

Paramagnetic Resonance Spectra of Eu^{++} in CdSe and CdTe

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The paramagnetic resonance spectra of Eu^{++} in the semiconducting compounds CdSe and CdTe have been measured at 77°K. The results obtained are compared with those obtained by Dorain for Eu^{++} in CdS and with results for Eu^{++} in other crystals. The parameters describing the spectrum are found to be much less sensitive to changes in covalent bonding than are the parameters describing the behavior of the $3d^5$ configuration of Mn^{++} in these compounds. The variations in the parameters for Eu^{++} from compound to compound are compared with existing theories for the variations.

INTRODUCTION

THERE have been very few paramagnetic resonance spectra of rare-earth ions reported in semiconducting crystals. Dorain has observed Eu^{++} in CdS.¹ A resonance attributed to Gd^{3+} in ZnS powders has since been shown to be due to Cr^{+} .²

In this paper paramagnetic resonance measurements of Eu^{++} in CdSe and CdTe are reported. These are the smallest band gap materials, 1.8 and 1.5 eV, respectively, in which a rare-earth ion resonance has been observed. One of the purposes in undertaking this study was to see whether there was any lattice distortion resulting from substituting a Eu^{++} ion of ionic radius 1.2 Å for the Cd^{++} ion whose radius is 1.02 Å.³ Distortions of Mn^{++} -doped zincblende and wurtzite lattices have been postulated to explain paramagnetic resonance measurements in compounds where the Mn^{++} ion substitutes for the smaller Zn^{++} ion.⁴ In the Al_2O_3 lattice, Geschwind and Remeika have been able to substitute Gd^{3+} for Al^{3+} where there is almost a 2 to 1 ratio in ionic size.⁵ Their resonance results indicated that there was a local lattice distortion at the Gd^{3+} site in Al_2O_3 .

Information concerning the crystalline field and any lattice distortions may in principle be derived from the fine structure splitting of the Eu^{++} spectrum. There is, however, some uncertainty in how the spin Hamiltonian parameters characterizing the fine-structure splitting are related to the crystalline-field potential. The ground state ${}^8\text{S}_{7/2}$ of the $4f^7$ electronic configuration of Eu^{++} (or Gd^{3+}) is to first order unaffected by the crystalline field. The splitting of this state comes about through higher order perturbations, the nature of which depends on the spin-orbit coupling and spin-spin coupling as well as on the symmetry and magnitude of the crystalline-field potential at the Eu^{++} site.⁶ The situation is

analogous to the ${}^6\text{S}_{5/2}$ state of the $3d^5$ configuration of Mn^{++} . However, because of the different configurations, the nature of the higher order perturbations will be different in the two cases. Following the theoretical work of Watanabe,⁷ and of Gabriel, Johnston, and Powell,⁸ the fine-structure splitting of the ground state of Mn^{++} in a cubic field is well understood. However, for Mn^{++} in fields of lower symmetry than cubic the dependence of the fine-structure splitting on the crystalline-field potential is, at the present time, not completely understood.⁹ The relation between the spin Hamiltonian parameters describing the fine-structure splitting of Eu^{++} and the crystalline-field potential has not been as fully investigated either theoretically or experimentally as has the case of Mn^{++} . As a result, crystalline-field effects on the Eu^{++} spectrum are, at best, only qualitatively understood at the present time.

For Eu^{++} in a site of cubic symmetry, the perturbations that can lead to splitting of the ground state have been summarized by Lacroix.¹⁰ He finds that the perturbations involving excited states of the $4f^7$ configuration are too small to account for the observed splittings. Excited states involving the $4f^65f$ and $4f^55d^2$ configurations must be used. These perturbations are linear in the crystalline-field potential. The observed splittings of the ground state of Gd^{3+} in several fluorite lattices are indeed found to be more nearly linear rather than quadratic in the crystalline field.¹¹ The agreement is qualitative. Calculations on the basis of a point-charge model show significant departures from a quantitative agreement with a linear dependence.

The higher order perturbations that can lead to splitting of Eu^{++} in a field of trigonal symmetry have been summarized by Hutchinson, Judd, and Pope.¹² Some of these are linear, and others quadratic in the

¹ P. B. Dorain, *Phys. Rev.* **120**, 1190 (1960).

² R. S. Title, *Phys. Rev. Letters* **4**, 502 (1960); J. Dieleman, R. S. Title, and W. V. Smith, *Phys. Letters* **1**, 334 (1962).

³ V. M. Goldschmitt, *Trans. Faraday Soc.* **25**, 253 (1929).

⁴ C. Kikuchi and G. H. Azarbayejani, *J. Phys. Soc. Japan* **17** Suppl. **B1**, 453 (1962); R. S. Title, *Phys. Rev.* **131**, 2503 (1963).

⁵ S. Geschwind and J. P. Remeika, *Phys. Rev.* **122**, 757 (1961).

⁶ J. H. Van Vleck and W. G. Penney, *Phil. Mag.* **17**, 961 (1934); R. Lacroix, *Helv. Phys. Acta.* **30**, 374 (1957).

⁷ H. Watanabe, *Progr. Theoret. Phys. (Kyoto)* **18**, 405 (1957).

⁸ J. R. Gabriel, D. F. Johnston, and M. J. D. Powell, *Proc. Roy. Soc. (London)* **A264**, 503 (1961).

⁹ W. J. Nicholson and G. Burns, *Phys. Rev.* **129**, 2490 (1963); A. M. Germanier, D. Gainon, and R. Lacroix, *Phys. Letters* **2**, 105 (1962).

¹⁰ R. Lacroix, *Proc. Phys. Soc. (London)* **77**, 550 (1961). *Helv. Phys. Acta.* **30**, 374 (1957).

¹¹ J. Sierro, *Phys. Letters* **4**, 178 (1963).

¹² C. A. Hutchinson, Jr., B. R. Judd, and D. F. D. Pope, *Proc. Phys. Soc. (London)* **B70**, 514 (1957).

crystalline field potential. The results obtained by Hutchinson *et al.*¹² for Gd^{3+} in diluted GdCl_3 led them to conclude that the dominant parameter in the fine-structure splitting b_2^0 depends primarily on the square of the crystalline-field potential in the case of GdCl_3 . Experiments carried out by others on Gd^{3+} and Eu^{++} in various crystals indicate that a linear dependence of b_2^0 on crystalline-field potential may be more important in some cases.^{1,13} Since in both cubic and trigonal symmetry the nature of the dependence of the spin Hamiltonian parameters on the crystalline-field potential is not completely understood, any information about the crystalline field derived from these parameters, such as lattice distortions, must be considered as merely qualitative at the present time.

A comparison is made of the results obtained in this paper for Eu^{++} in CdSe and DdTe with those obtained by Dorain for Eu^{++} in CdS .¹ Both the spin Hamiltonian parameters and the hyperfine structure parameters for Eu^{151} and Eu^{153} are found to be much less sensitive to changes in the covalent bonding than in the case of the $3d^5$ configuration of Mn^{++} in these compounds.¹⁴ This is not too surprising since the $4f^7$ configuration is in an inner shell of electrons and would be less affected by changes in the character of the bonding than the outer $3d^5$ configuration of Mn^{++} .

The values of the spin Hamiltonian parameters obtained point out the difficulty in relating these parameters to the crystalline-field potential, and as a result no information about lattice distortions is derivable from the results.

EXPERIMENTAL

The crystals used in this study were grown by J. A. Kucza. The CdSe crystals were vapor grown and the CdTe crystals were grown from the melt. Europium was added as EuSe in the case of CdSe , and as the metal in the growth of the CdTe crystals. The CdSe crystals were easily cleaved along (1010) planes and CdTe crystals along (110) planes. This simplified the alignment of the crystals. Experiments were carried out at 77 and 4.2°K. The spectra were also observable at room temperature. However, the linewidths at room temperature were too broad to resolve completely the hyperfine structure lines of Eu^{151} and Eu^{153} .

THE THEORY OF THE SPECTRUM

The spin Hamiltonians appropriate for Eu^{++} in the C_{4v} symmetry of CdSe , and the T_d^2 symmetry of CdTe have been previously given in the literature.^{1,15} Since several notations have been used, the Hamiltonians are repeated here to establish the notation being used.

For the C_{4v} symmetry of CdSe ,

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

For economy in notation the following substitutions are usually used:

$$\begin{aligned} b_2^0 &= 3 B_2^0 & b_4^0 &= 60 B_4^0 & b_6^0 &= 1260 B_6^0 \\ b_4^3 &= 3 B_4^3 & b_6^3 &= 36 B_6^3 & b_6^6 &= 1260 B_6^6. \end{aligned} \quad (1a)$$

In these expressions the parameters b_n^m should be regarded as parameters which express the fine-structure splitting of the spectrum. As stated in the Introduction, the exact relation between these parameters and the crystalline-field potential is yet to be established. The expressions for the transitions between the levels resulting from the Hamiltonian of Eq. (1) acting on the $^8S_{7/2}$ state of Eu^{++} have been given by Low and Zusman¹⁶ for the magnetic field both parallel and perpendicular to the c axis.

For the cubic T_d^2 symmetry of CdTe , the appropriate Hamiltonian is given by

$$H = g\beta\mathbf{H}\cdot\mathbf{S} + B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4), \quad (2)$$

where the following substitutions are usually made:

$$b_4 = 60 B_4 \quad \text{and} \quad b_6 = 1260 B_6.$$

The splitting of the $^8S_{7/2}$ state resulting from the Hamiltonian of Eq. (2) has been given by Lacroix¹⁰ in a different notation. (For the above notation see Ref. 15.) The equations for use at constant frequency and variable magnetic field are wrong as far as sign is concerned for the $\pm 5/2 \leftrightarrow \pm 3/2$ and $\pm 7/2 \leftrightarrow \pm 5/2$ transitions as given by Low.¹⁷ Use of these equations would lead to errors in the signs of the parameters.

The terms to be added to the above transitions because of the hyperfine interaction with Eu^{151} and Eu^{153} have been given by Lacroix,¹⁰ correct to terms of third order.

THE RESULTS

CdSe

From measurements made with the magnetic field \mathbf{H} parallel to the c axis, the spin Hamiltonian parameters b_2^0 , b_4^0 , and b_6^0 , and the hyperfine structure parameters A^{151} and A^{153} may be determined both in magnitude and in relative sign. In addition, terms of second order may be used to obtain $|b_4^3|$.⁵ The parameter $|b_6^6|$ is determined from measurements made with the magnetic field perpendicular to the c axis.⁵ The terms in b_6^6 in the

¹⁶ W. Low and A. Zusman, Phys. Rev. **130**, 144 (1963).

¹⁷ W. Low, *Paramagnetic Resonance in Solids* (Academic Press Inc., New York, 1960), p. 115, Eq. (19.4); W. Low, Phys. Rev. **109**, 265 (1958). Care must be exercised in use of Eq. (5) in this reference for although it appears to be similar in form to the equations for use at constant frequency and variable field, it is, as written, valid only for the case of constant field H_0 and variable frequency.

¹³ M. Weger and W. Low, Phys. Rev. **111**, 1526 (1958).

¹⁴ R. S. Title, Phys. Rev. **130**, 17 (1963).

¹⁵ J. M. Baker, B. Bleaney, and W. Hayes, Proc. Roy. Soc. (London) **A247**, 141 (1958).

TABLE I. The paramagnetic data (all except g are in units of 10^{-4} cm^{-1}) for Eu^{++} in CdSe and CdS at 77°K .

	g	A^{151}	A^{153}	b_2^0	b_4^0	b_6^0	$ b_2^3 $	$ b_6^3 $
CdSe	1.9893 ± 0.0007	-23.19 ± 0.13	-10.22 ± 0.07	$+239.7 \pm 2.0$	-2.75 ± 0.09	$+0.24 \pm 0.09$	11.7 ± 5.0	2.4 ± 1.0
CdS	1.992 ± 0.001	22.50 ± 0.10^a	10.04 ± 0.10^a	-336.6 ± 0.5	-11.6 ± 0.1	$+0.69 \pm 0.3$

^a Absolute value.

Hamiltonian of Eq. (1) causes a cosine variation in the fine structure lines in this direction with a period of 60 deg .¹⁸

The results obtained at 77°K are given in Table I where, for comparison, the results of Dorain for Eu^{++} in CdS¹ are also included. The absolute signs given in the table are found by measuring the relative intensities of the fine structure lines at liquid helium temperatures. The levels with negative quantum numbers will be more fully occupied at liquid helium temperatures and the transitions involving these levels will be more intense.¹⁸ The signs for the parameters for Eu^{++} in CdS in Table I are opposite to that which Dorain reports. His observation that with \mathbf{H} parallel to the c axis, the fine structure lines at low magnetic fields were more intense implies that b_2^0 is negative^{5,12} and not positive as he reports.

In the case of Eu^{++} in CdSe, it was found that the fine structure lines at high magnetic fields were more intense at 4.2°K with \mathbf{H} parallel to the c axis, indicating that b_2^0 is positive in this case. Since the position of the lines at 77°K had indicated that A^{151} , A^{153} , and b_4^0 had opposite signs to b_2^0 , these quantities are all negative.

The sign of b_2^0 for Eu^{++} in CdS is opposite to that of Eu^{++} in CdSe, whereas b_4^0 is negative in both crystals.

The negative sign found for the hyperfine parameters A^{151} and A^{153} in CdSe agrees with the only previous sign determination, that by Blumberg and Eisinger for Eu^{++} in CaF_2 .¹⁹

At liquid helium temperatures, the hyperfine parameters of Eu^{151} and Eu^{153} in CdSe were found to be of the same magnitude as at 77°K , within experimental error, as was the parameter b_4^0 . The parameter b_2^0 increased by about 2% to $243.5 \pm 2.0 \times 10^{-4} \text{ cm}^{-1}$ and b_6^0 increased to $0.62 \pm 0.2 \times 10^{-4} \text{ cm}^{-1}$.

CdTe

The parameters obtained at 77°K are given in Table II. These were derived from observations of the variation of the spectrum in the (110) plane. The signs

TABLE II. The paramagnetic data (all except g are in units of 10^{-4} cm^{-1}) for Eu^{++} in CdTe at 77°K .

g	A^{151}	A^{153}	b_4	b_6
1.9917 ± 0.0007	-23.19 ± 0.15	-10.25 ± 0.10	-7.66 ± 0.10	-0.12 ± 0.14

¹⁸ B. Bleaney, H. E. D. Scovil, and R. S. Trenam, Proc. Roy. Soc. (London) A223, 15 (1954).

¹⁹ W. E. Blumberg and J. Eisinger, Bull. Am. Phys. Soc. 6, 141 (1961).

of the fine structure parameters b_m and the hyperfine parameters A^{151} and A^{153} were determined to be the same. The sign was fixed as negative by noting that at 4.2°K with the magnetic field parallel to the [001] direction, the $-7/2 \leftrightarrow -5/2$ transition occurs at low magnetic fields. The negative signs found for the A values agree with the negative signs found for A^{151} and A^{153} in CdSe and CaF_2 .

In both CdSe and CdTe a satellite structure was observed in the hyperfine lines in the $1/2 \leftrightarrow -1/2$ transition at 4.2°K . In CdSe the structure was visible at 77°K . The structure was incompletely resolved and was not analyzed.

DISCUSSION OF THE RESULTS

The g Values

The g values for Eu^{++} in CdSe and CdTe are less than the free-electron value of 2.0023 and fall in the range of 1.989–1.995 that has been reported for Eu^{++} and Gd^{+++} in other crystals. The departure from the free-electron value has been attributed to a partial breakdown of Russell-Saunders coupling which will cause a small admixture of the first excited state ${}^6P_{7/2}$ into the ground state ${}^8S_{7/2}$.¹⁵ The g value is given by $g = (1 - \alpha^2)g({}^8S_{7/2}) + \alpha^2g({}^6P_{7/2})$, where α is the amount of admixed ${}^6P_{7/2}$ state in the ground state and is given by

$$\alpha = \frac{(14)^{1/2}\lambda}{E_p - E_s},$$

where λ is the spin orbit coupling and $E_p - E_s$ is separation of the ${}^6P_{7/2}$ state from the ${}^8S_{7/2}$ state. The fact that the g values for Eu^{++} in CdSe and CdTe fall in the range measured for other crystals indicates that the separation of the ${}^6P_{7/2}$ state from the ${}^8S_{7/2}$ is unaltered in CdSe and CdTe, and is equal to $\sim 32\,000 \text{ cm}^{-1}$ or 4 eV. One would therefore not expect, and one does not see, the optical spectrum of Eu^{++} in these crystals, since the lattice with a band gap of 1.8 eV for CdSe and 1.5 eV for CdTe would itself absorb any exciting light.

The A Values

A^{151} and A^{153} are negative both in CdSe and CdTe, in agreement with the results of Blumberg and Eisinger for Eu^{++} in CaF_2 .¹⁹ Watson and Freeman have suggested that the hyperfine interaction for the ${}^8S_{7/2}$ ground state of Eu^{++} arises chiefly from a spin polariza-

TABLE III. Hyperfine structure parameters A in units of 10^{-4} cm^{-1} for Eu^{++} and Mn^{55} in the three cadmium compounds and in three fluorite lattices.

Crystal	Eu^{151}	Eu^{153}	Mn^{55}	Reference
CdS	(-) 22.50	(-) 10.04	-66.0	1, a
CdSe	-23.19	-10.22	-62.2	this paper, 14
CdTe	-23.19	-10.25	-57.5	this paper, b
CaF_2	-34.5	-15.3	-97.8	15
SrF_2	-34.0	-15.2	-93	c, 24
SrCl_2	(-) 34.5	(-) 15.5	-81.2	25

^a See Ref. 26.

^b J. Lambe and C. Kikuchi, Phys. Rev. **119**, 1256 (1960).

^c R. S. Title, Phys. Letters **6**, 13 (1963).

tion of the ns^2 configurations by the $4f^7$ configuration.²⁰ One would, therefore, not expect that the sign of this interaction would vary from crystal to crystal if spin polarization is the main contribution to the magnetic field at the nucleus. There is a contribution due to the admixed ${}^6P_{7/2}$ state; however, this contribution is comparatively small.¹⁵

To facilitate comparison of the hyperfine results, Table III has been constructed. In the table the results for the three cadmium compounds and also for three fluorite lattices are included. The A value for Mn^{55} in these lattices is also given in the table. An examination of the europium results shows that within each group, either the zincblende and wurtzite lattices of the cadmium compounds or the fluorite lattices of the second half of the table, the A values of each isotope of europium agree with each other within 3%. However, the results for the zincblende and wurtzite lattices are about 33% lower than those in the fluorite lattices. This is to be contrasted with the A values for Mn^{55} which are also some 33% lower in the zincblende and wurtzite lattices, but which show significant variation within each group itself. In the zincblende and wurtzite group, the magnitude of A of Mn^{55} decreases by 13% in going from CdS to CdTe, and in the fluorite lattices decreases by 17% in going from CaF_2 to SrCl_2 . In the case of Mn^{55} , both the changes within each group and the 33% change between the two groups has been attributed to changes in the degree of covalent bonding with neighboring anions.^{21,22} The wave function of the $3d^5$ configuration will spread out when the bonding is more covalent. This leads to a smaller exchange interaction with the ns^2 core electrons, and since this is the mechanism that gives rise to the magnetic field at the nucleus of Mn^{55} , a smaller hyperfine interaction is observed when the bonding is more covalent. In the fluorite lattice Cl anions are more covalently bonded than F ions, and this accounts for the lower A value for Mn^{55} in SrCl_2 as compared to SrF_2 . Similarly, in the cadmium compounds the Te ion is associated with the

more covalent bond and has the smaller A value. A similar mechanism has been suggested to account for changes in the Eu^{151} and Eu^{153} A values in going from lattice to lattice.^{1,15,20,23} However, as an examination of Table III reveals, there is some difficulty in applying this concept to the europium results. There is, in contrast to Mn, very little variation with changes in covalent bonding within a specific lattice type. However, there is as much variation in the Eu A values as for Mn^{55} in going from the fluorite to the zincblende and wurtzite lattices. In addition, if, following Watson and Freeman,²⁰ one attributes the hyperfine interaction to a spin polarization of the ns^2 core electrons by the $4f^7$ configuration, then one would have to postulate that core electrons are themselves affected by changes in the covalent bonding, since the $4f^7$ configuration is itself an inner shell configuration. This seems unlikely. There is, however, the possibility that only the outermost $5s^25p^6$ electron shells are affected by changes in covalent bonding and it is the exchange interaction of the $4f^7$ configuration with this shell that leads to changes in the Eu A values with covalent bonding. One would further have to postulate that the effect of an increase in covalent bonding on the $5s^25p^6$ shell is not appreciable within a particular lattice type, but varies considerably when the lattice type is changed. In the absence of detailed calculations of the spin polarization of core electrons for rare-earth ions,²⁰ no definite conclusions can be drawn. The problem does not arise for the $3d^5$ configuration of Mn^{55} since it itself is the outermost shell of electrons (next to the valence electrons).

The b_n^m Parameters

Comparison of the parameters b_n^m obtained for the three cadmium compounds will be made by comparing first the results for the two wurtzite crystals CdS and CdSe. The parameters b_4^0 and b_6^0 in these crystals cannot be directly compared with b_4 and b_6 of CdTe since b_4^0 and b_6^0 may contain contributions from the noncubic parts of the field. In the case of the fluorite lattices Gd^{3+} has been seen in both cubic and noncubic symmetries in the same crystal.²⁴ In some of the cases $b_4^0 \sim b_4$, but usually b_4^0 differs from b_4 , indicating a significant noncubic contribution to b_4^0 .

An examination of the results for the wurtzite crystals shows that b_2^0 changes sign from negative to positive in going from CdS to CdSe. As stated in the Introduction, Hutchinson, Judd, and Pope showed that contributions to the parameter b_2^0 may come from terms both linear and quadratic in the crystalline field potential.¹² In addition, the linear term is proportional to $1/R^3$, where R is the separation of the charge on the impurity from that on the neighboring anions, whereas the quadratic term involving chiefly terms of sixth

²⁰ R. E. Watson and A. J. Freeman, Phys. Rev. **127**, 2058 (1962); Phys. Rev. Letters **6**, 277 (1961).

²¹ O. Matumura, J. Phys. Soc. Japan **14**, 108 (1959).

²² J. S. Van Wieringen, Discussions Faraday Soc. **19**, 118 (1955).

²³ A. J. Shushkus, Phys. Rev. **127**, 2022 (1962).

²⁴ J. Sierro, Phys. Letters **4**, 178 (1963); J. M. Baker and F. I. B. Williams, Proc. Phys. Soc. (London) **78**, 1340 (1961).

order in the crystalline field potential would be expected to vary as $1/R^{14}$.¹² A change in sign in b_2^0 in going from CdS to CdSe can come about as a result of nearly equal but opposite in sign linear and quadratic contributions. Since these have different dependences on R , a decrease in lattice size in going from CdSe to CdS could cause the quadratic term to be dominant in CdS. The results indicate that the linear contribution would have to be positive. One of the linear contributions suggested by Hutchinson *et al.*¹² is given by

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

where ζ is the spin-orbit coupling constant, $A_2^0 \langle r^2 \rangle$ is the radial factor in the second-order term of the crystalline-field potential and proportional to $1/R^3$, and W_P and W_D are the energies of the ${}^6P_{7/2}$ and ${}^6D_{7/2}$ levels, relative to the ${}^8S_{7/2}$ ground state. Since $A_2^0 \langle r^2 \rangle$ is expected to be negative for the wurtzite lattice, the contribution of (3) will in fact be positive. To account quantitatively for the results obtained in CdS and CdSe, the factor $A_2^0 \langle r^2 \rangle$ would have to be of the order of $450 \times 10^{-4} \text{ cm}^{-1}$, which is about three times larger than the value of $A_2^0 \langle r^2 \rangle$ found in the double nitrates and trichlorides.¹² The value of $A_2^0 \langle r^2 \rangle$ is very sensitive to charge distribution²⁵ and its high value may possibly reflect an increase in covalent bonding in CdS and CdSe.

It is rather interesting to note that the axial field parameter $D(=b_2^0)$ for Mn⁵⁵ also changes sign from $-130.7 \times 10^{-4} \text{ cm}^{-1}$ in ZnS²⁶ to $+15.2 \times 10^{-4} \text{ cm}^{-1}$ in CdSe.¹⁴

A comparison of the parameters b_4^0 and b_6^0 between CdS and CdSe would require a separation of the cubic and noncubic contributions to these parameters. The parameter b_4^0 is negative in both CdS and CdSe as is b_4

in CdTe. The sign of b_4 would be expected to be the same in the zincblende lattice as in the fluorite lattice. For Eu⁺⁺ in CaF₂ it had been found¹⁵ that b_4 has the same sign as A^{151} and A^{153} which Blumberg and Eisinger had found to be negative.¹⁹ Low had reported b_4 for Gd³⁺ in CaF₂ as positive,¹⁷ which on the basis of the linear dependence of b_4 on crystalline-field potential¹⁰ is inconsistent with the above results. A check made on a Gd³⁺-doped CaF₂ crystal revealed that at liquid helium temperatures with \mathbf{H} parallel to the $[001]$ direction, the $-7/2 \leftrightarrow -5/2$ transition occurs at low magnetic fields and, hence, b_4 is in fact negative and not positive as Low reported.¹⁷

The magnitude of b_4 obtained for Eu⁺⁺ in CdTe may be compared to the results for b_4 for Eu⁺⁺ in CaF₂ and SrCl₂,^{15,27} on the basis of a point-charge model and a linear dependence of b_4 on crystalline-field potential. The value of $b_4 = -7.66 \times 10^{-4} \text{ cm}^{-1}$ in CdTe is a little lower than one would expect on a linear dependence, but considerably larger than would be expected from a quadratic dependence of b_4 on crystalline-field potential. The reasonably good agreement with a linear dependence on the potential would indicate that the parameter b_4 is relatively insensitive to the effects of covalent bonding. This is in contrast to the parameter $a(=2b_4)$ for Mn⁵⁵ which has been found to be very dependent on the amount of covalency in the bond.¹⁴ The fair agreement of the result for b_4 in CdTe with the value calculated from the results in the fluorite lattice would also indicate that there is no appreciable lattice distortion about the Eu⁺⁺ ion in CdTe.

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²⁷ W. Low and U. Rosenburger, Phys. Rev. **116**, 621 (1959).

²⁵ G. Burns, Phys. Rev. **128**, 2121 (1962).

²⁶ J. Schneider, S. Sircar, and A. Rauber, Z. Naturforsch **18a**, 980 (1963).