

Optical Spectrum and Zeeman Effect of $\text{CaF}_2:\text{Eu}^{2+}$ †

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New measurements of the Zeeman effect and of the fluorescent lifetime as a function of temperature of Eu^{2+} in CaF_2 are reported. Estimates of the theoretical parameters are made, and it is shown that neither these estimated values nor the magnetic splitting support those simplified models, used to explain the Faraday rotation, that neglect either the crystal field or the Coulomb interaction between the $5d$ and the $(4f)^6$ electrons. Evidence is given that the relative intensity of the Zeeman components in emission is dominated by "spin-memory" effects rather than by thermalization between the Zeeman levels of the excited state.

I. INTRODUCTION

THE spin-allowed transitions involving the d electrons of ions in crystals usually give rise to broad absorption bands as a consequence of the large difference in ligand field interaction between the two states of different orbital wave function. This difference, according to the Franck-Condon principle, leads to a final state with appreciable vibrational excitation.¹ Consistent with this picture, the spin- and parity-allowed $f^n \rightarrow f^{n-1}d$ transitions of the divalent rare-earth ions in crystals are usually quite broad.² One of the exceptions is the 4130 Å line of Eu^{2+} in CaF_2 , which is sharp enough at low temperature to resolve the Zeeman components with attainable magnetic field.³⁻⁶

This paper presents new measurements of the $\text{CaF}_2:\text{Eu}^{2+}$ Zeeman effect that are in general agreement with those of Ref. 5 but are of greater precision. However, we differ with these authors' interpretation of the temperature dependence of the intensity of the Zeeman components of the emission spectrum. In addition, the lifetime of the excited state has been remeasured, this time as a function of temperature, and the difficulties in completing an adequate theoretical description are considered.

Because both $4f$ and $5d$ electrons are involved, the spin-orbit coupling constants and the crystal-field interaction of each of these kinds of electrons, and the coupling between them, appear in the Hamiltonian function. This large number of adjustable parameters and the very great number of states that occur in the f^6d configuration limit the utility of such calculations for explaining this spectrum. Nevertheless, results of approximate calculation are useful because they provide insight into the relative values of these interactions, and such a calculation is given in Sec. II. One approximation that has been used in the interpretation of the absorption spectra and Faraday rotations of the divalent rare-earth ions neglects the coupling between the $(4f)^{n-1}$ electrons and the $5d$ electron.^{2,7-10} On this model the structure of the first absorption band in Eu^{2+} is essentially the separation between the seven J levels of the 7F ground state of f^6 added to the promotion energy of one f electron to the e cubic orbital of the $5d$ state. It is of interest to see whether the Zeeman splitting of the lowest excited level is consistent with this model and to see whether this approximation can be justified theoretically.

The ground ${}^8S_{7/2}$ state of the Eu^{2+} ion in CaF_2 has been carefully studied by EPR and Endor techniques¹¹ that are of much higher resolution than the optical studies to be reported here, so that the g factor and crystal-field parameters of this state are known; our

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¹ M. H. L. Pryce, in *Phonons*, edited by R. W. H. Stevenson (Plenum Press, Inc., New York, 1966).

² D. S. McClure and Z. Kiss, *J. Chem. Phys.* **39**, 3251 (1963).

³ W. A. Runciman and C. V. Stager, *J. Chem. Phys.* **38**, 279 (1963).

⁴ B. P. Zakharchenya and A. Ya. Ryskin, *Opt. i Spektroskopiya* **14**, 309 (1963) [English transl.: *Opt. Spectry.* **14**, 163 (1963)].

⁵ B. P. Zakharchenya, I. B. Rusanov, and A. Ya. Ryskin, *Opt. i Spektroskopiya* **18**, 999 (1965) [English transl.: *Opt. Spectry.* **18**, 563 (1965)].

⁶ A. A. Kaplyanskii and A. K. Przhhevskii, *Opt. i Spektroskopiya* **19**, 597 (1965) [English transl.: *Opt. Spectry.* **19**, 331 (1965)].

⁷ J. D. Axe and P. P. Sorokin, *Phys. Rev.* **130**, 945 (1963).

⁸ T. S. Piper, J. P. Brown, and D. S. McClure, *J. Chem. Phys.* **46**, 1353 (1967). This paper goes beyond this approximation in interpreting the spectrum of Yb^{2+} in SrCl_2 , but considers its validity.

⁹ M. J. Freiser, S. Methfessel, and F. Holtzberg, *J. Appl. Phys.* **39**, 900 (1968).

¹⁰ K. G. Johnson and J. N. Sandoe, in *Proceedings of the Physical Society Conference Rare Earths*, Durham, England, 1966 (to be published).

¹¹ J. M. Baker and F. I. B. Williams, *Proc. Roy. Soc. (London)* **267A**, 283 (1962), and papers quoted therein.

TABLE I. Coulomb and spin-orbit splitting of the octet levels of the $\text{Eu}^{2+} 4f^6 5d$ configuration.^a

Coefficients of the Slater integrals in the term energy expressions												
L	$c(F_0)$	$c(F_2)$	$c(F_4)$	$-c(G_1)$	$-c(G_3)$	$-c(G_5)$	$E(L)^b$	$E(L) - E(5)$	ζ_{4f}^c	ζ_{5d}^c	λ^d	ΔE_{SO}
1	6	-24	-66	-14	84	462	-5349	1907	2/7	-1/7	21/2	2580
2	6	-6	99	21	84	462	-6187	1069	1/7	0	35/2	3540
3	6	11	-66	21	24	462	-4347	2909	3/28	1/28	49/2	4690
4	6	15	+22	21	84	462	-3927	3329	13/140	1/20	63/2	5880
5	6	-10	-3	21	84	252	-7256	0	3/35	2/35	77/2	7100

^a All energies are in cm^{-1} .^b $E(L)$ omits the contribution $6F_0$.^c Coefficients of the one-electron spin-orbit constants that give the many-electron factor λ .^d Coefficients of λ that give the total width ΔE_{SO} of the spin-orbit splitting of the term.

experiments are directed to the interpretation of the excited state.

Configurations with an odd number of electrons in a cubal environment appropriate to Ca sites in CaF_2 (O_h) give rise to wave functions that belong to the Γ_6 , Γ_7 , and Γ_8 representations of the cubic double group.^{5,12} The first two exhibit only the twofold Kramers degeneracy, while the last is fourfold degenerate. The splitting of the 4130 Å line under uniaxial stress^{3,13} and the Zeeman effect⁵ show that the upper state belongs to the Γ_8 representation. The magnetic splitting of Γ_8 levels is not, in general, isotropic, and a formula for its angular dependence has been derived by Judd¹⁴:

$$(W/\beta H)^2 = \frac{1}{4}(5\gamma^2 + 3\delta^2) \pm \gamma \left\{ \gamma^2 + \frac{1}{2}\delta^2 [9(l^4 + m^4 + n^4) - 3] \right\}^{1/2}, \quad (1)$$

where W is the energy shift, β is the Bohr magneton, H is the magnetic field intensity, γ and δ are parameters characterizing the splitting, and l , m , and n direction cosines between the field direction and the $\langle 100 \rangle$ axes. This splitting becomes isotropic if either γ or δ is zero, and it is instructive to consider the Zeeman pattern in these extremes. If $\delta = 0$, $\gamma \neq 0$ there are four equally spaced levels, the classic case for $S = \frac{3}{2}$ in the spin Hamiltonian if third-order spin terms are absent. If $\gamma = 0$, $\delta \neq 0$ the Γ_8 level splits into two doubly degenerate levels, a simple example of which is the 2E level of a d electron. For cases where both γ and δ are unequal to zero, an intermediate case will result that depends on the orientation of the magnetic field, the

greatest difference occurring between the $\langle 111 \rangle$ and $\langle 100 \rangle$ directions.

II. THEORY

Although a detailed analysis of the $\text{Eu}^{2+} 4f^7$ -to- $4f^6 5d$ transitions was not attempted because of its complexity, some results of approximate calculations are worth noting because they provide insight into the relative orders of magnitude of the three largest interactions—Coulomb, spin orbit, and crystal field.

First consider the ground state (${}^8S_{7/2}$) of the $4f^7$ configuration. This state is very little contaminated by the cubal crystal field V_{CF} , since V_{CF} preserves spin and parity and $4f^7$ has no other octets, while the next higher octets of the $4f^6 5d$ configuration are excluded because they are of opposite parity. Spin-orbit coupling V_{SO} admixes the ${}^6P_{7/2}$ state of $4f^7$ into the ground state. The lower-lying $4f^6 5d$ configuration also has a ${}^6P_{7/2}$ state, but this is not admixed because of its parity. The ground state, taking all first-order admixtures into account, is then

$$|0\rangle = |{}^8S_{7/2}\rangle + \alpha |{}^6P_{7/2}\rangle, \quad (2)$$

where $\alpha = 0.17$.¹¹

For the $4f^6 5d$ excited states we consider only the octet terms unless specifically otherwise noted. The possible L values are 1–5, as we can see by noting that they are formed by the coupling of an f hole to a d electron, which gives the decomposition $D^{(3)} \times D^{(2)}$.

An exact expression for the Coulomb energy of the $5d$ electron interacting with the $4f^6$ core was computed by analysis of the fd configuration and use of the diagonal sum rule to relate the fd results to the $4f^6 5d$ term splittings. These results are summarized in Table I. The first six columns give the coefficients of the Slater integrals in the term energy expression, i.e.,

$$E(L) = \sum_i c(F_i) F_i + \sum_i c(G_i) G_i. \quad (3)$$

¹² G. F. Koster *et al.*, *Properties of the Thirty-Two Point Groups* (M.I.T. Press, Cambridge, Mass., 1963). Group notation and selection rules were taken from this reference.

¹³ A. A. Kaplyanskii and A. K. Przhhevskii, *Opt. i Spektroskopiya* **13**, 882 (1962) [English transl.: *Opt. Spectry.* **13**, 508 (1962)].

¹⁴ B. Bleaney, *Proc. Phys. Soc. (London)* **73**, 937 (1959).

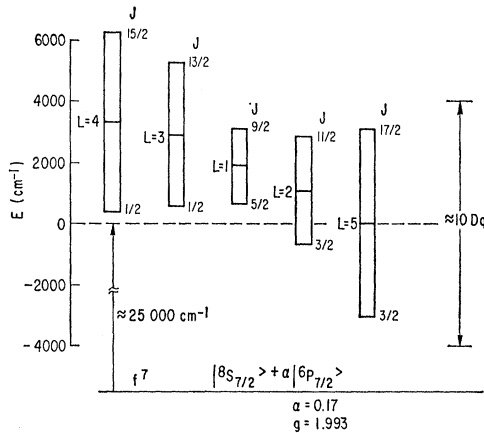


FIG. 1. Coulomb and spin-orbit splitting of the octet levels of the $\text{Eu}^{2+} 4f^6 5d$ configuration. The spin-orbit splitting is to first order only.

These expressions were derived independently with a general formula given by Judd¹⁵ for Coulomb interactions in an $l''l'$ configuration. Judd's formula was much more difficult to evaluate than straightforward application of the diagonal sum rule in the present case, but the results are in agreement, which provides confidence in their accuracy.

Numerical values of the term separations were obtained with parameters scaled from the Yb^{2+} parameters after McClure and Kiss²:

$$F_k(\text{Eu}^{2+}) = 0.8F_k(\text{Yb}^{2+}), \quad (4)$$

which gives, in cm^{-1} : $F_2 = 149.4$, $F_4 = 11.39$, $G_1 = 154.5$, $G_3 = 19.69$, and $G_5 = 3.29$. Column 7 gives the resulting numerical values of the term energies. We omit the term $6F_0$ common to every value of L . Note that Hund's rule is obeyed in that the lowest term is $L=5$. Since we are interested only in the term separations, the energy $E(5)$ is subtracted from all terms, and the final result for the term separations is given in column 8.

To obtain the splitting of these terms by spin-orbit coupling, we computed the relationship between the one-electron spin-orbit coupling parameters ζ_{4f} and ζ_{5d} and the term splitting factor λ ; these are also given in Table I. Columns 9 and 10 give the coefficients of the one-electron parameters in the expression for λ , e.g.,

$$\lambda(^8F) = (3/28)\zeta_{4f} + (1/28)\zeta_{5d}. \quad (5)$$

Column 11 gives the coefficient $S(2L+1)$, which, when multiplied by λ , gives the total width of the spin-orbit splitting of the term.

We obtained numerical values for ζ_{4f} and ζ_{5d} from the known values for the trivalent rare earths on the

basis that the spin-orbit parameters change very little with the state of ionization.¹⁶ Thus we take

$$\zeta_{4f}(\text{Eu}^{2+}) = \zeta_{4f}(\text{Eu}^{3+}) = 1415 \text{ cm}^{-1}.$$

ζ_{5d} increases gradually from 996 cm^{-1} for Ce^{3+} to 1220 cm^{-1} for Hf^{3+} .² We take the average for Eu^{2+} and obtain

$$\begin{aligned} \zeta_{5d}(\text{Eu}^{2+}) &= \frac{1}{2}[\zeta_{5d}(\text{Ce}^{3+}) + \zeta_{5d}(\text{Hf}^{3+})] \\ &= 1108 \text{ cm}^{-1}. \end{aligned}$$

Using these numerical estimates, we calculated the total widths of the spin-orbit split terms ΔE_{SO} ; these are given in column 12. This calculation is valid only to first order, since the interaction between terms is neglected.

Now let us consider the crystal-field interaction. Piper *et al.*⁸ have done a complete analysis of the $f^{13}d$ configuration taking Coulomb interaction, spin-orbit coupling, and crystal-field splitting of both the f and d electrons into account. They applied these results to the interpretation of the $\text{SrCl}_2:\text{Yb}^{2+} 4f^{14} \rightarrow 4f^{13}5d$ spectrum with the use of both the spectral positions and intensities. The best fit to the observed spectrum occurred for $Dq = 800 \text{ cm}^{-1}$, where Dq is the crystal-field splitting parameter for a single $5d$ electron. The quantity of physical interest is the energy separation of the e_g and t_{2g} orbitals in the crystal field, i.e., $10Dq = 8000 \text{ cm}^{-1}$. The value of $10Dq$ for $\text{SrCl}_2:\text{Yb}^{2+}$ would not be expected to be very different from that for $\text{CaF}_2:\text{Eu}^{2+}$; certainly it differs by less than a factor of 2.

The results of these calculations and the estimate of $10Dq$ are compared in Fig. 1. The centers of the vertical bars are the term centers before spin-orbit coupling; the length of the bars denotes the total spin-orbit width of the term to first order. The estimate of $10Dq$ is also shown on the same scale for comparison. The Coulomb interaction, spin-orbit coupling, and $10Dq$ are all of the same order of magnitude. To further complicate matters, an estimate of the position of the lowest-lying sextet levels of $4f^6 5d$ shows that they overlap the higher-lying octet levels. It therefore seems that the agreement between experiments and theoretical models^{2,7-10,27-29} that neglect either the Coulomb interaction or crystal-field splitting is fortuitous, perhaps due to the insensitivity of the measured effects to the details of the energy levels.

The only fully allowed transitions from the $^8S_{7/2}$ ground state to the $4f^6 5d$ configuration terminate on the $^8P_{5/2}$ and $^8P_{7/2}$ excited states. However, the 8P states are admixed by the crystal field into the other octets (except 8D) and by the spin-orbit coupling into many of the sextets and octets. The transition inten-

¹⁵ B. R. Judd, Phys. Rev. **125**, 613 (1962).

¹⁶ D. S. McClure, Advan. Solid State Phys. **9**, 400 (1959).

sities to these levels are proportional to the squares of the 8P admixture coefficients, which, because of the large overlap of the levels, should be quite large.

Since there are 280 octet states in f^6d , 188 of which are included in $47\Gamma_8$ levels, a calculation to find the energy levels, the admixture coefficients mentioned above, and the magnetic splitting would involve the diagonalization of a 47×47 matrix. Even if this were done, there would be some question as to whether the outcome would be adequate to explain the experimental results without the inclusion of the sextet states. For this reason we have not attempted to carry the calculation further.

III. EXPERIMENTAL RESULTS

The crystals used in these experiments were either supplied by Optovac Incorporated or grown at Aerospace Corporation. The absorption spectrum at room temperature, combining data from a Cary 14 spectrophotometer and a McPherson Vacuum uv monochromator, is shown in Fig. 2, which differs from earlier published results¹⁷ by its extension to shorter wavelength. Because the linewidth depends on concentration, it is necessary to use very dilute material in the Zeeman studies,³⁻⁵ and because of the large oscillator strength it is possible to work with such small concentrations. The Zeeman data were taken on a crystal nominally containing only 2 ppm, which was too little to analyze by the usual spectrochemical means but was correct to within an experimental error of $\pm 20\%$ by extrapolation of the strength of the absorption bands from more concentrated crystals, which could be analyzed. The fraction of the europium ions remaining in the trivalent state is unknown, but the strong red fluorescence typical of this ion was not observed in any of our crystals. The absorption spectra of the dilute crystal at room temperature and at 4°K

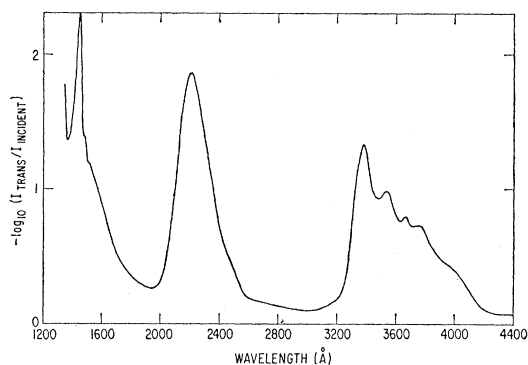


FIG. 2. Absorption spectrum of a 0.25-mm-thick sample of 0.4 mole % Eu^{2+} in CaF_2 at room temperature.

¹⁷ A. A. Kaplyanskii and P. P. Feofilov, *Opt. i Spektroskopiya* **13**, 235 (1962) [English transl.: *Opt. Spectry*, **13**, 129 (1962)].

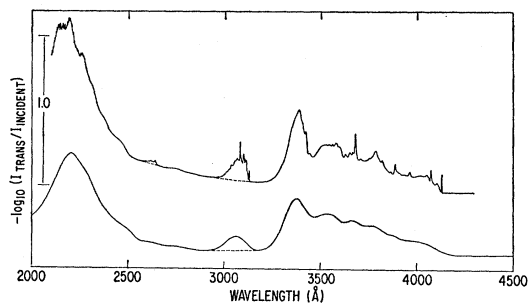


FIG. 3. Absorption spectrum of a 1.3-cm-thick sample of 2 ppm mole fraction of Eu^{2+} in CaF_2 at (a) room temperature, (b) 4.2°K . The resolution of the Cary 14 is not sufficient to show the true linewidth and maximum intensity of the 4130 \AA line. Elimination of transitions due to impurities, as shown by their absence in Fig. 2, has been indicated by the dashed line.

are shown in Fig. 3. The complexity of the low-temperature absorption spectrum is due to vibronic sidebands of the various electronic transitions, and it makes the interpretation^{6,9} of the "steps" in the room-temperature spectrum in terms of the various J levels of f^6 less certain. While some unresolved additional structure of the shorter-wavelength transitions could be observed when the crystal was placed in the magnetic field, only the 4130 \AA line is sharp enough for detailed study. In emission at 4°K in the absence of a magnetic field, there is the strong sharp line at $4130.04 \pm 0.04 \text{ \AA}$ and a number of relatively broad vibronic satellites on the long-wavelength side.¹⁸ There are also some very weak sharp lines within 3 \AA of the 4130 \AA line^{5,6} that are not observed in absorption and are believed to be due to Eu^{2+} ions coupled to point defects. These will not be discussed further.

For the measurement of the lifetime, the crystal was excited by a source of a few nsec duration.¹⁹ At 300°K the lifetime was $0.73 \pm 0.02 \mu\text{sec}$, in agreement with an earlier measurement.²⁰ At 77 and 4°K it was reduced to 0.635 ± 0.02 and $0.60 \pm 0.02 \mu\text{sec}$, respectively. At the lowest temperature the possibility of resonance trapping was not completely eliminated, so that the true lifetime might be even shorter. The reduction in lifetime as the temperature is decreased is probably due to the existence of states of lower oscillator strength lying just above the lowest excited level. Since the transitions visible in Fig. 2 at wavelengths shorter than that of the 4130 \AA line are stronger, this result gives support to published evidence for a forbidden transition from the ground state to a level about 88 cm^{-1} (15 \AA) above the lowest excited level.⁶

The Zeeman spectrum in absorption was photographed on a Bausch & Lomb dual grating spectrograph

¹⁸ M. V. Hobden, *Phys. Letters* **15**, 10 (1965).

¹⁹ R. C. Mackey, S. A. Pollack, and R. S. Witte, *Rev. Sci. Instr.* **36**, 1715 (1965).

²⁰ P. Feofilov, *Opt. i Spektroskopiya* **1**, 996 (1956).

TABLE II. Absorption spectrum of $\text{CaF}_2:\text{Eu}^{2+}$ at 4.2°K ($H=47.3$ kG).

$\bar{\lambda}$, Å	Comment ^a	Polarization ^b	Temp. Dep. ^c	Assignment	$\bar{\lambda}$, cm ⁻¹	
					Observed	Predicted ^d
a. Field along [111] axis						
4127.47	vw, sh	⊥ (also ?)	w	$\begin{cases} -\frac{5}{2} \rightarrow \text{C} \\ -\frac{5}{2} \rightarrow \text{D} \end{cases}$	24 221.1±0.1	$\begin{cases} 24\ 220.7 \\ 24\ 220.85 \end{cases}$
4128.14	m, d	⊥ (also ?)	s	$\begin{cases} -\frac{7}{2} \rightarrow \text{A} \\ -\frac{7}{2} \rightarrow \text{B} \end{cases}$	24 217.2	$\begin{cases} 24\ 217.25 \\ 24\ 217.4 \end{cases}$
4128.86	m, sh	⊥ (also ?)	w	$\begin{cases} -\frac{5}{2} \rightarrow \text{A} \\ -\frac{5}{2} \rightarrow \text{B} \end{cases}$	24 212.9	$\begin{cases} 24\ 212.7 \\ 24\ 212.9 \end{cases}$
4129.61	w, sh		w	$\begin{cases} -\frac{3}{2} \rightarrow \text{A} \\ -\frac{3}{2} \rightarrow \text{B} \end{cases}$	24 208.5	$\begin{cases} 24\ 208.35 \\ 24\ 208.5 \end{cases}$
4130.27	vvw	⊥ (also ?)	w	$\begin{cases} -\frac{1}{2} \rightarrow \text{A} \\ -\frac{1}{2} \rightarrow \text{B} \end{cases}$	24 204.7	$\begin{cases} 24\ 204.1 \\ 24\ 204.2 \end{cases}$
b. Field along [100] axis						
4126.89	vvw			$-\frac{7}{2} \rightarrow \text{C}$	24 224.5	24 224.4
4127.38	w	⊥		$-\frac{5}{2} \rightarrow \text{D}$	24 221.6	24 221.7
4127.66	vvw	⊥		$-\frac{5}{2} \rightarrow \text{C}$	24 220.0	24 220.1
4128.00	w	⊥		$-\frac{7}{2} \rightarrow \text{B}$	24 218.0	24 218.2
4128.25	m, d	⊥		$-\frac{7}{2} \rightarrow \text{A}$	24 216.5	24 216.6
4129.00	w			$-\frac{5}{2} \rightarrow \text{A}$	24 212.1	24 212.3
4129.50	w, sh	⊥		$-\frac{3}{2} \rightarrow \text{B}$	24 209.2	24 209.4
4129.75	vvw	⊥		$-\frac{3}{2} \rightarrow \text{A}$	24 207.7	24 207.8
4130.23	w			$-\frac{1}{2} \rightarrow \text{B}$	24 204.9	24 205.0
c. Field along [411] axis						
4127.41	w		w	$-\frac{5}{2} \rightarrow \text{D}$	24 221.4	24 221.4
4127.99	w		s	$-\frac{7}{2} \rightarrow \text{B}$	24 218.0	24 218.0
4128.26	w, d		s	$-\frac{7}{2} \rightarrow \text{A}$	24 216.5	24 216.7
4128.76	w		w	$-\frac{5}{2} \rightarrow \text{B}$	24 213.5	24 213.5
4129.00	mw, sh		w	$-\frac{5}{2} \rightarrow \text{A}$	24 212.1	24 212.1
4129.51	w		w	$-\frac{3}{2} \rightarrow \text{B}$	24 209.1	24 209.2

^a m, w, vw, vvw mean medium, weak, very weak, and extremely weak (barely detectable in our experiment). Sh means sharp [~ 0.13 Å (0.8 cm⁻¹)] FWHM, while d means diffuse [~ 0.36 Å (2.2 cm⁻¹)]. Those not marked are intermediate, nearer to the lower value.

^b ⊥ means $E \perp H$, || means $E \parallel H$.

^c w means weakens or disappears if the crystal is cooled from 4.2 to 3°K; s means remains approximately the same. A missing entry in column 2 or 3 means that the property in question was not measured.

^d Predicted using the parameters given in the text.

with the crystal in the field of a superconducting magnet capable of obtaining 47.3 kG. Strains in the windows of the Dewar made external polarizers useless, so we obtained polarization information by noting that with the light path parallel to the field, one obtains the $E \perp H$ spectrum, while with the light path perpendicular

to the field (done with mirrors), one obtains both the $E \perp H$ and $E \parallel H$ spectrum, so that the additional lines have $E \parallel H$. Since the selection rules predict that all allowed transitions are one or the other, but none are both, this suffices to identify the lines. (This technique is not adequate for H in the [111] direction because

some levels are so closely spaced that the individual transitions are not resolved. For this reason we have not attempted an assignment of the irreducible representation of the upper state for this orientation of the magnetic field, although there is no inconsistency of our experimental results with the assignments given in Ref. 5.) The orientation of the crystal was determined from the {111} cleavage planes, and the spectrum was measured with the magnetic field along a [111], [100], and [411] direction. Comparison of plates taken with 47.3 and with 25.0 kG showed the splitting to be linear in H to within the precision of measurement, so only the high field results will be reported. In Eq. (1) the splitting does not depend on the sign of γ or δ . The observed spectra at 4°K can be fitted within the experi-

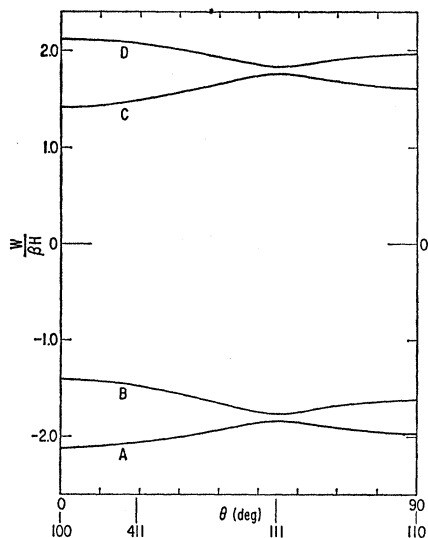


FIG. 4. Magnetic splitting of the $\text{CaF}_2:\text{Eu}^{2+}$ 4130 Å line as a function of angle of the magnetic field to the [100] axis in the (110) plane.

mental precision by $\nu_0 = 24\,206.0 \pm 0.1 \text{ cm}^{-1}$, $\gamma^2 = 0.125 \pm 0.01$, and $\delta^2 = 4.11 \pm 0.04$. The experimental results are compared to those predicted with these parameters²¹ in Table II. The convention is adopted that the four excited levels are labeled A–D in order of increasing energy. The angular dependence of the splitting for the field directed in the (110) plane, according to Eq. (1) with the parameters above, is illustrated in Fig. 4. The values of γ^2 and δ^2 from Ref. 5 are 0.09 and 4.05, respectively. The larger magnetic field available in our

²¹ These results can also be expressed, according to Ref. 14, by a spin Hamiltonian of the form $\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} + f\beta(H_x S_x^3 + H_y S_y^3 + H_z S_z^3)$, with either $|g| = 3.88$ and $|f| = 2.24$ or $|g| = 3.18$ and $|f| = 2.47$, g and f being of opposite sign in either alternative. The ambiguity is discussed in Ref. 14. We do not emphasize this point of view because the effective spins do not approximate to any real angular-momentum operators, and forcing the results into a spin-Hamiltonian formulation is a formal procedure without physical content.

TABLE III. Emission spectrum of $\text{CaF}_2:\text{Eu}^{2+}$ at 4.2°K ($H = 47.3 \text{ kG}$ directed along the [100] axis).

$\lambda, \text{Å}$	Comment ^a	Assign- ment	λ, cm^{-1}	
			Observed	Predicted ^b
4128.30	m, d	$A \rightarrow -\frac{7}{2}$	24 216.2 ± 0.3	24 216.6
4129.04	m	$A \rightarrow -\frac{5}{2}$	24 211.9	24 212.3
4129.45	s	$B \rightarrow -\frac{3}{2}$	24 209.5	24 209.4
{4129.73	mw	$A \rightarrow -\frac{3}{2}$	24 207.8	24 207.8
{4130.22	mw	$B \rightarrow -\frac{1}{2}$	24 205.0	24 205.0
4130.59	m	$C \rightarrow +\frac{3}{2}$	24 202.8	24 202.4
{4130.98	s	$B \rightarrow +\frac{1}{2}$	24 200.5	24 200.6
{4131.24	mw	$A \rightarrow -\frac{1}{2}$	24 199.0	24 199.0
{4131.83	m	$D \rightarrow +\frac{7}{2}$	24 195.5	24 195.2
{4132.02	w (shelf)	$A \rightarrow +\frac{3}{2}$	24 194.4	24 194.6
4132.75	m	$A \rightarrow +\frac{5}{2}$	24 190.1	24 190.1

^a s, m, mw, and w mean strong, medium, moderately weak, and weak. d means relatively diffuse. Bracketed transitions are not completely resolved, and the line indicated "shelf" is just detectable as a separate transition.

^b Predicted on the basis of Eq. (1) with the same parameters as used in the absorption spectrum.

experiment resulted in less overlap of the lines and thus somewhat more precise determination of their position, as well as simple increase of the magnetic splitting, so that we estimate our limits of error to be about half of those of Ref. 5.

The strong "no-phonon" emission line in the absence of a magnetic field was, within the precision of the experiment, at exactly the same wavelength as the absorption line. In a field of 47.3 kG directed along the [100] axis, the observed emission lines could be identified with transitions between levels previously determined from the absorption spectrum with the agreement shown in Table III. The spectrum was taken on a 1-m

TABLE IV. Magnetic field along [100] axis (c_{4h}).

m_g	Γ	Electric dipole selection rule						Excited electronic state	
		Γ	5	6	7	8	Level	Γ	
$-\frac{7}{2}$	5	5	π	σ	...	σ	A	8	
$-\frac{5}{2}$	8	6	σ	π	σ	...	B	6	
$-\frac{3}{2}$	7	7	...	σ	π	σ	C	5	
$-\frac{1}{2}$	6	8	σ	...	σ	π	D	7	
$+\frac{1}{2}$	5								
$+\frac{3}{2}$	8								
$+\frac{5}{2}$	7								
$+\frac{7}{2}$	6								

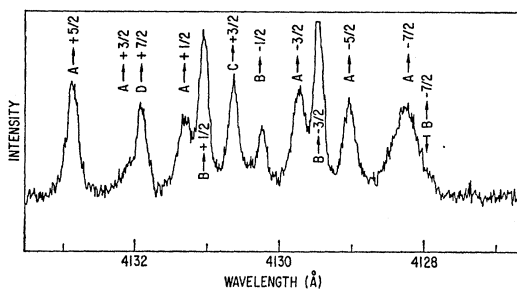


FIG. 5. Emission spectrum of $\text{CaF}_2:\text{Eu}^{2+}$ at 3.0°K ; propagation of the light near the $[110]$ direction, magnetic field 47.3 kG in the $[100]$ direction.

Jarrell-Ash monochromator equipped with an RCA 7265 phototube in the fourteenth order of the Harrison grating. The precision of the wavelength measurement is not as good as in the photographic technique used in absorption, so that $\bar{\lambda}$ in Table III has an estimated limit of error of $\pm 0.3\text{ cm}^{-1}$. For those lines observed in both emission and absorption, the linewidth is in good agreement (see Table I) and most of the additional lines are $\sim 0.8\text{ cm}^{-1}$ wide.

The selection rules in the presence of the magnetic field can be determined in the group appropriate to the reduced point symmetry by the use of Ref. 12. Since the excited levels were not all resolved when the field was in the $[111]$ direction, and because of the low-point symmetry when the field was in the $[411]$ direction, we limit discussion to the data taken with the field in the $[100]$ direction, which reduces the point symmetry to C_{4h} . The representations for the ground-state levels, in Table IV, are then given by column 1 and the selection rules by column 2. The data of Tables II and III then uniquely determine the upper state assignment with no violations. This assignment is given in Table IV, column 3, which is in agreement with Ref. 5.

When the temperature was lowered from 4.2 to 3.0°K , the emission lines originating on levels C and D became weaker relative to those originating on levels A and B, but not nearly so much as predicted for a Boltzmann distribution thermalizing in the excited state. (See Fig. 5.) This is true to an even greater degree in Fig. 3 of Ref. 5, where the spectrum is shown for $T = 1.7^\circ\text{K}$. The authors of Ref. 5 choose to interpret the weakening of the transitions from the higher-lying levels as evidence that the spin-lattice relaxation time is less than the lifetime of the excited state, so that thermalization is achieved. We believe that the deviations from the Boltzmann ratio are so striking that the

contrary is the case, and that the temperature dependence of these intensities is in fact due to "spin memory," i.e., the spin orientations, thermalized in the ground electronic state, survive to a considerable extent through the pumping process.²² This implies that the lower-lying ground states connect preferentially to the lower-lying excited states, which is quite reasonable since the lower-lying states in the magnetic field are those made up predominantly of low values of m_s . An EPR measurement of the excited state using optical detection²²⁻²⁶ seems promising for a definitive test,⁵ and such an experiment is under construction in our laboratory.

IV. DISCUSSION

The large g factor of ~ 3.8 is inexplicable if the Coulomb coupling between the $5d$ and the $(4f)^6$ electrons is ignored^{3,9} or if the crystal-field coupling is ignored.²⁷⁻²⁹ It therefore appears that both simple models are untenable, and agreement of the Faraday rotation with either of them^{9,27-29} is due to the insensitivity of this effect in the experimental region to the detailed nature of the energy levels. It appears that a calculation carried out along the lines of that of Ref. 8 will be necessary to yield further insight into the nature of this sharp level. Even though there are not enough identified levels to fit theory to experiment, the results with estimated parameters should be reliable enough to show whether any simplified view has reasonable validity.

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²² G. F. Imbusch and S. Geschwind, Phys. Rev. Letters **17**, 238 (1966).

²³ S. Geschwind, R. J. Collins, and A. L. Schawlow, Phys. Rev. Letters **3**, 245 (1959).

²⁴ S. Geschwind, G. E. Devlin, R. L. Cohen, and S. R. Chinn, Phys. Rev. **139**, A314 (1965).

²⁵ G. F. Imbusch and S. Geschwind, Phys. Letters **18**, 109 (1965).

²⁶ G. F. Imbusch, S. R. Chinn, and S. Geschwind, Phys. Rev. **161**, 295 (1967).

²⁷ Y. R. Shen, Phys. Rev. **133**, A511 (1964); **134**, A661 (1964).

²⁸ Y. R. Shen and N. Bloembergen, Phys. Rev. **133**, A515 (1964).

²⁹ J. C. Suits, B. E. Argyle, and M. J. Freiser, J. Appl. Phys. **27**, 1391 (1966).