

## Electron Paramagnetic Resonance of Europium (II) in Single Crystals of Cadmium Sulfide\*

PAUL B. DORAIN

*Brandeis University, Waltham, Massachusetts*

(Received July 5, 1960)

Paramagnetic resonance absorption measurements have been made with single crystals of cadmium sulfide containing europium (II). The results can be fitted to the usual spin-Hamiltonian for  $^8S$  state. The zero field splitting is about  $0.4 \text{ cm}^{-1}$ . A comparison of the results with present theories for the crystal field splittings of  $^8S$  is made.

### INTRODUCTION

PARAMAGNETIC resonance absorption spectra of manganese (II) in single crystals of cadmium sulfide and cadmium telluride have shown superhyperfine interaction of the 3d electrons with the nearest neighbor cadmium nuclei.<sup>1,2</sup> In a general effort to examine other paramagnetic impurities in CdS, we have observed the paramagnetic resonance of europium (II) in single crystals of cadmium sulfide. No superhyperfine interaction was found, but it is of interest to report the experimental results which may help to give a clearer insight into the nature of the mechanisms for the splitting of the configuration  $4f^7(^8S)$  by crystalline fields.

### THEORY SUMMARY

The ground state of Eu(II) which results from a  $4f^7$  configuration is  $^8S$ . The perturbation by an axial crystal field splits the  $^8S$  level into four doublets whose separation is usually quite small compared to the energies used in a typical electron paramagnetic resonance experiment.

Cadmium sulfide has a hexagonal crystal structure of the wurtzite type and has threefold and sixfold symmetry about the  $c$  axis. The most general Hamiltonian which may be used for a paramagnetic rare earth cation in such crystal is:

$$\mathcal{H} = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^3 O_4^3 + B_6^0 O_6^0 + B_6^3 O_6^3 + B_6^6 O_6^6, \quad (1)$$

where the  $O_l^m$  are operators which transform like  $Y_l^m$ , the spherical harmonics. Tables for these operators in which numerical constants are omitted are given by Stevens,<sup>3</sup> Elliott and Stevens,<sup>4</sup> Judd,<sup>5</sup> Baker, Bleaney, and Hayes,<sup>6</sup> and Jones, Baker, and Pope<sup>7</sup> for various values of  $l$  and  $m$ . The general procedure for obtaining the operators is given by Stevens. The coefficients,  $B_l^m$ ,

are determined from experiment. Following Bleaney *et al.*,<sup>8</sup> we define:

$$b_2^0 = 3B_2^0, b_4^0 = 60B_4^0, b_6^0 = 1260B_6^0, b_6^6 = 1260B_6^6.$$

For the case where  $H$  is parallel to the  $c$  axis of the crystal, we have the following levels if the contributions of the terms in  $B_4^3$ ,  $B_6^3$ , and  $B_6^6$  are neglected:

$$\begin{aligned} E_{\pm 7/2} &= \pm \frac{7}{2} g \beta H + 7b_2^0 + 7b_4^0 + b_6^0, \\ E_{\pm 5/2} &= \pm \frac{5}{2} g \beta H + b_2^0 - 13b_4^0 - 5b_6^0, \\ E_{\pm 3/2} &= \pm \frac{3}{2} g \beta H - b_2^0 - 3b_4^0 + 9b_6^0, \\ E_{\pm 1/2} &= \pm \frac{1}{2} g \beta H - 5b_2^0 + 9b_4^0 - 5b_6^0. \end{aligned} \quad (2)$$

Paramagnetic resonance is observed for the  $\Delta M = \pm 1$  transitions among these levels which give seven lines with an intensity ratio 7:12:15:16:15:12:7.

For the case where  $H$  is not parallel to the  $c$  axis, the spectrum becomes more complex. The usual technique is to transform the crystal field representation into the magnetic field representation because the magnetic field splittings are large compared to the crystal field splittings. The results become cumbersome and converge slowly except for  $g\beta H \gg b_2^0, b_4^0, b_6^0$ . In the present experiment, this condition is not fulfilled, and so the expressions will not be given.

The naturally abundant isotopes of europium are  $\text{Eu}^{151}$  and  $\text{Eu}^{153}$ . When one considers the interaction of the electron spin with the nuclear spin,  $I$ , the term  $H_n = A \mathbf{I} \cdot \mathbf{S}$  must be added to the Hamiltonian given in Eq. (1). The expression for the energy levels due to this additional term have been calculated to third order by Lacroix<sup>9</sup> for an isotopic value of  $A$ . If one uses the transition  $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$ , then the difference in energy between the  $m_I = -\frac{5}{2}$  and  $m_I = \frac{5}{2}$  transition is given by  $5A$ , if  $A$  is small.

### EXPERIMENTAL

All experiments were performed at 3.0 cm wavelength. The magnetic field was produced by a Varian 12-in. magnet and was measured with a proton resonance with water for the source of protons. The proton resonance frequency was counted with a Hewlett Packard 524B counter, which allowed one to put accurate field

\* This research was supported by the Aeronautical Research Laboratory, Air Research and Development Command.

<sup>1</sup> P. B. Dorain, *Phys. Rev.* **112**, 1058 (1958).

<sup>2</sup> J. Lambe and C. Kikuchi, *Bull. Am. Phys. Soc.* **5**, 158 (1960).

<sup>3</sup> K. W. H. Stevens, *Proc. Phys. Soc. (London)* **A65**, 209 (1952).

<sup>4</sup> R. J. Elliott and W. K. H. Stevens, *Proc. Roy. Soc. (London)* **A218**, 553 (1953).

<sup>5</sup> B. Judd, *Proc. Roy. Soc. (London)* **A227**, 552 (1955).

<sup>6</sup> J. M. Baker, B. Bleaney, and W. Hayes, *Proc. Roy. Soc. (London)* **A247**, 141 (1958).

<sup>7</sup> D. A. Jones, J. M. Baker, and D. F. D. Pope, *Proc. Roy. Soc. (London)* **A74**, 249 (1959).

<sup>8</sup> B. Bleaney, H. E. D. Scovil, and R. S. Trenam, *Proc. Roy. Soc. (London)* **A223**, 15 (1954).

<sup>9</sup> R. Lacroix, *Helv. Phys. Acta.* **30**, 374 (1957).

TABLE I. Hamiltonian parameters for Eu<sup>+2</sup> in various crystal lattices.

Crystal	Temp. °K	<i>g</i>	<i>A</i> <sup>151</sup> ×10 <sup>4</sup> cm <sup>-1</sup>	<i>A</i> <sup>153</sup> ×10 <sup>4</sup> cm <sup>-1</sup>	<i>b</i> <sub>2</sub> <sup>0</sup> ×10 <sup>4</sup> cm <sup>-1</sup>	<i>b</i> <sub>4</sub> <sup>0</sup> ×10 <sup>4</sup> cm <sup>-1</sup>	<i>b</i> <sub>6</sub> <sup>0</sup> ×10 <sup>4</sup> cm <sup>-1</sup>	Reference
CdS-Eu <sup>+2</sup>	295	1.992±0.001	23.03±0.10	10.32±0.10	342.9±0.5	11.9±0.1	-0.97±0.3	This paper
	77	1.992±0.001	22.50±0.10	10.04±0.10	336.6±0.5	11.6±0.1	-0.69±0.3	
SrCl <sub>2</sub> -Eu <sup>+2</sup>	R. T.	1.994±0.001	32.5	14.7				a
KCl-Eu <sup>+2</sup>	R. T.		32.56	14.38				b
CoF <sub>2</sub> -Eu <sup>+2</sup>	R. T.	1.989	34.5	15.4		57.9	0.5	c
SrS-Eu <sup>+2</sup>	R. T.	1.991	30.8	13.8				d
LaCl <sub>3</sub> -Eu <sup>+2</sup>	R. T.	2.0	38	17				e

Over-all splitting was 5220 gauss.

<sup>a</sup> W. Low, Phys. Rev. **101**, 1827 (1956); **116**, 621 (1959).<sup>b</sup> M. Abraham, R. W. Kedzic, and C. D. Jefferies, Phys. Rev. **108**, 58 (1957).<sup>c</sup> C. Rytter, Helv. Phys. Acta. **30**, 242 (1957); J. M. Baker, B. Bleaney, and W. Hayes, Proc. Roy. Soc. (London) **A247**, 141 (1958).<sup>d</sup> A. A. Manenkov, A. M. Prokhorov, P. S. Trukhlyayev, G. N. Vakovlev, Doklady Akad. Nauk. (U.S.S.R.) **112**, 623 (1957) [translation: Soviet Phys. (Doklady) **2**, 64 (1957)].<sup>e</sup> D. M. Gruen, J. G. Conway, and R. D. McLaughlin, J. Chem. Phys. **25**, 1102 (1956).

calibration markers on the chart recording of the electron paramagnetic resonance as the chart was being recorded. Linear interpolation between these field markers enabled the magnetic field to be determined with  $\pm 0.3$  gauss.

The electron resonance was detected by modulating at a frequency of 100 kc/sec the magnetic field to a depth small compared to the width of the resonance. The microwave signal was then amplified in a broadly tuned amplifier with a gain of about  $10^5$ . The resultant signal was phase sensitively detected using a 6AR8 beam switching tube which gives an additional gain of about 100. The resulting derivative signal of the absorption was observed visually on an oscilloscope or recorded with a strip chart recorder.

The cavity was a rectangular transmission cavity operating in the TE<sub>102</sub> mode which was coaxially fed.

The microwave frequency was measured using a Hewlett Packard X532A wavemeter and was checked against a residual hydrazyl signal.

The CdS-Eu crystal was grown from the vapor phase by the method given by Greene *et al.*<sup>10</sup> The europium (II) was incorporated in the CdS powder by adding EuSO<sub>4</sub> in the desired amount and mixing in a ball mill for several days. The single crystals which were grown from the vapor at a temperature of about 1100°C contained 0.1-mole percent Eu and were very dark, low conductivity crystals. The dark color seems to be characteristic of even very low concentrations of Eu<sup>+2</sup>.

The *c* axis of the crystal used in the experiment was determined by cleaving the crystal along two intersecting planes, the intersection of which is the *c* axis. This orientation was checked by taking a Laue x-ray photograph as the crystal was rotated about this axis, and comparing the result with the Laue pattern of a known oriented single crystal of pure CdS.

#### EXPERIMENTAL RESULTS

Resonance was observed at 77°K and 295°K at a frequency of about 9500 Mc/sec. When the *c* axis is parallel to the magnetic field, the parameters *g*, *b*<sub>2</sub><sup>0</sup>, *b*<sub>4</sub><sup>0</sup>, and *b*<sub>6</sub><sup>0</sup> may be determined by using Eq. (2). If the values

of *b*<sub>2</sub><sup>0</sup>, *b*<sub>4</sub><sup>0</sup>, and *b*<sub>6</sub><sup>0</sup> are calculated from the spacings between corresponding lines on either side of the  $M = -\frac{1}{2} \rightarrow \frac{1}{2}$  transition, then higher order effects from the terms such as *b*<sub>4</sub><sup>3</sup> are eliminated. The values of *b*<sub>2</sub><sup>0</sup>, *b*<sub>4</sub><sup>0</sup>, and *b*<sub>6</sub><sup>0</sup> are given in Table I.

The value of *A* was calculated from the transition  $M = -\frac{1}{2} \rightarrow \frac{1}{2}$ . The width of the lines was six gauss so that it was possible to measure directly the separation 5*A* from the spacings of the extreme lines to each isotope.

The sign of the parameters was determined from the resonance at 4°K with the *c* axis parallel to the magnetic field. The  $M = -\frac{7}{2} \rightarrow -\frac{5}{2}$  transition will occur at low magnetic fields and will be most intense if *b*<sub>2</sub><sup>0</sup> is positive. There were some saturation effects noticed at this temperature. It was not possible to determine the sign of *A* because the second order effects are small and are overpowered by broadening of the lines for transitions other than  $M = -\frac{1}{2} \rightarrow \frac{1}{2}$ .

#### DISCUSSION OF RESULTS

Table I gives several experimental results of Eu<sup>+2</sup> in various host lattices. The hyperfine parameters for Eu, CdS are about 25% less than those reported for more ionic crystals. This effect is explained by allowing the wave function to be spread out more in a covalent lattice than in an ionic lattice. The average value of  $r^{-3}$  is decreased which reduces the parameter *A*.

The mechanisms which have been proposed for the crystal field splitting for the configuration (4*f*<sup>7</sup>, <sup>8</sup>S) of Gd<sup>+3</sup> have been reviewed by Hutchison, *et al.*<sup>11</sup> They find that the mechanism which contributes most to the term *b*<sub>2</sub><sup>0</sup> in the spin-Hamiltonian may be schematically represented by:

$$\langle {}^8S_{7/2} | \Lambda | {}^6P_{7/2} \rangle \langle {}^6P_{7/2} | V | {}^6X_J \rangle \\ \times \langle {}^6X_J | V | {}^6P_{7/2} \rangle \langle {}^6P_{7/2} | \Lambda | {}^8S_{7/2} \rangle, \quad (\text{A})$$

where  $\Lambda$ , the spin-orbit interaction, couples the *S* state to a *P* state which, in turn, is coupled via the crystalline field to higher states, <sup>6</sup>X<sub>J</sub>. The splitting of the *P* state affects the splitting of the ground *S* state. This mechan-

<sup>10</sup> L. C. Greene, D. C. Reynolds, S. J. Cryzak, and W. M. Baker, I. Chem. Phys. **29**, 1375 (1958).

<sup>11</sup> C. A. Hutchison, Jr., B. R. Judd, and D. F. D. Pope, Proc. Phys. Soc. (London) **B70**, 514 (1957).

ism leads only to the term,  $b_2^0$ , in the spin-Hamiltonian. Since it has been found that the sixth-order terms in the potential are much larger than the others for rare earth ions, the size of  $b_2^0$  will be determined chiefly by these sixth-order terms. Hutchison used the temperature dependence of  $b_2^0$  as a test of the consistency of the theory. Since mechanism *A* is quadratic in  $V$ , and  $V$  varies as the inverse seventh root of the lattice spacings, the splitting should vary by the inverse fourteenth power of the lattice spacings. This effect gives rise to an increase in  $b_2^0$  of 10% in going from room temperature to liquid nitrogen temperature. The results for CdS-Eu show a small decrease of 1%. It appears that mechanism *A* is not a predominate factor in the term  $b_2^0$ .

A second mechanism described by Hutchison is represented schematically by

$$\langle {}^8S_{7/2} | \Lambda | {}^6P_{7/2} \rangle \langle {}^6P_{7/2} | \Lambda | {}^6D_{7/2} \rangle \\ \times \langle {}^6D_{7/2} | V | {}^6P_{7/2} \rangle \langle {}^6P_{7/2} | \Lambda | {}^8S_{7/2} \rangle, \quad (B)$$

where the only contribution to  $V$  is from  $A_2^0 \langle r^2 \rangle$ . The contribution from this mechanism may be shown to be

$$-12\zeta^3 A_2^0 \langle r^2 \rangle / 5W_p^2 W_D, \quad (3)$$

where  $W_p$  and  $W_D$  are the energies of  ${}^6P_{7/2}$  relative to  ${}^8S_{7/2}$ , and  $\zeta$  is the spin orbit coupling constant. The sign of  $A_2^0 \langle r^2 \rangle$  is very dependent upon the charge distribution of the ions around the cation. For a wurtzite type crystal, it should be negative, and Eq. (3) gives a positive contribution to  $b_2^0$ . In addition, the effect of temperature should be small, because  $A_2^0$  depends on the inverse third power of the lattice spacings. Therefore, Eq. (5) may be an important contribution to  $b_2^0$ .

A third mechanism proposed is represented by:

$$\langle 4f^7, {}^8S_{7/2} | V_{ss} | 4f^6 6p, {}^8D_{7/2} \rangle \\ \langle 4f^6 6p, {}^8D_{7/2} | V | 4f^7, {}^8S_{7/2} \rangle. \quad (C)$$

This mechanism leads only to  $b_2^0$  through  $A_2^0 \langle r^2 \rangle$  and is linear in the crystalline field.

The optical spectra of  $\text{Eu}^{+2}$  in various crystal lattices<sup>12</sup> is unlike that of  $\text{Gd}^{+3}$  in that, in addition to the narrow lines characteristic of transitions among  $4f$  levels, there are several broad bands which show interaction with the lattice vibration. Freed and Katcoff<sup>13</sup> have ascribed

these bands to transitions of the type  $4f^n \rightarrow 4f^{n-1}5p$ . It is reasoned that these transitions are very probable because the most stable oxidation state is +3 for the lanthanide ions. It appears that mechanism (C) is an important factor in the size of  $b_2^0$ , but the difficulty of the calculation prevents an estimate of this contribution to  $b_2^0$  at the present time.

Initially the experiment was done to see if the  $4f$  electrons in  $\text{Eu}^{+2}$  would show a superhyperfine interaction with the next nearest neighbor cadmium ions. Such an effect has been reported for CdS-Mn and CdTe-Mn<sup>1,2</sup> where, for both crystals, the interaction constant is 1.4 gauss. The value, 0.82 gauss, reported by Dorian is in error. Both  $\text{Mn}^{+2}$ ,  $3d^5$ , and  $\text{Eu}^{+2}$ ,  $4f^7$ , are S-state ions. It was expected that if a superhyperfine interaction were observed, it would be considerably smaller than that observed for  $\text{Mn}^{+2}$  because the wavefunctions for  $f$  electrons do not have a large spacial extension. No superhyperfine interaction was observed. The width for  $\text{Eu}^{+2}$  in CdS was 6 gauss for the  $\Delta M = -\frac{1}{2} \rightarrow \frac{1}{2}$  transition with a modulation depth of the magnetic field of less than 0.1 gauss. The minimum width observed for  $\text{Eu}^{+2}$  in other crystals is about 2 gauss. It appears, therefore, that no superhyperfine interaction was observed because (1) the superhyperfine interaction constant is small compared to that of  $\text{Mn}^{+2}$  and (2) the natural line width of  $\text{Eu}^{+2}$  is too large.

## CONCLUSIONS

The positions of the paramagnetic resonance lines of  $\text{Eu}^{+2}$  in a CdS single crystal can be described by the usual spin Hamiltonian. Of the crystal field parameters, the  $b_2^0$  term is the largest as is found for  $\text{Gd}^{+3}$  in other lattices. It was not possible to obtain the  $b_4^3$ ,  $b_6^3$ , and  $b_6^6$  terms in the usual manner because of this large term in  $b_2^0$ . Tentative conclusions from the results indicate that there is appreciable contribution to the  $b_2^0$  term from higher states coupled to the ground state via spin-spin interaction and second order crystal field terms. It appears that additional theoretical analysis must be done before further conclusions can be made regarding the splitting of S-state ions in predominantly covalent semiconductor lattices.

## ACKNOWLEDGMENT

It is a pleasure to thank Professor S. Czyzak of the University of Detroit for the crystals used in this experiment.

<sup>12</sup> W. A. Runcimann, *Reports on Progress in Physics* (The Physical Society, London, 1956), Vol. 21, p. 51, 52.

<sup>13</sup> S. Freed and S. Katcoff, *Physica* 14, 17 (1948).