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Paramagnetic Resonance and Relaxation

Hyperfine Structure in the Rare Earths

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The size of the hyperfine structure constants of the trivalent rare-earth ions in the fully magnetized state ($J_z=J$) is calculated from data on electron spin resonance in dilute salts. The results are compared with the available measurements (nuclear magnetic resonance, Mössbauer, but principally specific heat) on metals and garnets. Agreement is obtained for the metals within the exprimental errors.

1. Introduction

Measurements of the saturated electronic magnetic moment of rare earth metals indicate that the magnetic carrier is generally a trivalent lanthanide ion seated in a sea of conduction electrons. At low temperatures the metals mostly become ferromagnetic or antiferromagnetic, and the electronic magnetic moment (where known) assumes its maximum value $g_J\beta J$, where g_J is the Landé factor appropriate to the angular momentum J of the lowest state of the ground multiplet given by Russell-Saunders coupling for the trivalent ion. Similarly in the ferrimagnetic garnets the lanthanide ions are also in the trivalent state. In paramagnetic salts these ions are known to have large nuclear hyperfine couplings, which may also be expected in the cooperative phases of the metals and garnets. Some measurements of the hyperfine couplings have been made by means of the specific heat anomaly produced at very low temperatures, by means of nuclear magnetic resonance in the ferromagnetic state, and by Mössbauer experiments; we may anticipate a rapid extension of such measurements throughout the lanthanides. Most measurements have been interpreted in terms of an electronic magnetic field H_{eff} at the nucleus, but this assumes (1) that effects due to nuclear electric quadrupole interactions are negligible and (2) that we know the value of the nuclear magnetic moment. Unfortunately the latter have been deduced only from hyperfine measurements, and depend on calculated values of $\langle r^{-3}\rangle$ for the electrons; estimates by Bleaney[1] and Judd and Lindgren[2] of this quantity differ by 20 to 25%. Since the measurements are of hyperfine structure both for the cooperative phases and the paramagnetic salts, it seems better to make a direct comparison. This paper attempts to estimate the size of the hyperfine structure for the extreme electronic polarization $J_z=J$ from the available electron spin resonance data on dilute paramagnetic salts.

2. Measurements on Terbium

A large specific heat anomaly due to hyperfine interaction in terbium metal was first observed by Kurti and Safrata[3]; these measurements have been extended to lower temperatures by Heltemes and Swenson[4]. Nuclear magnetic resonance in terbium metal has been detected by Hervé and Veillet[5] at a frequency (extrapolated to 0°K) of 3190±15 Mc/s. The electron spin resonance data on paramagnetic salts of Tb^{3+} can be used to predict the size of the magnetic hyperfine structure, assuming that the metal behaves as an assembly of Tb^{3+} ions. If any contribution from conduction electrons is neglected, and the Tb^{3+} ions are assumed to have the same value of $\langle r^{-3}\rangle$ and the same contribution from core polarization as in the salts, the nuclear resonance frequency can be estimated as $\langle J_z\rangle$ (530±5) Mc/s. Here $\langle J_z\rangle$ is the average value of the angular momentum in the ferromagnetic state, and at 0°K we expect $\langle J_z\rangle$ to achieve its maximum value of $J=6$. This gives 3180

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± 30 Mc/s for the expected nuclear resonance frequency, which is in remarkably (and no doubt to some extent fortuitously) good agreement with the observed value.

In an electronic state with $J_z=J$, the distribution of electronic charge is rather far from spherical and a considerable electric field gradient at the nucleus can be expected. As the spin and orbit are strongly coupled, the principal axis of the gradient will be parallel to the direction of the electron magnetic polarization produced by the exchange and anisotropy forces. Taking this as the z axis, the Hamiltonian for the nuclei would have the form

$$\mathscr{H}=a'I_z+P\left\{I_z^2-\frac{1}{3}J(J+1)\right\},$$

where a' should vary as $\langle J_z\rangle$, which measures the electronic magnetization, and P as $\langle J_z^2-J(J+1)/3\rangle$, which is a measure of the average value of the electronic quadrupole moment. The nuclear resonance frequency should thus lie at $a'+P(2m_I-1)$ for the transition $I_z=m_I\leftrightarrow m_I-1$, and since P is rather large, it is apparent that the resonance observed by Hervé and Veillet must be the central $+1/2\leftrightarrow -1/2$ transition. Bleaney and Hill[6] have shown that a better fit to the specific heat data of Heltemes and Swenson at the lowest temperatures (where they are most accurate) can be obtained by assuming $P\approx 420$ Mc/s, a value consistent with a reasonable estimate of the nuclear electric quadrupole moment. Dr. R.J. Elliott (private communication) has pointed out, however, that this form of the quadrupole interaction, which is valid only when the electric field gradient lies along an axis of symmetry, must be modified for terbium by including a term $P'(I_x^2-I_y^2)$, where P' varies as $(1/3)\langle J_x^2-J_y^2\rangle$. Near $T=0°$K the electron moments lie normal to the hexagonal axis; taking the latter as the x-axis, we have $\langle J_x^2\rangle=0$, $\langle J_z^2\rangle=J^2$, giving $\langle J_y^2\rangle=J$. Hence

$$\frac{P'}{P}=\frac{-\frac{1}{3}J}{J^2-\frac{1}{3}J(J+1)}=-\frac{1}{2J-1}\,.$$

(For a metal such as dysprosium, where Dy^{3+} has half-integral electron spin, we have $\langle J_x^2\rangle=1/4$, $\langle J_z^2\rangle=J^2$ giving $\langle J_y^2\rangle=J-1/4$; hence in this case $P'/P=-1/(2J)$.)

Since P' is essentially an off-diagonal term, its effects are of order $(P')^2$ and are relatively small. For example, in terbium the central hyperfine resonance line would be displaced by less than 2 Mc/s, and the outer lines by still less.

3. Estimate of Hyperfine Structure Constants

Electron spin resonance data are available for all the stable isotopes of the lanthanides from measurements in dilute paramagnetic salts. In addition a few precision measurements have been made by atomic beam methods on atoms of praseodymium and thulium; these are in good agreement with the data from paramagnetic salts when the appropriate reductions have been made. The main uncertainties in these reductions come from (1) the contribution from core polarization and (2) admixtures of excited states with different J through the crystal field.

Atomic beam experiments on europium atoms (Pichanick, Sanders and Woodgate[7]) suggest that the core polarization effects in atoms are negligible. Solid state measurements on Eu^{2+} ions and Gd^{3+} ions show a somewhat larger effect, but if core polarization produces the same magnetic field at the nucleus per unit of electron spin for all ions in the lanthanide group (as holds to a good approximation for ions of the $3d$ group under similar conditions of bonding) then the effect will only be a few per cent. For Eu^{2+}, Endor measurements of Baker and Williams (unpublished) give $H_{\rm eff}=(-)0.8\times10^5$ gauss$\times S_z$. For other ions S_z must be replaced by $(g_J-1)J_z$. For example, on the assumptions mentioned above, in Tb^{3+} the contribution from this source to the measured nuclear resonance frequency would be about 200 Mc/s, compared with the observed value of 3180 Mc/s, or about 6%. For most other ions, except Sm^{3+}, $|g_J-1|$ is smaller and the effect should be proportionately smaller, especially as the field of the $4f$ electrons is appreciably greater in all other ions than in Tb^{3+}. Hence we shall assume that the core polarization contribution is the same as in the paramagnetic salts; this means that the observed hyperfine structures need only be scaled in proportion to J_z (i.e., the observed g-values) except for the effects of (2).

In paramagnetic salts, admixtures of excited states with different J show up because the anisotropy in the spin resonance gives different values of the effective g-value and hyperfine constant in different directions and their ratio is not constant, as would be the case if such admixtures were zero. The effect is most noticeable in the first half of the $4f$ group, and particularly so for samarium. In the ethyl sulphates the theory of Elliott and Stevens[8] can be used to eliminate such effects, but the uncertainties are greatest for praseodymium and samarium, being estimated as 5%. In the metals there may of course be similar effects.

Table I gives the results of calculations based on the available spin resonance data for paramagnetic salts with stable isotopes whose nuclear spin is not zero. The magnetic hyperfine constant a_0' is that appropriate to $T=0$°K, assuming that in the cooperative phase $\langle J_z \rangle$ has then assumed its maximum value and is equal to J. The estimates of the quadrupole coupling constant P are similarly obtained, assuming $\langle J_z^2-(1/3)J(J+1)\rangle = J^2-(1/3)J(J+1)$. Where the quadrupole coupling has not been measured for ion or atom, the value given includes the quadrupole moment Q as an unknown and is based on the values of Judd and Lindgren[2] for $\langle r^{-3}\rangle$; no Sternheimer-type correction has been applied. The value of a_0' and P are given in Mc/s, since they are most likely to be of interest in nuclear magnetic resonance or Mössbauer experiments.

The last two columns are of interest in specific heat measurements. The tail of the hyperfine specific heat anomaly may be expressed as a power series

$$\frac{C}{R}=\sum_{n=2}^{\infty} c_n T^{-n}\,, \tag{1}$$

in which the leading term is

$$c_2=\frac{1}{3}a_0'^2 I(I+1)$$

$$+\frac{1}{45}(P^2+3P'^2)I(I+1)(2I-1)(2I+3)\,. \tag{2}$$

The values of c_2 (in degree^2) are given in the last column, where P' has been assumed to be zero, after allowing for the natural abundance of the odd isotopes. The preceding column gives the overall width ($2Ia_0'$) of the hyperfine structure, since this gives an indication of the temperature at which higher terms in the series expansion become important. Since P is usually small compared with a_0', we can write to a good approximation

$$c_3=-\frac{1}{15}a_0'^2 PI(I+1)(2I-1)(2I+3)\,, \tag{3}$$

$$c_4=-\frac{1}{30}a_0'^4 I(I+1)(2I^2+2I+1)\,, \tag{4}$$

where a term in P^3 has been omitted in c_3 and terms in $a_0'^2P^2$, P^4 in c_4. Thus CT^2/R

Table I.

Ion	J	Isotope	I	a_0' (Mc/s)	P (Mc/s)	$2Ia_0'$ (°K)	CT^2/R (deg^2)
Pr IV	4	141	5/2	4300±200	− 3	1.02	0.12
Nd IV	9/2	143	7/2	960±20	<20	0.32	17×10^{-4}
		145	7/2	600±20	<20	0.20	
Sm IV	5/2	147	7/2	600±30	<20	0.20	10.7×10^{-4}
		149	7/2	500±25	<20	0.17	
Tb IV	6	159	3/2	+3180±30	$340Q$	0.456	$(291\pm6+2.2Q^2)\times10^{-4}$
Dy IV	15/2	161	5/2	− 820±20	+150±30	0.197	$(32.0\pm1.4)\times10^{-4}$
		163	5/2	+1140±20	+180±30	0.273	
Ho IV	8	165	7/2	+6500±60	+ 20±20	2.18	0.51
Er IV	15/2	167	7/2	930±20	$-23Q$	0.315	$(23.7\pm1+0.05Q^2)\times10^{-4}$
Tm IV	6	169	1/2	(−)2300±50	—	0.112	$(31\pm2)\times10^{-4}$
Yb IV	7/2	171	1/2	3100±10	—	0.145	$(15.9+0.43Q^2)\times10^{-4}$
		173	5/2	850± 5	$-140Q$	0.204	
Eu III	7/2	151	5/2	−360	−0.013	0.086	5.1×10^{-4}
		153	5/2	−160	−0.034	0.038	
Gd IV	7/2	155	3/2	41	?	0.006	2×10^{-6}
		157	3/2	56	?	0.008	

will start to deviate from a constant value at a temperature T where either

$$\frac{c_3}{c_2 T} = -\frac{1}{5}\left(\frac{P}{T}\right)(2I-1)(2I+3)\,, \qquad (5)$$

or

$$\frac{c_4}{c_2 T^2} = -\frac{1}{20}\left[\frac{(2Ia_0')^2}{T^2}\right]\left(1+I^{-1}+\frac{1}{2}I^{-2}\right), \qquad (6)$$

becomes no longer negligible. In holmium, for example, the effect of (6) gives a 10% drop in CT^2/R at $T=0.82(2Ia_0')=1.77$°K, and in thulium at $T=1.58(2Ia_0')=0.177$°K.

4. Discussion

Apart from the single nuclear magnetic resonance measurement on terbium, nearly all the available data come from specific heat measurements on metals. The data known to the author are summarized in Table II.

The main experimental error in determining CT^2/R arises from the uncertainty in the background specific heat which has to be subtracted from the measured values. (In some cases an anomaly in the region of 1 to 3°K has been observed which may be associated with the presence of oxygen; it is much smaller in the later measurements using improved samples.) Comparison of the results given in Table II with the calculated values of Table I is given in the following notes. It will be seen that there is no discrepancy outside the quoted errors.

Table II. Hyperfine Specific Heats of Rare Earth Metals.

Metal	Measured Value of CT^2/R (in units of 10^{-4} deg.^{2})	
Sm	13±2	Dreyfus, Goodman, Trolliet and Weil[15]
	10.3±0.5	Lounasmaa (unpublished)
Tb	280±10	Heltemes and Swenson[4]
Dy	24	Dash, Taylor and Craig[9]
	31.8±0.6	Lounasmaa and Guenther[10]
	26±2	Parks (unpublished)
Ho	5000±100	Gordon, Dempsey, and Soller[16]
Er	27±2	Parks (unpublished)

Notes on Table I and Table II

Nd. Unpublished measurements by C.A. Hutchison indicate that P is probably an order of magnitude smaller than the upper limits given. The contribution to CT^2/R from P is negligible, as is true also for Pr, Sm and Ho.

Sm. The effect of crystal field admixtures from the excited $J=7/2$ state is especially marked for the salts of samarium that have been measured. Elliott and Stevens[8] were able to fit the g-values only within 5 to 10%, though the effect on the hyperfine structure is less marked. Estimates of a_0' from the hyperfine structure constant for the parallel and perpendicular directions agree within 3%; so also do estimates from the chloride (Hutchison and Wong[11]) and the double nitrate. However an error of 5% is easily possible, which would lead to a possible error of 10% in the value of CT^2/R.

Tb. The value for P in terms of Q is based on Judd and Lindgren's value for $\langle r^{-3}\rangle$ which is some 20% smaller than that assumed by Bleaney and Hill[6] who show that $P=+0.02$°K$=420$ Mc/s gives the best fit with the data of Heltemes and Swenson.

Dy. The values given for P are based on the measurements of Park[12], but Mössbauer measurements on ^{161}Dy in garnet (Bauminger, Cohen, Marinov and Ofer[13]) suggest a value about twice as big for this isotope. This would increase the discrepancy between the observed values in Table II and that estimated in Table I, raising the latter to 33.8. However the interpretation of the Mossbauer result depends on the assumption that the magnetization follows a molecular field model at 85°K while Pauthenet's[14] measurement of the magnetization leads to a moment at 0°K of only 7.2 Bohr magnetons for Dy in the garnet instead of the expected 10 magnetons. Nevertheless it is interesting that if we combine Pauthenet's magnetic moments for 0°K and 85°K with the Mössbauer measurement of $a'=400\pm40$ Mc/s at 85°K, we obtain $a_0'=800\pm80$ Mc/s for 0°K, in good agreement with the value expected from spin resonance in paramagnetic salts.

Er. The values of P observed in three salts lead to rather different values for Q. Using Judd and Lindgren the values are 12 barns (ethylsulphate), 4 barns (chloride) and 6 barns (double nitrate); the latter two appear more reasonable than the first. If we take $Q=5$ barns, Table I leads to $CT^2/R=25.0\times10^{-4}$ deg^2, which is just within the experimental error of Parks's measurement.

Yb. The metal is non-magnetic, suggesting that the ion is Yb^{2+}, $4f^{14}$, which has a closed shell, but trivalent ions are present in garnets. Spectroscopic values of Q lie between 2 and 4 barns for ^{173}Yb, which would give an appreciable contribution to CT^2/R.

Eu, Gd. Eu IV has $J=0$, but Eu III, Gd IV ions are $4f^7$, $^8S_{7/2}$. The small hyperfine structures observed are due partly to a small break-down of Russell Saunders coupling and partly to core polarization.

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