

## Electron Paramagnetic Resonance of $\text{Eu}^{2+}$ in $\text{CaWO}_4$ †

J. BRONSTEIN AND V. VOLTERRA

*Department of Physics, The Hebrew University, Jerusalem, Israel*

(Received 14 September 1964)

Single crystals of  $\text{CaWO}_4$  doped with  $\text{Eu}^{2+}$  were investigated by electron paramagnetic resonance at 300, 77, 20, and 4°K. A spectrum of tetragonal symmetry was observed and fitted to the spin Hamiltonian for tetragonal symmetry. The values of the parameters are given for 300, 77, and 20°K. The absolute sign of the parameters was determined from observations at 4°K. The hyperfine splitting constants are  $A^{151} = -34.4 \pm 0.5$ ,  $B^{151} = -35.0 \pm 0.5$ ;  $A^{153} = -15.5 \pm 0.3$ ,  $B^{153} = -16.0 \pm 0.3$ ; all in  $10^{-4} \text{ cm}^{-1}$ .

### I. INTRODUCTION

MUCH experimental work has accumulated during the past few years on EPR of paramagnetic impurities in  $\text{CaWO}_4$ . Hempstead and Bowers<sup>1</sup> have published their work on two  $S$ -state ions, namely,  $\text{Mn}^{2+}$  and  $\text{Gd}^{3+}$ . We report here the results of an EPR investigation of  $\text{CaWO}_4:\text{Eu}^{2+}$ .

The ground state of  $\text{Eu}^{2+}$ , as that of the isoelectronic  $\text{Gd}^{3+}$  is  $(4f^7)^8S_{7/2}$ . In a crystalline field the ground-state degeneracy is removed owing to admixture with higher states.<sup>2,3</sup> In the tetragonal field of  $\text{CaWO}_4$ , the  $J = \frac{7}{2}$  state splits into four Kramers' doublets.

The tetragonal spectrum of rare-earth ions in  $\text{CaWO}_4$  is due to  $\text{Ca}^{2+}$  substitution. There are four  $\text{Ca}^{2+}$  ions in a unit cell with local symmetry  $S_4$ . There are two non-equivalent sites related by reflection in the (001) plane, which are thus magnetically equivalent. Therefore, only one tetragonal spectrum is expected.

The  $\text{Ca}^{2+}$  ion is surrounded by eight  $\text{O}^{2-}$  ions,<sup>4</sup> forming two distorted tetrahedra. The position of these oxygen ions has been recently determined by M. I. Kay *et al.*<sup>5</sup> and by A. Zalkin and D. H. Templeton.<sup>6</sup>

and

$$\begin{aligned} E_2^0 &= -\frac{1}{2}B_2^0, & E_4^2 &= \frac{5}{2}B_4^0 - \frac{1}{2}B_4^4, & E_6^2 &= -(105/32)B_6^0 - (5/32)B_6^4, \\ E_2^2 &= -\frac{3}{2}B_2^0, & E_4^4 &= (35/8)B_4^0 + (1/8)B_4^4, & E_6^4 &= -(63/16)B_6^0 + (13/16)B_6^4, \\ E_4^0 &= \frac{3}{8}B_4^0 + \frac{1}{8}B_4^4, & E_6^0 &= -(5/16)B_6^0 - (1/16)B_6^4, & E_6^6 &= -(231/32)B_6^0 - (11/32)B_6^4; \end{aligned} \quad (4)$$

the  $Y_n^m(x,y,z)$  used here are normalized so that all coefficients are integers with no common divisor.

The matrix elements of the  $O_n^m$  operators, which have not all been tabulated, may be calculated according to the Wigner-Eckhart theorem<sup>7</sup> using the formula

$$\langle \frac{7}{2}m | O_k^q | \frac{7}{2}m' \rangle = -\langle \frac{7}{2} || k || \frac{7}{2} \rangle (-1)^{7/2+k+m} \begin{pmatrix} k & \frac{7}{2} & \frac{7}{2} \\ q & m' & -m \end{pmatrix} (C_k^q)^{-1}. \quad (5)$$

Here  $C_k^q$  are normalization coefficients by which our  $Y_k^q$  have to be multiplied in order to be normalized in the

† The research reported in this document has been sponsored in part by the U. S. Air Force Office of Scientific Research, OAR, through the European Office of Aerospace Research, Grant No. AF EOAR 63-64.

<sup>1</sup> C. F. Hempstead and K. D. Bowers, *Phys. Rev.* **118**, 131 (1960).

<sup>2</sup> R. Lacroix, *Helv. Phys. Acta.* **30**, 374 (1957).

<sup>3</sup> J. H. Van Vleck and W. G. Penney, *Phil. Mag.* **17**, 961 (1934).

<sup>4</sup> R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers Inc., New York, 1957), Vol. II, Chap. 8, p. 6.

<sup>5</sup> M. I. Kay, B. C. Frazer and I. Almodovar, *J. Chem. Phys.* **40**, 504 (1964).

<sup>6</sup> A. Zalkin and D. Templeton, *J. Chem. Phys.* **40**, 501 (1964).

<sup>7</sup> U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic Press Inc., New York, 1959).

### II. THEORY

The general spin Hamiltonian for a  $^8S_{7/2}$  ion in a tetragonal field is

$$\begin{aligned} \mathcal{H} = & \beta g_{11} S_z H_z + \beta g_1 (S_x H_x + S_y H_y) \\ & + B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4 \\ & + A S_z I_z + B (S_x I_x + S_y I_y), \quad (1) \end{aligned}$$

where the  $O_n^m$  are operators which transform, as the spherical harmonics  $Y_n^m$ ;  $B_n^m$  are coefficients dependent upon the crystal field which is to be determined by experiment;  $S$  is an angular-momentum operator with  $S = \frac{7}{2}$ ; and  $I$  is the nuclear spin operator.  $\text{Eu}^{2+}$  has two isotopes of nearly equal abundance, both having  $I = \frac{5}{2}$ . Therefore, there are seven allowed electronic transitions ( $\Delta M = \pm 1$ ), and each one splits into twelve allowed hyperfine lines ( $\Delta m = 0$ ).

Taking the  $x$  axis as the quantization axis, the contribution to the Hamiltonian due to the crystal field has the form

$$\begin{aligned} E_2^0 O_2^0 + E_2^2 O_2^2 + E_4^0 O_4^0 + E_4^2 O_4^2 + E_4^4 O_4^4 \\ + E_6^0 O_6^0 + E_6^2 O_6^2 + E_6^4 O_6^4 + E_6^6 O_6^6, \quad (2) \end{aligned}$$

where the  $O_n^m$  are defined by

$$O_n^m(x,y,z) = O_n^m(z,x,y), \quad (3)$$

standard fashion,<sup>8</sup> and

$$\langle \frac{7}{2} \| 2 \| \frac{7}{2} \rangle = (15/2)(42/\pi)^{1/2}, \quad \langle \frac{7}{2} \| 4 \| \frac{7}{2} \rangle = 135(77/2\pi)^{1/2}, \quad \langle \frac{7}{2} \| 6 \| \frac{7}{2} \rangle = (4095/2)(33/2\pi)^{1/2}. \quad (6)$$

Taking the direction of the external magnetic field as axis of quantization, the off-diagonal matrix elements, at the 3-cm resonance, are much smaller than the diagonal ones. In this case second-order perturbation theory is sufficient in order to fit the results within experimental accuracy.

The resonance conditions in the  $z$  and  $x$  directions are given by the following expressions:

$$\begin{aligned} H_0 = H_{\pm 7/2} \pm 2(a-b) &+ \frac{P^2}{2[H_{\pm 7/2} \pm (a-c)]} - \frac{Q^2}{2[H_{\pm 7/2} \pm (b-d)]} - \frac{E^2}{2[2H_{\pm 7/2} \pm (a-d)]} \\ &- \frac{F^2}{2[2H_{\pm 7/2} \pm (b-c)]} + \frac{S^2}{2[3H_{\pm 7/2} \pm (a-b)]} - \frac{S^2}{2[3H_{\pm 7/2} \pm (b-a)]} + \text{hyperfine interaction correction (h.f.c.)}, \\ H_0 = H_{\pm 5/2} \pm 2(b-c) &+ \frac{P^2}{2[H_{\pm 5/2} \pm (a-c)]} + \frac{Q^2}{2[H_{\pm 5/2} \pm (b-d)]} + \frac{R^2}{2[H_{\pm 5/2} \pm (c-d)]} \\ &+ \frac{F^2}{2} \left[ \frac{1}{2H_{\pm 5/2} \pm (b-c)} - \frac{1}{2H_{\pm 5/2} \pm (c-b)} \right] + \frac{S^2}{2[3H_{\pm 5/2} \pm (b-a)]} + \text{h.f.c.}, \\ H_0 = H_{\pm 3/2} \pm 2(c-d) &- \frac{P^2}{2[H_{\pm 3/2} \pm (a-c)]} + \frac{Q^2}{2[H_{\pm 3/2} \pm (b-d)]} + \frac{F^2}{2[2H_{\pm 3/2} \pm (c-b)]} \\ &- \frac{E^2}{2[2H_{\pm 3/2} \pm (d-a)]} + \frac{R^2}{2} \left[ \frac{1}{H_{\pm 3/2} \pm (c-d)} + \frac{1}{H_{\pm 3/2} \pm (d-c)} \right] + \text{h.f.c.}, \\ H_0 = H_{1/2} &+ \frac{E^2}{2} \left[ \frac{1}{2H_{1/2} + d - a} - \frac{1}{2H_{1/2} + a - d} \right] + \frac{R^2}{2} \left[ \frac{1}{H_{1/2} + c - d} - \frac{1}{H_{1/2} + d - c} \right] \\ &- \frac{Q^2}{2} \left[ \frac{1}{H_{1/2} + b - d} - \frac{1}{H_{1/2} + d - b} \right] + \text{h.f.c.} \quad (7) \end{aligned}$$

Here  $H_{\pm M}$  denotes the  $\pm M \leftrightarrow \pm M \mp 1$  transition.

The correction due to the hyperfine interaction for the electronic transition  $M \rightarrow M-1$  is given by<sup>9</sup>

$$Km + \frac{B^2}{4H_0} \left( \frac{A^2 + K^2}{K^2} \right) [I(I+1) - m^2] + \frac{B^2}{2H_0} \left( \frac{A}{K} \right) m(2M-1). \quad (8)$$

The  $H_0$  appearing in the denominator is due to an approximate evaluation of the zero-order splitting of the levels which are admixed by the hyperfine interaction. As Lacroix<sup>2</sup> pointed out this approximation is not valid in the case of a large fine-structure splitting. In our case this splitting is quite small and therefore formula (8) is adequate.

The parameters in formulas (7) and (8) are given by

	$z$ axis	$x$ axis
$a$	$\frac{1}{2}(7b_2^0 + 7b_4^0 + b_6^0)$	$\frac{1}{32}(-56b_2^0 + 42b_4^0 + 70b_4^4 - 5b_6^0 - 21b_6^4)$ ,
$b$	$\frac{1}{2}(b_2^0 - 13b_4^0 - 5b_6^0)$	$\frac{1}{32}(-8b_2^0 - 78b_4^0 - 130b_4^4 + 25b_6^0 + 105b_6^4)$ ,
$c$	$\frac{1}{2}(-3b_2^0 - 3b_4^0 + 9b_6^0)$	$\frac{1}{32}(24b_2^0 - 18b_4^0 - 45b_4^4 - 45b_6^0 - 189b_6^4)$ ,
$d$	$\frac{1}{2}(-5b_2^0 + 9b_4^0 - 5b_6^0)$	$\frac{1}{32}(40b_2^0 + 54b_4^0 + 90b_4^4 + 25b_6^0 + 105b_6^4)$ ,
$P$	0	$\frac{1}{16}(21)^{1/2}(-8b_2^0 + 20b_4^0 - 20b_4^4 - 5b_6^0 - 5b_6^4)$ ,
$Q$	0	$\frac{1}{16}(5)^{1/2}(-24b_2^0 + 4b_4^0 - 4b_4^4 + 21b_6^0 + 21b_6^4)$ ,
$R$	0	$\frac{1}{16}(15)^{1/2}(-16b_2^0 + 16b_4^0 - 16b_4^4 - 7b_6^0 - 7b_6^4)$ ,
$E$	$(35)^{1/2}(b_4^4 + 3b_6^4)$	$\frac{1}{16}(35)^{1/2}(14b_4^0 + 2b_4^4 + 9b_6^0 - 39b_6^4)$ ,
$F$	$(3)^{1/2}(5b_4^4 - 7b_6^4)$	$\frac{1}{16}(3)^{1/2}(70b_4^0 + 10b_4^4 - 21b_6^0 + 91b_6^4)$ ,
$S$	0	$\frac{3}{8}(1001)^{1/2}(b_6^0 + b_6^4)$ ,
$H_0$	$h\nu/g\beta$	$h\nu/g\beta$ ,
$K$	$A$	$B$ ,

<sup>8</sup> J. L. Prather, Natl. Bur. Std. (U.S.) Monograph 19, 1961.

<sup>9</sup> W. Low, *Paramagnetic Resonance in Solids* (Academic Press Inc., New York, 1960), p. 60.

and

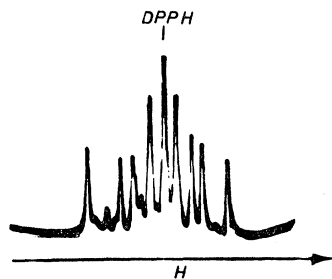
$$b_2^0 = 3B_2^0, \quad b_4^0 = 60B_4^0, \quad b_4^4 = 12B_4^4, \quad b_6^0 = 1260B_6^0, \quad b_6^4 = 60B_6^4. \quad (10)$$

### III. EXPERIMENTAL

Experiments were performed on several crystals purchased from Isomet Company and from Semi-Elements Inc., all with a nominal concentration of 0.1%. We oriented the crystals by x rays and polished them on the (001) and (110) planes. The measurements were made with a conventional X-band spectrometer at room, liquid-nitrogen, and liquid-hydrogen temperatures. Video detection was used at room and liquid nitrogen temperatures; low-power and superheterodyne detection were used at lower temperatures to avoid saturation.

All the crystals showed the same tetragonal spectrum. The [001] direction of the crystal is the tetragonal axis of the spectrum. In the (001) plane the maximum splitting of the spectrum was at  $(8 \pm 2)^\circ$  from the [100] direction, in good agreement with the  $(9 \pm 2)^\circ$  for  $\text{Gd}^{3+}$  and  $\text{Mn}^{2+}$  spectra.<sup>1</sup> This direction was chosen as the  $x$  axis of the  $\text{Eu}^{2+}$  spectrum. In both  $z$  and  $x$  directions the  $H_{7/2}$  transition appeared in the highest field, followed by the  $H_{-3/2}$ ,  $H_{-5/2}$ ,  $H_{1/2}$ ,  $H_{5/2}$ ,  $H_{3/2}$ ,  $H_{-7/2}$  transitions as the field was lowered. The  $H_{\pm 3/2}$  transition overlapped partially with  $H_{\pm 5/2}$  transition.

FIG. 1. The  $\frac{1}{2} \rightarrow -\frac{1}{2}$  transition of  $\text{Eu}^{2+}$  at 20°K with the external field parallel to the  $z$  direction. Not all of the twelve hyperfine lines are resolved. The weakest lines are forbidden nuclear transitions ( $\Delta m \neq 0$ ). The horizontal scale of the figure is not linear.



At low temperatures some forbidden electronic transitions were observed in the  $x$  direction. In addition forbidden ( $\Delta m \neq 0$ ) nuclear transitions were observed (see Fig. 1). The field of each individual line was measured by proton resonance. The center of each electronic transition and the hyperfine constants were then calculated using formula (8). The other parameters were calculated by iterations on (7). The first iteration

already produced the parameters within experimental error (see Table I), the zeroth approximation yielding  $b_2^0$ ,  $b_4^0$ , and  $b_6^0$  from the spectrum in the  $z$  direction, and  $b_4^4$  and  $b_6^4$  from the spectrum in the  $x$  direction.

The lines were identified as follows:

Different assignments of the transitions were tried in order to obtain

$$E_2^0 = -\frac{1}{2}B_2^0$$

as required by theory [see Eq. (4)]. The value of  $|M|$  for each transition given by this assignment was confirmed by the relative intensities of the transitions. From theory these are

$$\begin{array}{ccccccccc} H_{7/2}, & H_{-3/2}, & H_{-5/2}, & H_{1/2}, & H_{5/2}, & H_{3/2}, & H_{-7/2} \\ 7: & 15: & 12: & 16: & 12: & 15: & 7 \end{array}$$

in good agreement with the observed transitions.

The absolute signs of  $M$  were determined from observations at liquid-helium temperature, enabling the determination of the absolute sign of the  $b_n^{m's}$ .

### IV. RESULTS AND DISCUSSION

The results obtained are presented in Tables II and III. The sign of the hyperfine structure parameters was

TABLE I. Measured and calculated paramagnetic transitions of divalent europium in  $\text{CaWO}_4$ . Temperature = 300°K.

Transition	$H$ Parallel to the $z$ axis (gauss)		$H$ Parallel to the $x$ axis (gauss)	
	Observed	Calculated	Observed	Calculated
$\frac{7}{2} \rightarrow \frac{5}{2}$	3799.9	3799.9	3889.7	3886.6
$-\frac{1}{2} \rightarrow -\frac{3}{2}$	3533.1	3533.2	3594.4	3596.7
$-\frac{3}{2} \rightarrow -\frac{5}{2}$	3445.1	3445.3	3539.2	3537.5
$\frac{1}{2} \rightarrow -\frac{1}{2}$	3150.8	3151.2	3155.2	3155.7
$\frac{5}{2} \rightarrow \frac{3}{2}$	2874.6	2874.8	2778.7	2778.0
$\frac{3}{2} \rightarrow \frac{1}{2}$	2775.2	2775.4	2721.9	2724.2
$-\frac{5}{2} \rightarrow -\frac{7}{2}$	2530.2	2530.4	2446.1	2443.0
DPPH marker			3139.5	

TABLE II. Fine-structure Hamiltonian parameters of  $\text{Eu}^{2+}$ ,  $\text{Gd}^{3+}$ , and  $\text{Mn}^{2+}$  in  $\text{CaWO}_4$ . All  $b^i's \times 10^4 \text{ cm}^{-1}$ .

Ion	Temperature (°K)	$g_{11}$	$g_{\perp}$	$b_2^0$	$b_4^0$	$b_4^4$	$b_6^0$	$b_6^4$	Reference	Over-all splitting <sup>a</sup> $\times 10^4 \text{ cm}^{-1}$
$\text{Eu}^{2+}$	300	1.9907 $\pm$ 0.0006	1.9901 $\pm$ 0.0006	-31 $\pm$ 2	-289.1 $\pm$ 0.6	-371 $\pm$ 1	7.9 $\pm$ 0.6	1.5 $\pm$ 0.8	this paper	1044 $\pm$ 4
	80	1.9907 $\pm$ 0.0006	1.9901 $\pm$ 0.0006	+30 $\pm$ 2	-307.0 $\pm$ 0.6	-385 $\pm$ 1	9.1 $\pm$ 0.6	0.5 $\pm$ 0.8	this paper	1089 $\pm$ 4
$\text{Gd}^{3+}$	20	1.9907 $\pm$ 0.0006	1.9901 $\pm$ 0.0006	+54 $\pm$ 2	-311.6 $\pm$ 0.6	-383 $\pm$ 1	7.7 $\pm$ 0.6	1.7 $\pm$ 0.8	this paper	1093 $\pm$ 4
	77	1.9915 $\pm$ 0.0004	1.9916 $\pm$ 0.0004	-916.7 $\pm$ 1	-24.0 $\pm$ 0.2	(-) <sup>b</sup> 29.0 $\pm$ 0.2	-0.6 $\pm$ 0.3	0.0 $\pm$ 0.3	b	
$\text{Mn}^{2+}$	77	1.99987 $\pm$ 0.0001	1.99980 $\pm$ 0.0002	-137.6 $\pm$ 0.3	-1.2 $\pm$ 0.3	(-) <sup>b</sup> 2.3 $\pm$ 0.1			b	

<sup>a</sup> Neglecting hyperfine terms.

<sup>b</sup> C. F. Hempstead and K. D. Bowers, Phys. Rev. 118, 131 (1960). The definition of  $b_4^4$  in this paper is one-fifth that of Hempstead and Bowers, and their results were adapted accordingly.

TABLE III. Hyperfine structure constants of  $\text{Eu}^{2+}$  in various crystal hosts at room temperature.

Host	$A^{151}$	$B^{151}$	$A^{153}$	$B^{153}$	Reference
$\text{CaWO}_4$	$-34.4 \pm 0.5$	$-35.0 \pm 0.5$	$-15.5 \pm 0.3$	$-16.0 \pm 0.3$	this paper
$\text{CaF}_2$	$34.5 \pm 0.2$		$15.3 \pm 0.4$		a
$\text{SrCl}_2$	$34.5 \pm 0.3$		$15.5 \pm 0.3$		b
$\text{CaO}$	$29.63 \pm 0.1$		$13.05 \pm 0.2$		c
$\text{CdS}$	$23.03 \pm 0.1$		$10.32 \pm 0.1$		d
$\text{KCl}$	$32.56 \pm 0.06$		$14.38 \pm 0.03$		e
$\text{SrS}$	$30.8 \pm 0.2$		$13.8 \pm 0.2$		f
$\text{LaCl}_3$	38		17		g
$\text{CaF}_2$	$-34.3260 \pm 0.0004$		$-15.2349 \pm 0.0008$		h

<sup>a</sup> J. M. Baker, B. Bleaney, and W. Hayes, Proc. Roy. Soc. (London) **A247**, 141 (1958).

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

<sup>c</sup> A. J. Shuskus, Phys. Rev. **127**, 2022 (1962).

<sup>d</sup> P. B. Dorain, Phys. Rev. **120**, 1190 (1960).

<sup>e</sup> M. Abraham, R. W. Kedzie, and C. D. Jeffries, Phys. Rev. **108**, 58 (1957).

<sup>f</sup> B. Bleaney and W. Low, Proc. Phys. Soc. (London) **A68**, 55 (1955).

<sup>g</sup> D. M. Gruen, J. G. Conway and R. D. McLaughlin, J. Chem. Phys. **25**, 1102 (1956).

<sup>h</sup> J. M. Baker and F. I. B. Williams, Proc. Roy. Soc. (London) **A267**, 283 (1962) (ENDOR measurements) (calculated from their results  $A^{151} = -102.9096 \pm 0.0013$  Mc/sec, and  $A^{153} = -45.6730 \pm 0.0025$  Mc/sec, with  $c = 2.997928 \cdot 10^{10}$  cm/sec).

determined as follows: From formula (8) we see that the over-all splitting of the  $H_M$  transition is given by

$$5|K|[1+(K/2H_0)(2M-1)]. \quad (8a)$$

We found the splitting greater for  $M < 0$  transitions than for  $M > 0$  transitions beyond experimental error, thus proving that  $K$  is negative. This is in agreement with the sign found by Baker and Williams<sup>10</sup> from their ENDOR measurement of  $\text{Eu}^{2+}$  in  $\text{CaF}_2$  and with the positive sign found for  $\text{Gd}^{3+}$  in the same environment,<sup>1</sup> the magnetic moments of  $\text{Gd}^{155,157}$  and  $\text{Eu}^{151,153}$  being opposite in sign.<sup>10-12</sup> It must be noted that the values of  $|K|$  ob-

<sup>10</sup> J. M. Baker and F. I. B. Williams, Proc. Roy. Soc. (London) **A267**, 283 (1962).

<sup>11</sup> M. Pichanick, P. G. H. Sandars, and G. V. Woodgate, Proc. Roy. Soc. (London) **257**, 277 (1960).

<sup>12</sup> D. R. Speck, Phys. Rev. **101**, 1725 (1956).

tained in  $\text{CaWO}_4$  are greater than in many other crystals and are close to those for  $\text{CaF}_2$  (see Table III). This reflects less covalent bonding for  $\text{Eu}^{2+}$  in  $\text{CaWO}_4$ . The value of  $A^{151}/A^{153}$  is  $2.22 \pm 0.06$  compared with the value  $2.25312 \pm 0.00015$  obtained from the results of Baker and Williams.<sup>10</sup>

A comparison between the crystal field parameters for  $\text{Eu}^{2+}$  and  $\text{Gd}^{3+}$  shows the following features:

(1) In a field of cubic symmetry  $b_2^0 = 0$ ,  $b_4^0 = b_4^4$  and  $b_6^0 = -b_6^4$ . We found  $b_2^0 \neq 0$ ,  $b_4^4/b_4^0 = 1.25$  for  $\text{Eu}^{2+}$  while for  $\text{Gd}^{3+}$  this ratio is 1.21, showing that the symmetry is far from cubic. We found it difficult to investigate the third condition.

(2) While in  $\text{Eu}^{2+}$ ,  $b_4^0$  and  $b_4^4$  are the largest parameters, and  $b_2^0$  is small and even changes sign when the temperature is lowered, in  $\text{Gd}^{3+}$ , and also in  $\text{Mn}^{2+}$ ,  $b_2^0$  is much larger than the other parameters. We can find no explanation for this.

(3) The  $g$  factors for  $\text{Gd}^{3+}$  are closer to those of a free electron than those for  $\text{Eu}^{2+}$ , indicating that the admixture of higher levels is stronger in  $\text{Eu}^{2+}$ .

The temperature variation of the field parameters shows an increase of  $|b_4^0|$ ,  $|b_4^4|$  and  $b_2^0$  when the temperature is lowered, while  $b_6^0$  and  $b_6^4$  are practically constant. This variation is due to the variation in the crystal constants.

#### ACKNOWLEDGMENTS

We wish to thank Dr. B. S. Fraenkel for permission to use x-ray instrumentation for orienting the crystals, and Professor W. Low for suggesting the problem, and Professor Low and Dr. U. Ranon for reading the manuscript and for fruitful discussions.