

Spin-Orbit Splitting in CdS:Se Single Crystals

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Calculated values of the spin-orbit splittings from previously measured valence-band splittings in single crystals of CdS and CdSe at liquid-helium temperatures are 0.065 and 0.418 eV, respectively. In this investigation, spin-orbit splittings have been determined for solid solutions of CdS:Se single crystals from transmission measurements on thin platelets at 4.2°K. The single-crystal platelets of approximately 1μ thickness were grown from the vapor phase. Measurements which have been made on seven intermediate compositions indicate that the spin-orbit splittings vary in an approximately linear manner with composition. The average deviation from linearity is approximately 10% greater than the experimental uncertainties. It is believed that slight deviations from linearity may be due to (1) the deviation of CdS from the ideal c/a ratio in the wurtzite structure and (2) the greater contribution of ionic binding in CdS.

I. INTRODUCTION

THE interaction between the magnetic moment of the electron spin and orbital angular momentum may result in the splitting of energy states in crystals as it does in isolated atoms. Since the inner electrons in isolated atoms are chiefly responsible for the splitting, the splitting in the solid state is not unlike that in atoms. It is, therefore, expected that crystalline spin-orbit splittings will be reasonably sensitive to atomic number. Applications of group theory to the problem of spin-orbit interaction in crystals yields information describing the symmetries of the electronic wavefunctions and the way in which states degenerate in the absence of the interaction split when the perturbation is turned on.

Any calculation of the spin-orbit splitting in crystals must begin with some type approximation for the elec-

tronic wavefunctions. In the tight-binding approximation, the wavefunctions at the center of the Brillouin zone are taken to be linear combinations of atomic wavefunctions. In CdS, one assumes the bottom of the conduction band to be formed from the $5s$ levels of Cd, and the upper valence bands to be formed from the $3p$ levels of sulfur. The upper valence band states are constructed out of appropriate linear combinations of products of p_x , p_y , p_z hydrogen-like orbitals with spin functions. In the absence of both spin-orbit and crystalline field effects, these states are degenerate. The crystalline field of the wurtzite lattice partially removes this degeneracy, separating the p_z from the p_x and p_y orbitals. In the case of CdS, the c/a ratio is smaller than that in the ideal wurtzite lattice, indicating a tighter binding of the p_z orbital directed along the c axis. This then puts the p_z band below the p_x , p_y band in the valence band structure. The p_x , p_y band is further split by spin-orbit coupling. In this case it can be shown, if one assumes an approximately spherical potential in the neighborhood of the S atom, that the higher of the two split states is that one in which the electron spin and orbital angular momentum are parallel. This result is anticipated also from the atomic spin-orbit splitting, in which the $P_{3/2}$ state is known to have a greater energy than the $P_{1/2}$ state. This situation is shown in Fig. 1 (after Balkanski and des Cloizeaux),¹ where M is the quantum number representing the net angular momentum about the c axis.

The contributions of spin-orbit interaction and the crystalline field perturbation to the experimentally observable splittings E_1 and E_2 have been calculated in various LCAO (linear combination of atomic orbitals) approximations by several investigators.¹⁻³ In a treatment in which the wurtzite energy levels are treated as

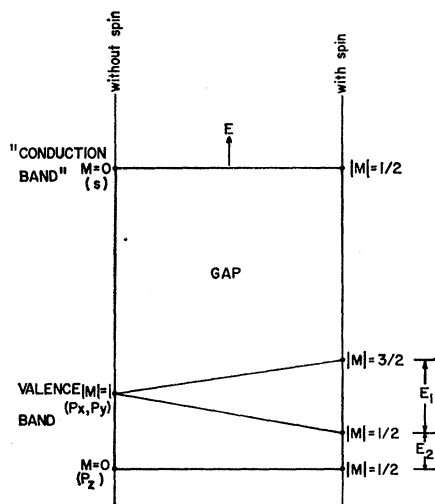


FIG. 1. Effect of the spin-orbit interaction on the valence band structure of CdS.

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¹ M. Balkanski and J. des Cloizeaux, *J. phys. radium* **21**, 825 (1960).

² S. Adler and J. Birman, General Telephone & Electronics Laboratory Report (unpublished).

³ J. J. Hopfield, *J. Phys. Chem. Solids* **15**, 97 (1960).

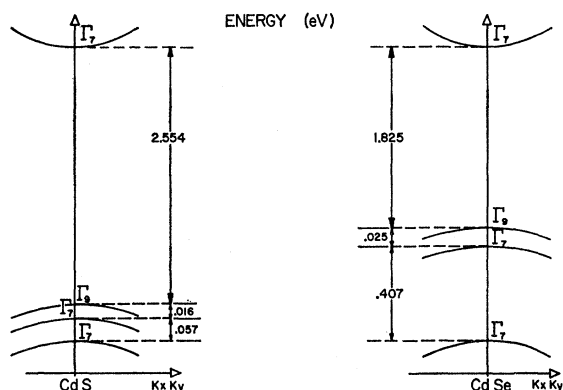


FIG. 2. Experimental values of the band separation in CdS and CdSe at 4.2°K.

perturbations of those in zinc blende, Adler and Birman have derived the relations

$$E_1 = -\frac{3}{2}\alpha + \frac{1}{2}\delta - \{2\alpha^2 + [(\alpha + \delta)/2]^2\}^{1/2},$$

$$E_2 = 2\{2\alpha^2 + [(\alpha + \delta)/2]^2\}^{1/2},$$

where α and δ represent the contributions of uniaxial field and spin-orbit interaction, respectively, to the splittings, E_1 and E_2 . If one puts $\alpha = -a$, and $\delta = b$, one has the results of Balkanski and des Cloiseaux,

$$E_1 = (3a + b)/2 - \frac{1}{2}[8a^2 + (a - b)^2]^{1/2},$$

$$E_2 = [8a^2 + (a - b)^2]^{1/2};$$

and if one puts $\delta = -\delta$, and $\alpha = \Delta/3$, there results the equations given by Hopfield,

$$E_1 = -\left(\frac{\delta + \Delta}{2}\right) - \left[\left(\frac{\delta + \Delta}{2}\right)^2 - \frac{2}{3}\delta\Delta\right]^{1/2},$$

$$E_2 = 2\left[\left(\frac{\delta + \Delta}{2}\right)^2 - \frac{2}{3}\delta\Delta\right]^{1/2}.$$

II. EXPERIMENTAL METHOD

In this investigation, the spin-orbit splitting as a function of composition in single crystals of CdS:Se solid solutions was determined at 4.2°K. Experimental values of the valence band splittings were used in conjunction with the equations of Adler and Birman to give values of the spin-orbit splitting.

Valence band splittings have been determined by transmission measurements at liquid helium temperatures for both endpoints of the solid solutions, CdS⁴ and CdSe.⁵ The band separations are given in Fig. 2. Since the spin-orbit coupling in Se is considerably greater than in S, it is natural to associate the splitting E_2 with this effect. In CdSe, this splitting is about 7 times its value in CdS. Splittings in intermediate solid solu-

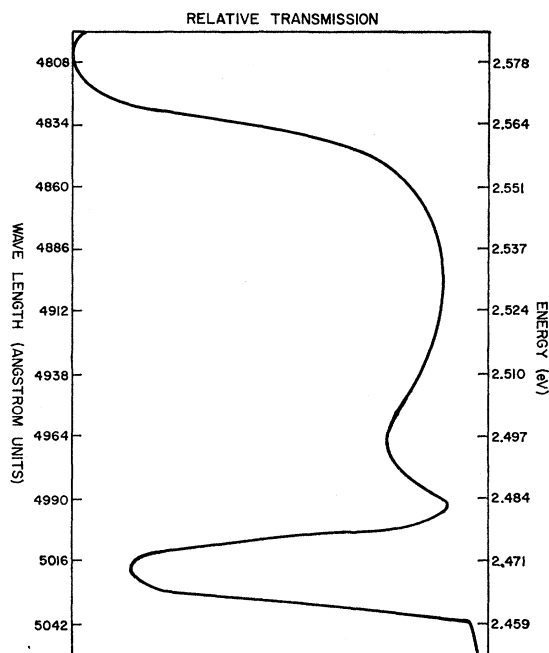


FIG. 3. Densitometer trace of the transmission spectrum of a CdS:Se single crystal containing 5 mole % CdSe. The two minima correspond to upper valence band absorptions.

tions were determined by transmission measurements made on very thin platelets (1 μ or less) grown from the vapor phase by Reynolds and Greene.⁶ A 55-W tungsten lamp was focused on the crystal which was mounted over a small hole in an aluminum plate and immersed in a helium Dewar. The transmitted light was analyzed with a 2-m Bausch & Lomb grating spectrograph, having dispersions of 4 and 8 Å/mm. Only very thin platelets show the three valence band structure, since very little light is transmitted with energies greater than the fundamental "gap." Experimental values determined in this way presumably correspond to absorptions from the valence bands to the ground state exciton level.⁷ A densitometer trace of the photograph of a typical crystal (5 mole % CdSe) is shown in Fig. 3. The homogeneity of the crystals analyzed is probably insured by the very fact that they showed the valence band structure; however, several samples of solid solutions, in the form of whiskers, were subjected to analysis using the electron probe method.⁸ The primary purpose of the analysis is to detect any inhomogeneities of the single crystals in a given run. These samples were submitted to the Mound Laboratory⁹ and were analyzed

⁶ D. C. Reynolds and L. C. Greene, *International Conference on Solid-State Physics, Brussels, June, 1958* (Academic Press Inc., New York, 1960).

⁷ All references to "band gap" will be understood to mean the separation between the top valence band and the ground state of the exciton.

⁸ L. S. Birks, *X-Ray Spectrochemical Analysis* (Interscience Publishers, Inc., New York, 1959), Chap. 7.

⁹ Operated by the Monsanto Research Corporation, Miamisburg, Ohio, for the Atomic Energy Commission.

⁴ D. G. Thomas and J. J. Hopfield, *Phys. Rev.* **116**, 573 (1959).

⁵ J. O. Dimmock and R. G. Wheeler, *Suppl. J. Appl. Phys.* **32**, 2271 (1961).

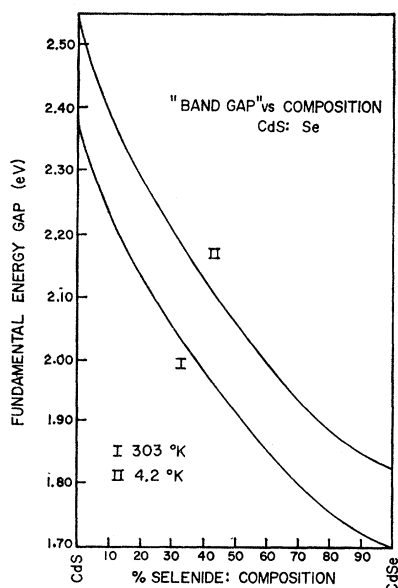


FIG. 4. Curve I: Variation of fundamental "band gap" with composition in CdS:Se single crystals at room temperature. Curve II: Assumed variation at 4.2°K, based on curve I.

under the supervision of Dr. C. R. Hudgens. In the opinion of Dr. Hudgens, no detectable inhomogeneities were found. Further experimentation is in progress, and a detailed report will be submitted for publication at a later date by Dr. F. L. Chan of this laboratory.

At the present time, a correlation of x-ray determinations of lattice parameter with chemical determinations of crystal compositions is in progress. Previous work at room temperature¹⁰ shows the variation of lattice parameter with concentration to be linear, while the variation of band gap with concentration deviates from linearity as shown in Fig. 4, curve I. If the deviations

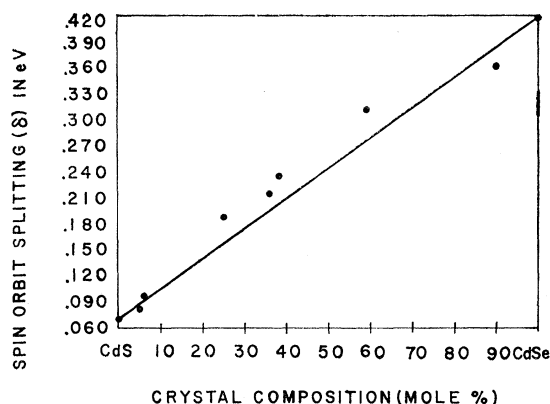


FIG. 5. Experimental dependence of spin-orbit splitting on composition of CdS:Se single crystals at 4.2°K.

¹⁰ Aeronautical Research Laboratory Eighth Quarterly Report (unpublished).

at 4.2°K are assumed to be proportional to those at room temperature, one can construct curve II. Tentative assignments of composition taken from this curve should be reasonably accurate, and were used here.

III. RESULTS AND DISCUSSION

Experimental values of " E_{gap} ", E_1 , and E_2 are given in Table I, together with the values of δ and α calculated from the inverse solutions of the equations of Adler and Birman:

$$\delta = \frac{1}{2}(2E_1 + E_2) + \frac{1}{2}[E_2^2 - 2E_1(E_1 + E_2)]^{1/2},$$

$$\alpha = -\frac{1}{6}(2E_1 + E_2) + \frac{1}{6}[E_2^2 - 2E_1(E_1 + E_2)]^{1/2}.$$

Solutions to these equations exist providing

$$E_2 \geq (1 + 3^{1/2})E_1.$$

It should be noted that only the positive values of the radical are consistent with the original equations. One finds that the spin-orbit splitting δ is always slightly

TABLE I. Experimental values of band separations in CdS:Se solid solutions at 4.2°K, and the calculated contributions of spin-orbit interaction and crystalline field to the valence band splittings.

Crystal composition	Experimental values " E_{gap} " (eV)	E_1 (eV)	E_2 (eV)	Calculated values δ (eV)	α (eV)
CdS	2.55	0.016	0.057	0.069	-0.009
5%	2.46	0.022	0.081	0.081	-0.016
6%	2.45	0.025	0.093	0.097	-0.015
25%	2.25	0.031	0.178	0.188	-0.017
36%	2.16	0.024	0.204	0.214	-0.013
38%	2.15	0.030	0.224	0.236	-0.016
59%	2.01	0.019	0.302	0.311	-0.010
90%	1.85	0.012	0.356	0.362	-0.006
CdSe	1.82	0.025	0.407	0.418	-0.013

greater than E_2 , which increases with mole % CdSe, while the crystalline field parameter α shows no regular variation. The variation of spin-orbit splitting with composition is very nearly a linear one, as shown in Fig. 5. The average deviation from linearity is about 10%, which is greater than the experimental uncertainties.

If one assumes the equations of Adler and Birman to be valid for the range of solid solutions examined, the deviations from linearity might be explained by at least two effects. First, the contribution of ionic binding in CdS is greater than that in CdSe. As a result, the electron will spend a greater portion of its time on the anion in CdS, and the spin-orbit coupling will be affected unequally in the solid solutions. Second, the deviation of the c/a ratio from the ideal in CdS, which is not the case in CdSe, reflects a tighter binding along the c axis. Again, this effect should contribute to the spin-orbit splitting in such a way as to produce some nonlinearity with composition.