Orthorhombic Electron-Spin-Resonance Spectra of Thulium Ions in CaF$_2$-I

P. A. FORRESTER AND S. D. McLAUGHLAN

Royal Radar Establishment, Malvern, Worcestershire, England

(Received 27 January 1965)

A new type of charge-compensation mechanism has been found in CaF$_2$ from a study of the electron-spin-resonance spectrum of the thulium ion. Irradiated crystals of CaF$_2$ which have been grown from a melt containing TmF$_3$ normally exhibit only a single isotropic spectrum which arises from Tm^{2+} ions in sites of cubic symmetry; but when the crystal is grown from a melt containing Tm$_2$O$_3$, highly anisotropic spectra with orthorhombic symmetry are found after irradiation. These lines can be fitted to a spin Hamiltonian of the form $\mathcal{3C}=\beta\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}+\mathbf{I}\cdot\mathbf{A}\cdot\mathbf{S}$, where the x, y, and z components of the g tensor lie along the mutually orthogonal directions $\langle110\rangle$, $\langle\bar{1}10\rangle$, and $\langle001\rangle$, respectively. The constants in the Hamiltonian are

$$g_{110}=2.51\pm0.01, \qquad g_{\bar{1}10}=0.36\pm0.01, \qquad g_{001}=5.71\pm0.01,$$
$$A_{110}=1300\pm30 \text{ Mc/sec}, \quad A_{\bar{1}10}=1100\pm400 \text{ Mc/sec}, \quad A_{001}=2570\pm30 \text{ Mc/sec}.$$

Various models which might give rise to the observed spectrum are discussed. Two alternative possibilities appear to exist: (1) The thulium ion is in the tetravalent state and is compensated by either a calcium ion vacancy or by additional F$^-$ and/or O^{2-} ions, or (2) the resonance arises from a Tm^{2+}-Tm^{3+} pair, with the two impurity ions occupying adjacent sites and bonded together by two substitutional O^{2-} ions.

1. INTRODUCTION

CALCIUM fluoride doped with thulium ions in the divalent state is of considerable interest as a laser material. The electron-spin-resonance (esr) spectrum of this system was first studied by Hayes and Twidell,[1] and their results have been confirmed by Pashinin, Prokhorov, and Udovenchik.[2] The ground state of the Tm^{2+} ion is $^2F_{7/2}$, and under the influence of a crystalline field of eightfold cubic symmetry, the $J=\frac{7}{2}$ level splits into two doublets Γ_6 and Γ_7 and a quartet Γ_8. The Γ_7 level lies lowest in energy, and transitions between the components of this doublet give rise to the observed spectrum. This consists of a single isotropic line at $g=3.45$, which is split into two hyperfine components of equal intensity by the interaction with the nuclear spin $I=\frac{1}{2}$ of the 100% abundant Tm^{169} isotope. We have found that the intensity of the lines from cubic sites is strongly dependent upon the manner in which the crystal is grown, and under certain conditions we have also observed highly anisotropic spectra which arise from thulium ions at sites with symmetry lower than cubic. Three different sets of spectra are observed altogether, and in this paper we shall report on a detailed investigation of one of these, which shall be referred to as spectrum I; the other spectra will be discussed in a separate paper.

2. EXPERIMENTAL NOTES

The experiments described below were performed at liquid-helium temperatures, usually with the bath pumped to about 1.5°K to avoid vibrations caused by bubbling of the helium. Two superheterodyne spectrometers operating at X and Q bands were used. The X-band spectrometer utilized an H_{011} rectangular cavity, made from standard waveguide, which resonated

at approximately 9000 Mc/sec. Matching of the cavity was achieved with a variable coupler of the type described by Gordon[3] which eliminated the need for a microwave bridge. The signal klystron was locked to the cavity, thus ensuring that the spectrometer was only sensitive to variations of χ''. The Q-band spectrometer was of similar design, but used a circular H_{111} cavity, resonating at approximately 35kMc/sec. Most of the measurements were made at X band, the Q-band apparatus mainly being used to check the g and A values in particular directions. The crystals were oriented either by x-ray methods, or when two good {111} cleavage planes could be found, by mounting on a precision Teflon wedge. An accuracy of $\pm\frac{1}{2}°$ was attained.

3. CRYSTAL PROPERTIES

The crystals used in our experiments were grown by Green of these laboratories by the Czochralski method. They were pulled from the melt at a rate of approximately 4 in./h from a vitreous carbon crucible in an atmosphere of 99.998% pure argon. Crystals were grown in which the thulium was added to the melt in the form both of TmF$_3$ and of Tm$_2$O$_3$. Since the segregation coefficients for both doping methods are not known accurately, our quoted thulium concentrations will refer to the quantity added to the melt. Crystals doped with the oxide were grown from melts containing 0.05 at.%Tm; those doped with the fluoride had concentrations ranging from 0.01 to 0.5 at.%. After growth, the crystals were annealed in a vacuum furnace which was programmed to make a single cycle between room temperature and 1100°C over a period of several hours. The annealed crystals were colorless, but exhibited weak optical absorption lines characteristic of Tm^{3+} ions.[4] At 1.5°K, no esr lines were observed

[1] W. Hayes and J. W. Twidell, J. Chem. Phys. 35, 1521 (1961).

[2] P. P. Pashinin, A. M. Prokhorov, and V. T. Udovenchik, Fiz. Tverd. Tela 5, 1221 (1963) [English transl.: Soviet Phys.—Solid State 5, 891 (1963)].

[3] J. P. Gordon, Rev. Sci. Instr. 32, 658 (1961).

[4] J. B. Gruber and J. G. Conway, J. Chem. Phys. 32, 1178 (1960).

which could be attributed to thulium ions, suggesting that the ions were in a valence state having an even number of $4f$ electrons. We therefore conclude that the thulium ions enter the lattice in the trivalent state when CaF_2 is doped with either TmF_3 or Tm_2O_3.

Trivalent ions in calcium fluoride can be converted to the divalent state by irradiation with x rays,[1] γ rays,[5] or high-energy electrons.[6] Our crystals were irradiated at room temperature by γ rays from a Co^{60} source, the dose ranging from 0.5 to 2 mrad. After irradiation, crystals doped with Tm_2O_3 exhibit quite different microwave resonance and optical absorption spectra from those doped with TmF_3. Crystals containing TmF_3 turned a light blue, whereas those containing Tm_2O_3 turned a deep red color. The optical absorption bands which produce these colorations in the two crystals will be reported on later. The esr spectrum of crystals doped with the fluoride shows two isotropic lines associated with Tm^{2+} ions situated at sites of cubic symmetry. We observe no other spectrum in such crystals which can be directly attributed to thulium, although in crystals grown from melts containing 0.2 at.% Tm, a strong zero-field resonance is observed at X band extending over several hundred gauss, which may possibly be associated with clusters of Tm ions. In irradiated crystals doped with Tm_2O_3 the intensity of lines corresponding to cubic sites is very weak. However, we do find intense and highly anisotropic spectra which we attribute to Tm ions at sites of lower symmetry. In the following sections we shall discuss the origin of the simplest of these spectra.

4. THE SPIN HAMILTONIAN

The angular variation of the spectrum may be interpreted in terms of the spin Hamiltonian

$$\mathcal{H}=\beta\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}+\mathbf{I}\cdot\mathbf{A}\cdot\mathbf{S}. \tag{1}$$

The effective spin $S=\frac{1}{2}$, and similarly the nuclear spin $I=\frac{1}{2}$. A quadrupolar term is not necessary since $I<1$. The splitting of the electron lines into two hyperfine components of equal intensity provides a convenient label for the thulium ion since there is no other naturally occuring member of the rare-earth series with a 100% abundant isotope with $I=\frac{1}{2}$. The Hamiltonian may be expanded into Cartesian components as follows:

$$\mathcal{H}=\beta[g_xH_xS_x+g_yH_yS_y+g_zH_zS_z]$$
$$+A_xS_xI_x+A_yS_yI_y+A_zS_zI_z. \tag{2}$$

If the hyperfine structure is ignored for the present, and we take the center of the two components as the position of the electron line, the angular variation of the spectrum may be described simply by the relations

$$h\nu=g\beta H, \quad \text{where} \quad g=[(lg_x)^2+(mg_y)^2+(ng_z)^2]^{1/2} \tag{3}$$

[5] Z. J. Kiss, in *Lasers and Applications*, edited by W. S. C. Chang (Ohio State University Press, Columbus, Ohio, 1963), p. 7.

[6] J. R. O'Connor and H. A. Bostick, J. Appl. Phys. **33**, 1868 (1962).

TABLE I. The parameters of the spin Hamiltonian for spectrum I of thulium ions in CaF_2.

$g_{110}=2.51\pm0.01$	$g_{\bar{1}10}=0.36\pm0.01$	$g_{001}=5.71\pm0.01$
$A_{110}=1300\pm30$ Mc/sec	$A_{\bar{1}10}=1080\pm400$ Mc/sec	$A_{001}=2570\pm30$ Mc/sec

and l, m, and n are the direction cosines of the applied magnetic field with respect to the crystalline axes x, y, and z. In the present case, six such sets of crystal axes are required to describe the observed spectrum; these are made up of all the ways of combining a $\langle001\rangle$ direction and two mutually perpendicular $\langle110\rangle$ directions to form a right-handed system of axes, and we choose the $\langle001\rangle$ direction to be the z axis. Each of the six sets is equally probable, so that for an arbitary orientation of the external magnetic field six pairs of lines are observed.

Expansion of the secular determinant derived from Eq. (2) leads to a quartic equation for the eigenvalues which cannot be readily solved analytically. The six parameters of Eq. (2) are best determined from the experimental results by numerical methods on a digital computer. The values of the six parameters were obtained by an optimization program which adjusted the initial values until a best "least-squares" fit to a total of thirty experimental points was produced. These values are given in Table I. Transitions are observed through the perturbation $g_xH_x'S_x+g_yH_y'S_y$, where H' is the rf magnetic field in the cavity resonator. Since $g_y=g_{\bar{1}10}$ is very small, a component of H' must exist along the x axis for transitions to be observed. The value of $A_{\bar{1}10}$ has rather a large error since our measurements were made in the region between 0 and 5 kG, where the energy levels are not very sensitive to variations of $A_{\bar{1}10}$. Greater accuracy could be obtained by making measurements either at high fields ($\sim$ 18 kG) along the $\langle\bar{1}10\rangle$ directions, or at low frequencies comparable with the zero-field splitting.

5. THE ANGULAR VARIATION OF THE SPECTRUM

We have studied the angular variation of the spectrum as the external magnetic field H was rotated in the three principal crystal planes (100), (110), and (111). With H lying in the (100) plane, and making an angle α to the $[0\bar{1}1]$ direction, there are four sets of lines, two of which are doubly degenerate. Ignoring the nuclear splitting, the angular dependence of the lines is given by the following equations:

$$g=[g_{110}^2\cos^2\alpha+g_{\bar{1}10}^2\sin^2\alpha]^{1/2}, \tag{4a}$$

$$g=[g_{110}^2\sin^2\alpha+g_{\bar{1}10}^2\cos^2\alpha]^{1/2}, \tag{4b}$$

$$g=[g_{001}^2\cos^2(45-\alpha)+\tfrac{1}{2}g_{110}^2\cos^2(45+\alpha)+\tfrac{1}{2}g_{\bar{1}10}^2\cos^2(45+\alpha)]^{1/2}, \tag{4c}$$

$$g=[g_{001}^2\cos^2(45+\alpha)+\tfrac{1}{2}g_{110}^2\cos^2(45-\alpha)+\tfrac{1}{2}g_{\bar{1}10}^2\cos^2(45-\alpha)]^{1/2}. \tag{4d}$$

The lines described by Eqs. (4a) and (4b) are singly degenerate and have an intensity which we shall call weight 1, whereas the lines described by Eqs. (4c) and (4d) are doubly degenerate and are described as having weight 2. By using these relations and an approximate solution to the secular determinant derived from Eq. (2), we have obtained theoretical curves for the expected angular variation of the spectrum. The variation as H is rotated in the (100) plane is shown in Fig. 1; the small circles are experimental points which are in excellent agreement with the theoretical curves shown as solid lines in the diagram. With the magnetic field directed along the [001] direction, one line of weight 2 occurs with $g=g_{001}$, and the other lines coalesce to a triple point of weight 4 with $g=2^{-1/2}g_{110}$. With H directed along the [011] direction, one line occurs at about 18 kG, which is outside our experimental range, a second line with weight 1 occurs with $g=g_{110}$, and the other two lines cross with an effective $g=\frac{1}{2}[2g_{001}^2+g_{110}^2]^{1/2}$ with weight 4. By measuring these four sets of points precisely, the initial values for the parameters g_{001}, g_{110}, A_{001}, and A_{110} were obtained for the optimization program.

In order to observe all the possible transitions, there must be a component of the rf magnetic field H' along the x direction ($\equiv\langle110\rangle$) for each site. In our system H' also lay in the (100) plane and was directed about 20° away from the [001] axis, which enabled all the lines plotted in Fig. 1 to be observed in a single experiment.

The appearance of the spectrum with H directed along the [011] axis is shown in Fig. 2. The two pairs of lines occurring with effective g values of g_{110} and $\frac{1}{2}[2g_{001}^2+g_{110}^2]^{1/2}$ are marked as spectrum I. The weaker lines labeled as spectrum II appear to be related to the lines of spectrum I, but this has not yet been fully established. The other intense lines shown as spectrum III vary rapidly with angle in this region and consequently are very broad; they arise, we believe, from another type of compensation which has rhombic symmetry. These two spectra will be discussed in a separate paper. Two very weak lines arising from Tm^{2+} ions in cubic sites can also be seen, and their intensity
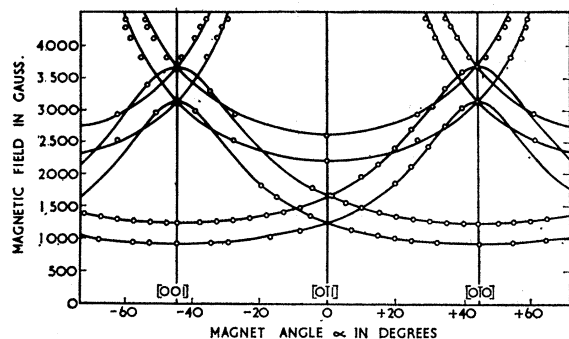

FIG. 2. The absorption spectrum of thulium ions in CaF_2 at 8934 Mc/sec when H is directed along the [011] axis. Note the intensity of the lines from ions in cubic sites.

relative to the other lines gives some idea of the rarity of such sites in crystals doped with Tm_2O_3. The recording was obtained from a crystal which had been heated to 500°C for several hours. This treatment bleached the crystal clear, and destroyed the resonance spectrum, but after subsequent re-irradiation, the esr lines reappeared with the same symmetry and intensity as before. No cubic lines were observed in this crystal prior to this treatment. These facts demonstrate that the basic compensation of the Tm^{3+} ions exists in a highly stable form, even at high temperatures.

The angular variation of the spectrum when H is rotated in the (110) plane is shown in Fig. 3. If α again denotes the angle between H and the [$\bar{1}$10] direction, the angular relationships are

$$g=[g_{001}^2\sin^2\alpha+g_{110}^2\cos^2\alpha]^{1/2},\qquad(5a)$$

$$g=[g_{001}^2\sin^2\alpha+g_{\bar{1}10}^2\cos^2\alpha]^{1/2},\qquad(5b)$$

$$g=[\tfrac{1}{2}g_{001}^2\cos^2\alpha+\tfrac{3}{4}g_{110}^2\cos^2(\alpha-\delta)$$
$$+\tfrac{3}{4}g_{110}^2\cos^2(\alpha+\delta)]^{1/2},\qquad(5c)$$

$$g=[\tfrac{1}{2}g_{001}^2\cos^2\alpha+\tfrac{3}{4}g_{110}^2\cos^2(\alpha+\delta)$$
$$+\tfrac{3}{4}g_{\bar{1}10}^2\cos^2(\alpha-\delta)]^{1/2},\qquad(5d)$$

where $\delta=\tan^{-1}2^{1/2}=54.7°$. The lines described by Eqs. (5a) and (5b) have weight 1, and those by Eqs. (5c) and (5d) have weight 2. Note that the transitions corresponding to Eq. (5a) are not shown in Fig. 3 since they were not observed in our experiment. An H_{01} rectangular cavity was used with the specimen lying on the base so that the rf magnetic field H' lay in the horizontal plane and was directed along the [$\bar{1}$10] direction. The line described by Eq. (5a) has its x axis in the vertical direction, and so never has a component lying along H'. It could therefore only be observed by placing the crystal in a region of the cavity where a

FIG. 1. The angular variation of the resonance field for spectrum I of thulium ions in CaF_2, when H is rotated in the (100) plane. Data taken at 8675 Mc/sec.
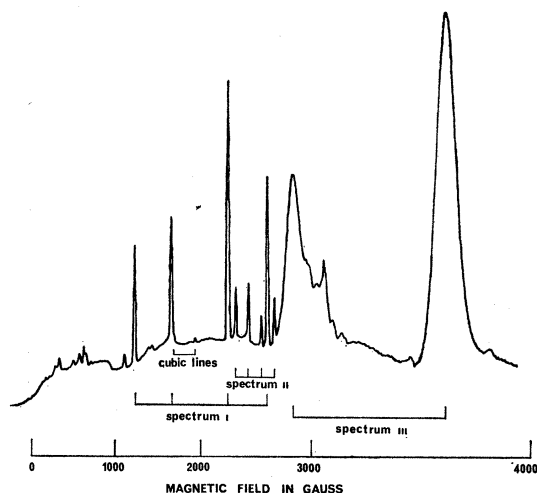
vertical component of H' exists, but this would have been difficult experimentally and we did not consider it to be worthwhile. The two curves corresponding to Eqs. (5c) and (5d) reach their maximum values of magnetic field when H is directed about 10° away from the [001] axis, even though these directions do not correspond to one of the principal directions of the g tensor because of the unusual manner in which the three g values are coupled together.

With H lying in the (111) plane, and making an angle α with the [$\bar{1}$10] direction, there are six sets of lines, each of equal weight, whose effective g values are given by the relations

$$g=[\tfrac{2}{3}g_{001}{}^2\sin^2\alpha+g_{110}{}^2\cos^2\alpha+\tfrac{1}{3}g_{\bar{1}10}{}^2\sin^2\alpha]^{1/2}, \quad (6a)$$

$$g=[\tfrac{2}{3}g_{001}{}^2\sin^2\alpha+\tfrac{1}{3}g_{110}{}^2\sin^2\alpha+g_{\bar{1}10}{}^2\cos^2\alpha]^{1/2}, \quad (6b)$$

$$g=[\tfrac{2}{3}g_{001}{}^2\cos^2(\alpha+30)+g_{110}{}^2\sin^2(\alpha+30) \\ +\tfrac{1}{3}g_{\bar{1}10}{}^2\cos^2(\alpha+30)]^{1/2}, \quad (6c)$$

$$g=[\tfrac{2}{3}g_{001}{}^2\cos^2(\alpha+30)+\tfrac{1}{3}g_{110}{}^2\cos^2(\alpha+30) \\ +g_{\bar{1}10}{}^2\sin^2(\alpha+30)]^{1/2}, \quad (6d)$$

$$g=[\tfrac{2}{3}g_{001}{}^2\cos^2(\alpha-30)+g_{110}{}^2\sin^2(\alpha-30) \\ +\tfrac{1}{3}g_{\bar{1}10}{}^2\cos^2(\alpha-30)]^{1/2}, \quad (6e)$$

$$g=[\tfrac{2}{3}g_{001}{}^2\cos^2(\alpha-30)+\tfrac{1}{3}g_{110}{}^2\cos^2(\alpha-30) \\ +g_{\bar{1}10}{}^2\sin^2(\alpha-30)]^{1/2}. \quad (6f)$$

These relations are plotted in Fig. 4. Experimental points are plotted on the curves corresponding to Eqs. (6a), (6c), and (6e); each of these lines has its x axis lying in the horizontal (111) plane. The x axes of the remaining lines are inclined at an angle $\cos^{-1}3^{-1/2}$ to the (111) plane containing H', and consequently their intensity is considerably lower than the other lines, and only a few experimental points have been identified with certainty.

6. THE CHARGE COMPENSATION

The CaF$_2$ lattice can be represented as a simple cubic array of F$^-$ ions with Ca^{2+} ions at the center of every alternate cube. When a rare-earth ion enters the
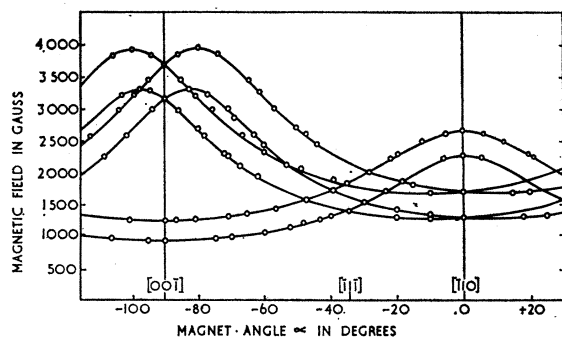
FIG. 3. The angular variation of the resonance field for spectrum I of thulium ions in CaF$_2$ when H is rotated in the (110) plane. Data taken at 8675 Mc/sec.
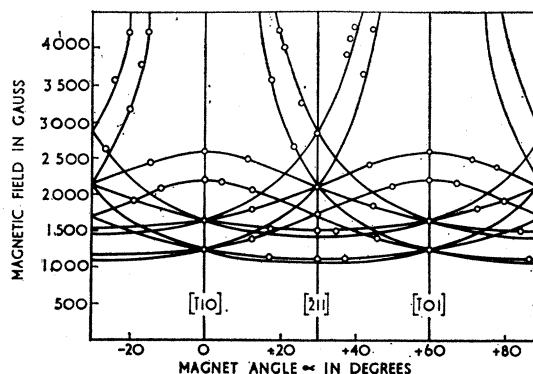
FIG. 4. The angular variation of the resonance field for spectrum I of thulium ions in CaF$_2$, when H is rotated in the (111) plane. Data taken at 9038 Mc/sec.

lattice there is a considerable body of evidence from esr studies and from x-ray work to support the view that the impurity ion replaces a Ca^{2+} ion and occupies its lattice site. With the impurity ion in the divalent state, the charge distribution in the crystal is unaltered and such ions are often found in sites of cubic symmetry.[7] If the ion is in any other valence state other charges must be introduced into the lattice to keep the crystal as a whole electrically neutral. An ion in the trivalent state introduces an extra positive charge, and this must be balanced by the addition of an extra negative charge. Two ways of achieving this have been observed. An additional F$^-$ ion can enter the lattice in an interstitial site[8]; these sites are the alternate centers of the fluorine cubes not occupied by Ca^{2+} ions. Alternatively, an O^{2-} ion can replace one of the F$^-$ lattice ions.[9] One case of a tetravalent ion in CaF$_2$ has been reported; Yariv[10] found a trigonal spectrum from U^{4+} ions in which each impurity ion was compensated by two O^{2-} ions which replaced two of the adjacent lattice F$^-$ ions.

Because of the mutual attraction of the impurity ion and its charge-compensating ion, the state of lowest energy occurs when the two ions are as near as possible to each other in the lattice. Thus, the local cubic symmetry at the site of the impurity ion is distorted by the presence of the adjacent compensating elements, and this is reflected in the symmetry of the esr spectrum. In the case of compensation by an interstitial F$^-$ situated at the nearest-neighbor site, an axial distortion is produced along the $\langle 001 \rangle$ directions. With

[7] W. Hayes and J. W. Twidell, *Proceedings of the First International Conference on Paramagnetic Resonance* (Academic Press Inc., New York, 1962), Vol. I, p. 163; W. Hayes, G. D. Jones, and J. W. Twidell, Proc. Phys. Soc. (London) **81**, 371 (1963); W. Hayes and J. W. Twidell, *ibid.* **82**, 330 (1963); C. Ryter, Helv. Phys. Acta **30**, 353 (1957).
[8] B. Bleaney, P. M. Llewellyn, and D. A. Jones, Proc. Phys. Soc. (London) **B69**, 858 (1956); J. M. Baker, W. Hayes, and M. C. M. O'Brien, Proc. Roy. Soc. (London) **A254**, 273 (1960).
[9] J. Sierro, J. Chem. Phys. **34**, 2183 (1961); P. A. Forrester and C. F. Hempstead, Phys. Rev. **126**, 923 (1962).
[10] A. Yariv, Phys. Rev. **128**, 1588 (1962).

compensation by O^{2-} ions, this axial distortion lies along the $\langle 111 \rangle$ directions. Fields of orthorhombic symmetry have been recently reported by Mahlab *et al.*,[11] which arise from a F^- ion situated at a third-nearest-neighbor interstitial site from a U^{3+} impurity.

Thus, local departures from cubic symmetry may be accounted for by the proximity of charge-compensating elements. The spectrum described in Secs. 4 and 5 has orthorhombic symmetry, and we must therefore look for a model for the site of the thulium ion which has C_{2v}, or lower, point symmetry. This model must involve distortions of the basic cubic symmetry which lie along a $\langle 001 \rangle$ direction, and two mutually perpendicular $\langle 110 \rangle$ directions. Compensation may therefore involve the presence of more than one charge.

The first problem is to determine the valence state of the thulium ion. The resonance spectrum only occurs in irradiated crystals, and therefore it seems unlikely that the lines originate from the trivalent ion. Furthermore, the spectrum appears to arise from transitions within a Kramers doublet which indicates that the number of electrons in the system is odd. The two simplest possibilities are that the trivalent thulium ion either captures or ejects an electron during the γ irradiation and thus becomes either divalent or tetravalent.

In crystals doped with TmF_3, only divalent ions are observed after γ irradiation, but this need not necessarily be so in crystals doped with Tm_2O_3. An ion in the tetravalent state would require two negative charges to maintain electrical neutrality, and the proximity of these charges could give rise to the required symmetry of the crystal field. A divalent ion does not require compensation, and at first sight one might not expect to find such ions at sites of low symmetry. If, however, the resonance arises from a $Tm^{2+}-Tm^{3+}$ pair, with the two ions occupying adjacent lattice sites, the Tm^{3+} ion, together with its charge-compensating ion, could produce the observed symmetry at the Tm^{2+} site. These two possibilities are discussed in more detail below.

A. The Tetravalent Model

A thulium ion in the tetravalent state would be isoelectronic with Er^{3+} and Ho^{2+}, which have eleven $4f$ electrons, and a $^4I_{15/2}$ ground state. In a purely axial field, the $J=15/2$ ground state splits into a set of degenerate doublets characterized by $|\pm J_z\rangle$. Since, however, the crystal field is not entirely axial in this case, admixtures of the other $|J_z\rangle$ states, with J_z differing by 2, 4, 6, etc., would occur, and with knowledge of only the g values, it is not possible to calculate the full ground-state eigenfunction since there are too many unknown parameters. However, the observed g values would appear to be consistent with an ion in the tetravalent state.

---

[11] E. Mahlab, W. Low, V. Volterra, and A. Yariv, Phys. Rev. **131**, 920 (1963).
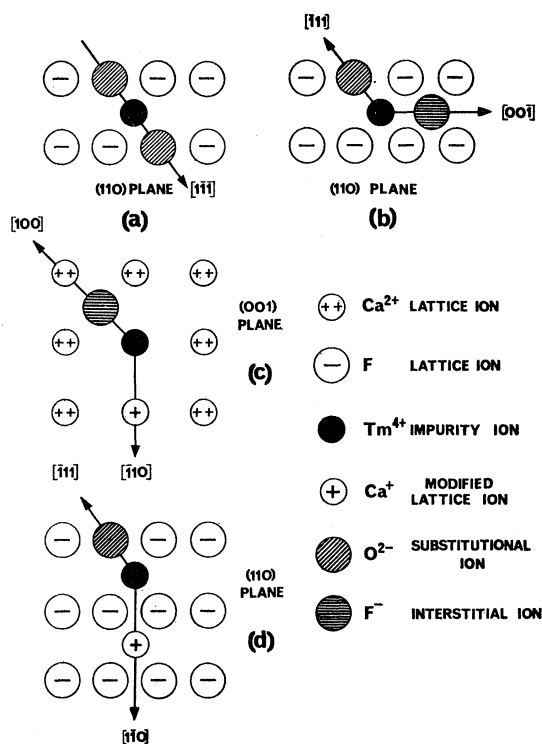

FIG. 5. Models illustrating some of the possible types of site for a substitutional tetravalent impurity ion in CaF_2.

We have not been able to devise a really satisfactory model for the charge compensation to give the required symmetry. Since the lattice is known to contain oxygen, one would expect that the simplest way to neutralize a tetravalent ion would be to replace two of the neighboring F^- lattice ions by O^{2-} ions; the state of lowest energy then occurs when the ions form a linear chain lying along a body diagonal of the crystal[10] as shown in Fig. 5(a). However, this model has C_{3v} symmetry. An alternative compensation mechanism would be by an interstitial F^- ion and a substitutional O^{2-} ion. A linear array is not possible in this case, and the lowest energy configuration is as shown in Fig. 5 (b). The three charges lie in a {110} plane, and reduce the cubic symmetry to C_{1v}, but since esr spectra are insensitive to the signs of the crystal field, the resultant spectrum would have C_{2v} symmetry.

Compensation could also be produced by a modification of an adjacent calcium ion site in some way. If a neighboring calcium ion were removed completely, the effective double negative charge of the resultant vacancy would compensate the two excess positive charges of the tetravalent ion, and would produce a distortion of the correct symmetry. Alternatively, it is possible that the neighboring calcium ion could capture the electron ejected by the Tm^{3+} ion during its conversion to the Tm^{4+} state. If the second charge on the Tm^{4+} ion were compensated by either a F^- ion situated on any of the

neighboring interstitial sites, or an O^{2-} ion replacing one of the adjacent F^- lattice ions, the required reduction of symmetry would be produced. Two of the possible variants of this model are shown in Figs. 5(c) and 5(d). This model would require the production of magnetic Ca^+ ions which might also be expected to show an esr spectrum. With the thulium added in the form of the oxide, one would expect to find some of the ions compensated by oxygen alone, as was found by Yariv in the case of U^{4+}, even if other forms of compensation also occurred. However, we find no such axial spectrum. The calcium ion vacancy seems to be the most plausible method of compensating, but since the role played by the oxygen does not appear to be crucial to any of the models, we conclude that this orthorhombic spectrum does not arise from Tm^{4+} ions.

For a particular level of a given ion, the trace of the g tensor should remain constant provided that the departure from cubic symmetry is not too great.[12] The g value of the Er^{3+} ion, which is isoelectronic with Tm^{4+}, is found to be 6.78 in cubic sites,[13] while that of Tm^{2+} is 3.45.[1] The mean g value of our spectrum is 2.86, which is much nearer to that of the Tm^{2+} ion than of the Tm^{4+} ion. It is comparable with the mean values of 2.93, 2.97, and 3.01 found by Ranon[14] for the Yb^{3+} ion (which is isoelectronic with Tm^{2+}) at various types of sites in $CaWO_3$. This is another indication that we should look for a charge-compensation model involving the Tm^{2+} ion.

B. The Tm^{2+}-Tm^{3+} Pair Model

If two trivalent impurity ions are located at adjacent substitutional lattice sites, each ion is subjected to an axial field, directed along the $\langle 110 \rangle$ direction joining them, superimposed upon the cubic field. Since the $\langle 110 \rangle$ axis has only twofold symmetry, a distortion along this direction reduces the point symmetry to C_{2v}. Irradiation would then convert a fraction of the impurity ions to the divalent state thus producing the observed spectrum. However, if the impurity ions were distributed randomly over the lattice, the probability of finding two ions occupying adjacent sites would be very small with impurity concentrations as low as 0.05%. Upon irradiation, therefore, one might expect to find a high proportion of Tm^{2+} ions in sites of cubic symmetry or with a simple axial type of compensation. This, however, is not the case, since a large majority of the thulium ions exhibit spectra with orthorhombic symmetry.

Since the two trivalent ions would be mutually repulsive, some additional binding agent would be necessary to produce a stable unit. The two excess positive charges of the impurity ions could be balanced by the addition of an interstitial O^{2-} ion, and this might
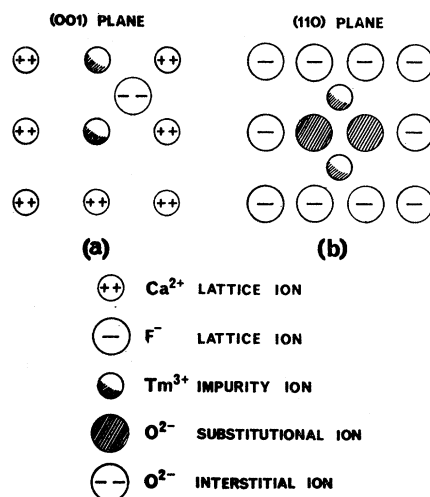
[12] H. R. Lewis and E. S. Sabisky, Phys. Rev. **130**, 1370 (1963).
[13] U. Ranon and W. Low, Phys. Rev. **132**, 1609 (1963).
[14] U. Ranon and V. Volterra, Phys. Rev. **134**, A1483 (1964).

FIG. 6. Models showing how a Tm^{3+}-Tm^{3+} pair could be formed in the CaF_2 lattice. One of the elements of the pair would then collect an electron to form the resonant center.

occupy one of the two interstitial sites common to both trivalent ions. These three ions would lie in a {100} plane, as shown in Fig. 6(a). Alternatively, two O^{2-} ions could replace two lattice F^- ions; the most stable arrangement would occur when the two F^- ions common to the two Tm^{3+} ions are replaced by O^{2-} ions. These four ions would lie in a {110} plane, as shown in Fig. 6(b), and form a quadrupolar charge distribution. This arrangement has the required symmetry, and the highly planar charge distribution might explain why one g_{110} is very small. This model seems to us to be the one most likely to occur. We assume that the Tm_2O_2 complex is particularly stable and enters the lattice as a neutral entity, and that this is the principal form in which thulium enters the lattice when CaF_2 is doped with Tm_2O_3. Irradiation with γ rays converts some of the ions to the divalent state. The resultant complexes are then overcompensated but they appear to be highly stable over long periods of time. We believe that a second, rather more complicated, spectrum observed in this type of crystal can also be explained by a variation of this model, but a detailed analysis of this spectrum is not yet complete.

Further evidence for the existence of Tm^{2+}-Tm^{3+} pairs in CaF_2 has been provided by Kiss,[15] who found a fluorescence spectrum in the 1.8 $-2\ \mu$ region. The normal fluorescence spectrum of Tm^{2+} ions in cubic sites occurs at about 1.1 μ, and arises from transitions between the $^2F_{5/2}$ and the $^2F_{7/2}$ levels. Kiss proposed that the 1.8 μ fluorescence originates from a transition between the $^3F_4$ level of a Tm^{3+} ion and the $^2F_{5/2}$ level of a Tm^{2+} ion on an adjacent lattice site. The frequency of the observed line corresponds very closely to the known energy separation between these two levels, and the line is split into two components, the separation of which

[15] Z. J. Kiss, Phys. Rev. **127**, 718 (1962).

almost exactly matches the splitting of the Γ_7 and Γ_8 components of the $^2F_{5/2}$ level. We have looked for the esr spectrum of such pairs in CaF_2 crystals doped with up to 0.5 at.% of Tm in the form of TmF_3 and have found no such lines. Since TmF_3 is normally produced chemically from Tm_2O_3, it would seem possible that the crystals used by Kiss, which were doped with the fluoride, actually contained a small amount of the oxide as well, and that the fluorescence spectrum which he observed arose from the Tm_2O_2 complex which we postulate. We have recently observed weak fluorescence lines between 1.8 and 2.2 μ from CaF_2 doped with Tm_2O_3, but have not yet been able to determine whether these lines are identical with those observed by Kiss.

7. THE GROUND-STATE EIGENFUNCTION

The electric potential produced by the charge distribution surrounding the impurity ion can be expanded in a series of spherical harmonics $Y_l^m(\theta,\phi)$. For a field of C_{2v} symmetry, this expansion takes the form

$$V=A_2^0Y_2^0+A_2^2Y_2^{\pm2}+A_4^0Y_4^0+A_4^2Y_4^{\pm2}+A_4^4Y^{\pm4}_4$$
$$+A_6^0Y_6^0+A_6^2Y_6^{\pm2}+A_6^4Y_6^{\pm4}+A_6^6Y_6^{\pm6},$$

where the A_l^m are numerical constants to be evaluated. The Y_l^0 terms split a given J manifold into doublets characterized by $|\pm J_z\rangle$, and the other terms mix in other $|J_z\rangle$ states of which the J_z value differs by 2, 4, and 6. Thus, the most general form for a doublet derived from a $J=\frac{7}{2}$ state in this field is given by

$$\left|{\alpha \atop \beta}\right\rangle=a\left|\pm\tfrac{7}{2}\right\rangle+b\left|\pm\tfrac{3}{2}\right\rangle+c\left|\mp\tfrac{1}{2}\right\rangle+d\left|\mp\tfrac{5}{2}\right\rangle.$$

The g values between the two components of the doublet are obtained from operators of the form $g_x=2g_J\langle\alpha|J_x|\beta\rangle$, etc., which lead to the following relations:

$$g_x=(16/7)[(7)^{1/2}ad+(15)^{1/2}bc+2\sqrt{3}bd+2c^2],$$
$$g_y=(16/7)[(7)^{1/2}ad+(15)^{1/2}bc-2\sqrt{3}bd-2c^2],$$
$$g_z=(8/7)[7a^2+3b^2-c^2-5d^2].$$

Using the experimental g values from Table I, and the relationship $a^2+b^2+c^2+d^2=1$, we obtain the following ground-state eigenfunction,

$$\left|{\alpha \atop \beta}\right\rangle=0.870\left|\pm\tfrac{7}{2}\right\rangle+0.132\left|\pm\tfrac{3}{2}\right\rangle$$
$$+0.448\left|\mp\tfrac{1}{2}\right\rangle+0.174\mp\tfrac{5}{2}\rangle.$$

Since there are four equations and four unknowns there is unfortunately no cross check on this result. Nor is there sufficient data to work back to the potential coefficients A_l^m, and this must await a detailed optical study of the excited states.

8. CONCLUSIONS

Irradiated crystals of CaF_2 doped with thulium ions in the form of Tm_2O_3 exhibit esr spectra which are considerably different from those doped with TmF_3. At least three sets of spectra are found arising from thulium ions located at sites of orthorhombic or lower symmetry, and the results of a detailed study of one of these spectra are presented in this paper. Various mechanisms which might give rise to this spectrum are discussed. The most likely explanation is that during the process of crystal growth Tm^{3+} ions enter the lattice in pairs and occupy nearest-neighbor sites. We propose that these ions are bonded into a highly stable unit by two O^{2-} ions which replace the two lattice F^- ions common to the two Tm^{3+} ions. However, it would be highly desirable to have some additional evidence for this model. With the external magnetic field directed along the (110) direction, certain lines appear to be just resolved into at least seven components, which we assume to be a superhyperfine structure produced by the overlap of the electronic wave function with the neighboring fluorine nuclei. It should be possible using the electron-nuclear-double-resonance technique to measure this interaction more precisely, and thus to use the neighboring nuclei as probes to determine the nature of the Tm^{2+} environment.

Other rare-earth ions may enter the CaF_2 lattice in a similar manner when introduced as the oxide. We are currently studying the spectra of ytterbium, dysprosium, and terbium ions, and from a preliminary analysis we believe that some of the observed spectra may also arise from ion pairs.