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Calculated Spin-Orbit Splittings of Some Group IV, III-V, and II-VI Semiconductors

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The spin-orbit splittings of the valence and conduction bands of the group-IV semiconductors Si, Ge, and α-Sn, the III-V compounds AlSb, GaP, GaAs, GaSb, InP, InAs, and InSb, and the II-VI compounds ZnS, ZnSe, ZnTe, and CdTe have been obtained at the Γ, X, and L symmetry points in the Brillouin zone. The calculations were made using a relativistic orthogonalized plane wave (ROPW) model. The energies presented are differences in eigenvalues of the Dirac Hamiltonian where the exchange correlation potential operator was approximated by the cube root of the electron density with coefficients suggested by Slater and by Kohn, Sham, and Gaspar (KSG). The calculated values are compared with values obtained from experiments and from previous $\vec{k}\cdot\vec{p}$ calculations. The validity of the two-thirds rule for the ratio of the L-point to Γ-point valence-band spin-orbit splitting is examined. The effects of hydrostatic pressure on the spin-orbit splittings are also presented.

I. INTRODUCTION

The purpose of this paper is to present calculated crystalline spin-orbit splittings obtained from solutions of the Dirac equation. The Dirac equation is solved using a relativistic orthogonalized-plane-wave (ROPW) formalism with a crystalline potential which is a superposition of isolated-atom potentials.[1,2] This study includes the effect of using a crystalline self-consistent potential and the effect of different exchange approximations upon the calculated splittings. The spin-orbit splittings for a wide variety of semiconductors (Si, Ge, α-Sn, AlSb, GaP, GaAs, GaSb, InP, InAs, InSb, ZnS, ZnSe, ZnTe, and CdTe) are given in order to check (or establish) trends as well as to give their individual values. Also, the hydrostatic pressure effect upon the spin-orbit splittings is calculated and compared with experiment.

Observations of spin-orbit splittings throughout the Brillouin zone have been made using optical reflectivity,[3] electroreflectance,[4] and absorption[5] spectra. These measurements determine the value of the splittings to within a few hundreds of an eV. In fact the very small increases in the spin-orbit splitting due to hydrostatic pressure have been measured.[6]

On the theoretical side, the spin-orbit splittings have been calculated using the OPW formalism and first-order perturbation theory by Liu[7] for Si and Ge. Herman *et al.*[8] obtained the valence-band Γ-point splitting by scaling atomic spin-orbit splittings for these compounds. Cardona and co-workers (Ref. 4) have used the $\vec{k}\cdot\vec{p}$ perturbation-theory method in which some band information including one or several spin-orbit splittings must be used as input to allow determination of the adjustable parameters. Once these parameters are determined, the band structure throughout the zone can be extrapolated. This works quite well in some cases, but fails at times as will be pointed out later.

The method used in this paper is a "black box" computer program into which the lattice constant and atomic numbers are fed, and out of which comes an unadjusted relativistic band structure. This approach has been utilized by Herman and co-workers[1,2,9] using a relativistic OPW formalism with an isolated-atom crystalline potential and by Eckelt,[10] and Madelung and Treusch[11] who use the Korringa-Kohn-Rostoker (KKR) formalism with a muffin-tin potential derived from a superposition of isolated-atom crystalline potentials.

In Sec. II A, the relativistic OPW formalism is briefly presented. Special attention is given to the insensitivity of the isolated-atom potential model to the shape of the extended tail of the core charge

density. Section II B introduces the characteristic nonrelativistic and relativistic band structures for these materials. The rationale of the two-thirds rule for the ratio of the top-valence-band spin-orbit splitting at the L point to that at the Γ point is also reviewed. The insensitivity of the calculated spin-orbit splittings upon OPW convergence, the exchange-correlation potential coefficient, and upon self-consistent charge rearrangement are discussed in Sec. II C. The spin-orbit splittings are presented and discussed in Sec. III A. The two-thirds rule is compared with calculational results. General trends from compound to compound are pointed out. In Sec. III B, isolated-atom spin-orbit splittings are given for the atoms making up the various crystals. Their relative contribution to the crystalline splittings is shown. Section III C presents the dependence of the calculated spin-orbit splittings upon hydrostatic pressure. The calculated results roughly confirm experimental findings. The most important points of the paper are then summarized in Sec. IV.

II. COMPUTATIONAL MODEL

A. Theory

The work in our laboratory on nonrelativistic self-consistent orthogonalized-plane-wave (SCOPW) band calculations has led to results which permit realistic comparisons with available experimental data for the band structure and related properties for a wide range of compounds.[12–16] It is possible to calculate the effects of pressure on band structure, deformation energies, spin-orbit splittings, effective masses, valence and conduction band densities of states, the imaginary part of the dielectric constant (ϵ_2), and x-ray form factors with no adjustments to fit experiment.

In spite of some measure of success in this laboratory and by other investigators, much remains to be learned. Perhaps the most controversial and active area concerns the approximations used to handle exchange and correlation in crystals.[15,17–23] Another area which has received much less attention is that of relativistic effects. One can certainly use first-order perturbation theory in nonrelativistic band calculations to take account of relativistic and spin-orbit effects. On the other hand, Herman and his co-workers have taken a more fundamental approach by developing band calculations in a fully relativistic formalism.[1,2] It is our contention that this approach must be pursued further before a final decision is made on the exchange-correlation problem. For the heavier compounds, a serious question can be raised about making refinements to nonrelativistic calculations. In short, exchange studies should be done with relativistic calculations. For the heavy II-VI, III-V, and group-IV compounds and atoms, relativistic corrections are at least as large as the differences introduced by varying the coefficient in a $\rho^{1/3}$ exchange approximation. Our goal is to reformulate the SCOPW technique using relativistic electronic wave functions which are solutions of the Dirac equation.

We have some reservations about the overlapping-isolated-atom-potential model with regard to the energy eigenvalues. However, the spin-orbit splittings, which compare well with experiment, are relatively insensitive to the exchange parameter used [Slater or Kohn-Sham-Gaspar (KSG)] and to the convergence with respect to the number of OPW's used.

In addition to the fact that an exchange approximation must be made in order to carry out calculations and that care must be exercised to insure convergence, there are two problems peculiar to the non-self-consistent model. The first is that the model neglects the valence charge density rearrangement that takes place when isolated atoms are brought together to form a crystal. No correction is made for this error in the isolated-atom model. The second problem arises in the treatment of the crystal potential. The potential is formed from a superposition of isolated-atom potentials. However, the core states at a given lattice site are perturbed by the overlap of the valence atomic wave functions centered at different lattice sites. A correction is made in terms of a "core shift" by adding up all the isolated-atom total potentials at a site due to the neighboring sites.[24] Therefore, the potential of an isolated atom is modified by the addition of a constant potential. The core wave functions are unchanged and all the core energy levels at a given lattice site are shifted downward by a common amount.

It is at first rather disturbing to observe that after the first few shells of neighbors, the main contribution to the core shift comes from the tail of the $\rho^{1/3}$ exchange potential. Thus, one can obtain considerable variation in the core shifts depending on how far out one carries the sum over the unrealistic exchange tail. This would seem to indicate that the calculated eigenvalues are very sensitive to a rather unphysical part of the model. Fortunately, this problem is not serious because the exchange tail also contributes to the valence electron potential energy at large r. The potential energy for $K = 0$ is an additive term in all valence electron eigenvalues.[24] The exchange tail shifts all core and valence eigenvalues by the same amount and does not affect relative energy differences. This fact removes the dependence of the model on the long-range-exchange tail provided that the $V(K = 0)$ integral is carried out just as far as the core shift sum.

All of these problems raise some doubts about

the energy eigenvalues generated by the isolated-atom model and self-consistency is a must if no adjustments are to be made. However, we find that the spin-orbit splittings obtained with this model are insensitive to all of the drawbacks of the model. This is true because the spin-orbit interaction is a phenomenon which takes place in the core. In this region, the persistent exchange tail, the valence charge-density rearrangement, and plane wave convergence are not important parameters. The spin-orbit splitting is also relatively insensitive to the coefficient of the $\rho^{1/3}$ exchange term because the exchange potential is small in the core compared to the Coulomb potential. The core levels themselves are certainly sensitive to this coefficient, but the smaller spin-orbit splittings are less so in absolute value.

The Dirac Hamiltonian for an electron in a central field $V(\vec{r})$ is

$$H = -(2/q)i\,\vec{\alpha}\cdot\vec{\nabla} + (2/q^2)\beta + I_4 V(\vec{r}) \quad ,$$

where q is the fine-structure constant and $\vec{\alpha}$, β, and I_4 are the operators

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}; \quad \beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix}; \quad I_4 = \begin{pmatrix} I_2 & 0 \\ 0 & I_2 \end{pmatrix} \quad .$$

The three 2×2 Pauli matrices are represented by $\vec{\sigma}$ and I_2 is the 2×2 unit matrix. In order to find the eigenvalues of this Hamiltonian by the method of orthogonalized plane waves, it is assumed that the eigenfunctions are Slater determinants of one-electron wave functions, as in the nonrelativistic problem. The states are four component functions in which the equations satisfied by the large and small components of the radial wave functions are found by the variational principle. The complete one-electron functions are taken to be a finite linear combination of plane waves which are orthogonalized to the core states.

Following the development of Herman, Kortum, Ortenburger, and Van Dyke, one can obtain the eigenvalues of the Dirac Hamiltonian. The overlapping atomic potential and core eigenvalues are calculated with programs adapted from those of Liberman, Waber, and Cromer.[25] We are indebted to Dr. Liberman for supplying us with his programs.

The order of the matrices that must be solved to find the energy eigenvalues is greatly reduced by using symmetrized orthogonalized plane waves. This is an important factor in the relativistic formalism because the inclusion of spin doubles the matrix size. The linearly independent members of the stars including spin at the Γ, X, and L points in the reduced zone are determined and then the projection-operator method is used to determine linear combinations of the plane waves which are the symmetrized OPW's. We have presented a summary of the symmetrization techniques in Ref. 26.

B. Relativistic Band Structure

All of the compounds considered in this paper have the zinc-blende tetrahedral crystal symmetry. The diamond crystal structure (for Si, Ge, and α-Sn) is a special case of zinc-blende symmetry in which anion and cation are identical. Zinc-blende notation will be used throughout this paper. The zinc-blende Brillouin zone is illustrated in Fig. 1. Figures 2(a) and 2(b) give the schematic nonrelativistic and relativistic band structures for this group of compounds at Γ, X, and L. The top nonrelativistic valence band has p-like symmetry at Γ. At X and L, the p-like band is split by the crystal field into an x, y, and z band. The bottom conduction band at Γ (Γ_{1c}) is s like. The next higher conduction band is p like and again shows crystal field splitting at X and L. The doubly and triply degenerate nonrelativistic bands are then spin-orbit split as shown in Fig. 2.

The two-thirds rule, first derived by Roth and Lax,[27] states that the spin-orbit splitting of the top valence band at L (the L_{3v}) is two-thirds of the spin-orbit splitting of the top valence band at Γ (the Γ_{15v}). The derivation of this relation is indicated in Fig. 3. The top valence band at Γ in the nonrelativistic limit consists of the triply degenerate x, y, z basis functions. Adding spin basis functions α and β and diagonalizing the operator H_{so} ($H_{so} = \Delta\vec{L}\cdot\vec{S}$) yields the $j=\frac{1}{2}$ and $\frac{3}{2}$ basis functions which are split in energy by $\frac{3}{2}\Delta$. The situation is different at L where the nonrelativistic crystal field splits off the z basis function (L_{1v}) from the doubly degenerate x, y basis functions (L_{3v}). Adding α and β spin functions to the x, y functions and diagonalizing H_{so} then produces a spin-orbit splitting Δ of the L_{3v}. Deviations from the two-thirds rule are then to be expected because of the much weaker spin-orbit coupling between the L_{3v} states and the L_{1v} state. One would expect

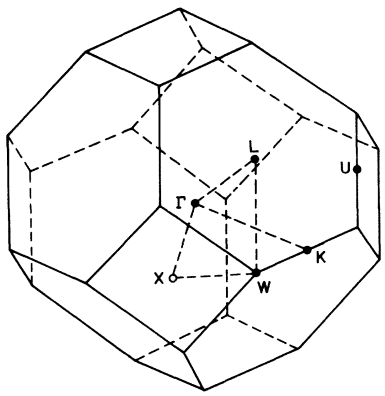

FIG. 1. The zinc-blende Brillouin zone with high-symmetry points labeled.

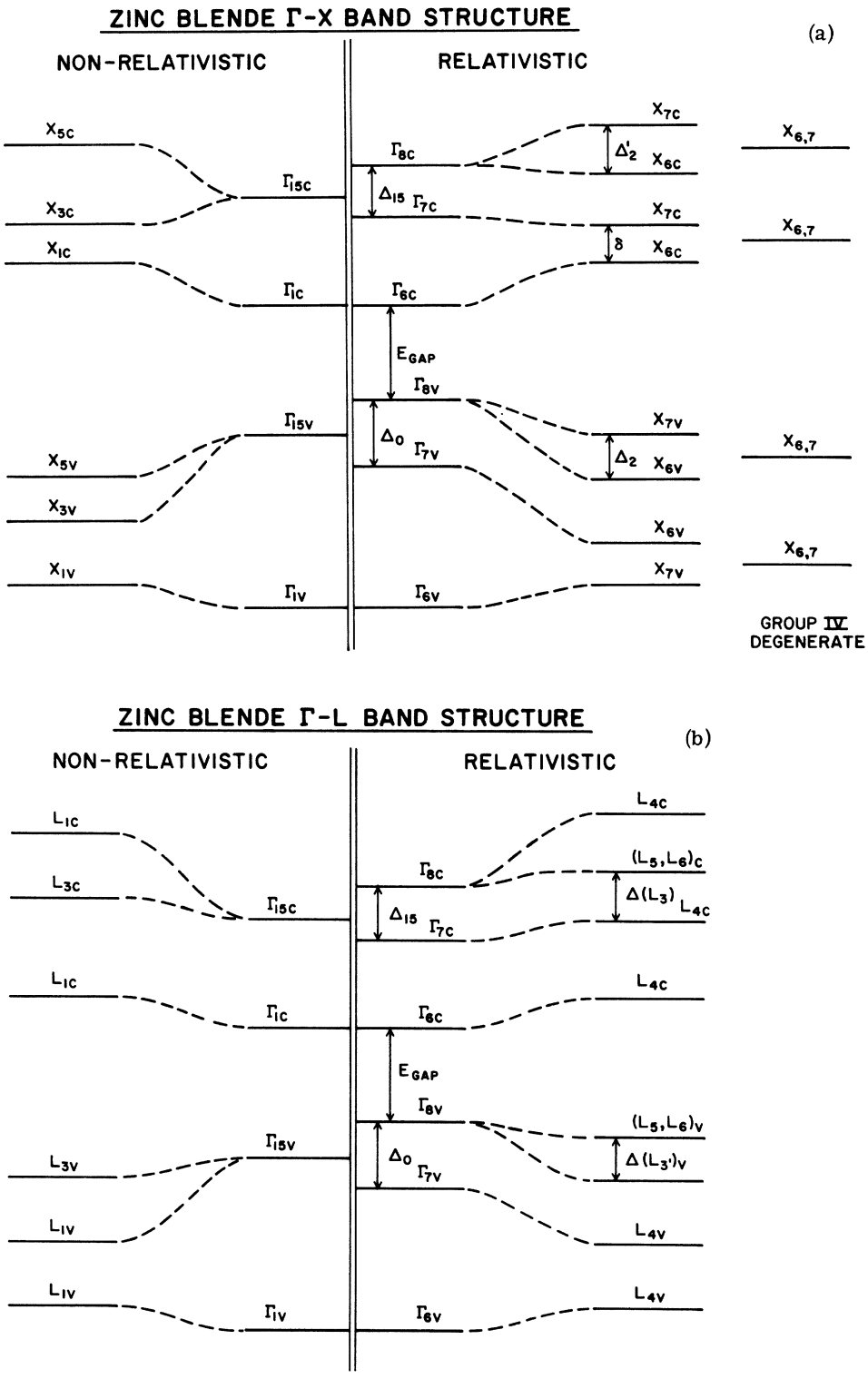

FIG. 2. (a) Schematic nonrelativistic and relativistic band structure along Γ-X for zinc-blende symmetry. Spin-orbit splitting notation follows that of Cardona *et al.* (Ref. 4). (b) Schematic nonrelativistic and relativistic band structure along Γ-L for zinc-blende symmetry. Spin-orbit splitting notation follows that of Cardona *et al.* (Ref. 4).

the bottom L_{4v} (L_{1v}) to push up the L_{4v} (L_{3v}) state, decreasing the L point splitting, and thus decreasing the ratio below two-thirds. This in fact happens.

The situation is quite different for the top valence band at X. Group theory demands that there be no spin-orbit splitting of the top X_{5v} for group-IV compounds. The X_{5v} spin-orbit splitting thus re-

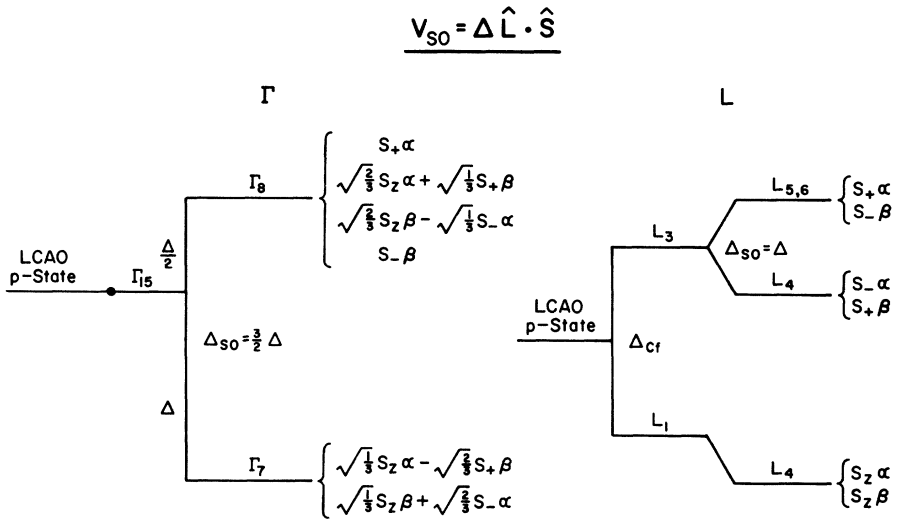

FIG. 3. Spin-orbit splitting of the top valence-band P state at Γ and L for zinc-blende symmetry. Representative wave functions involve the p-like functions s_z, $s_+ = (s_x + i s_y)/\sqrt{2}$, $s_- = (s_x - i s_y)/\sqrt{2}$, and the spin functions (α, β).

flects the dissimilarity of anion and cation.

C. Approximations

It is important to consider the dependence of the calculated spin-orbit splittings upon the convergence of the OPW series, and upon the exchange-correlation effective potential. We are also able to evaluate the dependence on the isolated-atom vs the self-consistent potential.

229 plane waves at the Γ point and an equivalent number at X and L were used in the OPW wave-function expansion for all the compounds. All of the band energy differences for compounds presented in this paper are converged to within 0.2 eV, while the spin-orbit splittings are converged to within 0.02 eV. Table I illustrates the convergence of the InAs eigenvalues and spin-orbit splittings. This convergence behavior is typical for all these compounds, indicating that a sufficient number of plane waves was used in the wave-function expansion.

The uncertainty in the spin-orbit splittings due to approximations to the effective exchange-correlation operator must also be considered. The best-known approximations are Slater's, where the eigenvalues match excitation energies quite closely, and Kohn-Sham-Gaspar's, where the charge density closely matches the Hartree-Fock charge density. To illustrate the dependence of the spin-orbit splittings upon the exchange-correlation approximation, calculations are presented throughout the paper for both approximations. The dependence of the spin-orbit splittings upon the exchange-correlation approximation ranges from 0.01 to a maximum of 0.06 eV for the compounds investigated.

The use of an isolated-atom potential rather than a self-consistent crystal potential is a more serious matter. The eigenvalue differences change up to an eV between the two models. However, the spin-orbit splittings, which depend primarily upon the potential in the inner core region, are much less sensitive to details of the crystalline potential. Table II illustrates this lack of sensitivity by comparing ZnSe spin-orbit splittings derived from the isolated-atom model with those derived from a fully self-consistent model. Details of the self-consistent model and detailed ZnSe self-consistent results will

TABLE I. Convergence of OPW energy levels at the Γ point for InAs. All entries are in eV.

No. of plane waves	113	137	181	229
Γ_{6c}	−26.42	−26.42	−26.42	−26.42
Γ_{8c}	−30.27	−30.32	−30.34	−30.35
Γ_{7c}	−30.73	−30.78	−30.81	−30.81
Γ_{6c}	−35.29	−35.29	−35.29	−35.30
Γ_{8v}	−35.52	−35.61	−35.70	−35.72
Γ_{7v}	−35.88	−35.97	−36.07	−36.10
Γ_{6v}	−47.15	−47.15	−47.15	−47.15
Γ_{8v}-Γ_{7v}	0.35	0.36	0.37	0.38
Γ_{8c}-Γ_{7c}	0.46	0.46	0.47	0.47

TABLE II. Relativistic OPW (ROPW) and self-consistent relativistic OPW (SCROPW) spin-orbit splittings for ZnSe. All entries are in eV.

	ROPW	SCROPW
Δ_0	0.449	0.464
Δ_{15}	0.145	0.167
Δ_2	0.199	0.198
$\Delta(L_{3'})$	0.266	0.258
$\Delta(L_3)$	0.063	0.082
$\Delta(L_{3'})/\Delta_0$	0.59	0.56

TABLE III. Calculated and experimental values of the spin-orbit splittings in crystals of Si, Ge, and α-Sn. The label S refers to ROPW calculations using Slater's exchange approximation and KSG refers to Kohn-Sham-Gaspar exchange. All entries are in eV.

	ROPW							
	S	KSG	Expt[a]	OPW[b]	OPW[c]	OPW[d]	$\vec{k}\cdot\vec{p}$[e]	$\vec{k}\cdot\vec{p}$[f]
			Δ_0					
Si	0.05	0.05	0.04[f]		0.046	0.042		
Ge	0.30	0.30	0.29[f]		0.28	0.29		
α-Sn	0.67	0.66		0.65	0.64			
			Δ_{15}					
Si	0.03	0.04			0.035		0.051	0.06
Ge	0.24	0.22			0.21		0.36	0.36
α-Sn	0.54	0.49		0.48	0.48		1.06	0.97
			$\Delta(L_{3'})$					
Si	0.03	0.03			0.03			0.02
Ge	0.19	0.19	0.20		0.18			0.16
α-Sn	0.44	0.43	0.48		0.41			0.43
			$\Delta(L_3)$					
Si	0.00	0.02						0.02
Ge	0.11	0.10						0.10
α-Sn	0.27	0.22	0.31[g]					0.28
			$\Delta(L_{3'})/\Delta_0$					
Si	0.60	0.60			0.65			
Ge	0.63	0.63			0.64			
α-Sn	0.66	0.65			0.64			

[a]Experimental numbers given for $\Delta(L_{3'})$ and $\Delta(L_3)$ are actually Δ_1 and Δ_1'.
[b]See Ref. 9.
[c]See Ref. 2.
[d]See Ref. 7.
[e]See Ref. 28.
[f]See Ref. 4.
[g]See Ref. 9.

be published in a separate paper. As can be seen from the table, self-consistent charge rearrangement changes the spin-orbit splittings by about 0.02 eV or less. This conclusion is substantiated by unpublished self-consistent results for Ge, GaAs, and CdTe.

We thus conclude that the spin-orbit splittings presented in this paper have a maximum uncertainty of ± 10%, due to calculational approximations which involve truncating the plane-wave series, approximating the correct many-body exchange-correlation effective potential, and neglecting self-consistent charge rearrangement.

III. RESULTS AND DISCUSSION

A. Spin-Orbit Splittings

The calculated values of the spin-orbit splittings are given in Tables III-V. The notation is the same as that of Cardona, Shaklee, and Pollack.[4] Experimental estimates are included in the table for Δ_0, $\Delta(L_3)$, and Δ_2, as well as Δ_1 values. It is generally agreed that Δ_1 is the splitting of the top valence band along the Λ line near the L symmetry point. For comparison, other calculational results are included for Δ_{15}, $\Delta(L_{3'})$, $\Delta(L_3)$, and Δ_2 where available.

A large enough number of samples of the tetrahedrally bonded semiconductors have been calculated to establish trends which differ somewhat from those obtained by the empirical approach of Ref. 4. This is mainly in the calculated relativistic OPW Δ_{15} value compared to the $\vec{k}\cdot\vec{p}$ value. Also the interesting ratio of the $\Delta(L_{3'})$ / Δ_0 of these compounds is contained in the tables and discussed. To be noted also in the following is the rather good agreement between the relativistic OPW calculated values of Δ_0 and the experimental measurements. Δ_0 is generally the best known experimental value.

1. *Group*-IV *Elements*

The agreement between the ROPW calculations and the measured spin-orbit splittings shown in Table III is quite good as pointed out above. It appears to matter very little which exchange approximation (Slater or Kohn-Sham-Gasper) is used except in the case of the α-Sn value. For the latter, the Slater exchange value is 0.27 eV as compared to the 0.22-eV value obtained with the use of the Kohn-Sham-Gasper approximation. The experimental value[9] is 0.31 eV which does favor the Slater results. Also in α-Sn, the $\Delta(L_{3'})$ value is ~ 0.05 eV less than the Δ_1 experimental value. A ROPW calculation was made at the midpoint of the Λ line

TABLE IV. Calculated and experimental values of the spin-orbit splittings in III-V zinc-blende crystals. The label S refers to ROPW calculations using Slater's exchange approximations and KSG refers to Kohn-Sham-Gaspar exchange. All entries are in eV.

	ROPW S	ROPW KSG	Expt[a, b]	OPW[c]	$\vec{k}\cdot\vec{p}$[b]	$\vec{k}\cdot\vec{p}$[d]
			Δ_0			
AlSb	0.67	0.64	0.75			
GaP	0.09	0.09	0.10			
GaAs	0.35	0.34	0.34	0.32		
GaSb	0.68	0.66	0.80	0.64		
InP	0.12	0.13	0.11			
InAs	0.38	0.37	0.43			
InSb	0.77	0.75	0.82	0.72		
			Δ_{15}			
AlSb	0.11	0.09			0.10	0.24
GaP	0.18	0.17		0.18	0.17	0.22
GaAs	0.20	0.19			0.26	0.29
GaSb	0.29	0.26		0.26	0.31	0.39
InP	0.45	0.43			0.74	0.82
InAs	0.47	0.44			0.67	0.74
InSb	0.47	0.43		0.43	0.78	0.94
			$\Delta(L_{3'})$			
AlSb	0.38	0.36	0.40		0.34	
GaP	0.06	0.06	0.10		0.09	0.072
GaAs	0.21	0.21	0.23	0.20	0.18	0.22
GaSb	0.41	0.39	0.46	0.37	0.39	
InP	0.09	0.11	0.15		0.14	0.11
InAs	0.25	0.26	0.28		0.28	
InSb	0.49	0.47	0.50	0.44	0.50	0.40
			$\Delta(L_3)$			
AlSb	0.07	0.05			0.09	
GaP	0.06	0.05			0.08	
GaAs	0.10	0.08		0.08	0.11	
GaSb	0.16	0.14		0.13	0.16	
InP	0.20	0.17			0.24	
InAs	0.22	0.19			0.25	
InSb	0.24	0.20		0.20	0.33	
			Δ_2			
AlSb	0.31	0.29			0.28	
GaP	−0.02	−0.02			0.01	
GaAs	0.10	0.09		0.08	0.07	
GaSb	0.26	0.24		0.37	0.29	
InP	−0.07	−0.08			0.21	
InAs	0.05	0.02			0.03	
InSb	0.21	0.18		0.16	0.09	
			$\Delta(L_{3'})/\Delta_0$			
AlSb	0.57	0.56				
GaP	0.67	0.67				
GaAs	0.60	0.62		0.63		
GaSb	0.60	0.59		0.58		
InP	0.75	0.85				
InAs	0.66	0.70				
InSb	0.63	0.63		0.61		

[a]Experimental numbers given for $\Delta(L_{3'})$ and $\Delta(L_3)$ are actually Δ_1 and Δ_1'.
[b]See Ref. 4.
[c]See Ref. 2.
[d]See Ref. 28.

to see if the spin-orbit value was appreciably different from that at the L point. A value of 0.45 eV was obtained using Slater's exchange approximation which is not large enough to conclude that the splitting is greater along Λ than at the L point.

The ROPW value of Δ_{15} is always significantly less than the $\vec{k}\cdot\vec{p}$ calculation of Ref. 4. The cause of this discrepancy is perhaps that in the $\vec{k}\cdot\vec{p}$ calculation, only the bonding and antibonding s and p states were considered to contribute. The value

TABLE V. Calculated and experimental values of the spin-orbit splittings in II-VI zinc-blende crystals. The label S refers to ROPW calculations using Slater's exchange approximation and KSG refers to Kohn-Sham-Gaspar exchange. All entries are in eV.

	ROPW S	ROPW KSG	Expt[a]	OPW[b]	KKR[c]	KKR[d]	$\vec{k}\cdot\vec{p}$[e]
			Δ_0				
ZnS	0.10	0.11	0.07[f]		0.08	0.0	
ZnSe	0.45	0.44	0.45[f]		0.42	0.42	
ZnTe	0.95	0.92	0.93[f]	0.88	0.93	0.93	
CdTe	0.95	0.93	0.81[g,h]	0.86	0.90	0.90	
			0.92[i]				
			Δ_{15}				
ZnS	0.15	0.14		0.14	0.14		
ZnSe	0.15	0.14			0.14		0.20
ZnTe	0.15	0.14			0.12		
CdTe	0.36	0.33		0.33	0.35		0.63
			$\Delta(L_{3'})$				
ZnS	0.04	0.05			0.05		
ZnSe	0.27	0.26	0.25[h]		0.27		0.26
ZnTe	0.56	0.54	0.57[h]	0.50	0.54		
CdTe	0.59	0.57	0.57[h]	0.51	0.54		0.92
			$\Delta(L_3)$				
ZnS	0.04	0.03			0.05		
ZnSe	0.06	0.06			0.05		
ZnTe	0.09	0.09		0.07	0.04		
CdTe	0.18	0.15	0.16[h]	0.15	0.14		
			Δ_2				
ZnS	0.03	0.02			0.03		
ZnSe	0.20	0.17			0.22		
ZnTe	0.43	0.39		0.37	0.44		
CdTe	0.40	0.35	0.35[h]	0.32	0.38		
			$\Delta(L_{3'})/\Delta_0$				
ZnS	0.40	0.45			0.63		
ZnSe	0.60	0.59			0.64		
ZnTe	0.58	0.58		0.57	0.58		
CdTe	0.62	0.61		0.59	0.60		

[a]Experimental numbers given for $\Delta(L_{3'})$ and $\Delta(L_3)$ are actually Δ_1 and Δ_1'.
[b]See Ref. 2.
[c]See Ref. 10.
[d]See Ref. 11.
[e]See Ref. 28.
[f]See Ref. 29.
[g]See Ref. 30.
[h]See Ref. 31.
[i]See Ref. 4.

of Δ_{15} is then determined by requiring that X_{4v} remain degenerate. In Ref. 9, the $\vec{k}\cdot\vec{p}$ Δ_{15} value matches that of ROPW. This was achieved by adding another parameter in the calculation.

The two-thirds rule for the ratio $\Delta(L_{3'})/\Delta_0$ holds approximately for the group-IV elements. However, there appear to be two trends in the data. First, the value of the ratio becomes larger for heavier elements (see Table III). Second, in all three cases the ratio is slightly less than the two-thirds value.

2. III-V *Compounds*

The Δ_0 data for these compounds demonstrate that the spin-orbit splitting of the valence band at the Γ point is strongly influenced by the anion (e.g., see GaP-InP or AlSb-InSb in Table IV). The influence of the cation on Δ_0 is to make the value somewhat larger for heavier cations. For example, the Slater exchange result for AlSb is 0.67 eV, while it is 0.68 eV for GaSb and 0.77 eV for InSb. The valence-band spin-orbit splitting at the L point $[\Delta(L_{3'})]$ is also dominated by the anion. As at the Γ point, the splitting is somewhat larger for heavier cations. This influence of the cation causes the $\Delta(L_{3'})/\Delta_0$ ratio to deviate from the value of $\frac{2}{3}$.

The conduction-band spin-orbit splittings $[\Delta(L_3)$ and $\Delta_{15}]$ are dominated by the cation. The effect of the anion is to increase the splitting for the heavier ions. This effect is more pronounced in the Ga compounds than in the In compounds because the In compounds have larger conduction band splittings due to the In itself.

The values of the valence-band splittings at the X point Δ_2 are listed as negative for the phosphorous compounds. The X_{7v} and X_{6v} energy levels do indeed cross over which suggests that the cation contribution to the splitting is opposite in sign to that of the anion. The fact that the other compounds in the Ga and In sequence give a positive value for Δ_2 indicates that the major contribution to the valence-band splitting is due to the anion as mentioned for the Γ and L points.

3. II-VI *Compounds*

As before, the ROPW calculated Δ_0 values of the II-VI compounds given in Table V agree quite well with experiment. The splitting is strongly influenced by the anion as in the case of the III-V compounds. Also, the Δ_{15} splitting is determined primarily by the cation. Similar to the III-V compounds, the cation has more of an influence on $\Delta(L_{3'})$ than on Δ_0. This causes the $\Delta(L_{3'})/\Delta_0$ ratio to deviate from $\frac{2}{3}$. The value of this ratio for ZnS seems to be anomalous. One would expect the ratio to be larger than ZnSe by comparison with III-V compounds, where compounds with a lighter anion give a larger $\Delta(L_{3'})/\Delta_0$ within a cation series. It should also be pointed out that the splittings for ZnS are quite small and the anomaly may result from calculational uncertainties in the results. The Δ_2 value for ZnS is positive compared to the negative value found for GaP and InP. However, it is small. The Δ_2 values show the same general behavior as found for the III-V compounds.

B. Atomic Spin-Orbit Splittings

The relativistic atomic programs of Liberman *et al.*,[25] which are used to calculate the starting atomic potential and the core eigenvalues, give the spin-orbit splittings of the atomic levels. The splittings of the p and d states of the isolated atoms which form the compounds discussed in this paper are given in Table VI. Slater's exchange approximation was used to calculate the numbers given in this table; however, Kohn-Sham-Gaspar's results are very similar. The OPW formalism requires a choice of which atomic states are to be taken as core states and which are valence states. The tightly bound core states are the isolated-atom states which are assumed to be unchanged in the crystalline environment. The loosely bound valence wave functions are considerably altered by the crystalline environment and are expanded in the OPW series. The horizontal lines in Table VI show the division of the atomic states between OPW core states and valence states.

The outer-core d-state splittings are especially interesting as reflectivity and absorption peaks are observed which involve these states. However in the crystalline environment, crystal field splitting is as important as spin-orbit splitting for the highest d states. As indicated, the crystal field splitting is ignored in the OPW model for core states so that one cannot infer much about crystalline results from atomic spin-orbit splittings for these states. The top-valence-band p states also experience combined crystal field and spin-orbit splittings in the crystal, and thus deviate considerably from the isolated atom values. On the other hand, the top-valence-band Γ_{15v} state is not crystal field split. One expects the crystalline spin-orbit splittings Δ_0 to be closely related to the spin-orbit splittings of the corresponding isolated atom anion states. (It is well established that the Γ_{15v} wave function is localized primarily around the anion sites.) One must also consider the crystalline enhancement of the spin-orbit valence-band splittings over the atomic values which results from a contraction of the valence state wave function about the core region when it is packed into a crystal.[7] The fact that our calculational results for Δ_0 agree so well with the outer p-state splitting of the corresponding atomic anion must be considered as fortuitous. The numbers in parentheses in Table VI are deduced from experimental optical spectra.[32] These splittings were ob-

TABLE VI. Calculated spin-orbit splittings of atomic levels. Slater's exchange approximation was used in all cases. All entries are in eV. Numbers in parenthesis give atomic spin-orbit splitting deduced from optical spectra (Ref. 32).

Atom	Al	Si	P	S	Zn	Ga	Ge	As	Se	Cd	In	Sn	Sb	Te
Level														
1s														
2s														
2p	0.48	0.70	0.99	1.35	24.6	28.5	32.8	37.6	42.9	195.8	214.5	234.5	256.0	278.9
3s	(0.014)	(0.028)	0.07	0.10 (0.071)	3.2	3.8	4.5	5.3	6.1	35.4	39.2	43.3	47.7	52.5
3p					0.40	0.46	0.64	0.80	0.97	6.98	8.1	9.1	10.05	10.69
3d						(0.10)	(0.18)	0.33	0.45 (0.31)	6.1	6.2	7.9	9.0	10.1
4s										0.70	0.95	1.14	1.35	1.47
4p											(0.27)	(0.42)	0.75	0.95 (0.60)
4d														
5s														
5p														

tained by use of the spin-orbit matrix elements given in Condon and Shortley.[33] In first-order perturbation theory for group-IV and -VI atoms, the atomic spin-orbit splitting is three times the splitting between the $J = 0$ and $J = 1$ levels, and is also 1.5 times the splitting between the $J = 1$ and $J = 2$ levels. An average of these two determinations is presented in the tables. Below germanium in the Periodic Table, these determinations agree within 25%, but the deviations get progressively worse, until for Te, the two numbers to be averaged are 0.02 and 0.88. As can be seen, crystalline enhancement does occur but is not reflected in our atomic calculations.

It is also interesting to examine the relative contribution of the various core spin-orbit splittings to the valence and conduction spin-orbit splittings, even though this represents a considerable simplification to the actual state of affairs. The valence OPW wave function can be written in the form

$$|\psi\rangle = |\Phi_{\mathrm{PW}}\rangle - |c\rangle ,$$

consisting of plane-wave terms and orthogonality terms involving the core wave functions. The spin-orbit expectation values then consist of four terms:

$$\langle\psi|H|\psi\rangle = \langle\Phi_{\mathrm{PW}}|H|\Phi_{\mathrm{PW}}\rangle - \langle\Phi_{\mathrm{PW}}|H|c\rangle - \langle c|H|\Phi_{\mathrm{PW}}\rangle + \langle c|H|c\rangle .$$

Liu[3] was first to observe that the predominant contribution to spin-orbit splitting comes from the last core-core expectation values. If one considers the relative contributions of the core spin-orbit splittings obtained merely by combining orthogonality coefficients with the core splittings, it is observed that for small k, the outer core p state contributes the most to the crystalline spin-orbit splitting, but deeper core p states become more significant for larger k.

C. Effects of Pressure on Spin-Orbit Splittings

Over the past few years, there have been theoretical[34] and experimental[6] attempts to specify the behavior of the spin-orbit splitting when the crystal

TABLE VII. Effect of hydrostatic pressure (1% decrease in lattice constant) on Δ_0 and Δ_{15} for Ge, GaAs, and ZnSe. Slater's exchange approximation was used in all cases. Energies are in eV.

	Δ_0	Δ_0 under pressure	% change in Δ_0	Δ_{15}	Δ_{15} under pressure	% change in Δ_{15}
Ge	0.2976	0.2982	+0.2%	0.2364	0.2370	+0.25%
GaAs	0.3508	0.3515	+0.2%	0.2002	0.2010	+0.4%
ZnSe	0.4493	0.4538	+1.0%	0.1454	0.1472	+1.2%

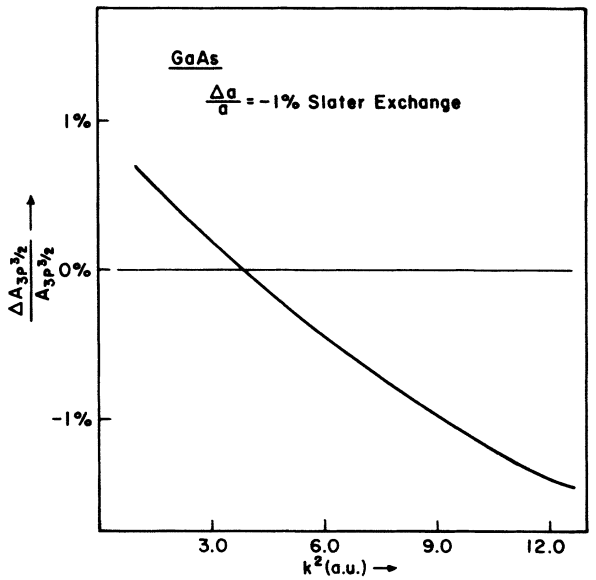

FIG. 4. Fractional change of OPW orthogonalization coefficient (see Sec. IIA) of the top core p state of GaAs at the Γ point as a function of k^2. A value $k^2 = 12.3$ corresponds to the use of 229 plane waves in the OPW expansion.

is subjected to hydrostatic pressure. Brust and Liu[34] used the OPW formalism to estimate the volume dependence of the valence-band spin-orbit splitting and obtained

$$\delta\Delta_{so}/\Delta_{so} \approx -4(\delta a/a),$$

where a is the lattice constant. This result can be anticipated if one considers the volume dependence due to renormalization of the wave function to depend on $1/a^3$ and the renormalization of the higher electron momentum to depend on $1/a$ ($3p$ electron state). Experimentally it has been found that instead of a factor of 4, a value closer to 1 ± 1 is more correct. Clearly, the spin-orbit splitting does not scale in a simple way with volume as derived by Brust and Liu.

In order to examine this problem, ROPW calculations were carried out with a 1% change in lattice constant for ZnSe, GaAs, and Ge. The results are presented in Table VII. In all cases the change in spin-orbit splitting Δ_0 was $\leq 1\%$. These results also support those of Cerdeira *et al.*[6] who used the KKR method to calculate the change in spin-orbit splitting.

It is apparent that the volume dependence of the valence-band spin-orbit splitting is not as simple as outlined by Brust and Liu. This is borne out experimentally and in more recent calculations including those presented here. One reason that $\delta\Delta_{so}/\Delta_{so}$ cannot scale in a simple way is demonstrated in Fig. 4. The $3p$ orthogonalization coefficients in the OPW treatment are k dependent and, in fact, change sign for larger k. The converged OPW calculations will give a different $3p$ contribution to Δ_{so} than the one OPW treatment of Brust and Liu. Also, Melz and Ortenburger[35] have pointed out that larger deviations from the $1/a^3$ volume dependence of the spin-orbit matrix element due to wave function renormalization are possible if the renormalization is assumed to occur outside rigid ion cores.

IV. SUMMARY

It has been demonstrated that the ROPW model is capable of yielding very good results for the spin-orbit splitting of crystals with the diamond or zinc-blende structure. The splittings are quite insensitive to self-consistent charge rearrangement, plane-wave convergence, and the coefficient in a $\rho^{1/3}$ exchange-correlation approximation. The two-thirds rule has been examined. It holds reasonably well and the deviations are explainable on the basis of spin-orbit coupling at the L point. Our results for the effect of hydrostatic pressure on spin-orbit splitting support the experimental results. The change is much smaller than predicted by earlier treatments.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 4 15 AUGUST 1971

Three-Phonon Scattering and Guthrie's Limits for Its Temperature Dependence*

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It is shown that one can explain the temperature dependence of the phonon conductivity of Ge in the entire range from 2 to 1000 °K if the three-phonon relaxation rate is given by $\tau_{3ph}^{-1} \propto g(\omega) T^{m(T)} e^{-\Theta/\alpha T}$. Three-phonon scattering processes are classified, after Guthrie, into two groups: class I, which involves the annihilation of carrier phonons by combination, and class II, which involves splitting of carrier phonons. At all temperatures, the values of $m(T)$ for both classes of processes lie either definitely below or close to the upper limit of $m(T)$ as obtained by Guthrie.

I. INTRODUCTION

Recently Guthrie[1] has given an expression for the three-phonon relaxation rate in the form

$$\tau_{3ph}^{-1} \propto g(\omega) f(T) \quad , \tag{1}$$

where $f(T) = T^m$ and $m = m(T)$. Further, $g(\omega) = \omega$ for transverse phonons, and $g(\omega) = \omega^2$ for longitudinal phonons. The value of m is found to be the same for both normal and umklapp processes. However, Klemens[2-4] has given an expression for umklapp processes:

$$\tau_{3ph}^{-1} \propto g(\omega) T^m e^{-\Theta/\alpha T} \quad . \tag{2}$$

At low temperatures he has taken $m = 4$ for transverse phonons and $m = 3$ for longitudinal phonons. These temperature dependences are in agreement with the findings of Herring.[5] At high temperatures, Klemens took $m = 1$ for both polarization branches. Except Joshi and Verma,[6] who have taken different values of m in the different temperature ranges ($m = 1-4$ for transverse phonons and $m = 1-3$ for longitudinal phonons), other workers have used the expressions given by Herring and Klemens. Since m, according to Guthrie, is a continuous function of temperature, $m = m(T)$, the use of different values of m in the different temperature regions is only a partial solution of the problem. In view of this inadequacy, we prefer to incorporate Guthrie's idea of the temperature dependence of m by writing the three-phonon scattering relaxation rate as

$$\tau_{3ph}^{-1} \propto g(\omega) T^{m(T)} e^{-\Theta/\alpha T} = B g(\omega) T^{m(T)} e^{-\Theta/\alpha T} \quad . \tag{3}$$