PHYSICAL REVIEW VOLUME 155, NUMBER 2 10 MARCH 1967

# Paramagnetic Resonance and Fluorescence of $Er^{3+}$ at Cubic Sites in ZnSe

J. D. KINGSLEY AND M. AVEN
*General Electric Research and Development Center, Schenectady, New York*

(Received 20 September 1966)

$Er^{3+}$ has been found at two distinct sites having cubic symmetry in ZnSe:Er, Cu. One of these is believed to be a simple Zn substitutional site, and in it the $Er^{3+}$ ground-state transforms as the $\Gamma_7$ representation of $T_d$ symmetry. The lowest excited state, at an energy of $6.5\pm1$ cm$^{-1}$, has $\Gamma_8$ symmetry. Electron-paramagnetic-resonance transitions have been seen at 14.1 GHz for both of these states. Because of their proximity, an applied magnetic field appreciably mixes these states, inducing an anisotropy into the $\Gamma_7$ resonance which has been measured at 9.3, 14.1, and 35.0 GHz. The $g$ factor of the $\Gamma_7$, obtained by extrapolating to zero magnetic field, is $5.950\pm0.005$. This implies that the appropriate Landé factor $g_J$ is $1.190\pm0.001$. The resonance of the $\Gamma_8$ state, when fitted to the calculations of Lea, Leask, and Wolf, gives a value of their parameter $x=-0.71$. We also find $B_4=-(1.9\pm0.3)\times10^{-3}$ cm$^{-1}$, $B_6=+(3.3\pm0.5)\times10^{-6}$ cm$^{-1}$, $A_4\langle r^4\rangle=-(43\pm6)$ cm$^{-1}$, and $A_6\langle r^6\rangle=+(1.6\pm0.2)$ cm$^{-1}$ for this center. The second $Er^{3+}$ defect, having cubic symmetry, has also been seen in resonance. It has a $\Gamma_8$ ground state and shows a strong line fluorescence, primarily from the $^4S_{3/2}$ state, which has a very broad excitation band. The crystal-field splittings of the $^4I_{15/2}$ and $^4I_{13/2}$ states have been determined from the emission spectra and fitted with the Lea-Leask-Wolf calculations. The fit is generally better than 1 cm$^{-1}$, which is the order of the deviations expected due to crystal-field mixing of adjacent free-ion states. In this center we find $x(^4I_{15/2})=+0.797$, $A_4\langle r^4\rangle=+113.1\pm0.7$ cm$^{-1}$, $A_6\langle r^6\rangle=+2.65\pm0.02$ cm$^{-1}$, and $g_J(^4I_{15/2})=1.184\pm0.001$. This center is believed to involve an $Er^{3+}$ interstitial at the center of a tetrahedron formed by four $Cu^+$ ions at Zn sites. Elementary point-charge calculations predict the observed crystal-field parameters of both centers surprisingly well.

## I. INTRODUCTION

A SHORT-RANGE energy transfer from noble metals to rare earths in several II-VI compounds has been reported by the authors and J. S. Prener.[1] It was concluded from qualitative changes in the rare-earth emission spectra that the separations between the two types of impurity were on the order of lattice spacings. It follows that an analysis of the symmetry of the rare-earth sites by means of optical and microwave spectroscopy may give some information concerning the location of the noble-metal and rare-earth impurities. This in turn is relevant to a more detailed understanding of the energy-transfer process.

In this paper we discuss the results of our spectroscopy of two defects in ZnSe:Cu, Er, both of which have the $Er^{3+}$ ion at sites having cubic symmetry. One of these cubic defects shows sensitized fluorescence, while no emission from the other center has been found. In addition to these sites, there are at least six noncubic Er sites, all of which show sensitized fluorescence, but these have not yet been studied in detail. Both cubic defects have been observed with electron paramagnetic resonance (EPR). The crystal-field splittings of the $^4I_{15/2}$ ground state and $^4I_{13/2}$ first excited state have been determined for the cubic center whose fluorescence spectrum has been found.

Until very recently there have been only a few EPR investigations of rare earths in II-VI compounds[2] and, to our knowledge, no detailed analyses of the optical spectra of these systems have been published. We have very recently learned of the EPR work of Watts[3] involving $Er^{3+}$ in ZnSe, ZnS, and CdTe. He has observed the ground-state resonance of $Er^{3+}$ at substitutional cation sites and his $g$ factors for ZnSe are similar to ours.

Although there is only meager prior experimental work which is relevant, there do exist rather complete analyses of the eigenfunctions and eigenvalues of $f$-electron states in cubic crystalline fields by Lea, Leask, and Wolf (LLW)[4] and by Ebina and Tsuya (ET).[5] Because we will make extensive use of these results, we summarize these authors's results and their notation in Sec. II.

## II. SUMMARY OF THE CRYSTAL-FIELD CALCULATIONS

Lea, Leask, and Wolf[4] and Ebina and Tsuya[5] performed machine computations of the cubic-crystal-field splitting of states of a $4f^n$ configuration having a definite total angular momentum $J$. Thus, starting with a set of basis functions of the form $|J,m_J\rangle$, they have provided us with the eigenfunctions and eigenvalues of a cubic-crystal-field perturbation of the form

$$\mathcal{H}_c=B_4(O_4^0+5O_4^4)+B_6(O_6^0-21O_6^4)$$

The $O_n^m$ are functions of the components of the total angular momentum.[4] Within a manifold of constant $J$,

---

[1] J. D. Kingsley, J. S. Prener, and M. Aven, Phys. Rev. Letters **14**, 136 (1965).

[2] R. S. Title, in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (North-Holland Publishing Company, Amsterdam, 1967).

[3] K. Watts (private communication).

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

[5] Y. Ebina and N. Tsuya, Repts. Res. Inst. Elec. Commun., Tohoku Univ. Suppl. **15** (1963). The reader should be aware that earlier articles on this subject by these authors contain numerous errors which have been corrected in this reference.

these functions are equivalent to terms of a spherical harmonic expansion of the crystal field.[6] The parameters $B_4$ and $B_6$ describe the strength of the crystal-field perturbation on a state of specific $L$, $S$, and $J$.[4–6] These parameters are related to those which, in principle, describe the interaction of a cubic crystal field on any state of a given $4f^n$ configuration by[6]

$$B_4 = A_4 \langle r^4 \rangle \beta, \quad B_6 = A_6 \langle r^6 \rangle \gamma.$$

The Stevens multiplicative constants $\beta$ and $\gamma$ are determined by the $L$, $S$, and $J$ of the free-ion state under consideration. The potential at the center of a tetrahedron of negative point charges has $A_4 < 0$, while that at the center of an octahedron of negative point charges has $A_4 > 0$. In both cases, $A_6 > 0$. For the ground state of $\mathrm{Er}^{3+}$, $\beta$ and $\gamma$ are both positive, so that corresponding $A_n$ and $B_n$ coefficients have the same signs.

In order that all ratios of the $B_4$ and $B_6$ parameters are spanned in the machine computations, LLW define two parameters $W$ and $x$ such that

$$B_4 F(4) = Wx, \quad B_6 F(6) = W(1 - |x|).$$

$W$ is an energy scale factor and $x$, which runs from $-1$ to $+1$, is determined by the ratio $B_4/B_6$. The primary utility of the numbers $F(4)$ and $F(6)$ is to maintain an approximately constant span for the eigenvalues for all values of $x$. For $J = 15/2$, $F(4) = 60$, $F(6) = 13\,860$ and for $J = 13/2$, they are 60 and 7560, respectively.

Since $W$ may be either positive or negative, all four possible combinations for the signs of $B_4$ and $B_6$ are included in the LLW results. Thus, they may be applied to describe the effect of any cubic field, octahedral or tetrahedral, on a $4f^n$ state having a definite $J$ value. However, by convention, the labeling of the odd-parity $\Gamma_6$ and $\Gamma_7$ states must be interchanged on going from an octahedral field to a tetrahedral field.[7] The labeling of the states given by LLW and ET is that appropriate to octahedral symmetry. Since ZnSe with $\bar{4}3m$ symmetry has no sites with inversion symmetry, the labeling appropriate to our centers is that for $T_d$ symmetry, even though we will show that one of the cubic sites has the $B_4$ and $B_6$ parameters which one would expect from an octahedron of negative point charges.

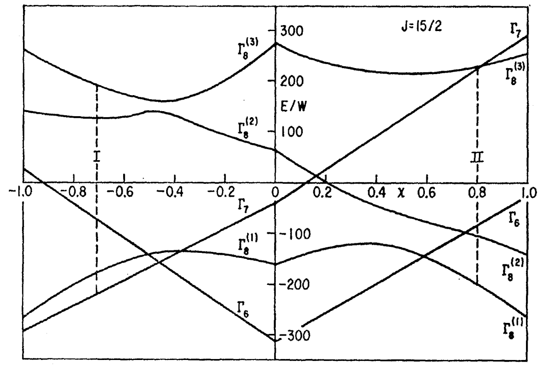

FIG. 1. The eigenvalues for the splitting of a $J = 15/2$ manifold by a tetrahedral crystalline field, as calculated by Lea, Leask, and Wolf (LLW). As is explained in the text, the labeling of the $\Gamma_6$ and $\Gamma_7$ states has been interchanged from that of LLW.

LLW tabulate the eigenvalues and eigenfunctions for the splitting of states having $J \leq 8$ and for $x$ values from $-1$ to $+1$ in intervals of 0.1. Since they chose the $\langle 100 \rangle$ axes as axes of quantization and these are fourfold axes, their wave functions have the form, for $J = 15/2$, of either

$$|\psi a\pm\rangle = a_1 |m_J = \pm 15/2\rangle + a_2 |\pm\tfrac{7}{2}\rangle + a_3 |\mp\tfrac{1}{2}\rangle + a_4 |\mp\tfrac{9}{2}\rangle \quad \text{(1a)}$$

or

$$|\psi b\pm\rangle = b_1 |\pm 13/2\rangle + b_2 |\pm\tfrac{5}{2}\rangle + b_3 |\mp\tfrac{3}{2}\rangle + b_4 |\mp 11/2\rangle. \quad \text{(1b)}$$

The $|\psi a+\rangle$ and $|\psi a-\rangle$ are Kramers conjugate states as are the $|\psi b+\rangle$ and $|\psi b-\rangle$ states. We will make frequent reference to the notation implied by Eqs. (1).

ET provide results for $J = 4$, 6, 8, $\frac{7}{2}$, and 15/2 and for $x$ from $-1$ to $+1$ in intervals of 0.25. They give eigenfunctions for both $\langle 100 \rangle$ and $\langle 111 \rangle$ axes of quantization and also include computations of the Zeeman splitting of the crystal levels by a uniform magnetic field, including $H$ fields strong compared to the crystal field.

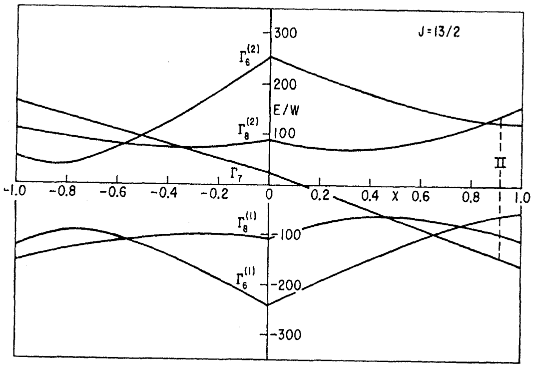

FIG. 2. The eigenvalues of a $J = 13/2$ manifold in a tetrahedral field (LLW).

---

[6] For a summary of computational techniques used in crystal-field theory see M. T. Hutchings, Solid State Phys. **16**, 227 (1964).

[7] Since $T_d$ is a subgroup of $O_h$ one may visualize, in principle, a reduction from $O_h$ to $T_d$ symmetry. In such a reduction the $\Gamma_{6g}$ and $\Gamma_{7u}$ representation of $O_h$ symmetry necessarily must be given the same label in $T_d$ symmetry. By convention this label is $\Gamma_6$. Similarly, $\Gamma_{7g}$ and $\Gamma_{6u}$ in $O_h$ both reduce to $\Gamma_7$ in $T_d$. The state labels given by LLW for integral $J$ values are appropriate for both $O_h$ and $T_d$ since only even-parity $4f^n$ states have integral $J$ values. However, the odd half-integer $J$ manifolds are necessarily odd-parity in $O_h$ crystal fields, thus requiring the interchange of labels in $T_d$ symmetry in order to conform to convention. For the great majority of calculations, this labeling is of no physical consequence but situations in which it could matter exist and it seems judicious to adhere to the convention. See, for example, G. E. Koster, J. A. Dimmock, R. G. Wheeler, and H. Statz, in *Properties of the Thirty-Two Point Groups* (The MIT Press, Cambridge, Massachusetts, 1963), pp. 101, 104.

In Figs. 1 and 2 we reproduce the LLW eigenvalues for $J=15/2$ and 13/2. The state labeling is that for $T_d$ symmetry.

## III. SAMPLE PREPARATION

The ZnSe crystals (with the zincblende structure, $\bar{4}3m$) were grown by vapor transport.[8] The Er was either incorporated during growth or subsequently diffused into grown crystals from liquid Se at 850°C for periods up to eight days. When the Er was incorporated during growth it was added to the powder charge as Er $(NO_3)_3$ or $ErCl_3$ in concentrations from $5\times10^{-4}$ to $2\times10^{-3}$ mole fraction. The Er concentration present in the samples in unprecipitated form was probably always less than $10^{-4}$ mole fraction. The concentrations were thus too small to permit investigation of the rare-earth absorption spectra. When the rare earth was added in the form of the nitrate it was found necessary to include $SrCl_2$ as a transporting agent. Cu was also either grown in or subsequently diffused in. The charge was prefired in $H_2Se$ and sintered in argon.

Untwinned single-crystal samples were cut from the boules and oriented by x-ray diffraction or by cleavage. When possible, the samples for resonance or Zeeman measurements were mounted on a cleaved surface and rotated about the ⟨110⟩ axis perpendicular to this surface with the magnetic field in the (110) plane. The samples were oriented to an accuracy of about 1°.

## IV. APPARATUS

Most of the resonance data were taken at 14.1 GHz on a spectrometer described by Ludwig and Woodbury.[9] Some measurements were also made at 9.3 and 35 GHz. In the resonance measurements the sample was cooled to 10, 4.2, or 1.4°K. The angular positions of the extrema of the resonance field could be determined to about 0.2°. The accuracy of the measurement of the $g$ factors of the strongly anisotropic $\Gamma_8$ resonances was in part limited by the imperfect orientation of the ⟨110⟩ axis perpendicular to the magnetic field. An angular error of 1° yields a $g$-factor error of about 0.002 for the observed resonances. The linewidths were typically 10 to 15 G at 14.1 GHz and this contributes an uncertainty in $g$ on the order of 0.003. The weaker and broader transitions were measured to about $\pm0.010$.

The fluorescence spectra were obtained with Jarrell-Ash $\frac{1}{2}$-m Ebert and 1-m Czerny-Turner spectrometers. The data were recorded both photoelectrically and photographically on the latter instrument. The instrumental resolution was about 0.1 Å in the visible and 0.2 Å in the near infrared. The sharper emission line positions were determined to about $\pm0.1$ cm$^{-1}$ through comparison to an Fe arc photographed simultaneously with the sample emission. The sample was excited with either a high-pressure Hg arc (G.E. AH-6) or a high-pressure Xe arc (PEK Labs X-75) suitably filtered. For measurements of excitation spectra, a Jarrell-Ash one-quarter meter $f/3.6$ Ebert monochromator was interspersed between the Xe arc and the sample. For the fluorescence measurements the sample was cooled to 77, 4.2, or 2°K.

The optical Zeeman measurements were obtained using a small iron core, superconducting coil, magnet capable of producing field strengths up to 42 kOe. The magnet and sample were both immersed in liquid helium at 2°K. The sample could be rotated while immersed to obtain angular-dependence data.

TABLE I. Cubic-site resonance transitions of $Er^{3+}$ in ZnSe (14.1 GHz, except * 9.3 GHz).

| | Transition | H‖⟨100⟩ | $h\nu/\beta H$ ⟨111⟩ | ⟨110⟩ |
|---|---|---|---|---|
| Center I | $a$ | 5.957 | 5.909 | 5.920 |
| | $b$ | 1.10* | 5.45 | 4.50 |
| | $c$ | 9.89 | 8.32 | 8.89 |
| Center II | $d$ | 5.596 | 2.958 | 3.700 |
| | $e$ | 11.53 | ... | ... |
| | $f$ | 2.93 | 4.77 | ... |
| | $g$ | 2.99 | ... | ... |

## V. EPR EXPERIMENTAL RESULTS

Seven resonance transitions of $Er^{3+}$ at cubic sites have been observed in ZnSe. The values of $h\nu/\beta H$ at 14.1 GHz at which they were found are shown in Figs. 3 and 4 and are listed in Table I for orientations of the

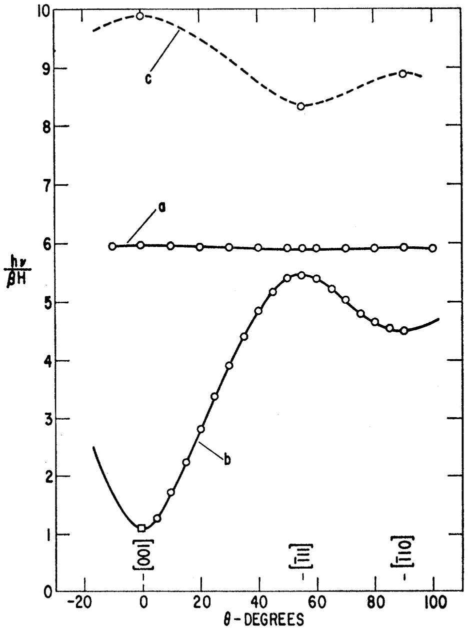

FIG. 3. The observed resonance transitions of center I. The data shown are for the $I=0$ isotopes and were taken at $\nu=14.1$ GHz except for the point indicated by the square.

---

[8] W. W. Piper and S. Polich, J. Appl. Phys. **32**, 1278 (1961).

[9] G. W. Ludwig and H. H. Woodbury, Phys. Rev. **113**, 1014 (1959).

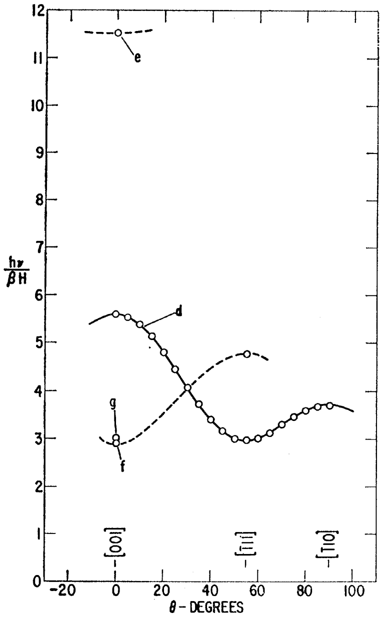

FIG. 4. The observed resonance transitions of center II at $\nu=14.1$ GHz. Only the data for the $I=0$ spectra are shown.

magnetic field along three principal directions. The various transitions have been assigned to center I or center II according to their occurrence in different samples and the interpretation to be presented subsequently. The two strongest transitions, $a$ and $d$, show both the Er nuclear-spin-zero spectrum and the 8-line spectrum of the $I=\frac{7}{2}$ $Er^{167}$ isotope, with the relative peak intensities of the two spectra being about 30 to 1, as one would expect from the natural abundances. The values of $h\nu/\beta H$ in Figs. 3 and 4 and Table I are for the $I=0$ spectra. Transitions $b$ and $c$ were found to be those of an excited state while the other five are all believed to be ground-state resonances. The intensity of resonance $b$ was measured between 4.2 and 1.4°K and the results were fit to

$$I=(1/T)e^{-\Delta/kT}$$

by choosing a value of the energy parameter $\Delta=6.5\pm1$ $\text{cm}^{-1}$.

Transitions $a$, $b$, $c$, and $d$ have an angular dependence characteristic of ions at cubic sites. This dependence is given approximately by

$$h\nu/\beta H=g+up(n_1,n_2,n_3)\,,$$

where $p(n_1,n_2,n_3)=1-5(n_1^2n_2^2+n_1^2n_3^2+n_2^2n_3^2)$, and the $n_i$ are the direction cosines of the magnetic field. For $H\perp[110]$, this becomes $p(\theta)=1-(5/4)\sin^2\theta(1+3\cos^2\theta)$ and $\theta$ is measured from the [001] axis in the (110) plane.

### A. Resonance of Center I

With the assumption that $J$ is a good quantum number, the Zeeman matrix elements become

$$g_J\beta\mathbf{H}\cdot\langle\psi_i|\mathbf{J}|\psi_k\rangle\,,$$

where $g_J$ is the Landé splitting factor. If $H$ is parallel to the $\langle 100\rangle$ axis of quantization, the $z$ axis, the displacement of the $k$th energy level, to first order in $H$, is given by

$$\Delta E_k=g_J\beta H_z\langle\psi_k|J_z|\psi_k\rangle\equiv g_J\beta H_zM_{kk}.$$

Referring to Eqs. (1) we see that the matrix element $M_{kk}$ has the form of either

$$M_{kk}=\pm[(\tfrac{15}{2})a_1^2+\tfrac{7}{2}a_2^2-\tfrac{1}{2}a_3^2-\tfrac{9}{2}a_4^2]$$

or

$$M_{kk}=\pm[(\tfrac{13}{2})b_1^2+\tfrac{5}{2}b_2^2-\tfrac{3}{2}b_3^2-(\tfrac{11}{2})b_4^2].$$

For $J=\frac{15}{2}$, the wave functions for the $\Gamma_6$ and $\Gamma_7$ states are determined by symmetry alone and in $T_d$ symmetry are given by

$$|\Gamma_6\pm\rangle=0.6332|\pm\tfrac{13}{2}\rangle+0.5819|\pm\tfrac{5}{2}\rangle-0.4507|\mp\tfrac{3}{2}\rangle-0.2393|\mp\tfrac{11}{2}\rangle,$$

$$|\Gamma_7\pm\rangle=0.5818|\pm\tfrac{15}{2}\rangle+0.3307|\pm\tfrac{7}{2}\rangle+0.7182|\mp\tfrac{1}{2}\rangle+0.1910|\mp\tfrac{9}{2}\rangle.$$

The matrix elements of $J_z$ for these two states are $\frac{17}{6}$ and $\frac{5}{2}$, respectively. If the free $Er^{3+}$-ion ground state were pure $^4I_{15/2}$, then the appropriate value of the Landé factor would be $g_J=\frac{6}{5}$. The (isotropic) $g$ factors of the $\Gamma_6$ and $\Gamma_7$ states of a pure $^4I_{15/2}$ manifold are thus 6.800 and 6.000 in $T_d$ symmetry. Because transition $a$ is comparitively isotropic and for it $h\nu/\beta H$ is only slightly less than 6, we conclude that it is the transition between the $|\Gamma_7+\rangle$ and $|\Gamma_7-\rangle$ states. Therefore, since transition $a$ is essentially temperature-independent between 1.4 and 4.2°K, center I has a $\Gamma_7$ ground state.

Figure 1 shows that the ground state of a $J=\frac{15}{2}$ manifold transforms as $\Gamma_7$ if $Wx<0$ and $|x|\approx1$. This will be the case if $B_4<0$ and $|B_4|\gg|B_6|$. More precisely, a $\Gamma_7$ lying lowest implies $B_4<0$ and $-5.1\times10^{-3}<B_6/B_4<+8.9\times10^{-4}$. Since the crystal field of a tetrahedron of negative point charges has a negative $B_4$, it is reasonable to assume that an ion at a Zn site, which is surrounded by a tetrahedron of four Se ions, would see a crystal field having a negative $B_4$. Thus, the resonance of center I is that which one would expect for $Er^{3+}$ at a substitutional Zn site.

It can be seen in Fig. 1 that whenever a $\Gamma_7$ lies lowest there is also a low-lying excited state with $\Gamma_8$ symmetry. Transitions $b$ and $c$, whose intensities decrease on cooling to 1.4°K, are thought to be transitions of this $\Gamma_8$ state. We will next show that the slight anisotropy of transition $a$ can be explained as being due to the mixing of these closely spaced $\Gamma_7$ and $\Gamma_8$ states by the applied magnetic field.

We consider first the effect of this mixing when $\mathbf{H}$ is along the axis of quantization. For $\mathbf{H}\|\langle100\rangle$, the $z$ axis, there are off-diagonal Zeeman matrix elements only between the $|\Gamma_7+\rangle$ state and the $|\Gamma_8a+\rangle$ state and between the $|\Gamma_7-\rangle$ and the $|\Gamma_8a-\rangle$ states. Consequently, we need diagonalize only the following 2×2 secular determinant;

$$\begin{array}{c|cc|} & |\Gamma_7+\rangle & |\Gamma\ a+\rangle \\ |\Gamma_7+\rangle & -g_J\beta HM_{11}-E & -g_J\beta HM_{12} \\ |\Gamma\ a+\rangle & -g_J\beta HM_{21} & -g_J\beta HM_{22}+\Delta-E \end{array}$$

where

$$M_{11}=\langle\Gamma_7+|J_z|\Gamma_7+\rangle=-\langle\Gamma_7|J_z|\Gamma_7-\rangle,$$
$$M_{22}=\langle\Gamma_8a+|J_z|\Gamma_8a+\rangle=-\langle\Gamma_8a-|J_z|\Gamma_8a-\rangle,$$
$$M_{12}=\langle\Gamma_7+|J_z|\Gamma_8a+\rangle=-\langle\Gamma_7-|J_z|\Gamma_8a-\rangle.$$

The roots are

$$\frac{E}{g_J\beta H}=\frac{1}{2}\Bigg\{\frac{\Delta}{g_J\beta H}-M_{22}-M_{11}$$
$$\pm\left[\left(\frac{\Delta}{g_J\beta H}-M_{22}+M_{11}\right)^2+4|M_{12}|^2\right]^{1/2}\Bigg\}.$$

If $\Delta\gg g_J\beta H$, then

$$E(\Gamma_7+)\simeq-g_J\beta HM_{11}-\frac{g_J\beta H|M_{12}|^2}{(\Delta/g_J\beta H-M_{22}+M_{11})}$$

and

$$E(\Gamma_8+)\simeq\Delta-g_J\beta HM_{22}+\frac{g_J\beta H|M_{12}|^2}{(\Delta/g_J\beta H-M_{22}+M_{11})}.$$

Similarly,

$$E(\Gamma_7-)\simeq+g_J\beta HM_{11}-\frac{g_J\beta H|M_{12}|^2}{(\Delta/g_J\beta H+M_{22}-M_{11})}$$

Consequently, the $\Gamma_7$ resonance condition, to order $H^2$, for $H\|\langle100\rangle$ is

$$\frac{h\nu}{\beta H}\simeq2g_JM_{11}-\left(\frac{g_J\beta H}{\Delta}\right)^2|M_{12}|^2(2g_JM_{11}-2g_JM_{22}).\quad(2)$$

The transition between the $|\Gamma_8a+\rangle$ and $|\Gamma_8a-\rangle$ states occurs when

$$\frac{h\nu}{\beta H}=2g_JM_{22}+\left(\frac{g_J\beta H}{\Delta}\right)^2|M_{12}|^2(2g_JM_{11}-2g_JM_{22}).\quad(3)$$

The predicted quadratic dependence of $h\nu/\beta H$ on magnetic field was verified by measuring the $\Gamma_7$ resonance at 9.3, 14.1, and 35 GHz. The results are given in Fig. 5 for **H** along the ⟨100⟩, ⟨110⟩, and ⟨111⟩ axes. Although Eq. (2) is valid only for **H**‖⟨100⟩, Fig. 5 shows that the results for all three field orientations can be fit to equations having the same form as (2) with a common zero-field intercept but slopes dependent on orientation. One may use the ET wave functions for a ⟨111⟩ axis of quantization and derive results similar in form to Eqs. (2) and (3), since for **H**‖⟨111⟩ the $|\Gamma_7+\rangle$ mixes with only one of the $\Gamma_8$ states. With the exception of $M_{22}$, the expressions for the ⟨100⟩ and ⟨111⟩ field orientations are identical.

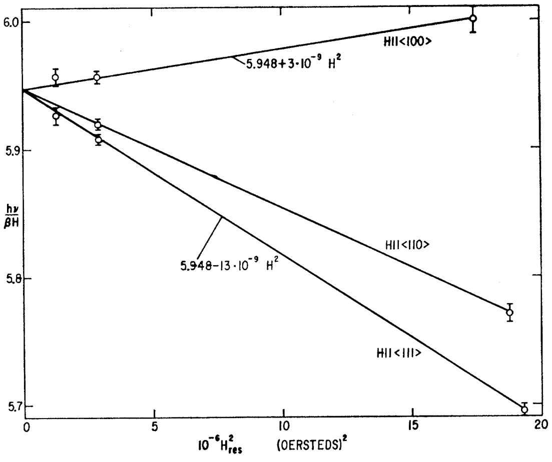

FIG. 5. $h\nu/\beta H$ for the $\Gamma_7$ resonance of center I as a function of the square of the magnetic field for three different orientations of the field.

We consider next the angular dependence of the $\Gamma_7$ resonance which is induced by the magnetic field mixing of the $\Gamma_7$ and $\Gamma_8$ states. Ham[10] has developed the following spin Hamiltonian, correct to order $H^3$, for a Kramers doublet which includes the perturbation of a nearby $\Gamma_8$:

$$\mathcal{H}_S=g_0\beta\mathbf{H}\cdot\mathbf{S}+\beta A[S_xH_x{}^3+S_yH_y{}^3+S_zH_z{}^3$$
$$-\tfrac{3}{5}(\mathbf{H}\cdot\mathbf{S})H^2]+\beta B(\mathbf{H}\cdot\mathbf{S})H^2,\quad(4)$$

where

$$g_0=2g_JM_{11},$$
$$A=-\tfrac{9}{2}g_J(g_J\beta M_{12}/\Delta)^2(\tfrac{1}{3}M_{33}-M_{22}),$$
$$B=g_J(g_J\beta M_{12}/\Delta)^2(\tfrac{1}{5}M_{22}+\tfrac{3}{5}M_{33}-2M_{11}),$$

and

$$M_{33}=\langle\Gamma_8b+|J_z|\Gamma_8b+\rangle.$$

The remaining notation is as before and the $z$ axis is a ⟨100⟩ axis. Resonance transitions between the $\Gamma_7$ Kramers conjugate states occur when

$$h\nu/\beta H=g_0+[\tfrac{2}{5}Ap(n_1,n_2,n_3)+B]H^2\quad(5)$$

to order $H^2$. $p(n_1,n_2,n_3)$ is the function previously defined. In Fig. 6 we show the angular dependence of the $\Gamma_7$ resonance in a {110} plane as measured at 14.1 and 35 GHz. The data can be fitted to a $p(\theta)$ dependence within experimental error. The data shown in Fig. 5 fit Eq. (5) with $A=+(23.4\pm1.0)\times10^{-9}$ and $B=-(6.8\pm0.5)\times10^{-9}$ Oe$^{-2}$.

We can calculate the $A$ and $B$ coefficients from the LLW wave functions by determining the four matrix elements $M_{11}$, $M_{22}$, $M_{33}$, and $M_{12}$. All of these except the first depend on the parameter $x$. The $\Gamma_8$ resonance results may be used to determine $x$, provided we consider the corrections to the experimental values of

---

[10] F. S. Ham (private communication).

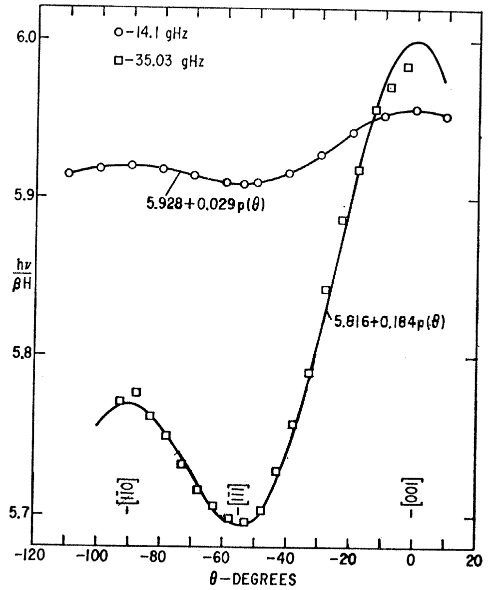

FIG. 6. The angular dependence of the $\Gamma_7$ resonance of center I in a {110} plane at 14.1 and 35.03 GHz.

$h\nu/\beta H$ due to the effects of the $\Gamma_7$-$\Gamma_8$ mixing. As it turns out this correction is not significant.

To interpret the $\Gamma_8$ resonance we must know the value of $g_J$, and an approximate value can be obtained from the data shown in Fig. 5. In the limit of zero magnetic field $(h\nu/\beta H)(\Gamma_7) \rightarrow 2g_J M_{11}$, as is indicated in Eq. (5). The results of Fig. 5 show that the zero-field extrapolation is $5.950 \pm 0.005$. Since $2M_{11} = 5$, independent of $x$, $g_J = 1.190 \pm 0.001$. We defer discussion of this value of $g_J$ until later.

With $\mathbf{H} \| \langle 100 \rangle$, transition $b$ occurs at $h\nu/\beta H = 1.10 \pm 0.01$. Using the LLW wave functions we have calculated the linear Zeeman splittings, for $\mathbf{H} \| \langle 100 \rangle$, for all three $\Gamma_8$ states, and for all values of $z$. Over the range of $x$ for which a $\Gamma_7$ lies lowest, there is only one transition of the lowest $\Gamma_8$ which could have $h\nu/\beta H = 1.10 \pm 0.01$. This is between the $|\Gamma_8^{(1)} b+\rangle$ and $|\Gamma_8^{(1)} b-\rangle$ at $x = -0.71 \pm 0.01$. Since for $\mathbf{H} \| \langle 100 \rangle$ neither of these states is mixed with the $|\Gamma_7 \pm\rangle$ states, their separation is linear in $H$ and no correction to the measured value of $h\nu/\beta H$ need be made.

Given the appropriate value of $x$ we can use the LLW results to determine the linear splitting of the $|\Gamma_8^{(1)} a\pm\rangle$ states and assign transition $c$. At $x = -0.71$, if $g_J = 1.190$, the linear splitting for $\mathbf{H} \| \langle 100 \rangle$ between the $|\Gamma_8^{(1)} a+\rangle$ and $|\Gamma_8^{(1)} a-\rangle$ states would imply $h\nu/\beta H = 9.91$, which is close to the value found for transition $c$. Since this pair of states is mixed with $|\Gamma_7 \pm\rangle$, we must consider the magnitude of the splitting between them which is cubic in $H$. As is indicated in Eqs. (2) and (3), the cubic splitting has the same magnitude at constant field but opposite sign for the $|\Gamma_7 \pm\rangle$ and $|\Gamma_8 a\pm\rangle$ states when $\mathbf{H} \| \langle 100 \rangle$. Since the resonances are measured at constant frequency, the experimental value for $[\frac{2}{5} A p(100) + B]$ shown in Fig. 5 for transition $a$ must be scaled to the field at resonance for transition $c$. It is found in this way that the correction to $(h\nu/\beta H)_{(c)}$ is only $-0.003$, less than the experimental uncertainty.

The mixing of the ${}^4I_{15/2}$ and ${}^4I_{13/2}$ states by the crystal field can induce $g$ shifts, on the order of 1%, which are different for the $\Gamma_7$ and $\Gamma_8$ states. This would be manifested as requiring different values of $g_J$ for the two states in order that the theoretical wave functions predict the observed resonances. By adjusting $g_J$ to fit transitions $b$ and $c$ to the LLW calculations at the same value of $x$, we could, in principle, find $g_J(\Gamma_8)$ and thus determine the degree of mixing between ${}^4I_{15/2}$ and ${}^4I_{13/2}$. Unfortunately, the $\Gamma_8$ resonance could not be measured with sufficient precision to justify this procedure. Figure 7 summarizes our interpretation of the resonance measurements of center I.

At $x = -0.71$ the LLW wave functions give $|M_{12}|^2 = 14.4$. We thus have theoretical values for all of the matrix elements which determine $A$ and $B$ in Eq. (4). Substituting these, and the value of $\Delta = 6.5 \pm 1$ cm$^{-1}$, we find $A = +(24.2 \pm 6) \times 10^{-9}$ and $B = -(5.6 \pm 1.4) \times 10^{-9}$. The uncertainty is due to the imprecise experimental value of $\Delta$. The calculated values bracket the experimentally determined parameters, which were $+23.4 \times 10^{-9}$ and $-6.8 \times 10^{-9}$, respectively.

We can further demonstrate that our assignments of the $b$ and $c$ transitions are correct by calculating their values for $\mathbf{H} \| \langle 111 \rangle$ and $\mathbf{H} \| \langle 110 \rangle$. The spin Hamiltonian of a $\Gamma_8$ correct to first order in $H$ is[11]

$$\mathcal{H}_S = g_J \beta [a \mathbf{H} \cdot \mathbf{S} + b(H_x S_x^3 + H_y S_y^3 + H_z S_z^3)],$$

where

$$a = (\tfrac{9}{4}) M_{22} - \tfrac{1}{12} M_{33},$$
$$b = -M_{22} + \tfrac{1}{3} M_{33}.$$

For $\mathbf{H} \| (n_1, n_2, n_3)$ the eigenvalues of this spin Hamil-

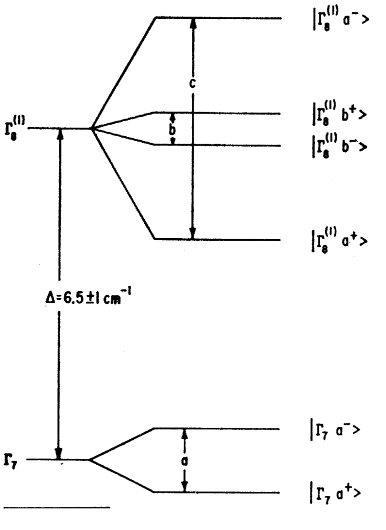

FIG. 7. The Zeeman levels and resonance transitions seen in center I.

---

[11] B. Bleaney, Proc. Phys. Soc. (London) A73, 939 (1959).

tonian are[11,12]

$$E=(g_J\beta H)y, \tag{6}$$

where

$$y^4-(M_{22}{}^2+M_{33}{}^2)y^2+M_{22}{}^2M_{33}{}^2+\tfrac{3}{16}(M_{22}-3M_{33})\times(3M_{22}-M_{33})(M_{22}+M_{33})^2\times(n_1{}^2n_2{}^2+n_1{}^2n_3{}^2+n_2{}^2n_3{}^2)=0.$$

The matrix elements are those previously defined. For $\mathbf{H}\|\langle 111\rangle$, Eq. (6) implies that transition $b$ is given to first order by $h\nu/\beta H=g_J(M_{22}+M_{33})$. Substituting the values previously deduced this becomes $h\nu/\beta H=5.495$. If the $\Gamma_7$ and $\Gamma_8$ wave functions are expressed in terms of a $\langle 111\rangle$ axis of quantization, it can be seen that the magnetic field mixes the lower of the $\Gamma_7$ states, $|\Gamma_7+\rangle$, with the higher of the two states between which transition $b$ occurs and the $|\Gamma_7-\rangle$ state with the lower of these states. Since the mixing decreases $h\nu/\beta H$ for the $\Gamma_7$ resonance from 5.950 to 5.909, $h\nu/\beta H$ for transition $b$ is reduced by $(5.909/5.45)^2(0.041)=0.048$. This predicts a value of 5.447 which agrees well with the observed value of 5.45.

For $\mathbf{H}\|\langle 111\rangle$ transition $c$ is unaffected by the $\Gamma_7$-$\Gamma_8$ mixing and Eq. (6) predicts $h\nu/\beta H=8.30$ while 8.32 was observed. The inclusion of the effect of the Zeeman mixing for an arbitrary orientation of the field is less trivial. Equation (6) predicts that transitions $b$ and $c$ should occur at $h\nu/\beta H=4.48$ and 8.88, respectively, when $\mathbf{H}\|\langle 110\rangle$. These are both close to the experimental values of 4.50 and 8.89 even though no correction for the mixing was made. No other transitions of this $\Gamma_8$ manifold were seen, presumably because the other energy separations are both sensitive to deviations from cubic symmetry and also have a strong quadratic dependence on magnetic field.

We found from the zero-magnetic-field $g$ factor of the $\Gamma_7$ state that $g_J=1.190\pm0.001$ while a pure $^4I_{15/2}$ state has $g_J=1.200$. About half of the difference between these values is due to the strong spin-orbit interaction which admixes other states with $J=15/2$ into the ground state. Wybourne[13] has calculated the free $Er^{3+}$ ion eigenstates and eigenfunctions. He gives for the ground state

$$0.9838|^4I_{15/2}\rangle+0.1783|^2K_{15/2}\rangle+0.0191|^2L_{15/2}\rangle,$$

which implies a Lande factor $g_J=1.194$. The wave function of Carlson and Crosswhite[14] gives $g_J=1.195$. Judd and Lindgren[15] give the wave function for the ground state of atomic Ho which has the same $4f$ configuration as $Er^{3+}$. They calculate $g_J=1.195$, the experimentally observed value for atomic Ho. It thus appears that a further reduction of $g_J$ by about 0.005 occurs when the $Er^{3+}$ ion is imbedded in the ZnSe host.

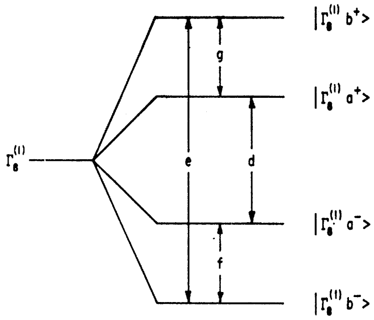

FIG. 8. The Zeeman levels and resonance transitions seen in center II.

The crystal field of the host can admix the $|^4I_{15/2},\Gamma_7\rangle$ and $|^4I_{13/2},\Gamma_7\rangle$ states. However, this produces a shift in $g_J$ which is a quadratic in the crystal-field strength since the Zeeman matrix element between these states, $\langle ^4I_{15/2},\Gamma_7|L_z+2S_z|^4I_{13/2},\Gamma_7\rangle$, can be shown to be zero. If the admixture is called $\alpha$, the corrected zero-magnetic-field $g$ value is

$$\begin{aligned}g_0&=2(1-\alpha^2)(1.195)\langle ^4I_{15/2},\Gamma_7+|J_z|^4I_{15/2},\Gamma_7+\rangle\\&\quad+2\alpha^2(1.108)\langle ^4I_{13/2},\Gamma_7+|J_z|^4I_{13/2},\Gamma_7+\rangle\\&=5.975-0.235\alpha^2.\end{aligned}$$

If this is to equal the experimental value of 5.950, then $\alpha=0.33$. Since the $^4I_{15/2}$ and $^4I_{13/2}$ states are separated by 6500 $cm^{-1}$ an admixture as large as 0.33 requires that the crystal-field matrix element between these states be 2200 $cm^{-1}$, which is unreasonably large. It thus appears that the observed difference between theory and experiment of 0.005 is due either to covalency[16] or orbit-lattice interactions.[17]

The values of $x=-0.71$ and $\Delta=6.5\pm1$ $cm^{-1}$ enable us to deduce from the eigenvalues of LLW that $W=+0.16\pm0.02$ $cm^{-1}$. We further find for center I that $B_4=-(1.9\pm0.3)\times10^{-3}$ $cm^{-1}$, $B_6=(3.3\pm0.5)\times10^{-6}$ $cm^{-1}$, and $B_6/B_4=-1.75\times10^{-3}$.

### B. Resonance of Center II

The four transitions of center II, $d$, $e$, $f$, and $g$ are all between states of one $\Gamma_8$ manifold. Consider first the values of $h\nu/\beta H$ for these transitions when $\mathbf{H}\|\langle 100\rangle$. Transitions $f$ and $g$ occur at nearly the same value of $h\nu/\beta H$ and the sum of the values of $h\nu/\beta H$ for transitions $d$, $f$, and $g$ is 11.52, which is only 0.01 less than $h\nu/\beta H$ for transition $e$. These observations imply that the transitions are as shown in Fig. 8, except for an ambiguity between $f$ and $g$.

As in the case of center I, we can use the $\Gamma_8$ resonance results to determine $g_J$ and $x$ for center II. We find that the entire angular variation of transition $d$ can be fitted to Eq. (6) with an rms deviation of 0.002. This

---

[12] Y. Ayant, E. Bélorizky, and J. Rosset, J. Phys. Radium **23**, 201 (1962).

[13] B. G. Wybourne, J. Chem. Phys. **34**, 279 (1961).

[14] E. H. Carlson and H. M. Crosswhite, Johns Hopkins Spectroscopic Report No. 19 (unpublished).

[15] B. R. Judd and I. Lindgren, Phys. Rev. **122**, 1802 (1961).

[16] W. Low and R. S. Rubins, Phys. Rev. **131**, 2527 (1963).

[17] M. Inoue, Phys. Rev. Letters **11**, 196 (1963).

corresponds to a random error in positioning the magnet of only 0.05°. With the same notation as before, we find $g_J=1.184\pm0.001$, $g_JM_{22}=2.798\pm0.003$, $g_JM_{33}=5.756\pm0.003$, and $x=0.7974\pm0.001$.

To first order in $H$, the Zeeman splitting between the $|\Gamma_8{}^{(1)}a-\rangle$ and $|\Gamma_8{}^{(1)}b-\rangle$ states should equal the splitting between the $|\Gamma_8{}^{(1)}a+\rangle$ and $|\Gamma_8{}^{(1)}b+\rangle$ stares, so that transitions $f$ and $g$ should occur at the same value of $h\nu/\beta H$. Furthermore, Eq. (6) indicates that the value of $h\nu/\beta H$ for transitions $f$ and $g$ when $\mathbf{H}\|\langle100\rangle$ should equal the value of $h\nu/\beta H$ for transition $d$ when $\mathbf{H}\|\langle111\rangle$. The difference between the three observed values could be due to a deviation from cubic symmetry. However, the discrepancies can be adequately explained by considering the shifts of the $|\Gamma_8{}^{(1)}a+\rangle$ states relative to the $|\Gamma_8{}^{(1)}b+\rangle$ states due to the magnetic field mixing of the low-lying excited states $|\Gamma_8{}^{(2)}\rangle$ and $|\Gamma_6\rangle$ with the ground state. Including this effect, we find for the $f$ and $g$ transitions $(\mathbf{H}\|\langle100\rangle)$,

$$\frac{h\nu}{\beta H}=g_J(M_{33}-M_{22})+g_J{}^2\beta H\biggl(\frac{|\langle\Gamma_8{}^{(1)}a+|J_z|\Gamma_8{}^{(2)}a+\rangle|^2}{E(\Gamma_8{}^{(2)})-E(\Gamma_8{}^{(1)})}-\frac{|\langle\Gamma_8{}^{(1)}b+|J_z|\Gamma_8{}^{(2)}b+\rangle|^2}{E(\Gamma_8{}^{(2)})-E(\Gamma_8{}^{(1)})}-\frac{|\langle\Gamma_8{}^{(1)}b+|J_z|\Gamma_6b+\rangle|^2}{E(\Gamma_6)-E(\Gamma_8{}^{(1)})}\biggr).$$

By using the LLW wave functions to calculate these matrix elements and inserting the energy differences determined from the fluorescence measurements, we find for the two values of $h\nu/\beta H$ 2.995 and 2.921. The quadratic dependence of the resonance transitions of $|\Gamma_8{}^{(1)}\rangle$ induced by the Zeeman mixing with the $|\Gamma_8{}^{(2)}\rangle$ and $|\Gamma_6\rangle$ states is smaller than these linear shifts by the order of $h\nu/\Delta\sim1/70$, and thus is much smaller than the experimental uncertainty.

Although the mixing by the crystal field of the ${}^4I_{13/2}$ excited state into the ground state does not effect the $g$ factor of the $\Gamma_7$ states, it does alter the $g$ factors of the $\Gamma_8$ states. We believe that the difference between $g_J=1.190$ for center I and $g_J=1.184$ for center II is due to this mixing. To estimate the degree of crystal-field mixing of the different Stark multiplets, which is required to explain the observed difference between the values of $g_J$ for center I and center II, we again assume that the corrected wave functions for the ground state have the form

$$|\Gamma_8a\pm\rangle=|{}^4I_{15/2},\Gamma_8{}^{(1)}a\pm\rangle+\alpha\bigl[|{}^4I_{13/2},\Gamma_8{}^{(1)}a\pm\rangle+|{}^4I_{13/2},\Gamma_8{}^{(2)}a\pm\rangle\bigr],$$

where $\alpha\ll1$. To first order in $\alpha$ the $g$ shift is given by

$$\begin{aligned}\Delta g={}&4\alpha\langle{}^4I_{15/2},\Gamma_8{}^{(1)},a+|L_z+2S_z|{}^4I_{13/2},\Gamma_8{}^{(1)}a+\rangle\\&+4\alpha\langle{}^4I_{15/2},\Gamma_8{}^{(1)}a+|L_z+2S_z|{}^4I_{13/2},\Gamma_8{}^{(2)}a+\rangle\\={}&-2.4\alpha.\end{aligned}$$

Experimentally $\Delta g\simeq-0.033$, so that $\alpha\sim0.014$. If the matrix element of the crystal field between the ${}^4I_{15/2}$ and ${}^4I_{13/2}$ states is $\langle15/2|V_c|13/2\rangle$, then

$$\alpha\sim\frac{\langle15/2|V_c|13/2\rangle}{E(15/2)-E(13/2)}=\frac{\langle|V_c|\rangle}{6500\text{ cm}^{-1}}\sim0.014.$$

Thus we conclude that the matrix element of the crystal field between the ${}^4I_{15/2}$ and ${}^4I_{13/2}$ states is $\sim90$ cm$^{-1}$, or the same order as the crystal-field splittings of either state.

### C. Fluorescence of Center II

In Fig. 9 we show the transitions of Er$^{3+}$ in ZnSe: Cu, Er which have been identified as occurring in one center. This center will be shown to be the same as the one found in resonance and previously labeled center II. All of these transitions terminate on either the ${}^4I_{15/2}$ or ${}^4I_{13/2}$ crystal-field multiplets. The transitions ${}^4F_{7/2}\rightarrow{}^4I_{15/2}$, ${}^4F_{7/2}\rightarrow{}^4I_{11/2}$, and ${}^4I_{11/2}\rightarrow{}^4I_{15/2}$ have also been seen for other Er$^{3+}$ (noncubic) defects in ZnSe but none of the lines in these groups could be definitely attributed to center II. Consequently the crystal-field splittings of only the ${}^4I_{15/2}$ and ${}^4I_{13/2}$ levels have been derived from the fluorescence spectra, but these data provide a reasonably critical test of the applicability of the LLW and ET calculations. No attempt was made to study the ${}^4I_{13/2}$ to ${}^4I_{15/2}$ transition. If the eigenvalues given by Wybourne[13] are reduced by 3%, they fit the seven levels given in Fig. 9 to an rms deviation of 100 cm$^{-1}$.

In Table II we list the crystal-field splittings of the ${}^4I_{15/2}$ state, as measured relative to the lowest crystal-field level. Transitions to the lowest three states of the ${}^4I_{15/2}$ multiplet from the ${}^4S_{3/2}$ state have widths at 4.2°K of about $\frac{1}{3}$ cm$^{-1}$ (instrumental) while the transi-

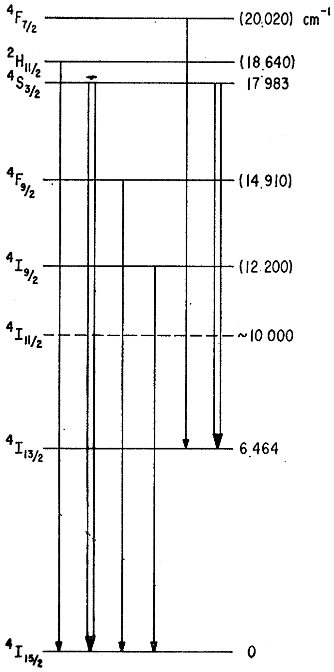

FIG. 9. The fluorescence transitions seen for center II. The strongest transitions are indicated by the double arrows. The energies in parentheses are those of the lowest level of a crystal-field multiplet. The other values are those of the centers of gravity for the crystal multiplets.

tions to the two highest levels have widths of 4.2°K of about 3 $cm^{-1}$. These latter transitions are probably lifetime-broadened by phonon emission from the $\Gamma_7$ and $\Gamma_8{}^{(3)}$ states of $^4I_{15/2}$ and their widths imply lifetimes on the order of $10^{-11}$ sec. Consequently the separations of the lowest three levels could be measured more precisely than the energies of the $\Gamma_7$ and $\Gamma_8{}^{(3)}$ states. We therefore interpolate the separations of the lowest three eigenvalues of LLW to fit the observed separations at a value of $x=0.7976\pm0.001$. The agreement between the values of $x$ determined in resonance and optically is remarkably good, better than the accuracy of either the EPR or optical measurement should imply. With $W=+0.378$ $cm^{-1}$, we calculate the energies shown in Table II. For the $^4I_{15/2}$ state of center II we thus find

$$B_4=+5.02\pm0.03\times10^{-3}\ \mathrm{cm}^{-1},$$
$$B_6=+5.48\pm0.03\times10^{-6}\ \mathrm{cm}^{-1},$$
$$B_6/B_4=1.09\times10^{-3}.$$

The $A_n\langle r^n\rangle$ parameters are given in Table III.

The fit shown in Table II lies just outside the estimated experimental accuracy in predicting the positions of the $\Gamma_7$ and $\Gamma_8{}^{(3)}$ levels. If this discrepancy is not due to an optimistic error limit, it may imply a differential shift of about 1 $cm^{-1}$ in the positions of the two higher states relative to the two lower states induced by crystal field mixing of the $^4I_{15/2}$ and $^4I_{13/2}$ states. These discrepancies between the experimental results and the theoretical values which are based on an electrostatic model may also be due to self-energy shifts caused by the interaction with the zero-point lattice vibrations.

TABLE II. Energies of $^4I_{15/2}$ crystal-field multiplet relative to the ground state ($cm^{-1}$).

| | $\Gamma_8{}^{(1)}$ | $\Gamma_8{}^{(2)}$ | $\Gamma_6$ | $\Gamma_7$ | $\Gamma_8{}^{(3)}$ | Center of gravity |
|---|---|---|---|---|---|---|
| Expt. | 0 | 36.0±0.1 | 43.9±0.1 | 162.3±0.5 | 165.1±0.5 | 76.0 |
| Calc. | 0 | 36.0 | 43.9 | 161.3 | 164.0 | 75.6 |
| | $x=0.7976$ | | | $w=0.378$ $cm^{-1}$ | | |

We have further demonstrated that the identified fluorescence lines and the observed spin resonance are due to the same $Er^{3+}$ defect by measuring optically the Zeeman splittings. The splitting of the lowest level, $\Gamma_8{}^{(1)}$, measured optically is shown in Fig. 10, along with plots of the splitting implied by the resonance results. The Zeeman measurements also confirmed that the state at 36.0 $cm^{-1}$ is a quartet and the state at 43.9 $cm^{-1}$ is a doublet. The transitions to the other two levels are too broad and the separation between them is too small to permit investigation of the Zeeman splittings.

If crystal-field theory is really applicable to ZnSe:Er, the values for the two parameters $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$ used to fit the splittings of the $^4I_{15/2}$ ground state should also apply to the splitting of the $^4I_{13/2}$ state. The splitting of a $J=13/2$ manifold by a cubic field is given by LLW in terms of $W$ and $x$ which are related in a simple way to $B_4$ and $B_6$ as previously discussed. Values of the proportionality factors between these parameters and $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$, the $\beta$ and $\gamma$ multiplicative constants are tabulated for the ground states of all the rare earths but not for the excited states. However, Prather[18] has given values of reduced matrix elements related to these constants. The values of the multiplicative constants for the different spin-orbit states of a given term can be related to each other provided one assumes pure $LS$ coupling.[19] The calculations of the various authors previously referred to indicate that the ground and first excited states of $Er^{3+}$ are more than 98% and 99% pure $^4I_{15/2}$ and $^4I_{13/2}$, respectively, so we should be able to apply these relations. From Elliot, Judd, and

TABLE III. The parameters $A_n\langle r^n\rangle$.

| | Experiment | | Calculated—Point Charges | | |
|---|---|---|---|---|---|
| | Center I | Center II | Subs. site[a] | Inter. site $A$[b] | Inter. site $B$[c] |
| $A_4\langle r^4\rangle$ | $-43\ \pm6$ $cm^{-1}$ | $+113.1\ \pm0.7$ | $-41.5$ | $+96.2$ | $+126$ |
| $A_6\langle r^6\rangle$ | $+1.6\pm0.2$ $cm^{-1}$ | $+2.65\pm0.02$ | $+2.6$ | $-1.5$ | $+1.5$ |

[a] $Er^{3+}$ at a $Zn^{2+}$ site surrounded by four $Se^{2-}$ ions 2.45 Å away (the interatomic separation in ZnSe).

[b] $Er^{3+}$ in the interstice surrounded by four $Zn^{2+}$ ions and six $Se^{2-}$ ions; no lattice relaxation (Zn ions 2.45 Å away, Se ions 2.82 Å away).

[c] Same as b except with a +1 charge on the Zn sites and a relaxation of the $Se^{2-}$ ions to the same $Er^{3+}$-$Se^{2-}$ separation of $a$) (2.45 Å).

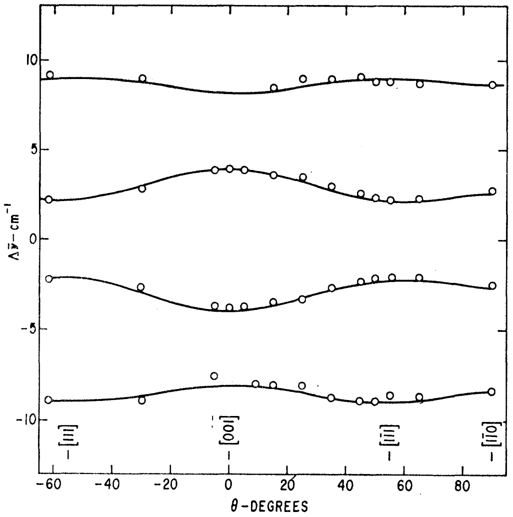

FIG. 10. The Zeeman splitting of the $\Gamma_8{}^{(1)}$ ground state of center II in a {110} plane for a field strength of 31 kOe. The solid lines are the splittings implied by the paramagnetic resonance transitions shown in Fig. 8. The points show the splitting determined optically.

---

[18] J. L. Prather, *Atomic Energy Levels in Crystals*, Natl. Bur. Std. Circ. No. **19** (U. S. Government Publishing and Printing Office, Washington, D. C., 1961).

[19] J. P. Elliott, B. R. Judd, and W. A. Runciman, Proc. Roy. Soc. (London) **A240**, 509 (1957).

Runciman,[19]

$$\rho(\nu)=(-1)^{J-J'}\frac{2J+1}{2J'+1}\left[\frac{(2J-\nu)!(2J'+\nu+1)!}{(2J'-\nu)!(2J+\nu+1)!}\right]^{1/2}\times\frac{W(LJLJ;S\nu)}{W(LJ'LJ';S\nu)},$$

where

$$\rho(4)\equiv\beta(J)/\beta(J'),\quad \rho(6)\equiv\gamma(J)/\gamma(J').$$

The values we require here for the Racah $W$ functions are not given in most tabulations, but may be computed from the simplified relations given by Biedenharn, Blatt, and Rose.[20] It should be pointed out here that the ratio of the Racah functions is not necessarily positive, as implied by LLW, so that the relative signs are not given by the first factor in the expression for $\rho(\nu)$. We find

$$\frac{\beta(^4I_{13/2})}{\beta(^4I_{15/2})}=\frac{B_4(^4I_{13/2})}{B_4(^4I_{15/2})}=+\frac{14}{11}$$

and

$$\frac{\gamma(^4I_{13/2})}{\gamma(^4I_{15/2})}=\frac{B_6(^4I_{13/2})}{B_6(^4I_{15/2})}=+\frac{7}{8}.$$

Thus, using the values of $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$ from the fit of the crystal-field splitting of the $^4I_{15/2}$ state we calculate that $W(^4I_{13/2})=+0.419$ cm$^{-1}$ and $x(^4I_{13/2})=+0.914$. These values are doubtless somewhat in error because of the assumption of pure $LS$ coupling. The eigenvalues obtained by interpolating the LLW results to these values of the parameters are shown in Table IV. The agreement is considered satisfactory in view of the accuracy of the interpolation (about 1%) and the accuracy of the experiment. Since the energy separation of the $^4I_{13/2}$ and $^4I_{11/2}$ states is only about one-half that of the $^4I_{15/2}$ and $^4I_{13/2}$ separation, we expect second-order shifts due to crystal-field mixing of the different terms to be twice as large for the $^4I_{13/2}$ crystal multiplet as for that of $^4I_{15/2}$, which may account for the discrepancies.

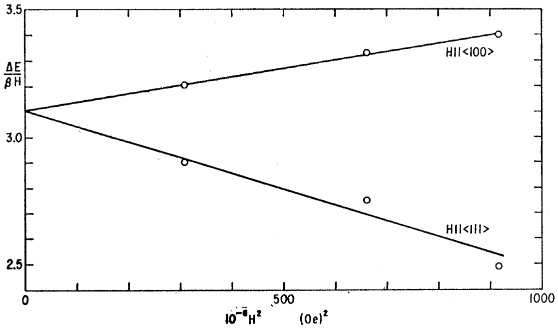

FIG. 11. The Zeeman splitting of $\Gamma_6^{(1)}$ of $^4I_{13/2}$ as a function of the square of the magnetic field.

Zeeman measurements confirmed that the degeneracies of the lowest three states are 2, 4, and 2. Measurements of the $g$ factors of these states are complicated by the smallness of the spacings between the $\Gamma_7$, $\Gamma_8^{(1)}$, and $\Gamma_6^{(1)}$ levels. The transitions studied to obtain the Zeeman splittings were always those from the $\Gamma_8(^4S_{3/2})$ state, so that a transition to a $\Gamma_8$ terminal state could produce up to 16 lines. Even though these lines have widths limited by the spectrometer, in order to clearly resolve the Zeeman patterns, fields of 15 kOe or more were usually required. Consequently, the Zeeman splittings were 20% or more of the crystal-field splittings and the nonlinear effects were significant. This is illustrated in Fig. 11, which shows the nonlinear, anisotropic splitting of the $\Gamma_6^{(1)}$ Kramers doublet.

We find the zero-magnetic-field value $g_0=5.2\pm0.2$ for the $\Gamma_7(^4I_{13/2})$ state. This implies $g_J=1.04\pm0.04$ while a pure $^4I_{13/2}$ state has $g_J=1.108$. For the $\Gamma_6^{(1)}(^4I_{13/2})$ state we find $g_0=3.1\pm0.1$. If we assume the same value of $g_J=1.04$, then for $\Gamma_6^{(1)}$

$$g_0(\Gamma_6^{(1)})=g_J\times(3.0\pm0.2).$$

The results of LLW interpolated to $x=+0.914$ imply

$$g(\Gamma_6^{(1)})=g_J\times3.08.$$

It should be observed that even though the $g$ factors have not been measured particularly precisely, the quoted values define $+0.9\leq x\leq+0.95$.

The $^4S_{3/2}$ level lies 17 983 cm$^{-1}$ above the center of gravity of the $^4I_{15/2}$ levels and its isotropic $g$ factor was measured to be $1.7\pm0.1$, which agrees with the value of 1.68 implied by the wave functions of Wybourne.[13]

The lowest three levels of each crystal multiplet have widths at 2°K which are instrument limited, or about $\frac{1}{3}$ cm$^{-1}$ for both groups. This is therefore an upper limit to the splitting of any of the low-lying $\Gamma_8$ states which might be induced by a deviation from perfect cubic symmetry. The spin resonance transitions $g$ and $f$ given in Table I place a still lower limit on the greatest possible noncubic splitting of the ground state of 0.01 cm$^{-1}$. Our spectroscopy has shown that these $\Gamma_8$ states are split on the order of 10 cm$^{-1}$ in the noncubic ZnSe:Cu, Er defects. We can conclude, therefore, that the deviations from cubic symmetry in center II are no more than $10^{-3}$ of those produced by substituting a different defect at one of the nearest neighbors.

TABLE IV. Energies of the $^4I_{13/2}$ crystal-field multiplet relative to their center of gravity (cm$^{-1}$).

| | $\Gamma_7$ | $\Gamma_8^{(1)}$ | $\Gamma_6^{(1)}$ | $\Gamma_6^{(2)}$ | $\Gamma_8^{(2)}$ |
|---|---|---|---|---|---|
| Expt | $-59.1\pm0.2$ | $-41.4\pm0.2$ | $-25.3\pm0.2$ | $51.3\pm1$ | $57.8\pm1$ |
| Calc | $-61.4$ | $-41.4$ | $-25.4$ | 53.2 | 58.2 |
| | | $x=+0.914$ | | $w=0.491$cm$^{-1}$ | |

---

[20] L. C. Biedenharn, J. M. Blatt, and M. E. Rose, Rev. Mod. Phys. **24**, 249 (1952).

## VI. DISCUSSION—STRUCTURE OF THE CENTERS

We have included in Table III elementary calculations of the parameters $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$ for three different sites. These calculations assume that the crystal-field splitting is purely electrostatic in nature and that the lattice is composed of spherical Zn and Se ions, with charges $+2$ and $-2$, respectively. We assume that these spheres do not overlap the rare-earth $4f$ wave functions, so that the $A_n$ may be calculated from a model consisting only of point charges. Only the first two shells of ions were included in the calculation. The values $\langle r^4\rangle = 1.13$ a.u. and $\langle r^6\rangle = 3.98$ a.u. were taken from the calculations of Freeman and Watson.[21]

For the first model, $Er^{3+}$ at a $Zn^{2+}$ site, we further assume that the four nearest $Se^{2-}$ neighbors remained at the positions they occupy in the perfect crystal. The values calculated for this model are surprisingly close to those observed, considering the extreme simplicity of the model. It would seem that the effects of covalency and screening are not particularly significant for the fourth-order parameter. The sixth-order parameter is more sensitive to lattice distortions and errors in the rare-earth wave functions used by Freeman and Watson, so we should not expect as good agreement as in the case of the fourth-order parameter.

In the second model of Table III the $Er^{3+}$ ion is placed in the interstitial site surrounded by a tetrahedron of four $Zn^{2+}$ ions and 6 $Se^{2-}$ ions. Both the ionic and covalent radii of the constituent atoms imply that there is sufficient space in the interstice for a trivalent rare earth. The sign and magnitude of the calculated fourth-order coefficient are satisfactory, but the sign of the sixth-order coefficient is wrong. The other two cubic sites obviously should also have opposite signs for the two coefficients. Since the fluorescence and resonance results indicate that both coefficients are unquestionably positive and since this simple point-charge model worked so well for center I, we are inclined to believe that the environment of the $Er^{3+}$ ion in center II is not simply the unaltered ZnSe lattice.

The six next-nearest neighbors to an interstitial site in the zinc-blende lattice are only 15% further away than the four nearest neighbors. If the positive charge of the rare earth attracts the negative next-nearest neighbors inward and repels the nearest neighbors outward sufficiently, the octahedral potential will dominate and both $A_n\langle r^n\rangle$ coefficients will be positive. Furthermore, if the rare earth were in an interstitial site there would be a local charge imbalance of $+3$ which the lattice would likely locally compensate through the association of other native defects or impurities. We have observed that when Cu is removed from our samples, both the fluorescence and resonance of center II disappear and the resonance of center I appears. Center II reappears when Cu is reintroduced and center I disappears. It may be that Cu is intimately involved in the structure of center II and provides the needed local charge compensation. So that the associated Cu would have no unpaired spins to alter the resonance spectra or low-lying optical transitions, we assume that it has the closed shell configuration $3d^{10}$ of $Cu^{1+}$. Since we have demonstrated that the symmetry seen by the rare earth is cubic to a high precision, we must surround the rare earth with a tetrahedron of 4, an octahedron of 6, a cube of 8, or a greater number of copper ions to preserve this symmetry. If we replace the four $Zn^{2+}$ ions nearest the interstitial site with four $Cu^{1+}$ ions, we form a complex which has a net effective charge of only $-1$. Furthermore, this weakens the negative contribution of the nearest neighbors to $A_6$. A point-charge model in which all six $Se^{2-}$ ions and four $Cu^{1+}$ ions are equidistant from the $Er^{3+}$ ion gives $A_n\langle r^n\rangle$ coefficients, in good agreement with experiment, as is shown in Table III. The agreement is made still better for both coefficients if we further permit a radially outward relaxation of the Cu ions. This is the simplest model of center II we have found, which is both consistent with our qualitative observations and also gives good quantitative agreement with the crystal-field parameters.

As a test of the proposed model the Cu was removed from one of our samples and Ag diffused into the sample. A new cubic defect was found which has $x = +0.67$. This definitely establishes the sensitivity of the crystal field to the compensating impurity and thus the proximity of the rare earth and noble metal.

It is interesting that we find the correct magnitude for the $A_n$ coefficients when we assume a strictly ionic model of the lattice with charges of $\pm 2$. The II-VI compounds are generally assumed to be partially covalently bonded with effective charges of between $\frac{1}{2}$ and 1.

## VII. SUMMARY

We believe that the results of our microwave and optical spectroscopy clearly demonstrate that $Er^{3+}$ can reside at two distinct cubic sites in ZnSe:Cu, Er. Furthermore, it has been shown that the results of Lea, Leask, and Wolf give an excellent first-order approximation to the eigenfunctions, eigenvalues, and $g$ factors of the 10 lowest crystal states of one of these centers. The mixing of nearby states by a magnetic field and the consequent nonlinear Zeeman splittings can be satisfactorily accounted for with the given eigenfunctions. The discrepancies between the calculated crystal-field splittings and the observed values, which are not much greater than the experimental accuracy in most cases, are on the order of magnitude for the shifts one would expect due to crystal-field mixing of free-ion states having different values of $J$.

The results of the spectroscopy of center II require that the $Er^{3+}$ ion be in a crystal field which is dominated by an octahedron of negative charges. An interstitial site has an octahedron of $Se^{2-}$ ions as next-nearest

---

[21] A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

neighbors but the tetrahedron of nearest $Zn^{2+}$ ions makes $A_6$ negative. Furthermore, this defect has an uncompensated charge of $+3$. We mitigate both of these deficiencies by replacing the four nearest $Zn^{2+}$ ions by four $Cu^{1+}$ ions. The latter substitution is suggested by the correlation of the presence of center II, as detected both in resonance and fluorescence, with the presence of Cu in our samples.

The resonances of center I are those expected for $Er^{3+}$ at a $Zn^{2+}$ site. The strong fluorescence of center II and the absence of fluorescence from center I is consistent with the existence of a short-range energy transfer from Cu to $Er^{3+}$ in ZnSe which we previously reported. Presumably, we could excite detectable fluorescence from center I if it were present in a concentration which provided sufficient optical absorption directly in the rare-earth lines.

Although we believe that we have presented strong evidence for the two specific models discussed, we also believe that a more detailed study of the rare-earth environment, such as electron-nuclear double resonance, would prove profitable.

## ACKNOWLEDGMENTS

We are particularly grateful to F. S. Ham for helpful discussions, for developing the spin Hamiltonian of Eq. (7), and for his critical reading of the manuscript. We thank E. B. Tucker and T. W. Moore for the resonance measurements at 9.3 and 35 GHz, and W. W. Piper and L. C. Kravitz for graciously providing the use of their 14.1-GHz spectrometer. Finally, we thank E. L. Kreiger, C. R. Trzaskos, W. Garwacki, and F. C. Mostek for their computational and technical assistance.

---

PHYSICAL REVIEW VOLUME 155, NUMBER 2 10 MARCH 1967

# Effect of Applied Electric Fields on the Ground State of $3d^3$, $3d^5$, and $3d^8$ Ions in $\alpha$-$Al_2O_3$

J. J. Krebs
*Naval Research Laboratory, Washington, D. C.*

(Received 20 October 1966)

The effect of applied electric fields on the ground states of $3d^3$, $3d^5$, and $3d^8$ ions in $\alpha$-$Al_2O_3$ has been studied. With the applied field $\mathbf{E}$ along the $c$ axis, the results can be explained by allowing the spin-Hamiltonian parameter $D$ (and $a-F$ for $Fe^{3+}$) to be a linear function of $E$. For an applied field of $10^6$ V/cm, the relative change in $D$ is of the order of 5% for a typical ion of these series. It seems likely, therefore, that the odd crystal-field components may make a significant contribution to $D$ for a number of these ions. A naive crystal-field model is unable to explain the variation in $\partial D/\partial E$ observed for the $3d^3$ and $3d^8$ ions, but these variations appear well correlated with the corresponding $g-g_{\text{free}}$ values. The correlation between the microwave and previously observed optical electric field effects is found to be quite poor, thus illustrating the complex nature of the ground-state effects.

## INTRODUCTION

The application of external electric fields offers a method of manipulating the energy levels of paramagnetic ions which are located in sites lacking inversion symmetry.[1] Early studies dealing with the ground state energy levels have centered on transition-metal impurities in silicon[2] and on $Cr^{3+}$ in $\alpha$-$Al_2O_3$ (ruby).[3,4] In this paper, the effect of applied electric fields on the ground state of ions of the $3d^3$ and $3d^8$ isoelectronic series in $\alpha$-$Al_2O_3$ is reported. In addition, new results are reported which considerably modify the previous interpretation[5] of such electric field effects (EFE) for the $3d^5$ ion $Fe^{3+}$ in $\alpha$-$Al_2O_3$. The work described is a logical extension of the earlier and more detailed studies of the EFE in ruby. With that work in mind, the $3d^3$ ions $V^{2+}$ and $Mn^{4+}$ and the $3d^8$ ions $Ni^{2+}$ and $Cu^{3+}$ were examined for an EFE and the results are found to be interpretable in terms of changes in the zero-field splitting parameter $D$ alone. There was no detectable change in the $g$ value or hyperfine constants of the ions in those cases where such changes could be separately examined.[6]

Considerable similarity exists between these two sets of isoelectronic ions as far as their optical and electron-paramagnetic-resonance (EPR) descriptions are concerned.[7] Although there is a difference in the spin

---

[1] N. Bloembergen, Science **133**, 1363 (1961).

[2] G. W. Ludwig and H. H. Woodbury, Phys. Rev. Letters **7**, 240 (1961); F. S. Ham, *ibid.* **7**, 242 (1961).

[3] J. O. Artman and J. C. Murphy, (a) Bull. Am. Phys. Soc. **7**, 14 (1962); (b) in *Proceedings of the First International Conference on Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963), p. 634; (c) J. Chem. Phys. **38**, 1544 (1963); (d) Phys. Rev. **135**, A1622 (1964).

[4] E. B. Royce and N. Bloembergen, Phys. Rev. **131**, 1912 (1963).

[5] J. J. Krebs, Phys. Rev. **135**, A396 (1964).

[6] Brief reports of this work has been given previously: J. J. Krebs, Bull. Am. Phys. Soc. **10**, 330 (1965); **11**, 203 (1966).

[7] See, e.g., H. Kamimura, Phys. Rev. **128**, 1077 (1962).