

where  $V_{ef}$  is an orthorhombic crystalline electric field potential,<sup>20</sup>  $\lambda$  is the spin-orbit coupling constant, and  $\mathbf{L}$  and  $\mathbf{S}$  are the orbital and spin angular momentum operators, respectively. Setting  $|1, \frac{1}{2}\rangle = (\pi_x + i\pi_y)\alpha$ ,  $|-1, -\frac{1}{2}\rangle = (\pi_x - i\pi_y)\beta$ , etc., where  $\alpha$  and  $\beta$  are spin functions, we rewrite Eq. (A1) in its matrix form:

$$\langle M_L, M_S | \mathcal{H}' | M_L', M_S' \rangle = \begin{bmatrix} \frac{1}{2}\lambda & \Delta & 0 & 0 \\ \Delta & -\frac{1}{2}\lambda & 0 & 0 \\ 0 & 0 & -\frac{1}{2}\lambda & \Delta \\ 0 & 0 & \Delta & \frac{1}{2}\lambda \end{bmatrix}, \quad (\text{A2})$$

where  $\Delta = \langle \pm 1, \pm \frac{1}{2} | V_{ef} | \mp 1, \pm \frac{1}{2} \rangle$  and where the constant diagonal element  $\langle \pm 1, \pm \frac{1}{2} | V_{ef} | \pm 1, \pm \frac{1}{2} \rangle$  has been omitted. The eigenvalues to this matrix are given by Eq. (4), and the four unnormalized eigenfunctions are given by

$$\begin{aligned} \psi_{1,2} &= |1, \pm \frac{1}{2}\rangle \mp \{ \lambda/2\Delta \mp [1 + (\lambda/2\Delta)^2]^{\frac{1}{2}} \} |-1, \pm \frac{1}{2}\rangle, \\ \psi_{3,4} &= |1, \pm \frac{1}{2}\rangle \mp \{ \lambda/2\Delta \pm [1 + (\lambda/2\Delta)^2]^{\frac{1}{2}} \} |-1, \pm \frac{1}{2}\rangle. \end{aligned} \quad (\text{A3})$$

The two extreme cases for these eigenfunctions, see Fig. 6, are obtained by permitting the ratio  $\lambda/2\Delta$  to either vanish or become very large.

Spectroscopic splitting factor values for cases corresponding to intermediate values of the ratio  $\lambda/2\Delta$  can be obtained by using slightly modified forms of expressions developed by Känzig and Cohen<sup>21</sup> for the  $\text{O}_2^-$  problem. For example, the axial component of the  $g$  value is given by

$$g_{zz} = g_e - 2 \left[ \frac{(\lambda/2)^2}{\Delta^2 + (\lambda/2)^2} \right]^{\frac{1}{2}} L, \quad (\text{A4})$$

where  $L$  is a factor close to unity (see reference 21). For the case of NO located at a negative-ion site in  $\text{KN}_3$ , the parameter  $\Delta$  would not be expected to be very large as compared to the spin-orbit coupling constant. Consequently, the  $g$  values would be expected to exhibit pronounced departures from the free-electron value. For example, using Eq. (A4) we find that departures of the order of 10% or so would result in the value of  $g_{zz}$  for a  $\lambda/2\Delta$  ratio of one tenth.

## Electron Spin Resonance of $\text{Gd}^{3+}$ and $\text{Eu}^{2+}$ in Single Crystals of CaO

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Single crystals of CaO doped with  $\text{Eu}^{2+}$  and  $\text{Gd}^{3+}$  have been investigated by paramagnetic resonance at X band. Measurements were made at 290, 77, and 4.2°K. The spectra of  $\text{Eu}^{2+}$  and  $\text{Gd}^{3+}$  can be described by a cubic spin Hamiltonian. The constants for the spectrum of  $\text{Gd}^{3+}$  at 290°K are  $g = 1.9913 \pm 0.0005$ ,  $b_4 = (+11.6 \pm 0.1) \times 10^{-4} \text{ cm}^{-1}$ ,  $b_6 = (-1.15 \pm 0.1) \times 10^{-4} \text{ cm}^{-1}$ . The over-all splitting of the ground state is  $(380 \pm 4) \times 10^{-4} \text{ cm}^{-1}$ . The constants for the spectrum of  $\text{Eu}^{2+}$  at 290°K are  $g = 1.9914 \pm 0.001$ ,  $b_4 = (+24.0 \pm 0.5) \times 10^{-4} \text{ cm}^{-1}$ ,  $b_6 = (-1.6 \pm 0.5) \times 10^{-4} \text{ cm}^{-1}$ ,  $|A^{151}| = (29.6 \pm 0.1) \times 10^{-4} \text{ cm}^{-1}$ , and  $|A^{153}| = (13.05 \pm 0.2) \times 10^{-4} \text{ cm}^{-1}$ . The over-all splitting of the ground state is  $(781 \pm 20) \times 10^{-4} \text{ cm}^{-1}$ . The splitting parameters are found to vary only slightly between 290 and 4.2°K.

### INTRODUCTION

PARTIAL removal of the eightfold spin degeneracy of  $4f^7$ ,  $^8S_{7/2}$  ions by cubic crystalline fields has been a subject of considerable interest in recent years. Low and Rosenburger<sup>1</sup> suggest that the splitting mechanism may be linear in the crystal field potential. An extrapolation of their data indicates that a splitting of about  $0.2 \text{ cm}^{-1}$  would be expected for  $\text{Gd}^{3+}$  and  $\text{Eu}^{2+}$  in CaO. A study of  $\text{Gd}^{3+}$ - and  $\text{Eu}^{2+}$ -doped CaO was undertaken to determine whether their suggested mechanism is operative in CaO. The crystal structure of CaO is face-centered cubic with lattice parameter  $a = 4.797 \text{ \AA}$ .

<sup>1</sup> W. Low and U. Rosenburger, Phys. Rev. **116**, 621 (1959).

### EXPERIMENTAL PROCEDURE

Paramagnetic resonance data were obtained using a Varian V-4500 spectrometer. Spectra were taken at room temperature, 77 and 4.2°K. Samples were placed on the side wall of a TE<sub>102</sub> rectangular cavity resonating at approximately 9.5 kMc/sec. A 12-in. rotating base magnet permitted the study of the angular variation of the spectra. The CaO crystals were obtained from Semi-Elements Inc. Impurities were introduced into the crystals with a concentration of approximately 0.05% by weight. Samples were cleaved into pieces approximately  $1 \times 4 \times 4 \text{ mm}$ . The orientation of the crystallographic axes was checked by means of x rays.

TABLE I. Constants for the spectrum of  $Eu^{2+}$  in CaO.

Temp. (°K)	$g$	$ A^{151} $ ( $10^{-4}$ cm $^{-1}$ )	$ A^{153} $ ( $10^{-4}$ cm $^{-1}$ )	$b_4$ ( $10^{-4}$ cm $^{-1}$ )	$b_6$ ( $10^{-4}$ cm $^{-1}$ )	$(32b_4-8b_6)^a$ ( $10^{-4}$ cm $^{-1}$ )
290	$1.9914 \pm 0.001$	$29.63 \pm 0.1$	$13.05 \pm 0.2$	$+24.0 \pm 0.5$	$-1.6 \pm 0.5$	$781 \pm 20$
77	$1.9917 \pm 0.001$	$30.09 \pm 0.1$	$13.42 \pm 0.1$	$+25.1 \pm 0.1$	$-2.1 \pm 0.5$	$820 \pm 20$
4.2	$1.9918 \pm 0.001$	$30.16 \pm 0.1$	$13.46 \pm 0.1$	$+25.7 \pm 0.5$	$-1.5 \pm 0.5$	$834 \pm 20$

<sup>a</sup> Over-all splitting of the ground state.

## EXPERIMENTAL RESULTS

Europium,  $Eu^{2+}$ 

The observed spectrum of  $Eu^{2+}$  has cubic symmetry and one ion in the unit cell. The angular variation of the spectrum can be described by the spin Hamiltonian in the notation of Baker *et al.*<sup>2</sup>:

$$H = g\beta\mathbf{H} \cdot \mathbf{S} + B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4) + AS \cdot \mathbf{I}, \quad (1)$$

where  $60B_4 = b_4$  and  $1260B_6 = b_6$  are the experimentally determined parameters. The spectrum of  $Eu^{2+}$  is complicated by the fact that each of the seven fine-structure lines shows hyperfine interactions with the two europium isotopes 151 and 153, each of which has a nuclear spin of 5/2. At room temperature the hyperfine structure of the  $1/2 \leftrightarrow -1/2$  transition is not completely resolved, but when the temperature of the crystal is lowered to 77°K, the structure is easily resolved. The hyperfine structure on the other fine-structure lines could not be resolved due to broadening and overlap. This prevented the determination of the sign of  $A$ . The signs of  $b_4$  and  $b_6$  were determined from measurements of the relative intensities of the fine-structure transitions at 4.2°K. The measured parameters are listed in Table I. With the field directed away from the principal axes, forbidden transitions of the hyperfine structure corresponding to  $\Delta m = \pm 1$  are observed. Such lines have also been observed for  $Eu^{2+}$  in  $CaF_2$ ,<sup>2,3</sup> but they were erroneously attributed to simultaneous transitions of the electronic spin of  $Eu^{2+}$  and the nuclear spin of an adjacent fluorine nucleus. In a recent paper by Bleaney and Rubins,<sup>4</sup> it was pointed out that these forbidden transitions would arise from splitting operators of any degree provided

that the magnetic field is not directed along an axis of twofold or higher symmetry.

Gadolinium,  $Gd^{3+}$ 

The spectrum of gadolinium observed shows cubic symmetry and one ion per unit cell. The angular variation of the spectrum can be described by the cubic spin Hamiltonian of Eq. (1). The width of the  $Gd^{3+}$  lines was of the order of 12 G and prevented the observation of hyperfine interaction with isotopes 155 and 157. The signs of  $b_4$  and  $b_6$  were determined from measurements of the relative intensities of the fine-structure transitions at 4.2°K. The measured parameters are listed in Table II.

## DISCUSSION OF RESULTS

A calculation for the ratio of cubic potentials at the Ca site in CaO and  $CaF_2$  based on a simple point-charge model leads to the expression

$$V(\text{CaO})/V(\text{CaF}_2) = (18/8)d_{\text{Ca-F}}^5/d_{\text{Ca-O}}^5. \quad (2)$$

This yields the result that the crystal field in CaO would be expected to be approximately twice that of  $CaF_2$ . A surprising result of this study is that the cubic field splitting of  $Gd^{3+}$  and  $Eu^{2+}$  is considerably smaller in CaO than that found in  $CaF_2$  (Table III). A second point of interest is the exceptional degree of covalent bonding exhibited by the  $Eu^{2+}$ . The sharp decrease in  $A$  for  $Eu^{2+}$  in going from  $CaF_2$  to CaO reflects an increase in covalent bonding. One would expect a reduction in hyperfine coupling as the ligand is changed from  $F^-$  to  $O^{2-}$ , but the value of the hyperfine coupling for  $Eu^{151}$  in CaO ( $29.6 \times 10^{-4}$  cm $^{-1}$ ) is even less than the value reported by Bleaney and Low<sup>5</sup> for SrS ( $30.8 \times 10^{-4}$  cm $^{-1}$ )

TABLE II. Constants for the spectrum of  $Gd^{3+}$  in CaO.

Temp. (°K)	$g$	$b_4$ ( $10^{-4}$ cm $^{-1}$ )	$b_6$ ( $10^{-4}$ cm $^{-1}$ )	$(32b_4-8b_6)^a$ ( $10^{-4}$ cm $^{-1}$ )
290	$1.9913 \pm 0.0005$	$+11.6 \pm 0.1$	$-1.15 \pm 0.1$	$380 \pm 4$
77	$1.9908 \pm 0.0005$	$+12.1 \pm 0.1$	$-1.16 \pm 0.1$	$395 \pm 4$
4.2	$1.9925 \pm 0.001$	$+12.2 \pm 0.1$	$-1.19 \pm 0.1$	$400 \pm 4$

<sup>a</sup> Over-all splitting of the ground state.<sup>2</sup> J. M. Baker, B. Bleaney, and W. Hayes, Proc. Roy. Soc. (London) **A247**, 141 (1958).<sup>3</sup> M. Dvir and W. Low, Proc. Phys. Soc. (London) **A75**, 136 (1959).<sup>4</sup> B. Bleaney and R. S. Rubins, Proc. Phys. Soc. (London) **77**, 103 (1961).<sup>5</sup> B. Bleaney and W. Low, Proc. Phys. Soc. (London) **68A**, 55 (1955).

TABLE III. Ground state splitting at 290°K of Eu<sup>2+</sup> and Gd<sup>3+</sup> in various crystals.

Crystal	Anion-cation distance in Å	<i>g</i>	<i>A</i> (10 <sup>-4</sup> cm <sup>-1</sup> )	(32 <i>b</i> <sub>4</sub> -8 <i>b</i> <sub>6</sub> ) <sup>a</sup> (10 <sup>-4</sup> cm <sup>-1</sup> )	Reference
Eu <sup>2+</sup> :CaF <sub>2</sub>	2.36	1.9927±0.001	151 34.07 153 15.1	1784±9	b
SrCl <sub>2</sub>	3.03	1.995 ±0.001	151 34.1 153 15.5	416±30	c
CaO	2.40	1.9914±0.001	151 29.6 153 13.05	781±20	This paper
Gd <sup>3+</sup> :CaF <sub>2</sub>		1.991 ±0.002		1491	d
ThO <sub>2</sub>	2.42	1.9913±0.0005		1755±3	e
SrCl <sub>2</sub>		1.9906±0.001		317±2	c
CaO		1.9913±0.0005		380±4	This paper

<sup>a</sup> Over-all splitting of the ground state.<sup>b</sup> See reference 2.<sup>c</sup> See reference 1.<sup>d</sup> See reference 7.<sup>e</sup> See reference 6.

where one would expect a fair degree of covalency to the bond. The strong covalency exhibited in CaO is difficult to explain since this does not appear to be the case for Gd<sup>3+</sup> in ThO<sub>2</sub><sup>6</sup> where the ligand is the same and the interionic distance is similar. At first glance one would assume that the reduction in crystal-field splitting could arise from covalency effects, but covalency has always implied increased cubic field effects contrary to what is observed. Deviations from the normal CaO parameters could give rise to this smaller than expected splitting, but x-ray measurements showed no detectable change. This still would not detect changes in the local parameters about the impurity ion for the small concentrations present in the crystals. An additional point that can be raised is that the Eu<sup>2+</sup> and Gd<sup>3+</sup> ions are in the interstitial sites where the symmetry is tetrahedral. This argument does not seem realistic since the EuO structure is isomorphous with CaO; and, therefore the Eu<sup>2+</sup> would be expected to be found in the octahedral sites rather than the smaller tetrahedral sites. From size considerations it appears that the Gd<sup>3+</sup> would prefer the same octahedral sites.

The temperature dependence of the splitting is found to be small, increasing slightly as the temperature of the crystal is lowered from 290 to 4.2°K. This small change with temperature has been construed as indicating a linear dependence on the crystal field. The sign of the cubic-field splitting for Eu<sup>2+</sup> and Gd<sup>3+</sup> in CaO is found to be positive just as that reported by Low<sup>6,7</sup> for Gd<sup>3+</sup> in ThO<sub>2</sub> and CaF<sub>2</sub>. If the cubic-field splitting is linear in terms of the crystal potential (as suggested by Low), the change in sign of the cubic potential which results in passing from eightfold cubic coordination in CaF<sub>2</sub> to sixfold cubic coordination in CaO is not re-

flected in the sign of the cubic-field splitting parameters. The splitting of the ground state of the 4*f*<sup>7</sup>, <sup>8</sup>S<sub>7/2</sub> configuration by cubic fields must, therefore, be due to a mechanism more complex than a simple linear dependence on the crystal potential.

*Note added in proof.* The signs of the cubic field splitting parameters for Eu<sup>2+</sup> and Gd<sup>3+</sup> in CaO which are listed above are in error and should be reversed to read -*b*<sub>4</sub> and +*b*<sub>6</sub>. Initially, the signs of the parameters were determined using Eq. (19.4) of Low.<sup>8</sup> These equations yield the erroneous result that the low field transition would be the *M* = -7/2 ↔ -5/2 for a positive value of *b*<sub>4</sub>. Unfortunately this result was checked against an erroneously labeled Fig. 2 of reference 7 which gave a result consistent with the above equations and also the positive value reported for *b*<sub>4</sub> in that paper. This consistency masked the error.

The negative value determined for *b*<sub>4</sub> in sixfold coordinated CaO as opposed to the positive value reported in eightfold coordinated CaF<sub>2</sub> does lend evidence that there is a linear dependence of the ground state splitting for <sup>8</sup>S state ions by cubic fields. There is a problem of explaining the unusually low ground state splittings found in CaO as compared to CaF<sub>2</sub>; for this does not appear to follow a simple linear dependence based on a simple point-charge model.

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<sup>7</sup> W. Low, Phys. Rev. **109**, 265 (1958).

<sup>8</sup> W. Low, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Suppl. 2: Paramagnetic Resonance in Solids, p. 115.

<sup>6</sup> W. Low and D. Shaltiel, J. Phys. Chem. Solids **6**, 315 (1958).