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Hydrostatic Pressure Coefficients and Deformation Potentials for II-VI Compounds

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Dedicated to Prof. Dr. Dr. h.c. P. GÖRLICH, on the occasion of his 65th birthday

Calculations of the pressure coefficients of the gaps and spin-orbit splittings at the Γ and L Brillouin zone points have been performed for cubic ZnS, ZnSe, ZnTe, and CdTe using the KKR method. Special emphasis was placed on the determination of the pressure coefficients of spin-orbit splittings. These coefficients were found to be considerably smaller than those predicted from the wave function renormalization due to the change of volume. We also calculated pressure coefficients and deformation potentials for the smallest gaps of hexagonal ZnO, ZnS, CdS, and CdSe. The results of the calculations are compared with experimental data.

Berechnungen der Druckkoeffizienten für die Bandabstände und Spin-Bahn-Aufspaltungen in den Punkten Γ und L der Brillouin-Zone wurden mit Hilfe der KKR-Methode durchgeführt. Besondere Betonung wurde auf die Bestimmung der Druckkoeffizienten für die Spin-Bahn-Aufspaltungen gelegt. Die berechneten Koeffizienten sind wesentlich kleiner als diejenigen, welche durch Normierungskorrekturen an den Wellenfunktionen auf Grund von Volumenänderungen vorausgesagt wurden. Es wurden auch Druckkoeffizienten und Deformationspotentiale der kleinsten Interbandabstände im hexagonalen ZnO, ZnS, CdS und CdSe berechnet. Die Ergebnisse unserer Rechnungen werden mit experimentellen Daten verglichen.

1. Introduction

In recent years there has been increasing interest in studying the effects of pressure on the electronic structure of semiconductors [1]. In particular recent experiments by Meltz [2] have determined a small increase in the spin-orbit splitting of the valence band in Ge and CdTe with hydrostatic pressure. Theoretical calculations of the magnitude of this shift were performed by Brust and Liu [3] using an OPW technique and by Meltz [2] with a simple perturbation approach. Both of these techniques yield the volume dependence of the spin-orbit splitting:

$$\frac{\delta\Delta}{\Delta} = -4 \frac{\delta a}{a}, \quad (1)$$

where Δ is the magnitude of the spin-orbit splitting and a is the lattice constant.

The value of $\delta\Delta/\Delta$ predicted by (1) turns out to be larger by about a factor of four than the experimental value. It is, therefore, of interest to see whether

another theoretical method yields for the volume dependence of the spin-orbit splittings a closer agreement with experimental values. We have used the KKR method to compute the pressure dependence of the uppermost valence bands and the lowest conduction band at the Γ and L points of the Brillouin zone for cubic ZnS, ZnSe, ZnTe, and CdTe. We have also performed similar calculations for the smallest gap at Γ of hexagonal ZnO, ZnS, CdS, and CdSe. We thus determined the hydrostatic pressure coefficients of the E_0 , Δ_0 , E_1 , and Δ_1 gaps of the cubic materials and of the smallest gap in the hexagonal compounds. For CdS and CdSe we also computed the dependence of the three smallest gaps on uniaxial stress and determined the deformation potentials C_1 , C_2 , C_3 , and C_4 . The calculated values are in close agreement with available experimental data.

2. Aspects of the Calculation

The effectiveness of the KKR method for calculating energy bands has been shown by Eckelt [4] who performed non-relativistic calculations of the II-VI compounds with zincblende structure. The method has since been generalized to include all relativistic effects to second order in the fine structure constant [5, 6, 7]. Eckelt [8] subsequently extended his results to include the spin-orbit coupling (mass velocity and Darwin terms being neglected) and computed spin-orbit splittings in these materials at several symmetry points in the Brillouin zone (including the Γ and L points). His results are in excellent agreement with experimental values from optical measurements [9, 10]. Meanwhile the KKR calculations have been applied to hexagonal II-VI compounds with success [11].

The most drastic limitation of the KKR method is the assumption of a muffin-tin potential, i.e. a potential that is spherically symmetric inside non-overlapping spheres surrounding each atomic site and constant elsewhere. The value of the constant potential outside the muffin-tin spheres is used as an adjustable parameter to bring the calculated value of the main gap at the Γ point into coincidence with experimental values. This is the only adjustable parameter used in the method.

An approximate formula for the value of the constant potential V_0 , taken to be the average value $\bar{V}_0$ of the atomic potentials outside the muffin-tin spheres, was proposed by Eckelt [4]. In order to bring the lowest energy gap into agreement with experiment it is usually sufficient to multiply $\bar{V}_0$ by a correction factor α close to unity. When spin-orbit coupling is considered (mass velocity and Darwin term neglected) we found that the best agreement between the calculated cubic $\Gamma_{8v}-\Gamma_{6c}$ gap and the experimental values was obtained with the α -values given in Table 1. This table also lists $V_0 = \alpha \bar{V}_0$, and the lattice constants at atmospheric pressure used in our calculations. It can be seen that α shows a systematic variation with lattice constant: In fact, if one plots α as a function of lattice constant a straight line results (Fig. 1). We shall refer to this result below.

The effect of a hydrostatic pressure P is to change the lattice constants according to

$$\frac{\Delta a}{a} = (S_{11} + 2 S_{12}) P \quad (2)$$

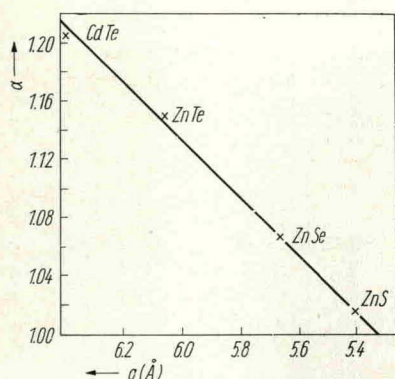
Table 1

Calculational parameters for cubic and hexagonal II-VI compounds.

V_0 was used for a full relativistic calculation in the hexagonal materials, while for cubic materials V_0 is that used for a calculation where only spin-orbit coupling is included

cubic	a (a.u.)*	V_0 (Ryd)	$\bar{V}_0$ (Ryd)	α	$S_{11} + 2 S_{12}$ (10^{-12} cm ² /dyn)				
CdTe	12.1172	-1.350	-1.120	1.205	0.79	[15]			
ZnTe	11.4745	-1.361	-1.185	1.149	0.66	[14]			
ZnSe	10.7042	-1.335	-1.252	1.066	0.57	[14]			
ZnS	10.2160	-1.335	-1.313	1.017	0.425	[14]			
hexagonal	c (a.u.)*	a (a.u.)*	V_0 (Ryd)	$\bar{V}_0$ (Ryd)	α	S_{11}	S_{12}	S_{13}	S_{33}
CdSe	13.2514	8.1266	-0.994	-1.164	0.86	2.338 [14]	-1.122 [14]	-0.572 [14]	1.735 [14]
CdS	12.6899	7.8185	-1.085	-1.217	0.89	2.069 [14]	-0.999 [14]	-0.581 [14]	1.697 [14]
ZnS	11.7845	7.2041	-1.135	-1.304	0.87	estimate from values for cubic ZnS of [14]			
ZnO	9.8393	6.1417	-1.705	-1.545	1.10	0.789 [16]	-0.343 [16]	-0.221 [16]	0.694 [16]

*) A.S.T.M. powder diffraction file.

Fig. 1. Dependence of $\alpha = V_0/\bar{V}_0$ on lattice constant

for cubic materials and according to

$$\frac{\Delta a}{a} = (S_{11} + S_{12} + S_{13}) P, \quad (3a)$$

$$\frac{\Delta c}{c} = (2 S_{13} + S_{33}) P \quad (3b)$$

for hexagonal materials. Here a and c are the unperturbed lattice constants and S_{ij} are the elastic compliances of the material. A uniaxial stress X parallel to the hexagonal c -axis changes the lattice constants according to

$$\frac{\Delta a}{a} = S_{13} X \quad \text{and} \quad \frac{\Delta c}{c} = S_{11} X. \quad (3c)$$

The values of S_{ij} used in our calculations are also shown in Table 1. The valence and conduction bands were computed along the Δ -axis for the cubic materials

Table 2
Energy gaps and spin-orbit splittings in cubic II-VI compounds (in eV)

Material	E_0		Δ_0		
	present work	exp.	present work	Eckelt [8]	exp.
CdTe	1.60	1.60	0.87	0.90	0.92 [17]
ZnTe	2.25	2.25 [17]	0.91	0.93	0.93 [17]
ZnSe	2.67	2.67 [18]	0.44	0.42	0.43 [17]
ZnS	3.58	3.66 [19]	0.075	0.08	0.071 [18]
	E_1		Δ_1		
	present work	exp.	present work	Eckelt [8]	exp.
CdTe	3.10	3.40	0.54	0.54	0.60 [17]
ZnTe	3.20	3.70 [17]	0.55	0.54	0.56 [17]
ZnSe	4.65	4.80 [18]	0.22	0.27	0.30 [18]
ZnS	5.63	5.80 [19]	0.05	0.05	—

and at the Γ point of the hexagonal compounds for several values of the lattice constants. Plotting the values of the gaps and spin-orbit splittings against pressure we get straight lines the slope of which determines the pressure coefficients.

3. Results for Cubic II-VI Compounds

In Table 2 the calculated values of the energy gaps and spin-orbit splittings are shown together with experimental data and earlier results of Eckelt [8]. The experimental data for E_0 have been used in the fitting procedure to determine the V_0 -values, as mentioned above. Our calculations were carried out with spin-orbit coupling included but mass velocity and Darwin correction neglected. The small deviations of our calculated spin-orbit splittings from Eckelt's results can be understood to be caused by small differences between the computational parameters a (lattice constant) and V_0 used in both calculations.

In Table 3 we compare the calculated pressure coefficients for E_0 , Δ_0 , E_1 , and Δ_1 with existing experimental data. Two sets of calculated values were obtained from different procedures. A certain gap or spin-orbit splitting E will change with a variation of the lattice constant according to

$$\frac{\partial E}{\partial a} = \left(\frac{\partial E}{\partial a} \right)_{V_0 \text{ fixed}} + \frac{\partial E}{\partial V_0} \frac{\partial V_0}{\partial a}; \quad (4)$$

we actually found $\partial E/\partial V_0$ to be independent of pressure and, therefore, we used the values for $P = 0$. The constant potential $V_0 = \alpha \bar{V}_0$ varies as

$$\frac{\partial V_0}{\partial a} = \bar{V}_0 \frac{\partial \alpha}{\partial a} + \alpha \frac{\partial \bar{V}_0}{\partial a}. \quad (5)$$

Our two computational procedures correspond to (i) varying $\alpha(a)$ according to

Table 3
Calculated and experimental pressure coefficients (in 10^{-6} eV/bar)

Material	E_0			Δ_0		
	α var.	α const.	exp.	α var.	α const.	exp.
CdTe	12.4	6.0	8.0 [20] 11.4 [21]	1.25	0.71	0.7 [2]
ZnTe	12.7	9.3	11.3 [20]	0.80	0.47	—
ZnSe	7.3	4.2	10.8 [22]	0.37	0.30	—
ZnS	8.3	6.3	5.7 [23] 6.3 [20]	-0.15	0.0	—
	E_1			Δ_1		
	α var.	α const.	exp.	α var.	α const.	exp.
CdTe	10.5	5.2	6.4 [20]	0.90	0.58	0.5 [2]
ZnTe	8.5	5.3	5.9 [20]	0.56	0.53	—
ZnSe	6.0	2.5	—	0.25	0.20	—
ZnS	6.9	4.3	—	-0.1	0.0	—

Fig. 1 and (ii) keeping α constant as a is varied. In the first case the second term on the right-hand side of (4) produces a correction of only 10% to the pressure coefficients and thus it reduces essentially to a calculation where V_0 is fixed.

Let us now turn to the pressure coefficients of the spin-orbit splittings. We shall represent them with the dimensionless quantity κ defined as

$$\frac{\delta \Delta}{\Delta} \approx -\kappa \frac{\delta a}{a}.$$

κ turns out to be the same for either Δ_0 or Δ_1 . The values obtained for κ are 1.8 for CdTe, 1.5 for ZnTe, and 1.2 for ZnSe. If we take the average of these three values we have $\kappa \approx 1.5$, which compares considerably more favorably with Meltz's experimental result of $\kappa \approx 1.0$ for both Ge and CdTe than with the estimate of Brust and Liu ($\kappa \approx 4$). We thought of explaining the discrepancy between our results and those of Brust and Liu as due to the admixture of core d-states in the valence bands. This admixture, which produces a negative contribution to the spin-orbit splitting [12], would be increased by the stress. This would also explain the negative sign found for κ in ZnS. In order to test this assumption, we calculated with the same method the value of κ for silicon. We also found $\kappa = 1.3$ in spite of the absence of d-electrons in the core. We thus conclude that the d-admixture is not the main reason for the low values of κ . The calculation of κ was also performed for germanium. The obtained value of $\kappa = 1.7$ was also in better agreement with the experimental work of Meltz than equation (1).

4. Results for Hexagonal II-VI Compounds

The calculations of the pressure dependence of the smallest gaps in the wurtzite type materials was carried out with the full relativistic version of the KKR method. In a previous paper [11] one of us obtained with this procedure crystal field and spin-orbit splittings in very good agreement with experimental values for ZnS, CdS, and CdSe. In the present work use was made of the fact that α is almost constant for these three compounds and hence it can be assumed to be independent of the lattice constants (see Table 1). This is true only in a full relativistic calculation. We should also point out that we have performed full relativistic calculations of the pressure coefficients of E_0 , Δ_0 , E_1 , and Δ_1 for cubic CdTe and ZnSe with α constant. Results in essential agreement with those of Table 3 with α variable were obtained.

The pressure dependence of the three smallest gaps of wurtzite type materials to first order in the deformation is described by [13]

$$E_A = C_1 \frac{\Delta c}{c} + C_2 \frac{2 \Delta a}{a} + C_3 \frac{\Delta c}{c} + C_4 \frac{2 \Delta a}{a}, \quad (6a)$$

$$E_B = C_1 \frac{\Delta c}{c} + C_2 \frac{2 \Delta a}{a} + \alpha_+ \left(C_3 \frac{\Delta c}{c} + C_4 \frac{2 \Delta a}{a} \right), \quad (6b)$$

$$E_C = C_1 \frac{\Delta c}{c} + C_2 \frac{2 \Delta a}{a} + \alpha_- \left(C_3 \frac{\Delta c}{c} + C_4 \frac{2 \Delta a}{a} \right); \quad (6c)$$

the constants C_1 , C_2 , C_3 , and C_4 are deformation potentials and $\alpha_{\pm}$ is given by

$$\alpha_{\pm} = \frac{1}{2} \left\{ 1 \pm \frac{\Delta_{cf} - \Delta_{so}}{(\Delta_{cf} - \Delta_{so})^2 + 8 \Delta_{so}^2}^{1/2} \right\}.$$

Δ_{cf} and $3 \Delta_{so}$ are the crystal field and spin-orbit splittings, respectively. The relative change of the lattice constants is given by equations (3a, b, c). The calculated variations of the band gaps E_A , E_B , and E_C under hydrostatic pressure were found to be equal among each other, i.e. in our computational method the deformation potentials C_3 and C_4 do not contribute to a shift of the band gaps. Thus for hydrostatic pressure (6a) splits into two equations:

$$E_A = C_1 \frac{\Delta c}{c} + C_2 \frac{2 \Delta a}{a} \quad \text{and} \quad 0 = C_3 \frac{\Delta c}{c} + C_4 \frac{2 \Delta a}{a}.$$

Two more equations follow from (6) for uniaxial stress along the hexagonal c -axis for which the variations of the three band gaps differ from each other. The four deformation potentials can be determined from these four equations. The results for CdS and CdSe are shown in Table 4 together with experimental values. The measurements with a stress along c for CdS [13] exhibit a crossing of the A and B exciton peaks for a uniaxial stress of 5.0×10^9 dyn/cm². This corresponds to a degeneracy of the uppermost two valence bands Γ_7 and Γ_9 , which is known as the quasi-cubic state. As can be seen in Fig. 2, the quasi-cubic state was calculated for a (0001) stress along c of 5.9×10^9 dyn/cm².

In Table 5 the calculated values of the hydrostatic pressure coefficients of the fundamental absorption edge in hexagonal ZnO, ZnS, CdS, and CdSe are compared with experimental data.

Table 4
Calculated and experimental deformation potentials (in eV) for
hexagonal CdS and CdSe

		C_1	C_2	C_3	C_4
CdS	calc.	-3.8	-3.3	-2.8	1.6
	exp. [11]	-1.7	-3.7	-2.7	1.5
CdSe	calc.	-0.3	-4.7	-4.1	1.9
	exp. [24]	-1.0	-4.1	-4.2	1.9

Table 5
Calculated and experimental pressure coefficients for
hexagonal II-VI compounds (in 10^{-6} eV/bar)

	ZnO	ZnS	CdS	CdSe
calc.	2.9	6.7	4.5	5.0
exp. [25]	2.7	6.3	4.5	6.0

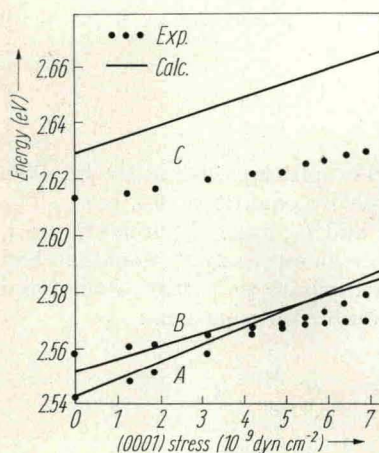


Fig. 2. Exciton energies from stress measurements in hexagonal CdS and calculated shifts of the band edges for (0001) stress

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