tb-Dy}	
Gd-Er	{ Gd-rich: ferromagnetic, $\theta \sim 30^\circ$ Er-rich: conical, $\theta \sim 30^\circ$
Tb-Er}	{ Tb- or Dy-rich: ferromagnetic in $c$ -plane, $\theta = 90^\circ$ Around 50/50 Tb/Er or Dy/Er: spiral in $c$ -plane. $\theta = 90^\circ$ Er-rich: conical, $\theta < 90^\circ$
Dy-Er}	

values of  $\theta$ . Taking these magnetic structures into account, we shall analyse our n.m.r. results.

First we shall show the results of our measurements of the frequency difference between the neighbouring lines,  $\nu_Q$ , which is equal to  $2P/h$ . *Figure 2* shows the results of the resonance of  $^{163}\text{Dy}$  in various Dy alloys. The experimental plots are divided into two groups. All the alloys belonging to the lower-frequency group have  $\theta = 90^\circ$ , although some are ferromagnetic and some are spiral, while two alloys belonging to the high-frequency group are conical, with  $\theta$ s differing considerably from  $90^\circ$ . In the low-frequency group  $P$  changes smoothly against the concentration. Since  $\theta = 90^\circ$  in all these alloys, this change arises from the change in  $P_c$  due to the change in

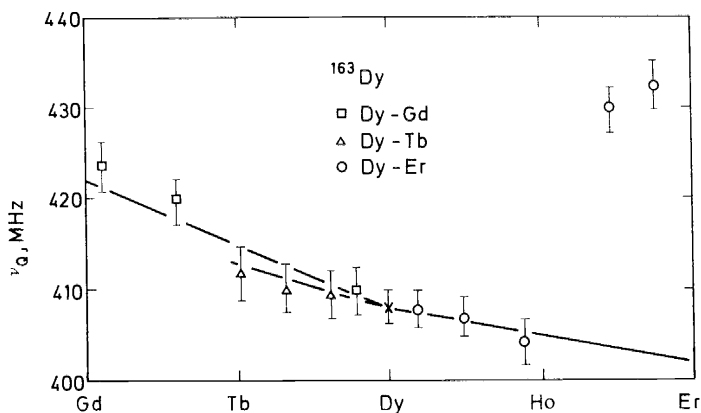


Figure 2. Values of  $\nu_Q$  of  $^{163}\text{Dy}$  in various Dy alloys

the lattice constants. The values of  $a$  and  $c$  were not determined accurately in alloys, but fairly accurate values are available for pure metals. If we assume that the changes in  $a$  and  $c$  are linear with the concentration, then we can calculate the values of  $a$  and  $c$  in all these alloys. Neglecting small magnetostriction effects in the case of ferromagnets and also small effects due to anisotropic thermal contraction, we use the values of  $a$  and  $c$  in paramagnetic phases in the following discussion. Using the formula given by Das and Pomerantz and assuming that  $P_c$  is proportional to the field gradient produced by the lattice charges as discussed already, we can calculate the relative change in  $P_c$  against the concentration of the alloys. The solid lines shown in Figure 2 for Gd–Dy, Tb–Dy and Dy–Er alloys are values obtained in this way with an appropriate proportionality constant. The agreement with the experimental plots seems satisfactory. From this proportionality constant the absolute value of  $P_c$  is determined for each of these alloys and  $P_{4f}$  is then determined. Then, using these values of  $P_c$  and  $P_{4f}$ , the angle  $\theta$  for the high-frequency group can easily be calculated. The experimental results for  $\nu_Q$  in Tb and Er alloys were similarly analysed.

The values of  $P_{4f}$  and  $P_c$  for Tb, Dy and Er metals obtained by these analyses are shown in Table 3, as well as the values of  $P_{4f}$  for free ions given by Bleaney<sup>6</sup>, which were obtained by the analysis of e.s.r. data on various salts. It should be emphasized that the values of  $P_{4f}$  in metals agree very well with those in free ions, indicating that the trivalent ions in these metals and alloys are almost in the same states as free ions. Because  $P_c$  depends upon

Table 3. Values of  $P$ ,  $P_{4f}$  and  $P_c$  for Tb, Dy and Er (in MHz)

Metal	$P$ (exper.)	$P_{4f}$ (exper.)	$P_{4f}$ (Bleaney)	$P_c$ (exper.)
Tb	336	383	386	94
Dy	204	227	228	46
Er	– 54.5	– 66	– 67.6	18

the quadrupole moment and spin values of the nucleus, the electric field gradient  $q_c$  corresponding to  $P_c$  was calculated and the values of  $q_c$  for Tb, Dy and Er metals are shown in *Table 4*.  $q_c$  is expressed as

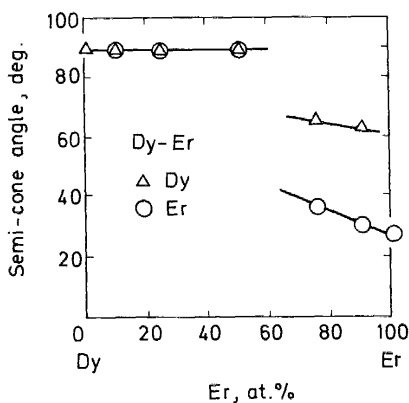
$$q_c = (1 - \gamma)q_1 + q_{\text{cond.}}$$

*Table 4.* Values of  $q_c$ ,  $q_1$  and  $q_c/q_1$

Metal	$P_c$ (MHz)	$q_c$ ( $10^{24}$ )	$q_1$ ( $10^{24}$ )	$q_c/q_1$
Tb	94	8.07	0.0149	540
Dy	46	7.04	0.0170	410
Ho	18	6.05	0.0178	340
Er	18	5.12	0.0182	280
Tm	47	3.61	0.0188	190

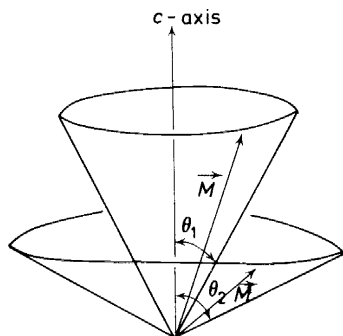
where  $\gamma$  is the Sternheimer coefficient,  $q_1$  the field gradient produced by the lattice charges and  $q_{\text{cond.}}$  that arising from the conduction electron charges. In this table the values for Ho calculated from the value of  $P$  obtained by Wagg and McCausland<sup>5</sup> and Tm obtained by Uhrich and Barnes<sup>8</sup> are also shown. The values of  $q_1$  shown in the table are those calculated from the lattice constants by use of the formula of Das and Pomerantz. The ratio  $q_c/q_1$  increases smoothly from Tm to Tb. The value of the Sternheimer coefficient was calculated to be about 70 in Tm<sup>9</sup> and this coefficient will not change much among heavy rare earth metals. Therefore these results indicate that the contribution of the conduction electron charges to the field gradient is larger than that arising from the lattice charges and increases smoothly from Tm to Tb. The conduction electron contribution may arise from the 5d parts in the wave functions of the conduction electrons and some calculations were already made<sup>10</sup>, but no definite conclusion was reached.

Now the results of the determination of the angle  $\theta$  will be discussed. *Figure 3* shows the results in Dy-Er alloys obtained by the procedure



*Figure 3.* Semi-cone angles for Dy and Er in Dy-Er alloys

discussed above. In the conical phase the values of  $\theta$  for Dy are very much different from those for Er. Neutron diffraction studies have been done in this alloy system by Millhouse and Koehler<sup>11</sup>, and it was shown that the average moments form a cone structure with the average semi-cone angle between  $30^\circ$  and  $40^\circ$ , depending upon the concentration. Therefore our results indicate that the magnetic moments of Dy and Er form a double cone. The average angles calculated from the angles for Dy and Er agree well with the results of neutron diffraction. The double cone structure is shown in *Figure 4*. Dy moments rotate on the surface of the cone  $\theta_2$ , while Er



*Figure 4.* Double cone structure.  $M$  corresponds to Er and  $M'$  to Dy

moments rotate on the cone  $\theta_1$ . Very similar results were obtained also in Tb-Er alloys.

Such a double cone structure probably arises from a large difference in one-ion anisotropy energies of Dy and Er; in Dy the anisotropy minimum is in the  $c$ -plane, while in Er it is nearly in the direction of the  $c$ -axis. Let us consider the simplest case, in which one Dy ion is added substitutionally in pure Er metal which has a conical structure with a semi-cone angle of about  $30^\circ$ . Owing to strong exchange interactions, the added Dy ion will also align with the same pitch as that of the parent Er, but owing to the anisotropy energy of the added ion, the direction of the magnetic moment of the added ion will tilt towards the direction of the anisotropy minimum. Thus the angle  $\theta$  of Dy will become much larger than  $30^\circ$  and a double cone structure will appear in these alloys. More direct determination of the angle  $\theta$  can be made by observing the anisotropy of  $\gamma$ -rays emitted from radioactive nuclei which are polarized along the direction of the  $4f$  moments of the parent ions at very low temperature. We have conducted such an experiment using a single crystal of Tb(18)-Er(82) alloy which contains a small amount of radioactive  $^{160}\text{Tb}$ . It was found that the semi-cone angle for  $^{160}\text{Tb}$  is about  $64^\circ$ , which agrees very well with the value obtained by n.m.r.<sup>12</sup>.

Next we shall discuss the hyperfine fields. *Figure 5* shows the hyperfine fields at  $^{163}\text{Dy}$  in various Dy alloys plotted against  $(\lambda - J)$ , after correcting a small contribution from the Lorentz field in the case of ferromagnets. It seems that the values for Gd-Dy and Dy-Tb alloys lie on a straight line, while those for Dy-Er alloys lie on another line with a slightly different

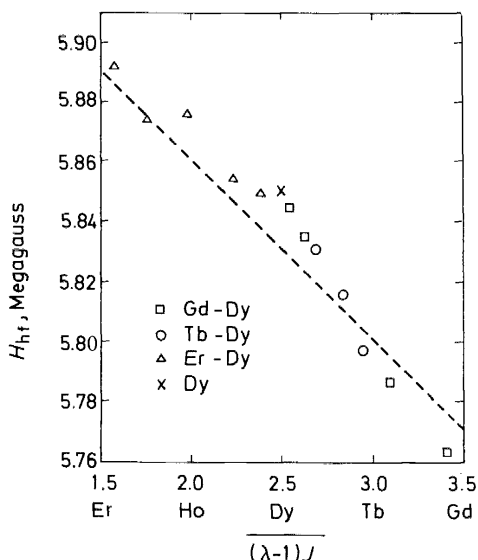


Figure 5. Hyperfine fields for  $^{163}\text{Dy}$  in various Dy alloys

inclination. Or, in rough approximation, the general trend may be represented by the dashed line shown in the figure. The values for Tb resonances in various Tb alloys also lie roughly on a straight line with the same inclination as that of Dy alloys. In the case of Er resonances in various Er alloys, the experimental points scatter in a wide range. Similar experiments have been done for Ho alloys by Mackenzie, McCausland and Wagg<sup>13</sup> and for Gd-Lu alloys by Zmora, Blau and Ofer<sup>14</sup>. The experimental points lie clearly on a straight line in each case. The values of  $h''$  defined in equation (1) were determined from the slopes of these linear changes and are shown in Table 5. These values do not exhibit much scatter.

The value of  $P_{4f}$  in metals and alloys is almost the same as that in the free ion, as already shown. Therefore,  $H_{4f}$  in metals and alloys too may be assumed to be nearly equal to that in the free ion. In Table 5 the values of  $H_{4f}$  given by Bleaney<sup>6</sup> are also shown. Then, using equation (1), the value of  $h'$  was calculated as shown in the table. The values of  $h'$  scatter considerably. For Er, because of large scattering of the experimental data from a linear relation, such analysis seems meaningless, but since  $H_{hf}$  is much smaller than

Table 5. Values of  $H_{hf}$ ,  $H_{4f}$ ,  $h'$  and  $h''$

Metal	$H_{hf}$ (MG)	$H_{4f}$ (MG)	$h''$ (MG)	$h'$ (MG)
Gd			- 0.074	+ 0.07
Tb	3.07	3.14(3)	- 0.060	+ 0.03(1)
Dy	5.85	5.70(9)	- 0.060	+ 0.12(4)
Ho	7.35	7.40(9)	- 0.083	+ 0.06(2)
Er	7.41	7.64(7)	?	?



$H_{4f}$ , even the sign of  $h'$  becomes negative, contrary to the cases of other metals.

As seen from this table, the contributions arising from the terms  $h'$  and  $h''$  are very much smaller than  $H_{4f}$ . Thus a small error in  $H_{4f}$ , or a small change in  $H_{4f}$  in metal and alloys as compared with that in the free ion, results in a large change in the value of  $h'$ . Moreover,  $h'$  and  $h''$  may depend upon the magnetic structure owing to possible change in the s-f exchange integral caused by the variation of the Fermi surface of the conduction electrons due to magnetic phase change, and they may also depend upon the nature of the wave functions at the Fermi surface, since s- and d-parts in the wave functions of the conduction electrons produce quite different hyperfine fields. The scattering of experimental points of Er from a linear change might be due to these causes, because many different magnetic phases appear in the Er alloys. Therefore, for more detailed discussions of the contributions of the conduction electron polarization on the hyperfine field, much more extensive and accurate experiments should be done.

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