[19]Approximately ten free paths, if the latter are energy independent. A variation in free path with energy would reduce this figure; however, as will be seen later, impurity-scattering effects are quite small in all of the specimens studied.

[20]Under simplified conditions (Ref. 7), the current distortion in the direction of the Hall field can be shown to depend exponentially on $w\beta n^{-1}(dn/dx)$, where dn/dx is the gradient of carrier concentration in the current direction, w is the specimen dimension along the Hall field, and β is the tangent of the Hall angle.

[21]See, for example, E. M. Conwell, Solid State Phys. Suppl. 9, 22 (1967).

[22]J. Yamashita and M. Watanabe, Progr. Theoret. Phys. (Kyoto) 12, 443 (1954).

[23]See p. 165 of Ref. 20 for a theoretical treatment of the zero magnetic field case.

[24]See, for example, the theory of E. N. Adams and T. D. Holstein [J. Phys. Chem. Solids 10, 254 (1959)] which, in the extreme quantum limit, yields $\mu_{ph} \sim H^{-5/2} \times T^{3/2}$ and $\mu_i \sim H^0 T^{3/2}$. Also, the expressions obtained by Kazarinov and Skobov (Ref. 15) give the following ratio for the scattering frequencies in quantizing fields: $\nu_i/\nu_{ph} \sim H^{-2}$.

[25]H. H. Wieder, J. Appl. Phys. 40, 3320 (1969).

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Volume Dependence of the Spin-Orbit Splitting in Representative Semiconductors from High-Pressure Electroreflectivity Measurements and Relativistic Orthogonalized-Plane-Wave Calculations

Peter J. Melz*†
Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts 02138

and

Irene B. Ortenburger
IBM Research Laboratories, San Jose, California 95114
(Received 18 December 1970)

By means of electroreflectivity measurements at room temperature and at 77 °K performed at pressures up to 10 kbar, we have experimentally determined the volume dependence of the Δ_0 and Δ_1 spin-orbit splittings in CdTe and the Δ_0 spin-orbit splitting in germanium. The volume dependence of the Δ_0 and Δ_1 (at L) spin-orbit splitting has also been obtained for Ge, GaAs, and CdTe from a relativistic orthogonalized-plane-wave (OPW) calculation. Our experimental and theoretical results are in agreement and indicate that the volume dependence of the spin-orbit splitting is considerably smaller than would be expected if the valence-electron density in the core region increased in proportion to the decrease in the crystal volume. These results are interpreted as an indication that the valence-electron density in the core region is little affected by the crystal volume and may be relatively unchanged from that of the free atom. The plausibility of the conclusion and some consequences are discussed. In some cases a reversible change in the electroreflectivity line shape as the pressure is cycled can give rise to erroneous results if the change in line shape is not taken into account. It is shown that all of our experimental results are consistent when reasonable corrections are made for the change in line shape, and it is suggested that such effects may not be accounted for in the experimental results of Bendorius and Shileika on GaAs which disagree with our calculated results.

I. INTRODUCTION

In the past few years, through a combination of experimental and theoretical efforts, the energy-band structure of many semiconducting crystals has become better known. Experimental investigations have usually involved optical studies and have recently been aided in accuracy and information content by the use of various modulation techniques,[1-4] while theoretical calculations[5-8] have made use of better initial models, improved calculational procedures and facilities, and well-established experimental information at isolated points in the Brillouin zone to calculate the optical constants for the crystal as well as the energy-band structure throughout the Brillouin zone.

The work reported in this paper is the result of using improved experimental and calculational techniques to investigate the pressure dependence of the spin-orbit splitting in representative semiconductors. The results are of interest both in terms of assessing which of various calculational

techniques gives an accurate description of spin-orbit–splitting effects and in interpreting how the density of the electron gas in the core region varies as the crystal volume is changed.

Adapting the electroreflectivity technique to high-pressure measurements would appear to be straightforward, though it is not immediately obvious what additional information can be obtained through such experiments. Modulation experiments performed under uniaxial stress[9,10] are in principle capable of yielding the same information as high-pressure experiments. For a determination of the volume-deformation-potential constants of a crystal, however, high-pressure experiments will be more accurate, since, in general, the change in volume produced by a high-pressure experiment is a factor of 3 larger than the change in volume produced by a comparable uniaxial stress experiment, and nonlinear effects[9,11] caused by symmetry-destroying strains are absent. As we shall see, this additional accuracy is essential if we are to give a meaningful interpretation to our results for the pressure dependence of the spin-orbit splittings.

Though electroreflectivity signals of high resolution can often be obtained, because of difficulties in relating the experimentally observed line shape to the energy of the transition giving rise to the line,[12] some uncertainty always exists in the true value of the energy gap. This difficulty would appear to be unimportant in high-pressure experiments where we are interested in the shift in the energy of a transition with pressure rather than an absolute energy. Unfortunately, because of changes in the surface field conditions caused by variations in the carrier concentration with pressure, in general the electroreflectivity signal shows a reversible change as the pressure is cycled. It is therefore important to attempt to avoid such effects, and where they are present attempt to estimate their effect before any conclusions are drawn from the experiment. Failure to do this resulted in an apparent decrease in the Δ_0 spin-orbit splitting in Ge with pressure, reported in a preliminary presentation of this work,[13] and may possibly be the source of our disagreement with the high-pressure electroreflectivity experiment of Bendorius and Shileika on GaAs.[14] This point is therefore given particular attention in the discussion of our experimental results.

In the past few years, as band-structure calculations for semiconductors have become more and more refined, there has been an increasing tendency to include effects due to spin-orbit coupling.[7,15–21] In general, results obtained by various methods of calculations are in reasonable agreement among themselves and with experiments for the valence-band splittings, but in the conduction bands, which are not so easily accessible experimentally, calculations by different techniques give splittings which may vary almost by a factor of 2, and in all cases are higher than the experimental estimates[22–24] which are available. Our experimental results for the pressure dependence of the spin-orbit splitting, therefore, provide an important additional check on the validity of various methods of treating spin-orbit effects.

II. EXPERIMENTAL APPARATUS AND TECHNIQUES

To perform electroreflectivity measurements at high pressures, a number of techniques previously developed by workers in the Gordon McKay Laboratory were employed with minor modifications.

A. Sample Preparation

Electroreflectivity samples were prepared in a manner similar to that described by Ludeke.[25] Samples of the material to be studied were cut, polished, and lightly etched to remove surface damage. An insulating layer of approximately 5000 Å of either SiO_2 or Al_2O_3 was then deposited on the highly reflecting surface by means of electron-beam-gun evaporation. Transparent electrodes were produced on top of the insulating layer either by deposition of SnO_2 by means of a vapor-transport technique or by electron-beam-gun evaporation of a transparent film of nickel metal. Contact was made to the transparent electrode either directly, using silver paste, or to a gold electrode evaporated on one corner of the transparent electrode.

Of the possible combinations of sample-preparation techniques used, the Al_2O_3 insulating layer in combination with the nickel electrode and gold contact provided the most reliable preparation procedure and best experimental results.

B. Pressure Apparatus

The pressure apparatus used has been described by Kosicki,[26] who referred to it as the "Raytheon" apparatus. Using standard techniques, it is capable of developing helium-gas pressures in excess of 12 kbar. The electroreflectivity samples were mounted in an optical transmission high-pressure vessel fitted inside an optical Dewar. In this configuration the high-pressure electroreflectivity experiment could be performed at liquid-nitrogen temperature to sharpen the electroreflectivity lines. In order to convert the reflectivity experiment to a transmission experiment with less complicated optics, a technique developed by Zallen and Paul[27] and Kosicki[26] was employed. The electroreflectivity sample was mounted at a 45° angle to the incident light beam so that the light reflected from the electroreflectivity sample was successively reflected at 45° from three mirrors of polished aluminum until it emerged from the opposite side of the high-pressure vessel in the same direction as

the incident beam. Electroreflectivity studies are usually performed near normal incidence, but our choice of 45° incidence did not appear to matter, since the line shapes we observed for CdTe were essentially identical to those observed at near-normal incidence by Ludeke and Paul[28] using samples cut from the same boule.

Because of the high accuracy desired, the pressure system had to be relatively leak free. In general, the change in pressure observed was less than 1% of the total applied pressure in 15 min. Also, to avoid systematic errors caused by the temperature dependence of the various transition energies, no measurements were taken until 15 min after the pressure in the vessel had been changed. This time interval allowed the interior of the vessel to return to the ambient temperature after energy had been added or removed from the system by compression or expansion of the gas. This precaution was particularly important at low pressures where the changes in gas volume were large, and noticeable hysteresis was observed if data were taken too soon after changing the pressure.

C. Optics and Electronics

The piezotransmission and electroreflectivity spectrometer described by Ludeke and Paul[28,29] was used with few minor modifications as dictated by the experiment. For experiments on CdTe, a xenon source and photomultiplier detector were used with an ac feedback technique employed to modify the supply voltage to the photomultiplier to keep the signal due to the reflected light constant. For experiments on Ge, a tungsten quartz-iodine source was used with a PbS detector. Since in this case the spectral output of the source and response of the detector were slowly varying with wavelength in the region of interest, no feedback was employed for the Ge experiments. Sinusoidal modulation of the field at the sample surface was used with no dc bias. Electroreflectivity signals were detected using standard phase-sensitive detection techniques.

TABLE I. Hydrostatic pressure shifts of CdTe optical transitions.

Transition and energy[a] (eV)	$\frac{dE}{dP}\left(10^{-6}\ \frac{\text{eV}}{\text{bar}}\right)$ This work	Langer[b]
E_0 = 1.49	8.3±0.5 (297 °K)	7.9
1.58	8.2±0.1 (77 °K)	
$E_0+\Delta_0$ = 2.52	8.9±0.2 (77 °K)	
E_1 = 3.40	7.0±0.4 (297 °K)	6.5
$E_1+\Delta_1$ = 3.95	7.5±0.5 (297 °K)	6.8
Δ_0 = 0.94	0.7±0.2	
Δ_1 = 0.55	0.5±0.7	0.3

[a]Energy of fiducial point of electroreflectivity line at 1 atm. This energy may differ from the true transition energy by 0.1 eV.

[b]See Ref. 32.

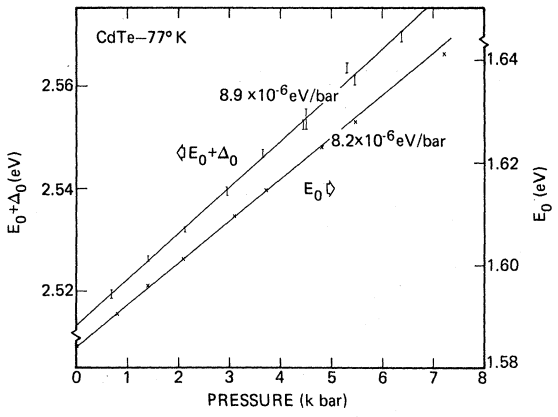

FIG. 1. Pressure shift of the E_0 and $E_0+\Delta_0$ electroreflectivity lines for CdTe at 77 °K.

III. EXPERIMENTAL RESULTS

A. CdTe

Cadmium telluride was initially chosen for this investigation because of its large spin-orbit splitting and high compressibility. The material used was p type and showed less than a factor of 2 change in resistivity when subjected to 10 kbar of pressure at 77 °K. This is to be compared with the orders-of-magnitude change in resistivity exhibited by n-type CdTe when subjected to comparable pressures at room temperature.[30] The p-type CdTe was therefore a good choice to avoid changes in electroreflectivity line shape caused by variations in the carrier concentration with pressure.

The shifts in the E_0, E_1, and $E_1+\Delta_1$ transitions[31] with pressure were determined at room temperature, while the shifts of the E_0 and $E_0+\Delta_0$ transitions with pressure were determined at 77 °K. The results of these experiments are summarized in Table I, with the data for the low-temperature experiments shown in Fig. 1. The electroreflectivity signal for the $E_0+\Delta_0$ transition was not sufficiently well resolved to justify a pressure experiment at room temperature, while the increase in resolution of the E_1 and $E_1+\Delta_1$ electroreflectivity signals[28] as the temperature is decreased was insufficient to gain additional information from the more difficult low-temperature experiment.

As can be seen from Table I, good agreement was obtained with the ordinary reflectivity measurements of Langer[32] where comparison is possible. Good agreement is also observed between the room-temperature and 77 °K data. The pressure coefficients of the spin-orbit splittings listed in Table

I take into account all available data from these experiments, but do not involve line-shape corrections. At room temperature only very slight changes in line shape and amplitude were observed, while at 77 °K the amplitude of the electroreflectivity signal decreased (reversibly) with pressure but did not change shape. Since similar changes were observed for both the E_0 and $E_0+\Delta_0$ lines, it was felt that no corrections were necessary.

As we shall see in Sec. IV, the changes in the spin-orbit splitting due to pressure observed in CdTe are considerably smaller than would be expected on the basis of simple arguments. A possible source of this discrepancy is that the valence-band spin-orbit splitting in CdTe is determined primarily by tellurium, that is, the valence electrons spend much more time in the vicinity of the tellurium ion than the cadmium ion. The application of a hydrostatic pressure could cause a redistribution of the valence change from the tellurium ion to the cadmium ion so that the spin-orbit splitting would not increase with pressure as rapidly as expected. This type of effect may equivalently be viewed as resulting from mixing of the occupied valence-band levels with higher-lying levels of the same symmetry under the influence of hydrostatic pressure.

B. Germanium

Symmetry demands that the redistribution of charge discussed above cannot take place in germanium, hence high-pressure electroreflectivity experiments were performed on this material for comparison. The effects observed could be expected to be approximately a factor of 6 smaller than those observed in CdTe because the spin-orbit splitting is three times smaller and germanium is only half as compressible as CdTe. Since observation of the pressure dependence of the Δ_1 splitting in CdTe was only barely possible because of the relatively broad high-energy electroreflectivity signal, meaningful observations of the pressure dependence of the Δ_1 splitting in germanium seemed futile, and effort was concentrated on the Δ_0 splitting.

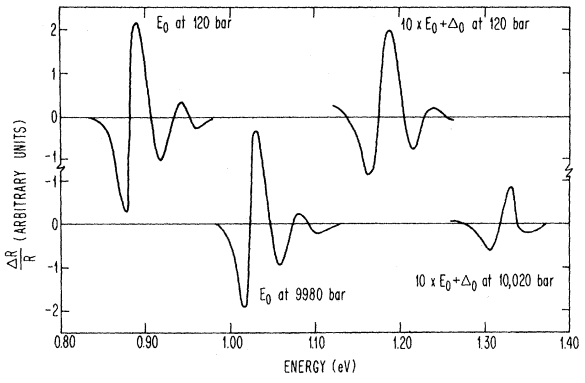

FIG. 2. Electroreflectivity lines shapes for the E_0 and $E_0+\Delta_0$ transitions in germanium at 77 °K at high and low pressure. Negligible change in line shape with pressure was assumed for this sample.

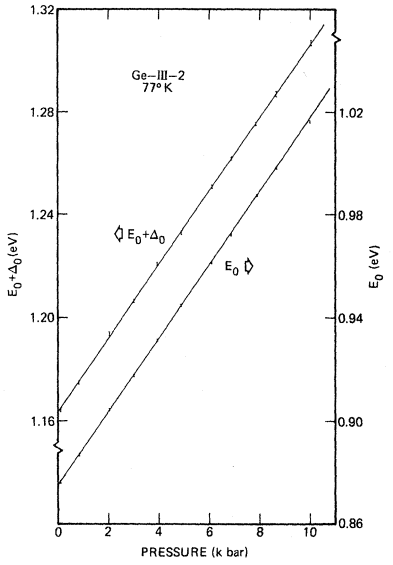

FIG. 3. Pressure shift of the E_0 and $E_0+\Delta_0$ electroreflectivity lines at 77 °K for the germanium sample giving the line shapes shown in Fig. 2. Both lines drawn through the data have slope 14.3×10^{-6} eV/bar.

Because of difficulties caused by the pressure variation of the electroreflectivity line shape, samples of different type and carrier concentration were used. One of these samples showed negligible change in the electroreflectivity line with pressure. The line shapes observed for this sample for the E_0 and $E_0+\Delta_0$ transitions at high and low pressure are shown in Fig. 2. The large number of oscillations observed indicates that the field was relatively uniform over the penetration depth of the light.[12, 33] It was assumed for this sample that, even though there were some amplitude changes in the electroreflectivity lines, the peak positions are faithfully related to the transition energies.

Figure 3 shows a plot of the shift of the E_0 and $E_0+\Delta_0$ electroreflectivity lines with pressure observed for this sample. This plot illustrates the difficulty involved in determining the volume dependence of the Δ_0 splitting in this manner, since both the E_0 and $E_0+\Delta_0$ lines appear to shift identically with pressure. To obtain a better perspective of the volume dependence of Δ_0, the data shown in Fig. 3 were "subtracted," that is, an energy of 14.2×10^{-6} eV/bar times the pressure of observation was subtracted from the observed energy of each electroreflectivity line. These subtracted data are shown in Fig. 4. The curved line drawn through

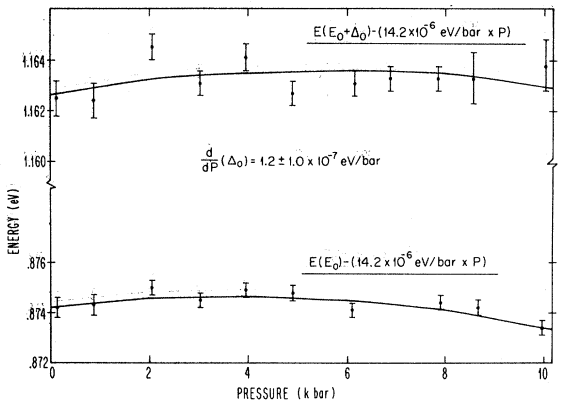

FIG. 4. Data shown in Fig. 3 with all energies reduced by 14.2×10^{-6} eV/bar times the pressure of observation. The curved line indicates the curvature to be expected in the data due to the nonlinear compressibility of germanium. The best fit to the data gives $d\Delta_0/dP = 1.2\pm1.0\times10^{-7}$ eV/bar.

the data points indicates the curvature in the data expected due to the first nonlinear term in the compressibility of germanium. The nonlinear term in the compressibility of germanium was computed from the third-order elastic constants determined by McSkimin and Andreatch[34] by the method described by Thomas.[35] Other possible contributions to the apparent nonlinear shift of the transition energies with pressure may be due to nonlinear variation in the resistance of manganin wire used to measure the pressure and nonlinear shift of the transition energy with volume. The importance of these effects was estimated from the nonlinear pressure coefficient of the resistance of manganin wire[36] and from the calculated variation of the germanium band structure with volume by Herman *et al.*[5] These nonlinear contributions proved to be of opposite sign and were both approximately a factor of 4 smaller than the expected contribution due to the nonlinear compressibility of the crystal. The subtracted data, therefore, should reflect faithfully the nonlinear compressibility of germanium; it can be seen that the curved line is a better fit to the data than a straight line would be.

From the fit to the subtracted data for the E_0 and $E_0+\Delta_0$ transitions for this particular sample, the pressure coefficient of the Δ_0 splitting is estimated to be $1\pm1\times10^{-7}$ eV/bar. The effect is less than 1% of the total shift of the observed transitions with pressure.

For experiments where the line shape had been observed to be a function of pressure, corrections were estimated to see if the data obtained from these experiments were consistent with data obtained when no corrections were considered necessary. The method of estimating corrections for line-shape changes is illustrated in Fig. 5. It is assumed that for the M_0 type of critical point which gives rise to the E_0 and $E_0+\Delta_0$ transitions in germanium, the low-energy portion of the electroreflectivity line is most faithfully related to the transition energy. The high-energy structure is much more affected by the field strength and is more sensitive to mixing effects of the two electro-optic functions.[12,33] The lowest energy peak was therefore assumed to indicate the transition energy. The effect of the changes in total line shape on the position of this peak was estimated by redrawing the line shape observed at high pressure in a manner which reproduced the line shape observed at low pressure. The shift in the lowest energy peak could then be estimated, as illustrated in Fig. 5. This procedure is admittedly somewhat arbitrary and much more faith should be placed on the results where these changes in line shape are absent. Nevertheless, as shown in Table II, by making corrections in this manner, the data obtained for the 77 °K experiments on three different samples showing greatly different line shapes are brought into coincidence. The room-temperature experiments are also consistent with the low-temperature data. Our best values from all experiments are $dE_0/dP = 14.3\pm0.1\times10^{-6}$ eV/bar and $d\Delta_0/dP = 1\pm1\times10^{-7}$ eV/bar. Our value of dE_0/dP is in agreement with the value of $13\pm1\times10^{-6}$ eV/bar obtained by Cardona and Paul[37] from high-pressure-transmission measurements.

IV. THEORY

The simplest possible model for the pressure dependence of the spin-orbit splitting is based on a scaling argument. If we consider spin-orbit effects to be a perturbation on the energy-band structure and consider an isolated level which is split

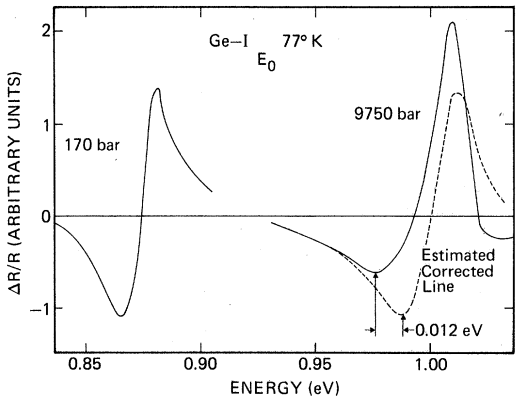

FIG. 5. Method of estimating corrections in the pressure coefficient of optical transitions necessary because of changes in the electroreflectivity line shape with pressure. In the case illustrated, the correction amounts to 10% of the total effect.

TABLE II. Summary of pressure experiments of germanium.

Sample	Transition	$\frac{dE}{dP}$ $\left(10^{-6}\frac{\text{eV}}{\text{bar}}\right)$	Temperature (°K)	Estimated correction $\left(10^{-6}\frac{\text{eV}}{\text{bar}}\right)$	Final value $\left(10^{-6}\frac{\text{eV}}{\text{bar}}\right)$
I	E_0	12.7±0.1	297		
	$E_0+\Delta_0$	12.6±0.4	297		
	E_0	13.2±0.1	77	1.2±0.4	14.4±0.4
	$E_0+\Delta_0$	12.8±0.1	77	1.6±0.4	14.4±0.4
II	$E_0+\Delta_0$	14.0±0.2	77	•••	14.0±0.2
	E_0	14.5±0.2	77	−0.6±0.2	13.9±0.3
III-2	$E_0+\Delta_0$	14.0±0.2	297		
	E_0	14.0±0.1	297		
	$E_0+\Delta_0$	14.4±0.1	77	•••	14.4±0.1
	E_0	14.3±0.1	77	•••	14.3±0.1
	Composite value: $\frac{d\Delta_0}{dP} = 1\pm1\times10^{-7}$ eV/bar				

by the spin-orbit interaction, a simple picture can be developed of how the spin-orbit splitting could be expected to vary with volume. In such an approach, the size of the spin-orbit splitting will ultimately depend on the matrix element

$$\Delta_{so} = \lambda\langle\psi|\vec{\nabla}V\times\vec{p}\cdot\vec{\sigma}|\psi\rangle\ , \tag{1}$$

where $|\psi\rangle$ is the electron eigenfunction obtained when spin-orbit effects are neglected, V is the crystal potential, $\vec{p}$ is the electron momentum, $\vec{\sigma}$ the electron spin, and λ contains only fundamental constants. Most of the contribution to this matrix element comes from the core region where $\vec{\nabla}V$ is large. In this region we expect the electron gas made up of the core electrons to be incompressible, and hence $\vec{\nabla}V$ should be relatively independent of volume. We expect two major contributions to the volume dependence of the spin-orbit matrix element: the largest coming from the renormalization of the wave function which should vary as $a^{-3/2}$, where a is the lattice constant, and the other from the higher electron momentum associated with confinement in a smaller volume, $|\vec{p}|$ varying as a^{-1}. To first order, one might expect

$$\delta\Delta_{so}/\Delta_{so} \approx -4\delta a/a\ . \tag{2}$$

This result and the underlying reasoning are in agreement with a somewhat more detailed estimate by Brust and Liu[38] of the volume dependence of the valence-band spin-orbit splitting at L in Ge, based on the orthogonalized-plane-wave (OPW) method.

The experimentally determined volume dependence at Γ in CdTe, assuming a compressibility $k = 2.36\times10^{-6}$ bar^{-1}, is

$$\frac{\delta\Delta_0}{\Delta_0}\frac{a}{\delta a} = -\frac{3}{k\Delta_0}\frac{d\Delta_0}{dp} = -1.0\ , \tag{3}$$

smaller by a factor of 4 than that predicted above. The volume dependences of the other spin-orbit splittings are similarly approximately equal to −1. In CdTe this could have been explained by a redistribution of valence charge density from the Te core to the Cd core. This explanation is not possible in Ge, and the similarity of the results for Ge and CdTe suggests that change in ionicity is not responsible for the small experimental value of $\delta\Delta/\Delta$.

Although the scaling argument is obviously an oversimplification, it was surprising to find it failing so badly. In order to understand the small pressure dependence of the spin-orbit splitting, calculations were needed in which the core region is treated correctly. Relativistic OPW energy-band calculations are known to give excellent values for the valence-band spin-orbit splittings in typical cubic semiconductors.[20] The errors in the spin-orbit splitting due to lack of self-consistency, imperfect convergence, and possible flaws in the model should be smaller than they might be in the other energy differences. Consequently, energy-band calculations, based on the trial crystal potential which is a superposition of Kohn-Sham free-atomic potentials, were performed for several values of lattice constant for the materials Ge, CdTe, and GaAs. The Lowdin partitioning scheme was used and the inner and outer matrices contained 113 and 283 plane waves at Γ, and 90 and 266 at L.

The calculated pressure coefficients dE/dp for various transitions are compared with the experimental results in Table III. The compressibilities used were $k = 1.33$, 1.25, and 2.36 ($\times10^{-6}$ bar^{-1}) for Ge, GaAs, and CdTe, respectively. The theoretical results for the spin-orbit splittings are nearly within experimental accuracy for CdTe and Ge. The agreement is not too bad for the other

TABLE III. Comparison of theoretical and experimental pressure coefficients in CdTe, Ge, and GaAs.

Transition	Transition energy [expt (eV)]	Spin-orbit splitting expt	Spin-orbit splitting calc	Pressure coefficient (10^{-6} eV/bar) expt	Pressure coefficient (10^{-6} eV/bar) calc
CdTe[a]: E_0	1.58			8.2±0.1	10.8
$E_0+\Delta_0$	2.52			8.9±0.2	11.9
E_1	3.40			7.0±0.4	6.7
$E_1+\Delta_1$	3.95			7.5±0.5	7.4
Δ_0		0.94	0.93	0.7±0.2	1.05
Δ_1		0.55	0.57	0.5±0.7	0.63
Ge[a]: E_0	0.87			14.3±0.1	12.0
$E_0+\Delta_0$	1.16			14.4±0.1	12.3
E_1					5.8
$E_1+\Delta_1$					6.0
Δ_0		0.29	0.29	0.1±0.1	0.23
Δ_1			0.19		0.15
GaAs[b]: E_0	1.44			11.3±0.2	9.6
$E_0+\Delta_0$	1.77			12.7±0.2	9.8
E_1	2.90			7.2±0.2	5.2
$E_1+\Delta_1$	3.12			7.5±0.2	5.4
Δ_0		0.34	0.34	1.4±0.2	0.20
Δ_1		0.22	0.21	0.3±0.1	0.13

[a]This work. [b]See Ref. 14.

transitions. It must be remembered that the lack of self-consistency and convergence have a greater relative effect on these other energy differences, since they are determined by the rearrangement of valence charge outside the cores. These are raw unadjusted energy-band calculations, and no attempt has been made to fit any experimental data. The volume dependence of the spin-orbit splittings $(\delta\Delta/\Delta)(a/\Delta a)$ is given in Table IV and compared with the experimental values. The simple theory predicted that this ratio should be about -4. It is interesting that the theoretical volume dependence is quite constant for the three materials. Similar numerical results have recently been obtained by Cerdeira *et al.*[39] using the Korringa-Kohn-Rostoker (KKR) technique, though they offer no explanation for the differences between their results and the simple model.

A simple explanation for the small volume dependence is possible if, when the unit-cell volume is decreased, the valence charge density in the core region is relatively unaffected, and all the renormalization of the wave function necessary to conserve the total charge takes place in regions of the unit cell outside the ion cores. This would not seem to be an excessive requirement for semiconductor crystals in which the cores occupy a small fraction of the total volume. If it is a good approximation that the core electrons are unaffected by a small decrease in lattice constant, then the fact that the valence wave functions already form a self-consistent solution in the core region will tend to keep the valence charge density in the core region unchanged.

In order to make this argument more plausible, consider the charge density associated with a single (nonrelativistic) OPW. By making a simple model for the orthogonality charge, one can show that it is possible to have large departures from the "$-3\delta a/a$" scaling law for the charge density in the core region. The exact expression for the charge density associated with a single unnormalized OPW of wave vector $\vec{\mu}$, $\phi(\vec{\mu},\vec{r})$ is

$$\rho_\mu(\vec{r}) = \phi^*(\vec{\mu},\vec{r})\phi(\vec{\mu},\vec{r}) / \int \phi^*(\vec{\mu},\vec{r})\phi(\vec{\mu},\vec{r})\,d\Omega \ , \tag{4}$$

where

$$\phi^*(\vec{\mu},\vec{r})\,\phi(\vec{\mu},\vec{r})$$

TABLE IV. Comparison of experimental and theoretical pressure and volume dependence of spin-orbit splittings.

Splitting	Pressure coefficient $\frac{d\Delta}{dP}\left(10^{-7}\frac{\text{eV}}{\text{bar}}\right)$ Theory	Pressure coefficient Experiment	Volume dependence $\frac{a}{\Delta}\frac{\delta\Delta}{\delta a}$ Theory	Volume dependence Experiment
Ge: Δ_0	2.3	1.2±1.0[a]	−1.8	−0.8±0.8[a]
Δ_1	1.5		−1.8	
GaAs: Δ_0	2.0	14.0±2.0[b]	−1.4	−10.0±2.0[b]
Δ_1	1.3	3.0±1.0[b]	−1.5	−3.2±1.0[b]
CdTe: Δ_0	10.5	7.0±2.0[a]	−1.5	−1.0±0.3[a]
Δ_1	6.3	5.0±7.0[a]	−1.4	−1.1±1.5[a]

[a]This work. [b]See Ref. 14.

$$= \frac{1}{\Omega} + \frac{1}{\Omega} \sum_{\vec{f}}^{\text{atoms}} \sum_{l}^{\substack{\text{core}\\ \text{levels}}} \sum_{\vec{d}}^{\substack{\text{direct}\\ \text{lattice}\\ \text{vectors}}} \sum_{n}^{\substack{\text{core}\\ \text{levels}}} \sum_{n'}^{\substack{\text{core}\\ \text{levels}}}$$

$$\times C_{n'lf}(\mu)\, C_{nlf}(\mu)\, R_{n'lf}(|\vec{r}-\vec{d}-\vec{f}|) R_{nlf}(|\vec{r}-\vec{d}-\vec{f}|)$$

$$- 2\delta_{nn'}\, C_{nlf}(\mu) R_{nlf}(|\vec{r}-\vec{d}-\vec{f}|) j_l(2\pi\mu|\vec{r}-\vec{d}-\vec{f}|) \tag{5}$$

and

$$\langle \mu | J | \mu \rangle \equiv \int \phi^*(\vec{\mu},\vec{r})\phi(\vec{\mu},\vec{r})\, d\Omega$$

$$= 1 - \frac{4\pi}{\Delta} \sum_{\vec{f}} \sum_{l} (2l+1) \sum_{n} C^2_{nlf}(\mu) \,. \tag{6}$$

R_{nlf} is a radial wave function, $C_{nlf}(\mu)$ is the corresponding orthogonality coefficient, and $\Omega = N^3\Delta$ is the volume of the crystal.

This charge density consists of a constant part plus a sum of corelike nonoverlapping charge densities centered on atomic sites. Let us model the corelike part by a function which is constant inside some radius which describes the core and which vanishes outside the cores. Let V be the volume of the crystal which is inside the core region. V is not a function of a (we are assuming that the cores are incompressible) while the total volume Ω is a function of a. The charge densities inside and outside the core region are

$$\rho^i = \frac{1-\rho}{\Omega(1-\rho V/\Omega)} \,, \tag{7}$$

$$\rho^0 = \frac{1}{\Omega(1-\rho V/\Omega)} \,. \tag{8}$$

The charge density inside the core depends on a through the volume Ω and through the orthogonality charge ρ. For fairly small V/Ω and fairly large ρ one can get considerable departures from the a^3 scaling law. If

$$\rho = \rho_0 (a_0/a)^n, \quad V/\Omega = \eta (a_0/a)^3 \,, \tag{9}$$

then, by differentiation with respect to a,

$$\frac{\delta\rho^i}{\rho^i} = \frac{(1-\eta\rho_0)\,\rho_0 n - (1-\rho_0)(3+\eta\rho_0 n)}{(1-\eta\rho_0)(1-\rho_0)} \frac{\delta a}{a} \,. \tag{10}$$

Brust and Liu have shown that in Ge the product of two orthogonality coefficients, i.e., ρ, scales as roughly (a_0/a).[11] For a typical OPW calculation in GaAs, the J matrix $\langle \mu | J | \mu \rangle$ is approximately 0.94 in the region of interest, so that $\eta\rho_0 = 0.06$. This is probably a reasonable value for Ge also. The core charge density in atomic Ge could be said to extend out no farther than 1.5 bohr, which gives $\eta = 0.09$. These numbers give

$$\delta\rho^i/\rho^i = -1.25\,\delta a/a \,. \tag{11}$$

A slightly smaller assumption of $\eta = 0.08$ gives

$$\delta\rho^i/\rho^i = -0.26\,\delta a/a \,. \tag{12}$$

There is a theoretical lower limit to η of 0.06 in this model since $\phi^*(\vec{\mu},\vec{r})\phi(\vec{\mu},\vec{r})$ is positive definite and $\eta\rho_0$ is known. Agreement with experiment and with the OPW results requires $\delta\rho^i/\rho^i \approx -0.5\,\delta a/a$, with another factor of $-1.0\,\delta a/a$ coming from the momentum renormalization.

These arguments are exceedingly crude, but they do show the possibility that the major part of the charge renormalization with a change in volume can be expected to come in the region outside the core, particularly in a crystal such as sphalerite, where the cores take up a small fraction of the total volume.

V. DISCUSSION AND CONCLUSIONS

Both our high-pressure electroreflectivity experiments and relativistic OPW calculations indicate that the volume dependence of the spin-orbit splittings considered is considerably lower than would be expected if the valence-electron density in the core increased in proportion to the decrease in volume of the unit cell. Our calculations are in disagreement with the experimental results of Bendorius and Shileika[14] on GaAs. Judging from our experience with changes in the electroreflectivity line shape in Ge, it seems possible that similar effects may have given rise to an erroneous conclusion in their experiments. This suggests that the electroreflectivity technique is perhaps not the best modulation technique to adapt to a high-pressure experiment and that another technique, such as energy modulation, might give less ambiguous results.

The principal conclusion we wish to draw from our experimental and theoretical results is that the valence-electron density in the core region is relatively unaffected by changes in the crystal volume. We have given a numerical plausibility argument based on the OPW formulation which supports this conclusion. From a physical viewpoint it can be argued that in the free atom the valence-electron density in the core region is the result of adjustment of a relatively high electron density (considering all the core levels) to a self-consistent configuration which minimizes the energy of the total configuration. It seems likely that the adjustments in the electron density which will occur when a number of atoms are brought together to form a crystal will occur in a manner which does little to upset the electron density in the core region, and that most of the adjustment will take place in the region outside the core where the total electron density is lower and a change in the valence-electron density can be made with a relatively small change in energy.

The above discussion is in variance with an argument of rather long standing due to Liu[15] which indicates that an increase in the valence-electron density in the core is responsible for the 50% increase in the Δ_0 splitting in germanium and similar semiconductors over the free-atom splitting. To make a valid comparison between the free-atom spin-orbit splitting and the splitting in the crystal, one cannot consider a single crystal state but must average over the Brillouin zone to take into account all the crystal states which evolve from the atomic states under consideration. A difference in the Δ_0 splitting and the atomic spin-orbit splitting is to be expected since the $\Gamma_{25'}$ and Γ_1 states at the center of the zone most closely approximate an sp^3 electronic configuration while the atomic configuration is s^2p^2.

It is likely that other experiments which are sensitive to the valence-electron density in the core region, such as the Knight shift, will reflect the lack of strong crystal-volume dependence which we have postulated.

Finally, it seems obvious that only calculations which treat the core region in a relatively realistic self-consistent manner can be expected to give valid results for spin-orbit splittings. It is true that all types of calculations will yield wave functions of the proper symmetry for calculating spin-orbit splittings, but only those calculations which do not assume a normalization of the wave function in the core region, but which calculate this normalization in a realistic manner, can be expected to give accurate results.

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†Present address: IBM Corp. K12/028, San Jose, Calif. 95114.

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PHYSICAL REVIEW B VOLUME 3, NUMBER 10 15 MAY 1971

Electron Mobility and Shallow Impurity Levels in In- and Cu-Doped CdS†

S. S. Li and C. I. Huang
Department of Electrical Engineering, University of Florida, Gainesville, Florida 32601
(Received 7 December 1970)

Electrical-conductivity and Hall-effect measurements were made between 300 and 4.2 °K on In-doped ($\sim 6\times10^{17}$ cm^{-3}) CdS single crystals. Normal band conduction was observed between 300 and 20 °K, while impurity-hopping conduction in a shallow-donor state (E_{D2}) dominated the conduction mechanism for $T<20$ °K. In the normal-band-conduction region, the best theoretical fit was obtained by using a two-shallow-impurity-level model. The result yields $E_{D1}=0.033$ eV for the In level with $N_{D1}=6\times10^{17}$ cm^{-3} and $E_{D2}=0.007$ eV for a level with unknown origin with $N_{D2}=1.3\times10^{17}$ cm^{-3}. The Hall mobility vs temperature was studied for both Cu- and In-doped CdS between 4.2 and 300 °K. It was found that the longitudinal optical phonons dominate the scattering of electrons for $T>200$ °K and $\mu_L\cong110(e^{(300\pm10)/T}-1)$ cm^2/V sec. A brief discussion of the scattering mechanism for $T<100$ °K is given for both In- and Cu-doped CdS.

I. INTRODUCTION

Although a considerable amount of work has been done on the photoconductive and luminescent properties in II-VI compounds, only a small part of this work has been on the conventional transport properties.

Much of the work on CdS has been concerned with the intrinsic scattering mechanism. Kroger *et al.*[1] attempted to fit their data to a simple expression for optical-mode scattering. Migazawa *et al.*[2] also attempted to fit their data with a combination of optical-mode and impurity scattering. Devlin[3] used the variational method to find the effect of two simultaneous scattering mechanisms on the Hall mobility. Fugita *et al.*[4] measured the Hall mobility under pulsed illumination using the Redfield[5] technique. Monikowa[6] measured the Seebeck coefficient of several n-type CdS crystals having room-temperature carrier concentrations of the order of 10^{15} cm^{-3}, and gave a value of 0.024 eV as the shallow-donor ionization energy. Woodbury[7] reported a double acceptor 0.09 eV below the conduction-band edge. Bradberry and Spear[8] observed trapping effects in their drift-mobility measurement due to a level 0.16 eV below the conduction band. They attributed this level to native defects, tentatively singly ionized sulfur vacancies. Buget and Wright[9] measured the temperature dependence of the carrier concentration in n-type CdS and found it determined by unknown donors with ionization energies of 0.45, 0.63, and 0.82 eV in different crystals.

Kroger and Vink[1] have studied the effect of additions of Cl and Ga which act as shallow donor after firing in Cd atmosphere, but the defects were in such high concentration that the samples were degenerate or indicated impurity-band conduction. Piper and Halsted[10] observed a donor level at 0.032 eV in samples with carrier density of 10^{15} cm^{-3}, which is sufficiently low to avoid impurity banding or screening effects. This energy is in close agreement with the value predicted on the assumption that the donor is hydrogenlike. Itakura and Toyada[11] measured the Hall effect in undoped CdS in which two donor levels were found: one 0.014 eV and the other 0.007 eV below the conduction-band edge.

The transport measurements reported in the literature so far yield a relatively well-understood knowledge with regard to the intrinsic scattering mechanism in CdS. Longitudinal optical- and acoustical-mode scattering dominate the scattering of electrons at high temperatures, while piezoelectric scattering dominates the scattering mechanism at low temperatures. Identification of impurity levels in CdS is still far from ideal owing to the fact that native defects resulting from nonstoicheo-