

Electron Spin Resonance of Er^{3+} in CaF_2

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Five different spectra of Er^{3+} in CaF_2 were observed. One spectrum corresponds to a field of cubic symmetry with $g=6.785\pm 0.002$; and one corresponds to a field of trigonal symmetry brought about by a substitution of O^{2-} ions for F^- ions, with $g_{11}=2.206\pm 0.007$, $g_{\perp}=8.843\pm 0.01$. A third spectrum, also of trigonal symmetry with $g_{11}=3.30\pm 0.01$, $g_{\perp}=8.54\pm 0.02$ is thought to be caused by a substitutional OH^- ion. A spectrum of tetragonal symmetry with $g_{11}=1.746\pm 0.002$ and $g_{\perp}=9.16\pm 0.01$ is believed to arise from sites of Er^{3+} ions with interstitial F^- ions in adjacent cubes. A fifth spectrum, for which the compensating ion is not identified, has tetragonal symmetry, with $g_{11}=7.78\pm 0.02$ and $g_{\perp}=6.254\pm 0.005$. The data permit the evaluation of the nuclear magnetic moment of Er^{167} as $\mu_N=0.56\pm 0.05$ nuclear magnetons.

INTRODUCTION

FROM many experiments by various authors it is well known that rare-earth ions can be substituted for the calcium ions in single crystals of calcium fluoride. The point symmetry at the site of the rare-earth ions may be either cubic, tetragonal, or trigonal.¹ The tetragonal point symmetry arises from charge compensation in which a fluorine ion occupies interstitially an adjacent cube, whereas the trigonal symmetry is caused by OH^- or O^{2-} ions substituted for fluorine ions at nearest-neighbor sites of the rare-earth ions. Recently, an orthorhombic point symmetry has been identified in the case of U^{3+} in CaF_2 .²

The case of Er^{3+} is of considerable interest. In some of the crystals at our disposal we have identified five different spectra corresponding to five different crystal field potentials. Three of these spectra are unambiguously assigned to different charge compensations.

Previous measurements of Er^{3+} in CaF_2 were reported by Baker *et al.*,³ and by Dvir and Low.⁴ The spectra reported by these authors correspond to two of the five observed by us.

In addition we include here information about the effects of heat treatment and gamma irradiation on the crystals and the correlation of these with the observed electron spin resonance (ESR) spectra.

THEORY

The configuration of Er^{3+} is $4f^{11}$ and the ground state of the free ion is $^4I_{15/2}$. In a crystal field of cubic symmetry, the $J=15/2$ level, is split into three quartets, Γ_8 and two doublets Γ_6 and Γ_7 . The lowest Stark level in an

eight coordinated cube may be either Γ_6 or Γ_7 depending on the ratio of the fourth- to sixth-order crystal field potential.⁵ In crystal fields of lower symmetry such as axial symmetry, the various quartets split into doublets. The spin Hamiltonian for Kramers doublets in an axial field can be written as

$$K = g_{11}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + AS_z I_z + B(S_x I_x + S_y I_y) + P[I_z^2 - 1/3I(I+1)],$$

where S is the effective spin $\frac{1}{2}$, and the z axis is parallel to the axial distortion. The first two terms correspond to the Zeeman splitting, the third and fourth to the nuclear hyperfine splitting, and the last gives the contribution of the nuclear quadrupole interaction. It can be shown that as long as only small axial distortions are present (small compared with the cubic crystal field parameters), the trace of the g tensor should be conserved,^{6,7} i.e., $g_{11} + 2g_{\perp} = 3g_c$, where g_c is the g value in the cubic field.

EXPERIMENTAL RESULTS

The measurements were made with a standard reflection ESR spectrometer at about 9000 Mc/sec and at 20°K. The crystals were obtained from a number of sources and contained, according to the source specifications, 0.01%–0.5% Er^{3+} .

The five spectra observed can be summarized as follows:

(a) An isotropic line with $g=6.78\pm 0.01$ and eight hyperfine lines due to Er^{167} ($I=7/2$) with $|A|=71.2\pm 1$ G. This spectrum has been previously found by Baker *et al.*,³ and by Dvir and Low⁴ and arises from a Γ_7 ground state in a cubic crystalline field.

(b) Tetragonal spectrum (I). The tetragonal axis is parallel to a cube axis and the g values are

¹ (i) W. Low, J. Phys. Soc. Japan **17**, Suppl. B-1, 440 (1962); (ii) J. Sierro, J. Chem. Phys. **34**, 2183 (1961).

² E. Nachlab, W. Low, V. Volterra, and A. Yariv, Phys. Rev. **131**, 920 (1963).

³ J. M. Baker, W. Hayes, and D. A. Jones, Proc. Phys. Soc. (London) **73**, 942 (1959).

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

⁵ K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).

⁶ U. Ranon, Ph.D. thesis, Hebrew University, Jerusalem, 1963 (unpublished).

⁷ H. R. Lewis and E. S. Sabisky, Phys. Rev. **130**, 1370 (1963).

TABLE I. g values and traces of the g tensor.

Site	a	b	c	d	e
g_{11}	6.785 ± 0.002	7.78 ± 0.02	1.746 ± 0.002	3.30 ± 0.01	2.206 ± 0.007
g_{\perp}	6.785 ± 0.002	6.254 ± 0.005	9.16 ± 0.01	8.54 ± 0.02	8.843 ± 0.010
$\frac{1}{3} \text{Tr } g$	6.785 ± 0.002	6.763 ± 0.010	6.686 ± 0.008	6.79 ± 0.02	6.63 ± 0.01

$g_{11} = 7.78 \pm 0.02$ and $g_{\perp} = 6.254 \pm 0.005$. This spectrum has also been observed by Baker *et al.*⁸

(c) Tetragonal spectrum (II). The axes are the same as in the previous spectrum but the g values are very anisotropic; $g_{11} = 1.746 \pm 0.002$ and $g_{\perp} = 9.16 \pm 0.01$.

(d) Trigonal spectrum (I). The trigonal axes are along the body diagonals of the cube and the g factors are $g_{11} = 3.30 \pm 0.01$ and $g_{\perp} = 8.54 \pm 0.02$.

(e) Trigonal spectrum (II). The axes are the same as for the previous spectrum but with the parameters: $g_{11} = 2.206 \pm 0.007$, $g_{\perp} = 8.843 \pm 0.010$

$$|A| = (77 \pm 6)10^{-4} \text{ cm}^{-1}, \quad |B| = (305 \pm 6)10^{-4} \text{ cm}^{-1}, \\ |P| < 5 \times 10^{-4} \text{ cm}^{-1}.$$

The g values are summarized in Table I, in which a third of the trace of the g tensor is listed for comparison.

The various crystals showed different spectra and may be classified into three categories:

(1) Crystals showing all the five spectra. The relative concentrations of Er^{3+} ions in the various sites are a:b:c:d:e = 30:30:10:1:9.

(2) Crystals showing spectra (a)–(d). The relative concentrations are a:b:c:d = 15:15:10:1.

(3) Crystals showing only the spectrum (e).

In order to identify the nature of the compensating ions which are responsible for the different sites we subjected the crystals to thermal treatments and gamma irradiation. The effects of these treatments were as follows:

(i) Heating at 750°C in vacuum or in an atmosphere of hydrogen for several hours did not produce any observable changes in the relative intensities of the spectra.

(ii) Heating at 1100°C in an atmosphere of hydrogen for several hours and slow cooling to room temperature affected the spectra of crystals of type 1 and 2 in the following way. The spectra (a)–(d) decreased in intensity, particularly the spectrum (c) which disappeared almost completely. On the other hand, an intense spectrum of type (e) appeared in both types of crystals. Chips from the surface of the crystals showed only the spectrum (e). Apparently, the remaining spectra (a)–(d) arose from the interior of the crystals. This also indicated that the effects of the heat treatment were due to a diffusion process. It was observed that the quartz tubes in which the crystals were heated had been corroded, apparently by hydrofluoric acid.

(iii) Heating at 1100°C in an oxygen atmosphere gave similar results as described in (ii) except that the process was not so efficient and the quartz tubes were not corroded.

(iv) Gamma irradiation at room temperature, of heat-treated and untreated crystals, did not produce any appreciable changes. Apparently no valence change was effected. This differs from results obtained for other ions such as Yb^{3+} , Ho^{3+} , Tm^{3+} , and Tb^{3+} , where valence can be changed by such a treatment.^{7–10}

DISCUSSION

We tentatively propose the following identifications of the various spectra. The spectrum (e) is associated with a substitutional O^{2-} ion as a nearest neighbor to the paramagnetic ion. The evidence is from the reactions (ii) and (iii); the substitutional fluorine ions are mobile at elevated temperatures and diffuse towards the surface. They react with hydrogen, which has been shown to diffuse into the CaF_2 crystals¹¹ to form HF. The hydrofluoric acid reacts with the quartz, releasing H_2O which at this high temperature dissociates into H^+ and OH^- . The OH^- ions diffuse into the crystal, occupying some of the corner positions of cubes surrounding the Er^{3+} ions. This gives rise to the trigonal spectrum (d). At prolonged heating, the OH^- dissociates into O^{2-} and H^+ ions. The O^{2-} now compensates for the charge of the Er^{3+} ion and causes a new trigonal field. The process is very similar to that proposed by Sierro,¹ who assumes the reaction $\text{OH}^- + \text{F}^- \rightarrow \text{HF} + \text{O}^{2-}$. This mechanism explains the fact that the main spectrum after prolonged heating in hydrogen is spectrum (e), it explains the reduction of the cubic and tetragonal spectra, the strong decrease of spectrum (d), and intensification of spectrum (e). It also explains the fact that the surface part of the crystals predominately shows the spectrum (e), since, as Bontinck¹² pointed out, OH^- will not stay near the surface during the hydrolysis but will diffuse into the interior of the crystal.

When the crystals are heated in oxygen, the substitution of F^- ions by O^{2-} proceeds more slowly. The probable reason is that since there is no hydrogen

⁸ W. Low and U. Ranon in *Proceedings First International Conference on Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963), p. 167.

⁹ W. Hayes and J. W. Twidell in Ref. 8, p. 163.

¹⁰ W. Hayes, G. D. Jones, and J. W. Twidell, Proc. Phys. Soc. (London) **81**, 371 (1963).

¹¹ J. L. Hall and R. T. Schumacher, Phys. Rev. **127**, 1892 (1962).

¹² W. Bontinck, Physica **24**, 650 (1958).

present, there is no efficient agent for the removal of the interstitial and other F^- ions.

We identify spectrum (c) as belonging to the site in which an interstitial F^- ion causes the charge compensation and gives rise to a tetragonal field. Baker *et al.* attributed spectrum (b) to such sites. The main reason for our assignment, is that the g tensor of (c) shows a large anisotropy and that $g_{11} < g_1$, whereas spectrum (b) shows a small anisotropy and $g_{11} > g_1$. We would expect that an interstitial F^- ion would give rise to a large anisotropy in g . Further, a negative charge compensation causing the axial distortion implies $g_{11} < g_1$ in Er^{3+} .

An axial field can be approximated by a crystal field of the second order, $B_2^0 O_2^0$, where the operator O_2^0 is given by $O_2^0 = \langle J | \alpha | J \rangle [J_z^2 - 1/3 J(J+1)]$.^{13,14} A simple point-charge calculation shows that the axial field caused by a negative charge in an adjacent cube gives $B_2^0 > 0$. Hence, the sign of $B_2^0 O_2^0$ depends on the sign of the matrix element of O_2^0 . The axial field yields only diagonal matrix elements when superimposed on the cubic field. Therefore, for positive B_2^0 and $\langle J | \alpha | J \rangle$, the axial distortion will increase the part of the smallest $|J_z|$ in the eigenfunction of the cubic field ground state. These functions ψ are linear combination of various $|J_z\rangle$. For Er^{3+} $\langle J | \alpha | J \rangle$ is positive and therefore the axial distortion will increase the coefficient of the $|J_z\rangle$ of the smallest $|J_z|$. Conversely, a negative axial field would increase the coefficient of $|J_z\rangle$ with the largest $|J_z|$. Now $g_{11} = 2\Lambda \langle \psi | J_z | \psi^* \rangle$, where Λ is the Lande g factor (6/5 for Er^{3+}), so that an increase in the coefficient of the smallest $|J_z|$ will give a g_{11} which is smaller than the cubic g factor. Assuming also that the trace of the g tensor is conserved, one gets $g_{11} < g_c < g_1$. It should be noted that these considerations apply as well to the case of a trigonal field caused by a negative charge; one needs only to take the axis of quantization along the axial distortion. Therefore the qualitative anisotropy of the g tensor should be the same for both the O^{2-} and F^- induced fields. This is in agreement with the observed

data of spectra (c) and (d). These considerations are consistent also with the anisotropy of the g factors found for other rare-earth ions where the charge compensation has been shown to arise from an interstitial F^- ion. For example, in the case of Ce^{3+} , $\langle J | \alpha | J \rangle$ is negative. The coefficient of the largest $|J_z|$ in ψ is, therefore, larger at the expense of other coefficients, so that $g_{11} > g_1$. This has indeed been found experimentally.^{3,15} For the ions Nd^{3+} and U^{3+} $\langle J | \alpha | J \rangle$ is negative, and experiments have shown $g_{11} > g_1$ for the F^- axial sites.¹⁶ For Yb^{3+} $\langle J | \alpha | J \rangle$ is positive and both the O^{2-} and F^- site spectra have $g_{11} < g$.⁶

We have no definite explanation for spectrum (b). Since the trace of the g tensor is the same as for all the other spectra, it must also arise from a Γ_7 doublet. Since $g_{11} > g_1$ one would suppose that there is a weak positive charge, possibly a H^+ ion or a hole, giving rise to an axial distortion.

The hyperfine structure constants A and B in spectrum (e) permit the evaluation of the nuclear magnetic moment of Er^{167} : Using the value of $\langle r^{-3} \rangle$ of Lindgren¹⁷ (70 \AA^{-3}) we obtain $|\mu_N| = 0.56 \pm 0.05 \text{ nm}$. In this calculation, admixtures of other ionic levels such as $^4I_{13/2}$ were neglected. Such admixtures may contribute a small amount to the wave functions. This is, of course, reasonable since the value of g_{11}/g_1 is within 1% equal to A/B in spectrum (e), and therefore, indicative of only small admixtures of the $J=13/2$ level to the ground state.

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¹⁷ I. Lindgren, Nucl. Phys. **32**, 151 (1962).

¹³ K. W. H. Stevens, Proc. Phys. Soc. (London) **A65**, 209 (1952).
¹⁴ R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 387 (1953).