

imply that the net rate of production of the carriers ($n=f\tau$), by whatever primary and secondary processes are involved, depends on the number of carriers already present. The above experiments do not, however, distinguish the dependence of the excitation rate f from that of the lifetime τ on the intensity of radiation.

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Paramagnetic Resonance Spectrum of Gadolinium in Hydrated Lanthanum Trichloride*

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The paramagnetic resonance spectrum of Gd^{3+} in $LaCl_3 \cdot 7H_2O$ was measured and found to agree quite well with a spin Hamiltonian with dominant coefficients $b_2^0 = \pm 0.0131 \text{ cm}^{-1}$, $b_2^2 = \mp 0.0075 \text{ cm}^{-1}$ at room temperature, and $b_2^0 = \pm 0.0099 \text{ cm}^{-1}$, $b_2^2 = \mp 0.0115 \text{ cm}^{-1}$ at liquid air temperature.

1. INTRODUCTION

THE paramagnetic resonance spectrum of Gd^{3+} in $LaCl_3 \cdot 7H_2O$ was investigated in the hope that this substance might be suitable for a maser operation. The long relaxation time of the Gd^{3+} ion and its estimated zero-field splitting ($0.1-0.3 \text{ cm}^{-1}$) appeared promising. These estimates seem to have been confirmed by experiment.

There has been considerable work on the absorption spectra of the hydrated rare earth ions including those of gadolinium.¹ It was hoped that these results might be of some help in interpreting the optical spectra. Moreover, gadolinium seemed to be a logical starting point for the investigation of other chlorides of this series having similar crystal structures.

2. CRYSTALLOGRAPHY AND EXPERIMENTAL TECHNIQUE

(a) $LaCl_3 \cdot 7H_2O$ is a triclinic crystal for which no crystallographic data seem to be available. Since the crystal has no magnetic axis of symmetry, the determination of its magnetic axes is somewhat more involved than in the trigonal and hexagonal crystals so far investigated. The directions of all the magnetic axes must be determined from the resonance spectrum. The method used here is as follows. The crystal is rotated independently around two nonparallel axes and the direction of maximum splitting of the resonance spectrum is determined. (This direction will be called henceforth the z axis.) The crystal is then rotated in a plane

perpendicular to the z axis and the positions of maximum and minimum splitting in this plane are measured (henceforth called x and y axes, respectively). These axes are found to be mutually orthogonal, as expected.

(b) A conventional 3-cm microwave spectrometer is used. One of the two axes of rotation mentioned above is furnished by the magnet which can be rotated in a horizontal plane. The second axis is obtained from a crystal mount in the cavity which can be rotated in a vertical plane (see Fig. 1). To avoid diminution of line strength due to nonorthogonality of the steady magnetic field H_0 and the rf magnetic field, the crystal is mounted in the cavity at a point where the rf magnetic field is vertical. The crystal mount is rotated by an aluminium disk graduated in degrees. The disk is detachable to facilitate work at liquid air temperatures. Accurate alignment of the disk is ensured by a pin and hole arrangement. Backlash is about 3° .

RESULTS AND INTERPRETATION

At room temperature, at a frequency of 9373 Mc/sec, absorption lines were found at the following magnetic fields (in gauss):

	913	1607	3097
	1789	2181	3157
	2618	2738	3339
z axis	3433	x axis 3329	y axis 3667
	4246	3991	4200
	5082	4728	(three coinciding
	6034	5514	lines)

The widths of the lines were of the order of 20–30 gauss.

The spin Hamiltonian which has been applied to this spectrum is

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¹ G. H. Dieke and L. Leopold, *J. Opt. Soc. Am.* **47**, 944 (1957).

$$\begin{aligned}
 3\mathcal{C} = & \beta(g_x S_x H_x + g_y S_y H_y + g_z S_z H_z) \\
 & + b_2^0 [3S_z^2 - S(S+1)] + \frac{1}{2} b_2^2 (S_+^2 + S_-^2) \\
 & + b_4^0 \{ (7/12) S_z^4 - [\frac{1}{2} S(S+1) - 5/12] S_z^2 \\
 & - \frac{1}{10} S(S+1) + (1/20) S^2 (S+1)^2 \} \\
 & + b_4^2 (7/12) [S_z^2 (S_+^2 + S_-^2) + (S_+^2 + S_-^2) S_z^2 \\
 & - (2/14) (S(S+1) + 5) (S_+^2 + S_-^2)] \\
 & + b_4^4 [(49/24) (S_+^2 + S_-^2)]. \quad (1)
 \end{aligned}$$

The normalization has been chosen to agree as much as possible with Bleaney *et al.*² The energy levels of the above Hamiltonian are calculated by a perturbation method to the third order in b_2^0 , b_2^2 , and to the first order in b_4^0 , b_4^2 , b_4^4 . The expression for the energy levels is

z axis:

$$\begin{aligned}
 E = & \beta g_z S_z H_z + b_2^0 [3S_z^2 - S(S+1)] \\
 & + \frac{1}{4} (b_2^2)^2 \{ (S+S_z)(S-S_z+1)(S+S_z-1) \\
 & \times (S-S_z+2) / [\beta 2g_z H_z + 12b_2^0 (S_z-1)] \\
 & - (S-S_z)(S+S_z+1)(S-S_z-1)(S+S_z+2) / \\
 & [\beta 2g_z H_z + 12b_2^0 (S+1)] \} \\
 & + b_4^0 \{ (7/12) S_z^4 - [\frac{1}{2} S(S+1) - 5/12] S_z^2 \\
 & - \frac{1}{10} S(S+1) + (1/20) S^2 (S+1)^2 \};
 \end{aligned}$$

x axis:

$$\begin{aligned}
 E = & \beta g_x S_x H_x - \frac{1}{2} (b_2^0 - b_2^2) [3S_x^2 - S(S+1)] \\
 & + \frac{1}{16} (3b_2^0 + b_2^2)^2 \{ (S+S_x)(S-S_x+1)(S+S_x-1) \\
 & \times (S-S_x+2) / [\beta 2g_x H_x - 6(b_2^0 - b_2^2)(S_x-1)] \\
 & - (S-S_x)(S+S_x+1)(S-S_x-1)(S+S_x+2) / \\
 & [\beta 2g_x H_x - 6(b_2^0 - b_2^2)(S_x+1)] \} \\
 & + [\frac{3}{8} b_4^0 - \frac{5}{2} b_4^2 + (35/8) b_4^4] \\
 & \times \{ (7/12) S_x^4 - [\frac{1}{2} S(S+1) - \frac{5}{2}] S_x^2 \\
 & - \frac{1}{10} S(S+1) + (1/20) S^2 (S+1)^2 \};
 \end{aligned}$$

y axis:

$$\begin{aligned}
 E = & \beta g_y S_y H_y - \frac{1}{2} (b_2^0 + b_2^2) 3S_y^2 - S(S+1) \\
 & + \frac{1}{16} (3b_2^0 - b_2^2)^2 \{ (S+S_y)(S-S_y+1)(S+S_y-1) \\
 & \times (S-S_y+2) / [\beta 2g_y H_y - 6(b_2^0 + b_2^2)(S_y-1)] \\
 & - (S-S_y)(S+S_y+1)(S-S_y-1)(S+S_y+2) / \\
 & [\beta 2g_y H_y - 6(b_2^0 + b_2^2)(S_y+1)] \} \\
 & + [\frac{3}{8} b_4^0 + \frac{5}{2} b_4^2 + (35/8) b_4^4] \\
 & \times \{ (7/12) S_y^4 - [\frac{1}{2} S(S+1) - \frac{5}{2}] S_y^2 \\
 & - \frac{1}{10} S(S+1) + (1/20) S^2 (S+1)^2 \}.
 \end{aligned}$$

The coefficients b_4^{-2} , b_4^{-4} of polynomials in S_x , S_y , S_z transforming like the imaginary components of the spherical harmonics Y_4^2 , Y_4^4 were not determined, since they do not effect the splitting along the *x*, *y*, and *z* axes in the first order.

Since the splitting (0.54 cm^{-1}) is comparable to the applied frequency (0.3 cm^{-1}), a successive approximation had to be applied. Firstly, the coefficients g_x , g_y , g_z , b_2^0 , b_2^2 , were calculated by the least square method using first order perturbation calculation which is linear in the coefficients. The second and third order corrections were calculated using these coefficients; the third order corrections are of the same order of magnitude as the second order corrections in this case. These corrections were applied to the lines $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ and corrected values of g_x , g_y , g_z were obtained. Using these *g* values and the second and third order corrections mentioned before, the corrected b_2^0 , b_2^2 were calculated. Next, the eigenvalues and derivatives of the eigenvalues with respect to the coefficients were computed, again by perturbation calculation to the third order. With these new eigenvalues and derivatives, a further correction to the coefficients was computed by least squares. The coefficients b_4^0 , b_4^2 , b_4^4 were estimated from the deviations of these corrected eigenvalues from the experimental data.

The values of the coefficients, thus calculated, are $g_x = 1.998 \pm 0.003$, $g_y = 2.000 \pm 0.003$, $g_z = 1.989 \pm 0.003$,

$$b_2^0 = \pm 0.01313 \pm 0.00005 \text{ cm}^{-1},$$

$$b_2^2 = \mp 0.00752 \pm 0.0002 \text{ cm}^{-1},$$

$$b_4^0 = \pm 0.0002 \pm 0.0001 \text{ cm}^{-1},$$

$$\frac{3}{8} b_4^0 - \frac{5}{2} b_4^2 + (35/8) b_4^4 = 0.0000 \pm 0.0001,$$

$$\frac{3}{8} b_4^0 + \frac{5}{2} b_4^2 + (35/8) b_4^4 = \pm 0.0002 \pm 0.0001.$$

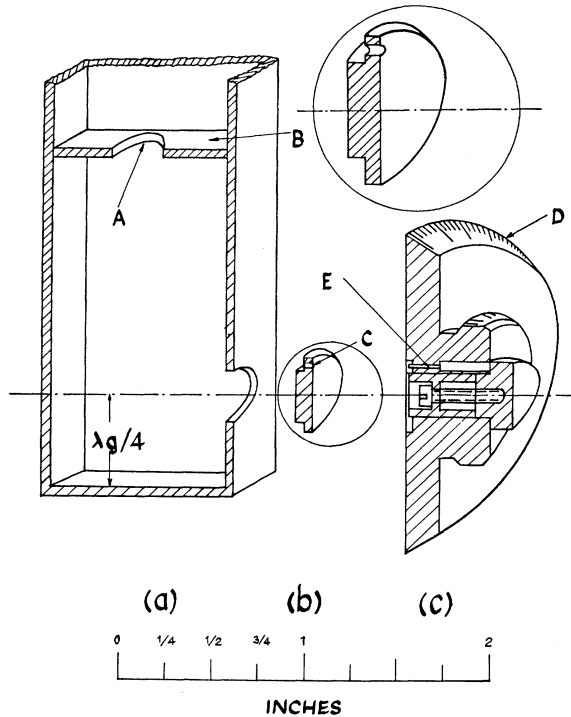


FIG. 1. Cavity arrangement. (a) Cavity; (b) crystal mount; (c) graduated disk; (A) iris; (B) metal plate; (C) positioning hole; (D) scale; (E) pin.

² Bleaney, Scovil, and Trenam, Proc. Roy. Soc. (London) A223, 19 (1954).

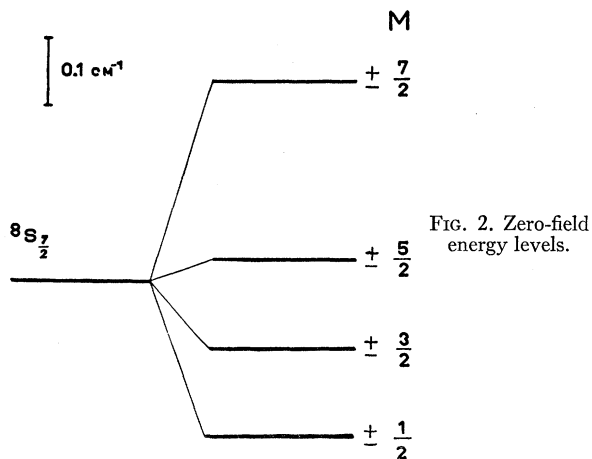


FIG. 2. Zero-field energy levels.

Thus, at zero field, the energy levels consist of four doublets with the relative separation of roughly 0.13, 0.13, and 0.28 cm^{-1} , as is shown in Fig. 2. Only the relative signs of the b parameters were determined. Thus the order of the levels has not been established. Agreement of the calculated with the observed values of energy levels is within 20 gauss. The deviations seem to be caused mainly by the neglect of fourth and fifth order terms in the perturbation calculation and by the neglect of terms in the spin Hamiltonian which transform like spherical harmonics of the sixth order ($Y_6^0, Y_6^2, Y_6^4, Y_6^6$).

Somewhat less accurate measurements were carried out at liquid air temperature. The splitting along the z axis was found to decrease, the lines at weakest and strongest fields being at 1287 and 5592 gauss. The splitting along the x axis however increased, the corresponding lines being at 1400 and 5625 gauss. The splitting along the y axis did not change significantly from the room temperature value. The magnetic axis rotated less than 5° from the room temperature directions. The coefficients b_2^0, b_2^2 at liquid air temperatures are thus found to be

$$b_2^0 = \pm 0.0099 \pm 0.003 \text{ cm}^{-1},$$

$$b_2^2 = \mp 0.0115 \pm 0.0007 \text{ cm}^{-1}.$$

These results should only be used with considerable reservations at still lower temperatures.

4. THEORY

The splitting of the $4f^7 {}^8S_{7/2}$ ground state of Gd^{3+} by the crystal field has been discussed by Van Vleck and

Penney.³ The splitting cannot be caused by a first order process for an S state, nor by second order perturbations in the crystal field and spin-orbit coupling. The selection rules ($\Delta L = \pm 1$, no change in parity for LS coupling; L odd, change in parity; or L even, no change in parity for matrix elements of the crystal field connecting any state with an S state) forbid interference of the two processes. LS coupling or the crystal field acting alone cannot produce any splitting of the 8S state. One therefore has to consider higher order perturbations. Each coefficient of the spin Hamiltonian has to be considered separately as there may be a number of mechanisms responsible for the magnitude and sign of each one. Pryce,⁴ for example, proposed a process

$$\langle 4f^7 {}^8S | W_{ss} | 4f^6 6p {}^8D \rangle \langle 4f^6 6p {}^8D | V_{\text{axial}} | 4f^7 {}^8S \rangle,$$

where W_{ss} is the operator of the spin-spin interaction and V_{axial} is the axial component of the electrostatic potentials. This mechanism can be seen to give rise to a splitting, as the matrix elements of the spin-spin interactions connect states with $\Delta L = \pm 2$ and same parity and then cause interference with the axial crystal field ($\Delta L = \pm 2$) in the second order. Other mechanisms operative within the $4f^7$ manifold or including higher excited configurations can be constructed. Some of these have been listed by Hutchison *et al.*⁵ It seems, at present, impossible to distinguish the mechanism of the splitting from the few coefficients determined from the paramagnetic resonance spectrum. The complex temperature dependence of the splitting points to the existence of a considerable number of mechanisms.

5. CONCLUSION

It is seen that the large zero field splitting (0.5 cm^{-1}) makes the perturbation calculation converge extremely slowly, so that quite considerable labor of computation is involved. Faster convergence could have been obtained by working at 1-cm wavelength, but unfortunately no adequate magnet was available. Alternatively, the manual labor of the calculations could have been diminished somewhat and slightly better accuracy obtained by use of an electronic computer.

³ J. H. Van Vleck and W. G. Penney, *Phil. Mag.* **17**, 961 (1934).

⁴ M. H. L. Pryce, *Phys. Rev.* **80**, 1107 (1950).

⁵ Hutchison, Judd, and Pope, *Phys. Soc. (London)* **B70**, 514 (1957).