

Paramagnetic Resonance of Tb^{3+} Ions in CaWO_4 and CaF_2

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The paramagnetic resonance absorption spectra of Tb^{3+} ions in single crystals of CaWO_4 and CaF_2 have been studied at 4.2°K over a wide range of frequencies from 4 to 50 kMc/sec. The observed spectra fit a simple spin Hamiltonian $\mathcal{H} = g_{\parallel}\beta H \cos\theta S_z + \Delta_x S_x + \Delta_y S_y + A S_z I_z$. Because the zero-field splittings in these crystals fall in the microwave region, direct measurement of the parameters in the Hamiltonian was possible and these were in excellent agreement with those obtained from the high-frequency measurements. In CaWO_4 , the parameters are $g_{\parallel} = 17.777 \pm 0.005$, $\Delta = (\Delta_x^2 + \Delta_y^2)^{1/2} = 8.131 \pm 0.006$ kMc/sec and $A = 6.284 \pm 0.005$ kMc/sec. In CaF_2 , there are two sets of spectra, one having axial symmetry about the cubic axes, and the other having axial symmetry about the body diagonals of the cube. The spectra with symmetry about the cubic axes are interpreted as resulting from Tb^{3+} ions which have a charge-compensating F^- ion occupying the nearest neighbor interstitial site. The spectra with symmetry about the body diagonals can arise from Tb^{3+} ions which have either (a) a charge-compensating F^- ion occupying the next-nearest interstitial site, or (b) a charge-compensating O^{2-} ion occupying the site of one of the eight F^- ions surrounding the paramagnetic ion. Our measurements do not allow us to distinguish between these two possibilities. The parameters in the spin Hamiltonian are, respectively: $g_{\parallel} = 17.77 \pm 0.02$, $\Delta = 5.134 \pm 0.006$ kMc/sec, and $A = 6.26 \pm 0.01$ kMc/sec; $g_{\parallel} = 17.28 \pm 0.01$, $\Delta = 31.67 \pm 0.02$ kMc/sec, and $A = 6.10 \pm 0.01$ kMc/sec.

1. INTRODUCTION

THE paramagnetic resonance absorption spectrum of Tb^{3+} ions has been observed in single crystals of calcium tungstate and calcium fluoride. The spectrum of Tb^{3+} ions has been observed previously by Baker and Bleaney¹ in yttrium ethyl sulfate and by Hutchison and Wong² in lanthanum chloride. Both these lattices have C_{3h} symmetry, whereas CaWO_4 has C_{4h} symmetry and CaF_2 is cubic. The electron configuration of the Tb^{3+} ion is $4f^8$ and the ground state of the free ion is 7F_6 . In a crystal field of complete axial symmetry the ground state splits into six doublets characterized by $J_z = \pm 6, \pm 5, \dots, \pm 1$, and a singlet with $J_z = 0$. The value of $g_{\parallel} - g_{\perp}$ for each doublet is $2\Delta J_z$, where Δ is the Landé factor and is $\frac{3}{2}$ for Tb^{3+} . In all cases observed so far $g_{\perp} \sim 0$ and g_{\parallel} is very nearly 18, which indicates that the lowest lying state is the $J_z = \pm 6$ doublet.

Departure from complete degeneracy of the doublets depends upon the degree of axial symmetry. For example, a field of threefold symmetry has matrix elements which connect states whose value of J_z differ by six; the degeneracy of the ground state is removed by the admixture of a component of the state $J_z = 0$. A field of fourfold symmetry can mix states whose J_z differs by four, and so the ground state would consist of an admixture of $J_z = \pm 6$ and $J_z = \pm 2$ wave functions. This admixture of excited states produces a zero-field splitting of the ground-state doublet and results in a reduction of g_{\parallel} from the pure $J_z = \pm 6$ value of 18.

The spectrum of the Tb^{3+} ion can be interpreted in terms of the following spin Hamiltonian:

$$\mathcal{H} = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \Delta_x S_x + \Delta_y S_y + A S_z I_z + B(S_x I_x + S_y I_y). \quad (1)$$

The effective spin is $S = \frac{1}{2}$, and the nuclear spin $I = \frac{3}{2}$ arises from the 100% abundant Tb^{159} isotope. Since the component of the g tensor perpendicular to the crystal axis g_{\perp} is zero or very nearly so, transitions of the type $\Delta m_s = \pm 1$, which occur when the rf magnetic field is perpendicular to the axis of quantization, have zero probability. Transitions are allowed, however, because of the admixture of the excited states with the ground-state wave functions. Transitions can be induced between the components of the wave functions for which $\Delta m_s = 0$ by an rf magnetic field parallel to the crystal axis. This admixture of the wave functions, which makes electronic transitions possible and which splits the ground-state doublet, is introduced into the Hamiltonian by the use of the terms $\Delta_x S_x + \Delta_y S_y$, which can be related to the off-diagonal elements of the crystal-field potential when the diagonal elements are known. A quadrupole term may also be necessary in the Hamiltonian. A large quadrupole interaction has been found for Tb^{160} in an ethyl sulfate crystal in a nuclear alignment experiment³ and such an interaction has also been inferred for Tb^{159} from specific heat measurements on the metal.⁴ The positions of the normal electron resonance lines for which $\Delta m_I = 0$ are not sensitive to the quadrupole coupling. The effect of this interaction would only be detectable in weak second-order transitions in which the nuclear spin flips simultaneously with that of the electron. Although weak lines were observed in the spectrum, it is felt that these arise from pairs of Tb^{3+} ions rather than from

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¹ J. M. Baker and B. Bleaney, Proc. Phys. Soc. (London) **A68**, 257 (1955); Proc. Roy. Soc. (London) **A245**, 156 (1958).

² C. A. Hutchison and E. Wong, J. Chem. Phys. **29**, 754 (1958).

³ C. E. Johnson, J. F. Schooley, and D. A. Shirley, Phys. Rev. **120**, 2108 (1960).

⁴ E. C. Heltemes and C. A. Swenson, J. Chem. Phys. **35**, 1264 (1961).

nuclear flip transitions. The quadrupole term has therefore been omitted from the Hamiltonian.

2. EXPERIMENTAL PROCEDURE

The experiments were performed at 4.2°K over a frequency range from 4 to 55 kMc/sec. In the frequency interval from 4 to 15 kMc/sec a helix slow-wave structure was wound on a cylindrically-shaped specimen. Magnetic resonance was observed as a change in the power transmitted through the helix as the resonance was traversed. Magnetic field modulation at 60 cps allowed display of the resonance lines on the oscilloscope using a crystal detector and a high-gain video amplifier. In the region from 25 to 55 kMc/sec the helix was replaced by a simple waveguide; the sample filled an RG96/U guide (cross section: 0.28 in. by 0.14 in.) for a length of about 0.25 in. At these high frequencies and at 4.2°K, samples of this size produced strong resonance signals (0.1 db or more). These two assemblies were used to study the behavior of the lines in the low-field region and to obtain direct measurements of the splittings of the energy levels in the zero-magnetic field.

Two high-sensitivity spectrometers operating at about 23 kMc/sec (*K* band) and 50 kMc/sec (*M* band) were used to obtain precision measurements, and to study the angular variation of the spectra. These spectrometers were of the cavity-reflection type and had variable couplers to match the cavities (operating in the cylindrical TE_{01} mode) to the input waveguides; this system, devised by Gordon,⁵ is considerably less sensitive to microphonics than the conventional microwave bridge since the matching is performed right at the cavity-coupling iris. Automatic frequency control was provided for both signal source and local oscillator. The *K*-band signal source was locked to a harmonic of a special crystal oscillator and the *M*-band source to a harmonic of a commercial ultra-stable microwave oscillator (which was itself locked to an Invar cavity). 2K33 klystrons provided microwave power at *K* band and backward-wave oscillators (made in this laboratory) at *M* band. A superheterodyne receiver was used, and the output was fed to either a high-speed strip chart recorder or an oscilloscope for display. The frequency of the microwave sources was measured with a Hewlett Packard transfer oscillator (100–220 Mc/sec) and electronic counter.

A modified Varian 12-in. electromagnet, rotatable about a vertical axis, provided fields up to 15.5 kgauss. Slow sweeps of the field were obtained by use of a function generator; for oscilloscope display field modulation of up to 50 gauss at 100 cps was obtained by large Helmholtz coils driven from an audio oscillator and power amplifier. The field was measured by a "Numar" proton-resonance probe, using the decade-electronic counter.

⁵ J. P. Gordon, Rev. Sci. Instr. **32**, 658 (1961).

The crystals were pulled from the melt by the Czochralski method and were kindly made available to us by Nassau.⁶ The concentration of Tb^{3+} ions varied from 0.1% to 0.005%. The crystals were oriented by x-ray techniques and the alignment after transfer to the cavity was known to $\pm \frac{1}{2}^\circ$. The accuracy of the measurements was limited only by the precision with which the proton resonance could be aligned with the electron-spin resonance signal; this was estimated to be about $\frac{1}{3}$ of the full line width, measured at the $\frac{1}{2}\chi_{\max}$ points.

3. SPECTRUM OF Tb^{3+} IONS IN $CaWO_4$

Each calcium ion in the calcium-tungstate lattice is surrounded by eight oxygen ions, each situated at a distance of approximately 2.5 Å. The point symmetry is S_4 . There are four calcium ions per unit cell,⁷ which occur in pairs, the symmetry of one type of site being obtained from the other by a reflection in the (001) plane passing through the Ca ion. The resonance spectra from paramagnetic impurities located at these two types of site would therefore be expected to be identical.

The observed spectrum of Tb^{3+} ions in $CaWO_4$ at constant frequency consisted of four equally-spaced lines, having a separation of 252.5 gauss. These lines were rather narrow, having a full width of 1.4 gauss at *K* band and 4.5 gauss at *M* band in a crystal with a nominal concentration of Tb^{3+} ions of 0.02%. With *H* directed along the *c* axis, the lines reached a minimum field, corresponding to an effective value of g_{11} of 18.928 when $\nu = 23.690$ kMc/sec. A plot of the mean of the four-line positions against $\sec\theta$, where θ is the angle between the applied field and the *c* axis, yielded a straight line, which enabled an upper limit of 0.15 to be set for the value of g_L . A similar plot of the line spacing against $\sec\theta$ also yielded a straight line showing that the hyperfine spacing is governed predominantly by the *A* term. Since g_L is nearly zero, it is difficult to get a reliable estimate for *B*. The spin Hamiltonian⁸ of Eq. (1) can thus be simplified to:

$$\mathcal{H} = g_{11}\beta H \cos\theta S_z + \Delta_x S_x + \Delta_y S_y + A S_z I_z. \quad (2)$$

The corresponding secular determinant can be factored and the exact solution is

$$E = \pm \frac{1}{2} [(g_{11}\beta H \cos\theta + Am)^2 + \Delta^2]^{\frac{1}{2}} \quad (3)$$

where

$$\Delta = (\Delta_x^2 + \Delta_y^2)^{\frac{1}{2}}.$$

From two precise sets of measurements at *K* band and *M* band, the three constants in Eq. (3) were determined; these values are shown in Table I.

⁶ K. Nassau and L. G. Van Uitert, J. Appl. Phys. **31**, 1508 (1960).

⁷ R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1948), Vol. II, Chap. 8.

⁸ B. Bleaney and K. W. H. Stevens, *Reports on Progress in Physics* (The Physical Society, London, 1953), Vol. 16, p. 108; K. D. Bowers and J. Owen, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. 18, p. 304.

TABLE I. Summary of paramagnetic resonance data for Tb⁺⁺⁺ ions in CaWO₄ and CaF₂.

Host lattice site	CaWO ₄	CaF ₂ (Complex type I)	CaF ₂ (Complex type II)
Symmetry axis	<i>c</i> axis	$\langle 100 \rangle$	$\langle 111 \rangle$
$g_{ }$	17.777 ± 0.005	17.768 ± 0.020	17.28 ± 0.01
g_{\perp}	< 0.15	< 0.25	< 0.25
Δ (from high-frequency data)	8.131 ± 0.006 kMc/sec	5.134 ± 0.006 kMc/sec	31.67 ± 0.02 kMc/sec
Δ (from zero-field data)	8.136 ± 0.010 kMc/sec
A (from high-frequency data)	6.284 ± 0.005 kMc/sec	6.26 ± 0.01 kMc/sec	6.10 ± 0.01 kMc/sec
A (from zero-field data)	6.32 ± 0.01 kMc/sec
Hyperfine spacing	252.5 ± 0.2 gauss	251.9 ± 0.4 gauss	252.2 ± 0.3 gauss
Observed zero-field resonance frequencies			
$m = \pm \frac{3}{2}$	12.495 ± 0.005 kMc/sec	10.75 ± 0.15 kMc/sec	32.995 ± 0.025 kMc/sec
$m = \pm \frac{1}{2}$	8.726 ± 0.005 kMc/sec	5.9 ± 0.1 kMc/sec	31.820 ± 0.025 kMc/sec
Linewidth at <i>K</i> band	1.4 ± 0.3 gauss	14.4 ± 0.5 gauss	
Linewidth at <i>M</i> band	4.5 ± 0.5 gauss	16 ± 1 gauss	24 ± 1 gauss

We have studied the behavior of the lines in the low-frequency region using the helix slow-wave structure. The experimental results, taken at $\theta = 0$, are shown in Fig. 1. The form of the curves remained the same as θ was varied but the values of H increased; however, the frequencies at which the various lines crossed remained the same. Equation (3) is seen to be obeyed rather closely. Each curve is a section of a hyperbola, one curve being obtained from another by a simple translation along the H axis. Physically, this means that the magnetic field which the electrons experience is the vector sum of the externally applied field and that due to the nucleus; as the nuclear orientation changes from one allowed state to the next, the resultant field changes by about 250 gauss. Thus, the hyperfine components are equally spaced in field, even at very low field values. The field of the nucleus in the $m = -\frac{1}{2}$ state just cancels the applied field when $g_{||}\beta H = A/2$, and in the $m = -\frac{3}{2}$ state when $g_{||}\beta H = 3A/2$; the electron resonance then occurs at the lowest possible frequency where $h\nu = \Delta$. The two zero-field resonances occur when

$$h\nu(\pm \frac{3}{2}) = [(9/4)A^2 + \Delta^2]^{\frac{1}{2}}$$

and

$$h\nu(\pm \frac{1}{2}) = [\frac{1}{4}A^2 + \Delta^2]^{\frac{1}{2}}$$

and the $m = +\frac{1}{2}$ level crosses the $m = -\frac{3}{2}$ level at $g_{||}\beta H = A/2$ when

$$h\nu = (A^2 + \Delta^2)^{\frac{1}{2}}.$$

By measuring these three frequencies we were able to obtain cross checks on the values of the constants A and Δ . The values are $\Delta = 8.131 \pm 0.006$ kMc/sec and $A = 6.32 \pm 0.01$ kMc/sec. The value of Δ is in excellent agreement with that obtained from the high-frequency measurements while the values of A differ by about 0.3% outside the expected errors.

As the angle θ between the applied field and the c axis was increased, the lines broadened; at *K* band the width increased from 1.4 gauss when $\theta = 0$, to about 15 gauss when $\theta = 60^\circ$. It should be pointed out that measurements of width are not too meaningful since the lines saturated very easily; even with an input power

of 10^{-8} w the lines showed evidence of some saturation when observed with 100 cps field modulation and oscilloscope presentation. As θ was further increased the line shape distorted, the peaks becoming somewhat flattened; at angles greater than about 70° , the lines became partially resolved into doublets, the highest field line being better resolved than the lowest field line. We interpret this as indicating that the two types of Ca site are not completely equivalent.

Besides the four main lines, other weaker lines have also been observed, which occur in the same field region as the main lines. The intensity of these satellite lines varied from crystal to crystal, being more intense in crystals of high concentration; in a crystal containing 0.02% Tb³⁺ ions the ratio of the heights of the satellite lines to the main lines was about 1 to 20. At *M* band, two sets of satellite lines were observed, one set having a width about equal to that of the main lines, the other set being much broader, with a width of about 30 gauss. At $\theta = 0$, the narrow line spectrum consisted of four lines, each displaced above the corresponding

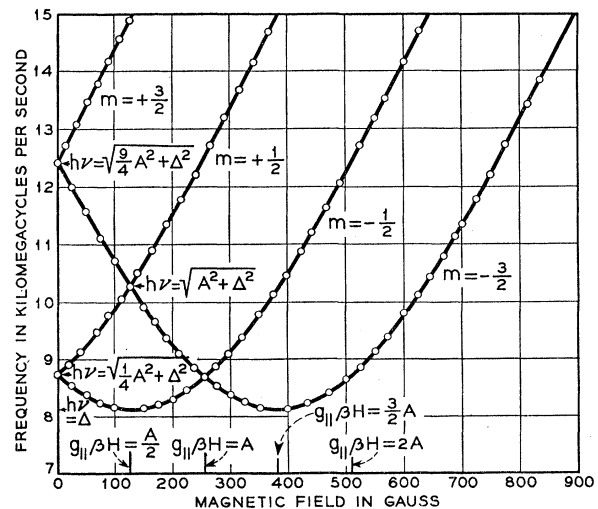


FIG. 1. The variation of the resonance frequencies of the hyperfine components of Tb³⁺ ions in CaWO₄ in the low-magnetic field region.

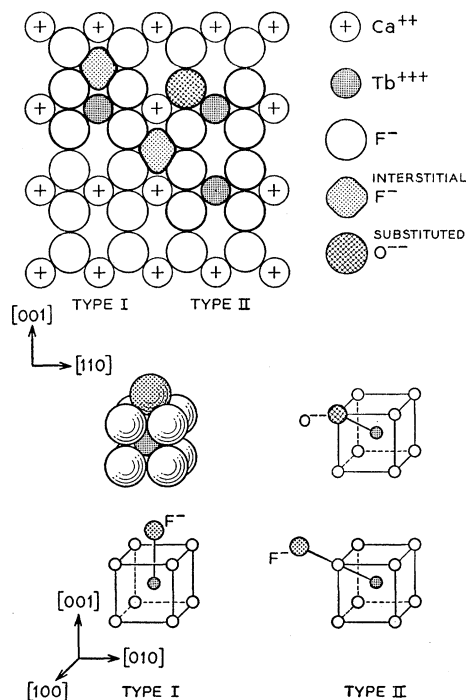


FIG. 2. Plane and perspective views of the two types of complex needed for charge compensation and for the observed symmetry of spectra.

main line by 30 gauss. As the angle θ was increased, each split into four components, which moved symmetrically in pairs about a mean position. The separation of these lines for a given value of θ , also depended upon the angle φ between the projection of H in the ab plane and the a axis. The broad lines had a hyperfine spacing of about 295 gauss and their center was displaced about 380 gauss below the center of the main lines. They also split into components as θ was increased, but these were difficult to resolve with our present sensitivity because of their width and low intensity. At 53.67 kMc/sec the effective values for g_{II} for the narrow and broad satellite lines were 17.74 ± 0.04 and 21.9 ± 0.01 , respectively. The narrow lines were also observed in the low-field region; they have zero-field splittings in the region below 12 kMc/sec. Further study will be needed to work out a detailed model to account for these satellite lines, but we believe from the present evidence that they arise from pairs of Tb^{3+} impurity ions, probably occupying adjacent Ca^{++} lattice sites, and possibly associated with a charge compensating Ca^{++} vacancy. Satellite lines, attributed to pairs of impurity ions, have also been observed by Mims⁹ in the spectrum of Ce^{3+} ions in $CaWO_4$. In crystals containing 0.05% Tb^{3+} ions there is, in addition to the resolved lines, a general background absorption in the low-frequency region which may

⁹ W. B. Mims (private communication).

possibly be associated with pairs of higher order or aggregates of impurity ions.

4. SPECTRUM OF Tb^{3+} IONS IN CaF_2

The calcium fluoride lattice is cubic, with two calcium ions and four fluorine ions to a unit cell. The calcium ions occupy positions at the corners and at the face centers of the unit cube and the eight fluorines are situated at sites of tetrahedral symmetry equivalent to $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. All the calcium ions are equivalent and each is surrounded by eight fluorine nearest neighbors which lie along $\langle 111 \rangle$ directions.

When a trivalent ion replaces a divalent calcium ion in the lattice the extra charge has to be compensated in some way. Bleaney, Llewellyn and Jones¹⁰ have studied the spectra of Nd^{3+} and U^{3+} in CaF_2 ; they considered various ways in which charge compensation might occur and concluded that the only satisfactory model was one in which an equal number of F^- ions enter the lattice in interstitial sites. This conclusion is supported by the x-ray work of Zintl and Udgard¹¹ and D'Eye and Martin¹² and by further paramagnetic resonance studies of other trivalent ions by Baker, Hayes, and Jones.¹³ Some of our results can be interpreted in a similar manner.

The interstitial site is the body-center position of the unit cube, which is equivalent to a site at the center of the cube edge, such as $(0, 0, \frac{1}{2})$. For a given Ca^{++} ion site, there are six nearest interstitial sites which lie along the $\langle 100 \rangle$ directions at a distance of 2.73 Å, and eight next-nearest interstitial sites which lie along the $\langle 111 \rangle$ directions at a distance of 4.72 Å. Since the Tb^{3+} ion and the compensating F^- ion are mutually attracted by their opposite charges, the most stable arrangement of the ions is obtained when each Tb^{3+} ion has a F^- ion occupying one of the six nearest interstitial sites. We shall refer to such a pair of ions as a "complex" of type I. However, the binding energy when the F^- ion occupies the next nearest interstitial site will be less than that for the nearest site, which itself is less than kT at 1200°C, since the pairs can be disordered at this temperature.¹⁴ Since the melting point of CaF_2 is above 1200°C, we might also expect to see spectra arising from these "complexes," which we shall refer to as type II. The effect of the complex is to superimpose a dipolar-electric field upon the normal crystal field of the lattice. For the type I complexes this axial field lies along one of the axes of the cube, whereas for the type II complexes, the field axis lies along one of the body diagonals. The type I

¹⁰ B. Bleaney, P. M. Llewellyn, and D. A. Jones, Proc. Phys. Soc. (London) **B69**, 858 (1956).

¹¹ E. Zintl and A. Udgard, Z. anorg. u. allgem. Chem. **240**, 50 (1939).

¹² R. W. M. D'Eye and F. S. Martin, J. Chem. Soc. (London) **349**, 1847 (1957).

¹³ J. M. Baker, W. Hayes, and D. A. Jones, Proc. Phys. Soc. (London) **73**, 942 (1959).

¹⁴ E. Friedman and W. Low, J. Chem. Phys. **33**, 1275 (1960).

complexes are thus subjected to a field of fourfold symmetry, while the type II complexes have threefold symmetry.

An alternative model for the type II complex should also be considered. Each Ca^{++} ion is surrounded by eight F^- ions which lie at the corners of a cube. If one of these F^- ions were to be replaced by an O^{--} ion, a complex having axial symmetry about one of the $\langle 111 \rangle$ directions would result. Such a substitution is feasible since the ionic radii of F^- (1.33 Å) and O^{--} (1.36 Å) are very similar. Feofilov¹⁵ has concluded from studies of the optical spectra of trivalent ions in CaF_2 that such a model would explain some of his observations. Although our crystals were grown under an inert atmosphere, it is possible that they contained small amounts of oxygen which might have been present in the inert gas as a trace of oxygen gas or water vapor. Figure 2 illustrates the various possibilities of complexes.

Let us define the axis of a complex as the direction of the F^- ion from the Tb^{3+} ion. Since all of the six possible sites for the F^- ion are energetically equivalent, we should expect to find an equal number of the complexes with their axes lying along each of the six directions. The resonance spectrum depends upon the angle θ between the externally applied field and the axis of each complex. Complexes which lie on a common axis give rise to a single spectrum, and as the complexes occur in pairs which differ only in the sign of their axes, we expect to find, for an arbitrary value of θ , three spectra from the type I complexes and four from the type II complexes.

We noted previously that the transition probability for these lines is maximum when the rf magnetic field lies along the axis of the complex and is zero when the field lies in the plane perpendicular to this axis. The three axes of the type I complexes are mutually perpendicular and in order to observe the three spectra simultaneously, there must be a component of the rf magnetic field along each of these axes. This caused some difficulty in the early stages of the work. For example, suppose that the rf magnetic field is vertical, as is the case when the sample is placed at the center of a vertical TE_{01} cylindrical cavity, and the external magnetic field is rotated in the horizontal plane; then, no absorption at all is observable at 24 kMc/sec if the crystal is oriented with a cube face lying in the horizontal plane. This is because the two complexes with axes in the horizontal plane have zero interaction with the vertical rf field, and the complex with the vertical axis is always orthogonal to the external field and hence shows no resonance since g_1 is zero. On the other hand, if the crystal is mounted with the $[111]$ axis vertical, the rf magnetic field then has equal components along the three axes and the three sets of lines appear with equal intensity.

¹⁵ I. V. Stepanov and P. P. Feofilov, Soviet Phys.—Doklady (English Trans.) **1**, 350 (1956); P. P. Feofilov, Doklady Akad. Nauk. S.S.S.R. **99**, 731 (1954).

The spectrum at 24 kMc/sec can be interpreted in terms of complexes of type I alone. As in $CaWO_4$, g_1 is zero to within the experimental error and g_{11} is a little less than 18. Each of the three pairs of sites gives rise to one absorption line which is split into four hyperfine components equally spaced in magnetic field. The angular variation of the centers of these hyperfine groups as the field is rotated in the (111) plane is shown in Fig. 3. The angle plotted φ is the angle of rotation of the magnet in the (111) plane and is zero when the component of H along the $[001]$ direction is largest. The angle θ_i between the magnetic field and the axis of each of the three complexes is given by the relations

$$\cos\theta_1 = \left(\frac{2}{3}\right)^{\frac{1}{2}} \cos\varphi,$$

$$\cos\theta_2 = \left(\frac{2}{3}\right)^{\frac{1}{2}} \cos\left(\varphi + \frac{2}{3}\pi\right)$$

and

$$\cos\theta_3 = \left(\frac{2}{3}\right)^{\frac{1}{2}} \cos\left(\varphi - \frac{2}{3}\pi\right).$$

Figure 3 was obtained by using these relations and Eq. (3). The small circles are experimental points and agree extremely well with the theoretical curves. At $\varphi=0$, θ_1 reaches the minimum angle, given by $\cos\theta_1 = \left(\frac{2}{3}\right)^{\frac{1}{2}}$ and $\cos\theta_2 = \cos\theta_3 = \left(\frac{1}{6}\right)^{\frac{1}{2}}$; the spectrum thus consists of two sets of lines, the degenerate set occurring at exactly twice the field of the other set. When $\varphi=30^\circ$, $\theta_1 = (180^\circ - \theta_2) = 45^\circ$ and $\theta_3 = 90^\circ$; the line corresponding to $\theta_3 = 90^\circ$ would only appear at infinitely high fields, while the other two lines cross in the low-field region. Because of the threefold symmetry and independence of the signs of the axes the spectrum repeats every 60° . Figure 4 shows recorder tracings of the spectrum when φ equals 0, 10° , 20° , and 30° .

The angular variation of the spectrum as the external field was rotated in the (110) plane was also studied. This plane has the advantage that the applied field can

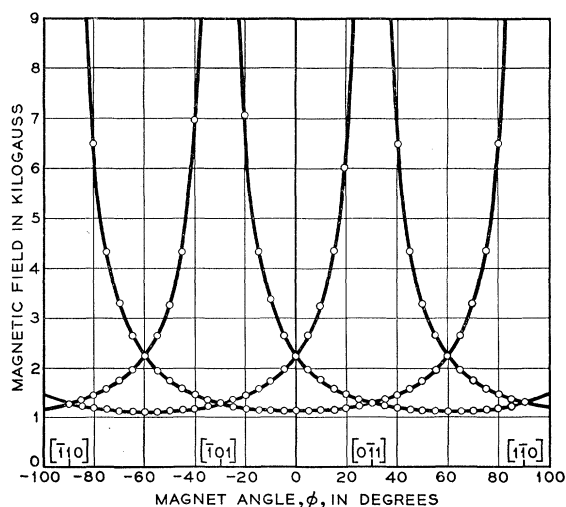


FIG. 3. The angular variation of the resonance field for type I complexes of Tb^{3+} ions in CaF_2 when H is rotated in the (111) plane. Data taken at 23.94 kMc/sec.

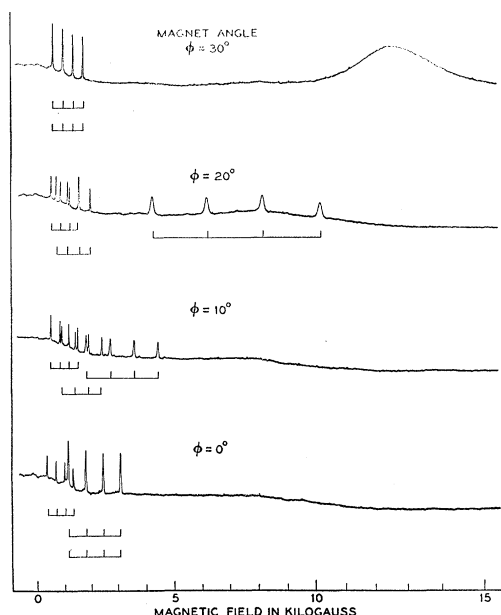


FIG. 4. The angular dependence of the spectra of Tb^{3+} ions in CaF_2 at K band. H is rotated in the (111) plane making various angles θ with respect to the $[001]$ axis. Note the background absorption in the low-field region and the broad line which appears at about $g=1.3$ when $\varphi=30^\circ$.

be directed along a cube edge, a face diagonal, and a body diagonal. The crystal was placed on the bottom of the TE_{01} cavity so that the rf magnetic field had components along all three axes. The corresponding angular relationships are

$$\cos\theta_1 = \cos\varphi$$

and

$$\cos\theta_2 = \cos\theta_3 = (1/\sqrt{2}) \sin\varphi,$$

where again φ is the angle of rotation of the magnet and is zero when H is along the $[001]$ direction. Two of the lines are thus coincident for all values of φ , while the other line can attain all possible values of θ . By setting φ to zero a precise measurement of the effective g_{11} was made.

The spectrum at 50 kMc/sec has also been studied with the external field lying in the (110) plane. By comparing the effective values of g_{11} at the two frequencies, the three constants in the spin Hamiltonian were calculated; these are shown in Table I. The zero-field splittings calculated from these data were $\nu(\pm\frac{3}{2}) = 10.68$ kMc/sec and $\nu(\pm\frac{1}{2}) = 6.01$ kMc/sec. The frequencies measured directly using the helix were $\nu(\pm\frac{3}{2}) = 10.75 \pm 0.15$ kMc/sec and $\nu(\pm\frac{1}{2}) = 5.9 \pm 0.1$ kMc/sec in excellent agreement with the calculated values.

At M band, a second series of spectra became apparent. These lines, which are about 24 gauss wide at $\theta=0$, reached extrema when the external field lay along the body diagonals and are interpreted as arising

from complexes of type II. At 49.43 kMc/sec the effective g_{11} was 22.505, which, assuming a real value of g_{11} of 18, means that Δ lies near 31 kMc/sec; this accounts for the absence of these spectra at 24 kMc/sec. A direct measurement of the two zero-field transitions gave $\nu(\pm\frac{3}{2}) = 32.995 \pm 0.025$ kMc/sec and $\nu(\pm\frac{1}{2}) = 31.820 \pm 0.025$ kMc/sec. From these data we can calculate $\Delta = 31.67 \pm 0.02$ kMc/sec and $A = 6.17 \pm 0.09$ kMc/sec. By using the accurate value of Δ to obtain the true value of g_{11} from the effective value, we can obtain a more accurate value of A from the spacing of the hyperfine lines at 50 kMc/sec. These values are also given in Table I.

The variation of the two sets of spectra as the external field is rotated in the (110) plane at 50 kMc/sec is shown in Fig. 5. The angular variation of the spectra from the type I complexes is shown as a dashed line and that of the type II complexes as a full line. The angular relationships for the four sets of type II complexes are

$$\cos\theta_1 = \cos(\varphi + \alpha),$$

$$\cos\theta_2 = \cos(\varphi - \alpha),$$

$$\cos\theta_3 = \cos\theta_4 = (1/\sqrt{3}) \cos\varphi,$$

where $\alpha = \tan^{-1}(1/\sqrt{2})$ and again $\varphi=0$ when H lies along the cube edge. The circles are experimental points. The lines of type II complexes are about one to five times more intense than those of type I, but we have not been able to make a reliable estimate of the relative numbers of the two types because of the difficulty of determining the precise configuration of the rf magnetic field over the sample. Recorder tracings of the observed spectra at M band are shown in Figs. 6 and 7.

In addition to the spectra described above, several other absorption features have been observed. As in

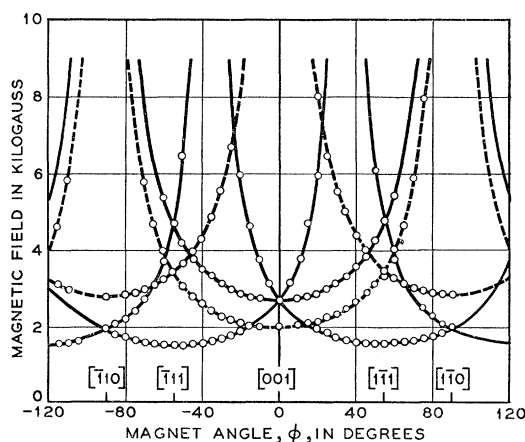


FIG. 5. Plot of the angular variation of the spectra of Tb^{3+} ions in CaF_2 when H is rotated in the (110) plane. Data taken at 49.95 kMc/sec. The spectra from the type II complexes are shown as solid lines and those from the type I complexes as dashed lines.

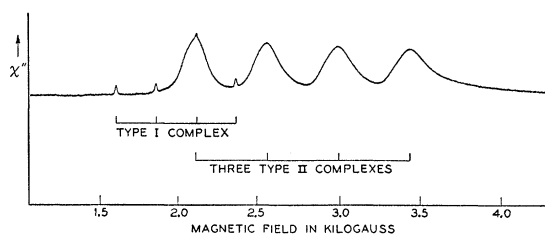


FIG. 6. The spectrum of Tb^{3+} ions in CaF_2 at 49.95 kMc/sec, showing the type I and type II spectra when H is directed along the $[001]$ axis.

$CaWO_4$, there is a general background of absorption in the low-field region which moves underneath the main lines. This may arise from complexes of higher order or aggregates of impurity ions. With the external field directed along one of the $\langle 110 \rangle$ directions, a broad line about 2800 gauss wide was observed at approximately $g=1.35$ at K band. The line appeared only when the rf magnetic field was perpendicular to the external field, and its peak height was then approximately equal to that of the two degenerate sets of lines of the type I complexes whose axes are inclined at 45° to the rf magnetic field. The line was strongly anisotropic and broadened rapidly as θ was increased, disappearing completely when H deviated from the $\langle 110 \rangle$ axis by more than 10° . We do not know the origin of this line, but we suspect that it arises from an impurity other than terbium.

Low¹⁶ has studied the spectra of various trivalent ions in CaF_2 and has reported lines which arise from ions situated in a pure cubic field where presumably the compensating F^- ion is not localized near the paramagnetic ion. We have searched for such a spectrum from Tb^{3+} ions in CaF_2 . Calculation¹⁷ shows, however, that the $J=6$ manifold splits in a cubic field of eight negative charges into $\Gamma_2 + \Gamma_4 + \Gamma_5 + \Gamma_1 + \Gamma_5 + \Gamma_3$ with the nonmagnetic singlet Γ_2 lying lowest. Paramagnetic resonance would, therefore, be observable only if the next highest level, the triplet Γ_4 , was also populated, which would require that the splitting be less than about 13 cm^{-1} ($e^{-E/kT}=0.01$ at 4.2°K). We have observed two very weak sets of four lines centered about $g=2$, but further study will be required to determine their origin.

5. CONCLUSIONS

When a trivalent impurity ion replaces a divalent ion in a lattice some form of charge compensation must occur to keep the crystal as a whole electrically neutral. In CaF_2 , our data indicate that charge compensation can be attained by at least two processes. Two

sets of spectra have been observed, which we have called type I and type II. The type I spectra have axial symmetry about the $\langle 100 \rangle$ cubic axes and are believed to arise from Tb^{3+} ions having an F^- ion occupying the nearest-neighbor interstitial site. The type II spectra have axial symmetry about the $\langle 111 \rangle$ body diagonals and can arise from Tb^{3+} ions which have either (a) an F^- ion occupying the next nearest-neighbor interstitial site, or (b) an O^{2-} ion located at the site of one of the eight F^- ion lattice sites surrounding the paramagnetic ion. Both these models have axial symmetry about the $\langle 111 \rangle$ axes and so we cannot distinguish between them from the symmetry of the paramagnetic-resonance spectrum. However, the parameter Δ , which is a measure of the strength of the crystalline-electric field, is much larger for the type II spectra than for the type I spectra. The distance between the Ca^{++} ion site and the two nearest interstitial sites is, respectively, 2.73 \AA and 4.72 \AA , whereas the distance from the Ca^{++} ion to the nearest normal F^- ion lattice site is 2.36 \AA . Thus an O^{2-} ion located at the normal F^- ion would be expected to produce a larger electric field at the site of the paramagnetic ion than an interstitial F^- ion at the next-nearest site. We therefore believe that the type II spectra probably arise from oxygen compensated terbium ions.

In $CaWO_4$, charge compensation does not appear to take place by means of interstitial-negative ions, which is reasonable since this lattice is much more tightly packed than that of CaF_2 . Compensation probably occurs by means of vacancies—one calcium vacancy neutralizing two trivalent ions. There is no evidence that the vacancies exist in the region of the Tb^{3+} ions from our measurements; if they do, the vector joining the Tb^{3+} ion to its associated vacancy must lie along the c axis of the crystal since the paramagnetic resonance spectrum is symmetrical about this axis. The existence of satellite lines may indicate the formation of pairs of ions, possibly in association with a vacancy, but further work is needed to clear up this point.

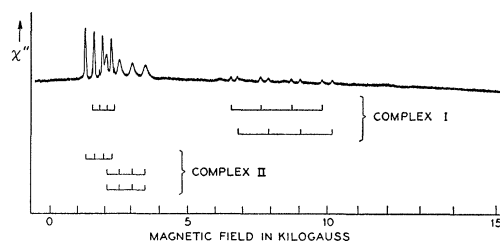


FIG. 7. The spectrum of Tb^{3+} ions in CaF_2 at 49.95 kMc/sec. H lies in the (110) plane and makes an angle $\phi=20^\circ$ with the $[001]$ axis. The two sets of lines of the type I spectra in the high-field region are not quite degenerate since the plane in which H moves is tilted slightly (by less than $\frac{1}{2}^\circ$) from the (110) plane. The fourth set of lines of the type II spectra, which are centered about 5750 gauss, is not visible in this recording because of their large line width at this orientation.

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Gamma Irradiation Effects on Electrets*

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Carnauba wax electrets were irradiated with gamma rays from a Co^{60} source. Doses varied between 0 and 5 megareöntgen (Mr). After irradiation the polarization of the electrets was determined by reheating them in short circuit and measuring the released charge. This charge was found to decrease roughly exponentially with dose, with a decay constant of the order of 1 Mr. A background effect due to Compton polarization is described.

I. INTRODUCTION

AN electret is a dielectric containing a "frozen-in" electric charge.¹ The charge is associated with a volume polarization though it is not clear whether this is a dipolar or an ionic effect. The "frozen-in" charge can be released by reheating of the sample; the release is accompanied by a depolarization current.² The current integral is a measure of the charge. It has been conjectured at an early stage that depolarization might also be brought about by x-ray or gamma-ray irradiation. However, so far no definite quantitative evidence is available since all measurements were influenced by the ionization of the air outside the electret. Recently, Myazdrikov³ has described a dosimeter for penetrating radiation based on the depolarization of electrets by gamma rays; in addition to a theoretical treatment he refers to some experimental results. But again the effect of the radiation on the volume polarization is neglected against the compensation of the surface charge due to saturation currents in the air above a free surface of the electret. The quantity measured is the surface charge as given by an induction plate method. According to our experience this is not a measure for the volume polarization of the electret. In the following, depolarization experiments are described which give the decrease of the "frozen-in" charge as a function of gamma-ray dose.

II. EXPERIMENTAL

The material used for the manufacture of the electrets was prime yellow carnauba wax. A series of disk-shaped samples was prepared. Dimensions were: thickness 2 cm, diameter 6 cm. Aquadag electrodes were applied to the top and bottom surfaces of each sample. Samples were polarized in the solid state. For this purpose they were heated to 70°C; after temperature equilibrium had been reached, a polarizing voltage of 10 kv was applied. The temperature was kept constant for 2 hr and then slowly lowered during the course of 3 hr. When it had fallen to 44°C, samples were short circuited and kept in this condition for 10 days at room temperature of about 30°C. Subsequently they were carried from Rio de Janeiro to Washington and irradiated in the Naval Research Laboratory Co^{60} irradiation facility.⁴ This consists of a hollow metal cylinder surrounded at its middle section by six Co^{60} sources with a total source strength of 8500 C. The dose rate at the center of the cylinder is 3.88×10^4 r/min. At a distance of 2 in. from the center in an axial direction it has decreased by 15% and at a distance of 2 in. in a radial direction it has decreased by 6%. Values given below refer to doses at the center. Different doses were obtained by changing the time of irradiation. For each irradiation intended to produce a given dose, two samples, one polarized and the other a nonpolarized blank, were sandwiched together, placed in a copper cylinder, and irradiated. Samples were then shipped back to Brazil. One to two months later each sample was reheated in a suitable capacitor already described in reference 2. The temperature was increased during 80 min from 30° to 75°C and subsequently kept con-

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² B. Gross, *J. Chem. Phys.* **17**, 866 (1949).

³ O. A. Myazdrikov, *Atomnaya Energ.* **8**, 64 (1960); *Kernenergie* **3**, 687 (1961); see also T. L. Wolfson and T. C. Dymant, *Health Physics* **7**, 36 (1961).

⁴ The authors express their gratitude to A. S. Schooley for making this work possible.