

given in Sec. 2, it follows from inspection that

$$a_{\pm}^2 + b_{\pm}^2 = a_+^2 + a_-^2 = b_+^2 + b_-^2 = 1,$$

and

$$a_+a_- + b_+b_- = a_+b_+ + a_-b_- = 0.$$

With the above information one obtains

$$U^{-1}T(v)U = \begin{pmatrix} \tau_{11}(v) & \tau_{12}(v) \\ \tau_{21}(v) & \tau_{22}(v) \end{pmatrix},$$

where

$$\begin{aligned} \tau_{11}(v) &= \gamma_- \omega_+ a_+^2 + \gamma_+ \omega_+ b_+^2, \\ \tau_{12}(v) &= \gamma_- \omega_+ a_+ a_- + \gamma_+ \omega_+ b_+ b_-, \\ \tau_{21}(v) &= \gamma_- \omega_- a_+ a_- + \gamma_+ \omega_- b_+ b_-, \\ \tau_{22}(v) &= \gamma_- \omega_- a_-^2 + \gamma_+ \omega_- b_-^2. \end{aligned} \quad (A2)$$

By using the fact that in the bulk limit $(\omega_-/\omega_+)^{N-t-2} \rightarrow 0$ for positive temperatures and $t=2, 3, \dots, N/2-1$, one finds

$$\begin{aligned} \langle S_{N/2-t}^2 S_{N/2}^2 \rangle \\ = (2S+1) \omega_+^{N-4} (16K^2 h^2 Z)^{-1} (\partial/\partial \lambda) \{ (\partial/\partial v) [(\tau_{11}^2(v) \\ + \tau_{12}^2(v)) D + (\omega_-/\omega_+)^{t-2} (a_+ a_- Y_+ + (a_+ b_- + b_+ a_-) Y_0 \\ + b_+ b_- Y_-) (\tau_{11}(v) \tau_{21}(v) + \tau_{12}(v) \tau_{22}(v))] \}_{v=1}. \end{aligned} \quad (A3)$$

From (A1) and (A2)

$$\begin{aligned} \partial \tau_{11}(v) / \partial v |_{v=1} &= \omega_+ K h (a_+^2 - b_+^2), \\ \partial \tau_{12}(v) / \partial v |_{v=1} &= \omega_+ K h (a_+ a_- - b_+ b_-), \\ \partial \tau_{21}(v) / \partial v |_{v=1} &= \omega_- K h (a_+ a_- - b_+ b_-), \\ \partial \tau_{22}(v) / \partial v |_{v=1} &= \omega_- K h (a_-^2 - b_-^2), \\ \tau_{11}(1) &= \omega_+, \\ \tau_{12}(1) = \tau_{21}(1) &= 0, \\ \tau_{22}(1) &= \omega_-; \end{aligned}$$

consequently

$$(\partial/\partial v) (\tau_{11}^2(v) + \tau_{12}^2(v)) |_{v=1} = 2\omega_+^2 K h (a_+^2 - b_+^2),$$

and

$$\begin{aligned} (\partial/\partial v) (\tau_{11}(v) \tau_{21}(v) + \tau_{12}(v) \tau_{22}(v)) |_{v=1} \\ = 2\omega_+ \omega_- K h (a_+ a_- - b_+ b_-). \end{aligned}$$

After referring back to (1), (3'), and the derivation of (2) one arrives at (9) by differentiating with respect to λ in (A3) and substituting

$$\begin{aligned} Z &= (2S+1) \omega_+^{N-2} D, \\ \sigma_{N/2} &= (-4K h S)^{-1} D^{-1} \partial D / \partial \lambda, \\ \sigma_{\text{host}} &= b_+^2 - a_+^2. \end{aligned}$$

Orthorhombic and Trigonal Electron-Spin-Resonance Spectra of Ce^{3+} Ions in CaF_2

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Two new electron-spin-resonance spectra, one having trigonal and the other having orthorhombic symmetry, have been observed in CaF_2 doped with small amounts of CeO_2 . The x and y axes of the orthorhombic spectrum lie in the (110) plane and are tilted by an angle $\delta = 13.8 \pm 0.2^\circ$ from the $[110]$ and the $[001]$ axes, respectively, and the z axis lies along the $[110]$ axis. The components of the g tensor for the two spectra are: orthorhombic, $g_x = 0.844 \pm 0.001$, $g_y = 0.22 \pm 0.05$, $g_z = 3.286 \pm 0.001$; trigonal, $g_{11} = 3.673 \pm 0.002$, $g_{12} \leq 0.3$.

1. INTRODUCTION

SINGLE crystals of CaF_2 containing trace impurities of paramagnetic ions often exhibit electron-spin resonance (ESR) spectra with symmetry lower than cubic. Such spectra arise because of the proximity of compensating charges which lower the point symmetry at the sites of the impurity ions. In previous papers,¹⁻³ we described spectra having orthorhombic symmetry which were observed in crystals of CaF_2 containing rare-earth (RE) ions which had been introduced into

the crystals in the form of the RE oxides. In the present paper, results on Ce^{3+} ions in CaF_2 doped with CeO_2 are described; in this system, two spectra of approximately equal intensity are observed, one having trigonal and the other having orthorhombic symmetry. Previous ESR studies of Ce^{3+} ions in CaF_2 have revealed ions situated in purely cubic sites,⁴ and ions having tetrahedral⁵ and trigonal⁶ symmetries, but the trigonal spectrum which we have observed is different from the one previously reported.

¹ P. A. Forrester and S. D. McLaughlan, Phys. Rev. **138**, 1682 (1965).

² S. D. McLaughlan, P. A. Forrester, and A. F. Fray, Phys. Rev. **146**, 344 (1966).

³ S. D. McLaughlan, Phys. Letters **20**, 486 (1966).

⁴ M. Dvir and W. Low, Proc., Phys. Soc. (London) **75**, 136 (1960).

⁵ J. M. Baker, W. Hayes, and D. A. Jones, Proc. Phys. Soc. (London) **73**, 942 (1959).

⁶ M. J. Weber and R. W. Bierig, Phys. Rev. **134**, 1492 (1964).

2. APPARATUS AND CRYSTAL GROWTH

The experimental apparatus has been described in the earlier papers.^{1,2} Measurements were made in the 9000-Mc/sec region using a superheterodyne spectrometer with the sample immersed in liquid helium at 1.5°K. The crystals were grown by the Czochralski method and were pulled at the rate of 4 in./h from a vitreous carbon crucible in an atmosphere of 99.998% pure argon.⁷ Cerium was added to the melt in the form of CeO₂, the level of doping being 0.05 at.-%.

The method and conditions of growth appear to be important in determining whether or not rhombic sites are produced. The addition of dopants in oxide form to the melt in the Stockbarger process does not usually produce rhombic sites. The conditions under which various types of site are produced will be discussed more fully in a later paper.⁸

3. EXPERIMENTAL RESULTS

The Ce³⁺ ion has a single electron in the 4*f* shell and the ground state is ²F_{5/2}. Crystal fields of symmetry lower than cubic split the $J = \frac{5}{2}$ level into three doublets, and transitions between the components of the lowest lying doublet can be treated as though they arise from an effective spin $S = \frac{1}{2}$. The spin Hamiltonian in Cartesian form is simply

$$\mathcal{H} = \beta [g_x H_x S_x + g_y H_y S_y + g_z H_z S_z]$$

and transitions at a frequency ν thus occur when

$$h\nu = g\beta H \text{ where } g = [(g_x h_x)^2 + (g_y h_y)^2 + (g_z h_z)^2]^{1/2}$$

and h_x , h_y , and h_z are the direction cosines of the applied field H with respect to the axes of the g tensor.

For the trigonal spectrum, the z axis lies along a

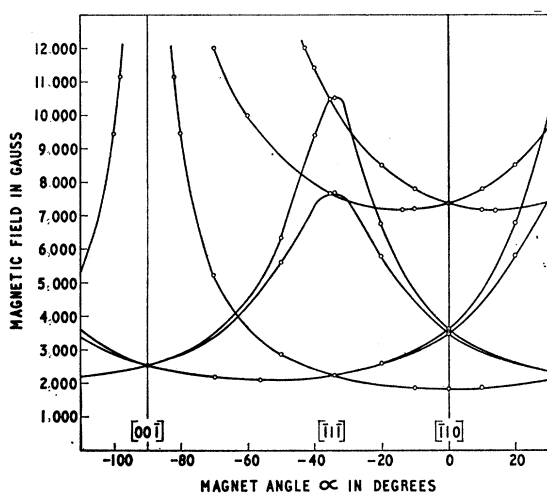


FIG. 1. The angular variation of the resonance field for the orthorhombic spectrum of Ce³⁺ ions in CaF₂ when H is rotated in the (110) plane. Data taken at 8470 Mc/sec.

⁷ The crystals were obtained from Barr and Stroud Ltd.

⁸ J. Kirton and S. D. McLaughlan (to be published).

body diagonal of the cube with $g_z \equiv g_{11}$, and the x and y axes lie in the corresponding {111} plane with $g_x = g_y \equiv g_{\perp}$. For an arbitrary orientation of the field H there are four spectra; equations relating the angular variation of the lines are well known, see for example Ref. 9, and will not be repeated here. The spectrum which we observe in the CeO₂:CaF₂ system can be described by the parameters $g_{11} = 3.673 \pm 0.002$ and $g_{\perp} \leq 0.3$. The value of g_{\perp} was obtained by extrapolation from a plot of H against $\sec\theta$ for fields up to 12 kG. This spectrum is different from that reported by Weber and Bierig⁶ for Ce³⁺:CaF₂, where the method of crystal growth was not specified; they found $g_{11} = 2.38 \pm 0.03$ and $g_{\perp} \leq 0.01$.

The z axis of the rhombic spectrum lies along the [110] axis and the x and y axes lie in the (110) plane and are tilted by an angle $\delta = 13.8 \pm 0.2^\circ$ from the [110] and [001] axes, respectively. There are 12 separate ways of choosing such a set of axes in a cubic system, and thus for an arbitrary orientation of H there are 12 different lines in the spectrum, each corresponding to a different orientation of H with respect to the 12 possible types of site. Some degeneracy occurs in planes of high symmetry; most of our experimental results were obtained with H rotated in the (110) plane, where seven different lines are observed. The angular variation of the spectrum with H in this plane is shown in Fig. 1, where the circles are experimental points and the solid lines are the calculated line positions using the following parameters:

$$g_x = 0.844 \pm 0.001, \quad g_y = 0.22 \pm 0.05, \\ g_z = 3.286 \pm 0.001, \quad \delta = 13.8 \pm 0.2^\circ.$$

The calculation of the angular variation of the spectrum is best performed in terms of a set of direction cosine matrices, each matrix relating the x , y , and z axes of the g tensor for one particular site to the cube axes of the crystal. The details of the method have been described fully in our earlier paper on the Yb₂O₃:CaF₂ system.²

4. THE GROUND-STATE EIGENFUNCTIONS

The crystalline electric field surrounding a paramagnetic ion can be expanded in terms of a series of spherical harmonics $Y_n^m(\theta, \phi)$. States in a given J manifold characterized by $|J, J_z\rangle$ are admixed by the $e^{im\phi}$ terms in the potential, and thus in a trigonal field where $m=3$, there are two possibilities for the form of the ground-state doublet derived from the $J = \frac{5}{2}$ manifold

$$|\frac{\alpha}{\beta}\rangle = |J = \frac{5}{2}, J_z = \pm \frac{3}{2}\rangle, \quad (1)$$

$$|\frac{\gamma}{\delta}\rangle = \cos\alpha |J = \frac{5}{2}, J_z = \pm \frac{5}{2}\rangle \pm \sin\alpha |J = \frac{5}{2}, J_z = \mp \frac{1}{2}\rangle. \quad (2)$$

The former leads to $g_{11} = 18/7$ and $g_{\perp} = 0$, while the latter gives $g_{11} = 6/7(6 \cos^2\alpha - 1)$ and $g_{\perp} = 18/7 \sin^2\alpha$. The

⁹ P. A. Forrester and C. F. Hempstead, Phys. Rev. 126, 923 (1963).

experimental values of $g_{11}=2.38$ and $g_1 \leq 0.1$ found by Weber and Bierig cannot be fitted to (2) but lie quite close to the theoretical values of $g_{11}=2.57$ and $g_1=0$ predicted by (1). They ascribed the lack of an exact fit to mixing from the $J=\frac{7}{2}$ manifold. In our case if we take $\alpha=15.3^\circ$, the wave function becomes

$$|\frac{7}{2}\rangle = 0.938|J_z = \pm\frac{5}{2}\rangle \pm 0.346|J_z = \mp\frac{1}{2}\rangle,$$

which leads to $g_{11}=3.673$ and $g_1=0.3$. The predicted values of g_1 is just within the experimental error.

In a field of twofold symmetry there is only one possible eigenfunction

$$|\frac{5}{2}\rangle = \pm p|\frac{5}{2}, \pm\frac{5}{2}\rangle \pm q|\frac{5}{2}, \pm\frac{1}{2}\rangle \pm r|\frac{5}{2}, \mp\frac{3}{2}\rangle,$$

and by using operators of the form $g_x = 2g_\lambda(\mu|J_x|\kappa)$ we can derive the following equations for the components of the g tensor:

$$\begin{aligned} g_x &= \pm 6/7(2\sqrt{5}pr + 4\sqrt{2}qr + 3q^2), \\ g_y &= \pm 6/7(2\sqrt{5}pr - 4\sqrt{2}qr + 3q^2), \\ g_z &= \pm 6/7(5p^2 + q^2 - 3r^2), \end{aligned}$$

where $p^2 + q^2 + r^2 = 1$. The best fit is obtained with the following eigenfunction:

$$|\frac{5}{2}\rangle = \pm 0.871|\pm\frac{5}{2}\rangle \pm 0.437|\pm\frac{1}{2}\rangle \mp 0.241|\mp\frac{3}{2}\rangle,$$

which predicts $g_x = -0.826$, $g_y = 0.197$, $g_z = 3.266$ and $p^2 + q^2 + r^2 = 1.008$. The fit is not quite perfect and reflects a slight admixture from the $J=\frac{7}{2}$ excited state.

5. DISCUSSION

Assuming an isolated $J=\frac{5}{2}$ manifold the Hamiltonian describing the crystal field potential of trigonal symmetry may be written as

$$H_{\text{trig}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^3 O_4^3,$$

where $B_n^m = \zeta_n A_n^m \langle r^n \rangle$ and ζ_n is the operator equivalent factor α , β for $n=2, 4$, respectively, as described by Elliott and Stevens.¹⁰ The trigonal field splits the $J=\frac{5}{2}$ manifold into three doublets which are located at

$$E(\pm\frac{3}{2}) = -B_4^0(2x+180),$$

and

$$E(\pm\frac{5}{2}, \mp\frac{1}{2}) = B_4^0\{(x+90) \pm 3[(3x-10)^2 + 10y^2]^{1/2}\},$$

where $x = B_2^0/B_4^0$ and $y = B_4^3/B_4^0$. For one of the $(\pm\frac{5}{2}, \mp\frac{1}{2})$ doublets to be lowest

$$10y^2 > 8000 + 240x - 8x^2.$$

Since α is negative for Ce^{3+} and A_2^0 is positive, as can be shown by a point charge calculation,¹¹ B_2^0 is negative. Hence, as B_4^3 is unaltered by any axial distortions, we can conclude that a large B_2^0 coefficient is required

to bring a $(\pm\frac{5}{2}, \mp\frac{1}{2})$ doublet lowest. This then indicates that the compensation associated with the trigonal sites in our crystals produces a much more severe axial distortion than that corresponding to the trigonal site reported by Weber and Bierig. A possible interpretation of this is that the compensation in our case consists of an O^{2-} ion on a nearest F^- ion site while in that of Weber and Bierig an F^- ion on a next nearest interstitial site is more probable. Assuming specific models for the trigonal centers, J. Kirton in an unpublished work has determined the crystal field components by point-charge calculations. Until the optical spectra corresponding to these sites are examined however, there is insufficient information to test the validity of these calculations.

The production of sites with rhombic symmetry seems to be characteristic of CaF_2 crystals grown by the Czochralski method from melts doped with RE oxides. Such spectra have now been observed from cerium, dysprosium, neodymium, thulium and ytterbium ions. It would seem likely that these spectra reflect a basic charge compensation mechanism which is common to ions of the RE series introduced into the crystal in this manner. However, the deduction of a satisfactory model for this compensation mechanism is not straightforward. In some cases, for example those of cerium and ytterbium, both orthorhombic and trigonal spectra are found in the crystals as grown, whereas with neodymium and thulium dopings, only orthorhombic spectra are found. Tetragonal spectra have not been observed in any of the RE oxide doped crystals which we have examined. Also, more than one orthorhombic spectrum can be observed from a given ion in the same crystal, as in the cases of thulium and ytterbium ions. The model must thus be capable of variants which could produce different orthorhombic spectra with different tilt angles δ . A crystal which had previously exhibited orthorhombic and trigonal spectra only showed the trigonal resonance after γ irradiation. Because of this and also the fact that orthorhombic spectra are generally accompanied by the simpler trigonal spectra it is tempting to postulate that the former are produced by some modification of the latter. Such sites are usually thought to arise from a substitution of an O^{2-} ion for one of the eight F^- ions surrounding the RE ion. Although there appears to be little real evidence to support this model, it seems not unlikely that such sites would be formed in oxide doped material. The addition of a second compensating ion to this site, such as a second O^{2-} ion substituting in the same F^- or more remote shells, could further reduce the site symmetry to give rise to the observed spectra.

The rotation of the x and y axes in the (110) planes suggests either (a) that the compensating ion, or ions, lie in this plane but in such a position that a higher symmetry site is not produced, or (b) that the compensation is produced by more than one ion, the dominant compensator lying along a $\langle 110 \rangle$ axis, and

¹⁰ R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A218**, 553 (1953).

¹¹ B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1963), p. 25.

thus involving a modification of a neighboring calcium site, with a second charge occupying a more distant site causing the twist of the x and y axes. Mahlab *et al.*¹² observed a spectrum from U^{3+} ions in CaF_2 with the same symmetry as that which we have observed from the RE oxide in CaF_2 and decided in favor of mechanism (a). They suggested that an F^- ion occupying an interstitial site in the fourth-nearest-neighbor position was responsible for their spectrum. It seems to us unlikely that F^- interstitial ions produce the rhombic sites which we observe since the simpler type of such compensation, leading to a spectrum with tetragonal symmetry, is not observed in our crystals.

Recently we have become aware of an independent study of RE-oxide-doped CaF_2 made by Russian workers.¹³ They have observed rhombic spectra from Dy^{3+} and Nd^{3+} ions having various tilt angles δ in the (110) plane. In the case of Dy^{3+} ions, only one ESR spectrum was observed in the crystals as grown, consisting of a rhombic spectrum with $\delta=17.5^\circ$. After γ irradiation a trigonal spectrum from Dy^{3+} ions and a rhombic spectrum, believed to be from Dy^{2+} ions, were produced. To explain these observations and results obtained from various heat treatments, Kask *et al.* proposed a model for the original rhombic site in which two of the nearest-neighbor F^- ions were replaced by O^{2-} ions along a $\langle 111 \rangle$ diagonal, together with the removal of one of the remaining six F^- ions to form a vacancy. This model gave a site with the correct symmetry which was electrically neutral. The production of the trigonal resonance after γ irradiation was explained as being due to the capture of an electron by the F^- vacancy; however, this idea relies upon the F^- vacancy plus an electron having the same properties as an F^- ion, but we would strongly question whether they can be so treated. For the Dy^{2+} resonance, the z component of the g tensor lay along a $\langle 110 \rangle$ direction, and since only six equivalent spectra were reported, the tilt angle δ must be zero. It was suggested that this spectrum arose from the capture by the Dy^{3+} ion of an electron during the irradiation, but since $\delta=0$ the Dy^{2+} ion is apparently situated in a site with higher symmetry than the original Dy^{3+} ion. It is not easy to see how these two sites can be simply related on their model.

Kask *et al.* had to invoke further variations of their model to explain their results from Nd^{3+} ions. In this case three rhombic spectra were observed in the crystals as grown. After γ irradiation, no trigonal lines were found but a new rhombic spectrum from Nd^{3+} ions

with $\delta=0$ was produced. They explained the presence of three different rhombic sites as resulting from a redistribution of the O^{2-} ions over the nearest-neighbor F^- shell; there are three different possible combinations for the O^{2-} pairs, which, coupled with the various sites for the vacancy, could produce a variety of rhombic sites. They suggested that the different types of rhombic site formed by Dy^{3+} and Nd^{3+} ions in CaF_2 might result from the different crystal structures of Dy_2O_3 and Nd_2O_3 . We feel that it is rather unlikely that the O^{2-} ions would occupy sites other than at opposing corners of the F^- cube since strong hybridization would be necessary to overcome their Coulomb repulsion. However, if such sites do occur, a migration of the vacancy during γ irradiation away from the immediate surroundings of the Nd^{3+} ion would explain the spectrum with $\delta=0$. Such a vacancy diffusion could also explain the conversion of the rhombic Dy^{3+} spectrum to the trigonal Dy^{3+} spectrum during γ irradiation, but to explain the production of the rhombic Dy^{2+} spectrum with $\delta=0$ a redistribution of the O^{2-} ions would apparently be necessary and this seems to us to be rather unlikely.

The model proposed by Kask *et al.* for the Dy^{3+} sites (a) explains why such sites are only formed in the presence of oxygen, and (b) points to a possible relationship between the rhombic and trigonal sites. However, the model does not explain satisfactorily all the experimental facts as discussed above, and we feel that the precise nature of the sites producing these rhombic spectra is still an open question which will only be resolved by further experimental evidence.

6. CONCLUSIONS

Two ESR spectra, one having trigonal and the other having orthorhombic symmetry, have been observed in crystals of CaF_2 grown by the Czochralski process from a melt containing small quantities of CeO_2 . These spectra are different from those previously reported for Ce^{3+} ions in CaF_2 , and reflect different types of charge compensation mechanism produced by the introduction of the cerium ions in the form of the oxide rather than as the, more normal, fluoride. The orthorhombic spectrum is similar in appearance to those found for other RE ions introduced in a similar manner, and is characteristic of a new type of charge compensation mechanism, the detailed nature of which we are still trying to elucidate.

ACKNOWLEDGMENTS

We are indebted to Adrian Fray for assistance with the experimental work and to Dr. J. Kirton for many stimulating discussions, and for informing us of his point-charge calculations on various models for the trigonal sites.

¹² E. Mahlab, W. Low, V. Volterra, and A. Yariv, *Phys. Rev.* **131**, 920 (1963).

¹³ N. E. Kask, L. S. Kornienko and A. O. Rybaltovskii, *Fiz. Tverd. Tela*, **7**, 3234 (1965) [English transl.: *Soviet Phys.—Solid State* **7**, 2614 (1966)].