scattering amplitude before squaring to compute a scattering cross section, an obvious point theoretically but one which has not usually been considered in detailed calculations. Further, we have shown how even in the long-wavelength limit the first Born approximation may be significantly in error. These two factors are of general importance in determining Rayleigh-scattering cross sections.

Note Added in Proof. A recent paper by M. Yussouff and J. Mahanty [Proc. Phys. Soc. (London) **85**, 1223 (1965)] discusses impurity scattering in the long-wavelength limit for a three dimensional model with equal nearest-neighbor central and noncentral forces. Their relaxation time is obtained from an unweighted total scattering cross section by application of the optical theorem and therefore contains no interference terms between scattering amplitudes corresponding to different irreducible representations of the point group of the impurity. We contend that a more detailed treatment of thermal conductivity with their model, in which the various scattering cross sections are consistently weighted according to their efficiency in destroying quasimomentum, will reveal results similar to those presented here.

Relativistic Effects on the Electronic Band Structure of Compound Semiconductors*†

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The effects of the three relativistic interaction terms, mass-velocity, Darwin, and spin-orbit coupling, on the electronic levels of covalent-bond compound semiconductors BN, SiC, AlP, and GaAs have been investigated. Quantitative relativistic shifts and spin-orbit splittings of the appropriate Bloch states at Γ, X, and L points in the Brillouin zone have been obtained using orthogonalized-plane-wave crystal wave functions. Comparisons between available experimental data and calculations of the spin-orbit splittings of GaAs show a maximum discrepancy of 11%. The inclusion of the relativistic shifts of the energy levels did not change very significantly the band structure obtained by the nonrelativistic calculations. These effects increase, however, as the atomic numbers of the constituent atoms increase.

I. INTRODUCTION

WHEN correlation effects are neglected, the system of electrons in a solid can be described by a one-electron equation, which is the well-known Hartree-Fock equation. However, no corresponding equation has been derived for the relativistic electrons. Thus we have to rely on the Dirac equation for an electron interacting with a crystal potential. After applying successive canonical transformations of the Foldy-Wouthuysen[1] type to the Dirac equation, the positive and the negative energy states can be decoupled to successively higher orders of α, where α is the fine-structure constant. To the order of α^2, there appear in the transformed Hamiltonian three extra terms in addition to the usual nonrelativistic kinetic energy and the crystal potential V:

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) - \frac{1}{2mc^2}\frac{\mathbf{p}^4}{4m^2} + \frac{\hbar^2}{8m^2c^2}\nabla^2 V(\mathbf{r})$$

$$+ \frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot(\nabla V(\mathbf{r})\times\mathbf{p}). \quad (\mathrm{I.1})$$

The first two terms in the above Hamiltonian give the nonrelativistic Hamiltonian and the last three terms are the mass-velocity term, the Darwin term, and the spin-orbit interaction term. The first of these acquired its name because it could be obtained by simply substituting into the nonrelativistic Hamiltonian the relativistic expression for the electron mass and then making a power-series expansion in terms of (v/c). The second term was named after Darwin[2] who first introduced it; it may be attributed to the interaction of the electron, whose coordinates fluctuate over distances comparable to a Compton wavelength with a somewhat smeared-out Coulomb potential. The last term de-

[1] L. L. Foldy and S. A. Wouthuysen, Phys. Rev. **78**, 29 (1950).

[2] C. G. Darwin, Proc. Roy. Soc. (London) **A118**, 654 (1928).

scribes the coupling between the spin and the orbital motion of the electron.

It is well known that all thermal, electric, and magnetic properties of semiconductors depend largely on their electronic energy-band structures, especially on such band parameters as the energy gaps, the position of the band edges in the Brillouin zone, and the detailed structures of the energy states around these band edges. In calculating these band parameters, the inclusion of the relativistic effects sometimes leads to important changes in the final results, especially in cases where the atomic numbers of the constituent atoms of the semiconductors are large. This can be seen in the following.

It has been found that, for most of the semiconductors, the valence-band edge is a p-like state and the conduction edge an s-like state. Under the spin-orbit interaction, a degenerate p-like state will split and an s-like state will remain uneffected. On the other hand, the inclusion of the mass-velocity and the Darwin correction terms will usually effect an s-like state more strongly than a p-like state. Thus, the splitting of the p-like valence-band edge plus the depression of the s-like conduction-band edge may significantly alter the values of energy gaps and other band parameters calculated by neglecting such corrections. This alteration can become very pronounced in semiconductors composed of atoms with high atomic numbers. For these semiconductors, the spin-orbit splitting and other relativistic shifts may become quantitatively comparable to or even larger than the energy gap itself. Therefore, the inclusion of these effects in the calculation of energy bands becomes absolutely essential.

This subject has attracted the attention of several authors. The group-theoretical analyses of the spin-orbit splittings of the energy bands for crystals of diamond and zincblende structures have been made by Elliott,[3] Dresselhaus,[4] and by Parmenter.[5] Liu[6] has carried the investigation one step further by making a quantitative study of the spin-orbit coupling for several semiconductors of diamond structure. For crystals of heavy elements, Conklin, Johnson, and Pratt[7] have shown that in PbTe the band structure calculated relativistically looked quite different from that calculated nonrelativistically. Herman, Kuglin, Cuff, and Kortum,[8] in the meantime, have introduced a systematic method for estimating the magnitude of all three relativistic terms.

The present investigation is devoted to a quantitative evaluation of the effects of the three relativistic terms on the one-electron bands of selected III-V and IV-IV compound semiconductors, namely BN, SiC, AlP, and GaAs, all of which crystallize in zincblende structure. The problem is approached by perturbation calculations on the one-electron crystal wave functions represented by linear combinations of orthogonalized plane waves (OPW). For the compound semiconductors listed above, OPW-type wave functions have been calculated by Bassani and Yoshimine[9] without the relativistic effects. Our calculations are based on their wave functions.

An OPW function consists of a smoothly varying plane-wave part and a rapidly oscillating core part. The relativistic matrix elements between core parts dominate over those involving plane waves. Therefore, the relativistic corrections applied to the crystal bands for heavy elements ($Z > 10$) could be approximated by an expression in terms of the relativistic corrections applied to the free atomic-core states apart from certain overlap integrals. This prescription has been followed consistently in this work except with light elements ($Z < 10$) in which case the matrix elements between two sets of plane waves must be considered.

The spin-orbit splittings obtained in these calculations and those obtained from the available experimental data do not differ from each other by more than 11%.

II. RELATIVISTIC TERMS TREATED BY PERTURBATION THEORY

It has been mentioned earlier that the three relativistic terms in the Hamiltonian (I.1) are of the order of α^2 and therefore small in comparison with the nonrelativistic Hamiltonian H_0. This suggests that these three terms may be treated with perturbation theory.

The unperturbed eigenfunctions of H_0 are represented by OPW functions, each of which consists of a plane-wave part and a core part:

$$\psi_k{}^\alpha(\mathbf{r}) = \sum_K a_\alpha(\mathbf{k}+\mathbf{K}) \,|\,\mathbf{k}+\mathbf{K}\rangle^\alpha$$
$$+ \sum_s \sum_{nlm} b^{\alpha,s}{}_{k,nlm}\phi^s{}_{nlm}(\mathbf{r}), \quad (II.1)$$

where α denotes the symmetry of the wave function belonging to a given irreducible representation. The first term in (II.1) is a Fourier expansion in terms of plane waves with wave vector $\mathbf{k}+\mathbf{K}$, $\mathbf{K}$ being the reciprocal lattice vector. It is written in such a form that certain plane waves are grouped together to form a symmetrized combination $|\mathbf{k}+\mathbf{K}\rangle^\alpha$, which takes the form

$$|\mathbf{k}\rangle^\alpha = \frac{1}{\sqrt{\Omega}} \sum_{R[k]} F^\alpha(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (II.2)$$

where the summation $R[k]$ is taken over the set of $\mathbf{k}$'s connected by symmetry operations in the group of wave vectors. The coefficients F^α have specific values so that $|\mathbf{k}\rangle^\alpha$ should transform like the specified irreducible representation. The symmetrized combination $|\mathbf{k}\rangle^\alpha$ is normalized to one over the crystal volume Ω.

[3] R. J. Elliott, Phys. Rev. **96**, 266, 280 (1954).
[4] G. Dresselhaus, Phys. Rev. **100**, 580 (1955).
[5] R. H. Parmenter, Phys. Rev. **100**, 573 (1955).
[6] L. Liu, Phys. Rev. **126**, 1317 (1962).
[7] J. B. Conklin, Jr., L. E. Johnson, and G. W. Pratt, Jr., Phys. Rev. **137**, A1282 (1965).
[8] F. Herman, C. D. Kuglin, D. F. Cuff, and R. L. Kortum, Phys. Rev. Letters **11**, 541 (1963).
[9] F. Bassani and M. Yoshimine, Phys. Rev. **130**, 20 (1963).

The second term in (II.1) is the core part resulting from orthogonalizing the wave function to the occupied core states specified by quantum numbers (nlm). For the compound semiconductors discussed in this work, we use the superscript s to denote the two different atomic elements involved. The crystal core function ϕ^s_{nlm} is expressed in terms of the normalized atomic-core functions χ^s_{nlm}, which are assumed to be undisturbed by the crystal fields, as

$$\phi^s_{nlm}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_n} e^{i\mathbf{k}\cdot\mathbf{R}_n} \chi^s_{nlm}(\mathbf{r}-\mathbf{R}_n-\mathbf{d}_s), \quad \text{(II.3)}$$

where N is the number of unit cells in the crystal and $\mathbf{d}_s$ represents the position vector of the sth atomic site with respect to the lattice point $\mathbf{R}_n$. [For instance, in the zincblende structure, $\mathbf{d}_s$ has two values, $\mathbf{d}_1 = (a/8)(\bar{1},\bar{1},\bar{1})$ and $\mathbf{d}_2 = (a/8)(1,1,1)$.] Since $\psi_\mathbf{k}^\alpha$ in (II.1) should be made orthogonal to ϕ^s_{nlm}, the coefficient $b^{\alpha,s}_{\mathbf{k},nlm}$ takes the form:

$$b^{\alpha,s}_{\mathbf{k},nlm} = -\sum_\mathbf{K} a_\alpha(\mathbf{k}+\mathbf{K})\langle\phi^s_{nlm}|\mathbf{k}+\mathbf{K}\rangle^\alpha. \quad \text{(II.4)}$$

The overlap integral between a symmetrized combination of plane waves and a crystal-core orbital can be conveniently expressed in terms of the commonly defined orthogonalization coefficient $A^s_{nl}(\mathbf{k})$[9] as follows:

$$\langle\phi_{nlm}|\mathbf{k}\rangle^\alpha = \sum_{R[\mathbf{k}]} e^{i\mathbf{k}\cdot\mathbf{d}_s} F^\alpha(\mathbf{k}) A_{nl}(\mathbf{k}) Y_l^m(\mathbf{k}|\mathbf{z}), \quad \text{(II.5)}$$

where Y_l^m is the spherical harmonics and $\mathbf{z}$ specifies a crystalline direction chosen as the quantization axis for all the atomic-core orbitals.

Since the crystal wave functions are represented by OPW functions (II.1), each of which consists of a plane-wave part and a core part, matrix elements between any two of these OPW functions will have three parts. The first of these parts will involve two sets of plane waves; the second will involve a set of plane waves and a set of ion cores, and the third will involve two sets of cores. The importance of these three relativistic terms, however, is appreciable when the electron is close to the nucleus where the OPW function is dominated by its core part and diminishes rapidly as it gets away from this core region. This domination of the core part in the region close to the nucleus becomes more pronounced in the atoms with greater atomic number. Liu[6] has shown that for the spin-orbit splitting in Si, the core-core term contributes to about 96% of the entire matrix element. Thus for crystals whose constituent ion cores having atomic numbers around or higher than this, we can safely neglect the plane wave part in (II.1) and write

$$\psi_\mathbf{k}^\alpha(\mathbf{r}) = \sum_{s=1}^{2} \sum_{nlm} b^{\alpha,s}_{\mathbf{k},nlm}\phi^s_{nlm}(\mathbf{r}). \quad \text{(II.6)}$$

With this simplified crystal wave function (II.6), the perturbation matrix elements appear in a very simple form:

$$\langle\psi_\mathbf{k}^\alpha|H'|\psi_\mathbf{k}^{\alpha'}\rangle = \sum_{s=1}^{2} \sum_{nlm} \sum_{n'l'm'} b^{\alpha,s}_{\mathbf{k},nlm}{}^* b^{\alpha',s}_{\mathbf{k},n'l'm'}$$
$$\times\langle\chi^s_{nlm}|H'|\chi^s_{n'l'm'}\rangle. \quad \text{(II.7)}$$

The assumption has been made that atoms in the crystal do not overlap. Here H' is the perturbing Hamiltonian which includes the spin-orbit interaction, the mass-velocity, and the Darwin corrections:

$$H' = H_{so} + H_{mv} + H_d, \quad \text{(II.8a)}$$

$$H_{so} = \mathbf{h}\cdot\boldsymbol{\sigma}, \quad \text{(II.8b)}$$

$$\mathbf{h} = \frac{\hbar}{4m^2c^2}(\boldsymbol{\nabla}V(\mathbf{r})\times\mathbf{p}), \quad \text{(II.8c)}$$

$$H_{mv} = -\frac{1}{2mc^2}\frac{\mathbf{p}^4}{4m^2}, \quad \text{(II.8d)}$$

$$H_d = \frac{\hbar^2}{8m^2c^2}\boldsymbol{\nabla}^2 V(\mathbf{r}), \quad \text{(II.8e)}$$

where $\boldsymbol{\sigma}$ in the second of the above equations represents the Pauli spin matrices.

From the above equations we see that the mass-velocity term is proportional to $\mathbf{p}^4$ and the Darwin term to $\boldsymbol{\nabla}^2 V(\mathbf{r})$ which are rather difficult to handle in actual calculations. For an approximation in the nonrelativistic limit, however, the kinetic energy of an electron in a certain state can be expressed in terms of its unperturbed energy eigenvalue in that state minus the potential energy experienced by it, i.e.,

$$\mathbf{p}^2 \simeq 2m[E_n - V(\mathbf{r})].$$

In this approximation the mass-velocity term becomes

$$\frac{-1}{2mc^2}\left\langle\chi_n(\mathbf{r})\left|\frac{\mathbf{p}^4}{4m^2}\right|\chi_{n'}(\mathbf{r})\right\rangle$$
$$\simeq \frac{-1}{2mc^2}\langle\chi_n(\mathbf{r})|(E_n - V(\mathbf{r}))$$
$$\times(E_{n'} - V(\mathbf{r}))|\chi_{n'}(\mathbf{r})\rangle. \quad \text{(II.9)}$$

As for the Darwin term, we may use the Green's theorem and arrive at

$$\frac{\hbar^2}{8m^2c^2}\langle\chi_n(\mathbf{r})|\boldsymbol{\nabla}^2 V(\mathbf{r})|\chi_{n'}(\mathbf{r})\rangle$$
$$= \frac{-\hbar^2}{8m^2c^2}\{\langle\boldsymbol{\nabla}\chi_n(\mathbf{r})|\boldsymbol{\nabla}V(\mathbf{r})|\chi_{n'}(\mathbf{r})\rangle$$
$$+ \langle\chi_n(\mathbf{r})|\boldsymbol{\nabla}V(\mathbf{r})|\boldsymbol{\nabla}\chi_{n'}(\mathbf{r})\rangle\}. \quad \text{(II.10)}$$

As mentioned previously, the mass-velocity and the Darwin terms are important near the nucleus where

only s-like atomic orbitals give rise to any appreciable charge density. For this reason, in crystal we would only expect the s-like levels to be affected appreciably by these terms. Since for the s-like state there always exists in the OPW function a $l=0$ core part, the plane-wave part in the OPW can always be neglected in the calculation of the effects due to these two relativistic perturbations, and (II.6) is sufficient.

As for the spin-orbit term, although it is of the nature of r^{-3}, it is in the meantime proportional to the angular momentum. (For the atomic case, it takes the form of $\lambda \mathbf{s} \cdot \mathbf{l}$.) Therefore, it vanishes for the s state. For crystals of light elements where there exists no occupied atomic-core orbital with angular momentum equal to or greater than one, the approximated expression (II.6) is no longer sufficient to describe the electron wave function in the calculation of the spin-orbit splitting. In such cases, the OPW function for a p-like state only possesses the plane-wave part. Hence, for a crystal of light elements where there exists only an s-core orbital, the spin-orbit matrix element must be separately treated in the following manner.

We assume that the crystal potential can be represented by a sum of all the atomic potentials centered around the lattice points and they have spherical symmetry with respect to their respective atomic sites. We further assume that there is no overlap between the two atomic potentials V_1 and V_2. The perturbation matrix elements of the spin-orbit interaction, H_{so}, for any crystal having ion cores of orbital angular momentum not higher than $l=0$ (i.e., $Z<10$) becomes

$$\langle \psi_{\mathbf{k}}^{\alpha}\beta_i | H_{so} | \psi_{\mathbf{k}}^{\alpha'}\beta_j \rangle$$

$$= \frac{\hbar}{4m^2c^2N\Omega_0} \langle \sum_{\mathbf{K}_i} a_\alpha(\mathbf{k}+\mathbf{K}_i)e^{i(\mathbf{k}+\mathbf{K}_i)\cdot\mathbf{r}} |$$

$$\nabla V(\mathbf{r}) \times \mathbf{p} | \sum_{\mathbf{K}_j} a_{\alpha'}(\mathbf{k}+\mathbf{K}_j)e^{i(\mathbf{k}+\mathbf{K}_j)\cdot\mathbf{r}} \rangle$$

$$\cdot \langle \beta_i | \boldsymbol{\sigma} | \beta_j \rangle$$

$$= \frac{i\hbar^2}{4m^2c^2\Omega_0} \sum_{s=1}^{2} \sum_{\mathbf{K}_i} \sum_{\mathbf{K}_j} a_\alpha^*(\mathbf{k}+\mathbf{K}_i)a_{\alpha'}(\mathbf{k}+\mathbf{K}_j)$$

$$\times e^{i(\mathbf{K}_j-\mathbf{K}_i)\cdot\mathbf{d}_s} \langle \beta_i | \boldsymbol{\sigma} | \beta_j \rangle$$

$$\cdot \int_{\Omega_0} e^{i(\mathbf{K}_j-\mathbf{K}_i)\cdot\mathbf{R}_s} \frac{\partial V_s}{\partial R_s} \left(\frac{\mathbf{R}_s}{|\mathbf{R}_s|} \times (\mathbf{k}+\mathbf{K}_j) \right) d\tau_0,$$

where the integration is taken over the unit cell of volume Ω_0. $\mathbf{R}_s$ is the radius vector of an electron with respect to the origin of the sth atom and $|\beta_i\rangle$ denotes the eigenstate of the spin operator σ_z. If for each term under the double summation, $\sum_{\mathbf{K}_j} \sum_{\mathbf{K}_i}$, the direction of $\mathbf{K}_{ji}=\mathbf{K}_j-\mathbf{K}_i$ is selected as the zenith, the above equa-

tion can be simplified to

$$\langle \psi_{\mathbf{k}}^{\alpha}\beta_i | H_{so} | \psi_{\mathbf{k}}^{\alpha'}\beta_j \rangle$$

$$= \frac{-\pi\hbar^2}{m^2c^2\Omega_0} \sum_{s=1}^{2} \sum_{\mathbf{K}_j} \sum_{\mathbf{K}_i} a_\alpha^*(\mathbf{k}+\mathbf{K}_i)a_{\alpha'}(\mathbf{k}+\mathbf{K}_j)e^{i\mathbf{K}_{ji}\cdot\mathbf{d}_s}$$

$$\times \int_0^\infty \frac{\partial V_s}{\partial r} j_1(K_{ji}r)r^2 dr \left(\frac{\mathbf{K}_{ji}}{|\mathbf{K}_{ji}|} \times (\mathbf{k}+\mathbf{K}_j) \right)$$

$$\cdot \langle \beta_i | \boldsymbol{\sigma} | \beta_j \rangle, \quad (\text{II.11})$$

where the spherical Bessel function of the first order, $j_1(K_{ji}r)$, results from expanding the exponential in Legendre polynomials.

Since each term under the double summation depends on the direction of $(\mathbf{k}+\mathbf{K}_j)$ relative to $\mathbf{K}_{ji}$, the performance of the summation is a tedious job. The labor of performing such sum increases with the increase of the number of plane waves employed in the construction of the crystal wave function, but can be reduced with the aid of an electronic computor.

III. PERTURBATION MATRICES AT SYMMETRY POINTS

The compound semiconductors which are included here in our discussion all crystallize in zinc-blende (sphalerite) structure. Since the zinc-blende structure belongs to the cubic system, it is more convenient to express the atomic orbitals χ_{nlm} in an OPW crystal wave function in terms of the cubic harmonics, which take the following form:

$$\chi_{ns}(\mathbf{r}) = \left(\frac{1}{4\pi}\right)^{1/2} \frac{P_{ns}(r)}{r}, \quad (\text{III.1a})$$

$$\chi_{nx}(\mathbf{r}) = \left(\frac{3}{4\pi}\right)^{1/2} \frac{P_{np}(r)}{r} \frac{x}{r}, \quad (\text{III.1b})$$

$$\chi_{nyz}(\mathbf{r}) = \left(\frac{15}{4\pi}\right)^{1/2} \frac{P_{nd}(r)}{r} \frac{yz}{r^2}, \quad (\text{III.1c})$$

$$\chi_{nx^2}(\mathbf{r}) = \left(\frac{5}{4\pi}\right) \frac{P_{nd}(r)}{r} \frac{x^2}{r^2}, \quad (\text{III.1d})$$

where $P_{nl}(r)/r$ is the radial part of the atomic wave function of the (nl) electron.

The type of core orbitals contained in the OPW function of a particular crystal state is determined by the symmetry of that state. For the states which transform like different irreducible representations at points $\Gamma[\mathbf{k}=(0,0,0)]$, $L[\mathbf{k}=(\pi/a)(1,1,1)]$, and $X[\mathbf{k}=(2\pi/a) \times (1,0,0)]$, the core parts of the space-wave functions are found to be as described in the following paragraphs. The irreducible representation symbols have been used to denote the core part of the wave functions with superscripts specifying the symmetry type.

There are three degenerate functions for the irreducible representation Γ_{15}, the following and its two cyclic permutations in the order x-y-z:

$$|\Gamma_{15}{}^{yz}\rangle=\sum_s\sum_n\ (b^s{}_{\Gamma_{15},np}|\phi_{nx}{}^s\rangle+b^s{}_{\Gamma_{15},nyz}|\phi^s{}_{nyz}\rangle)\ .\quad\text{(III.2)}$$

The first summation on s is to sum over the contributions from the two different atoms and the second summation is over the appropriate principal quantum numbers of all the occupied atomic core states. The wave function for the irreducible representation Γ_1 is nondegenerate. It is

$$|\Gamma_1\rangle=\sum_s\sum_n\ b^s{}_{\Gamma_1,ns}|\phi^s{}_{ns}\rangle\ .\quad\text{(III.3)}$$

Similarly for the irreducible representation X_1, the wave function is

$$|X_1\rangle=\sum_n\ (b^1{}_{X_1,ns}|\phi^1{}_{ns}\rangle+b^1{}_{X_1,nx^2}|\phi^1{}_{nx^2}-\tfrac12\phi^1{}_{ny^2}-\tfrac12\phi^1{}_{nz^2}\rangle$$
$$+b^2{}_{X_1,np}|\phi^2{}_{nx}\rangle+b^2{}_{X_1,nyz}|\phi^2{}_{nyz}\rangle)\ ,\quad\text{(III.4)}$$

and for the irreducible representation X_3, we have

$$|X_3\rangle=\sum_n(b^1{}_{X_3,np}|\phi^1{}_{nx}\rangle+b^1{}_{X_3,nyz}|\phi^1{}_{nyz}\rangle$$
$$+b^2{}_{X_3,ns}|\phi^2{}_{ns}\rangle+b^2{}_{X_3,nx^2}|\phi^2{}_{nx^2}$$
$$-\tfrac12\phi^2{}_{ny^2}-\tfrac12\phi^2{}_{nz^2}\rangle)\ .\quad\text{(III.5)}$$

The two degenerate functions for the irreducible representation X_5 are

$$|X_5{}^{y+z}\rangle=\sum_s\sum_n\ (b^s{}_{X_5,np}|\phi^s{}_{ny}+\phi^s{}_{nz}\rangle$$
$$+b^s{}_{X_5,nyz}|\phi^s{}_{nzz}+\phi^s{}_{nxy}\rangle)\ ,\quad\text{(III.6a)}$$

$$|X_5{}^{y-z}\rangle=\sum_s\sum_n\ (b^s{}_{X_5,np}|\phi^s{}_{ny}-\phi^s{}_{nz}\rangle$$
$$+b^s{}_{X_5,nyz}|\phi^s{}_{nzz}-\phi^s{}_{nxy}\rangle)\ .\quad\text{(III.6b)}$$

For L point, we have the nondegenerate irreducible representation L_1,

$$|L_1\rangle=\sum_s\sum_n\ (b^s{}_{L_1,ns}|\phi^s{}_{ns}\rangle+b^s{}_{L_1,np}|\phi^s{}_{nx}+\phi^s{}_{ny}+\phi^s{}_{nz}\rangle$$
$$+b^s{}_{L_1,nyz}|\phi^s{}_{nyz}+\phi^s{}_{nzx}+\phi^s{}_{nxy}\rangle)\ ,\quad\text{(III.7)}$$

and the two degenerate functions for the irreducible representation L_3:

$$|L_3{}^{x-y}\rangle=\sum_s\sum_n\ (b^s{}_{L_3,np}|\phi^s{}_{nx}-\phi^s{}_{ny}\rangle$$
$$\times b^s{}_{L_3,nyz}|\phi^s{}_{nyz}-\phi^s{}_{nzx}\rangle$$
$$+b^s{}_{L_3,nx^2}|\phi^s{}_{nx^2}-\phi^s{}_{ny^2}\rangle)\ ,\quad\text{(III.8a)}$$

$$|L_3{}^{x+y-2z}\rangle=\frac{1}{\sqrt3}\sum_s\sum_n\ (b^s{}_{L_3,np}|\phi^s{}_{nx}+\phi^s{}_{ny}-2\phi^s{}_{nz}\rangle$$
$$+b^s{}_{L_3,nyz}|\phi^s{}_{nyz}+\phi^s{}_{nzx}-2\phi^s{}_{nxy}\rangle$$
$$+b^s{}_{L_3,nx^2}|\phi^s{}_{nx^2}+\phi^s{}_{ny^2}-2\phi^s{}_{nz^2}\rangle)\ .\quad\text{(III.8b)}$$

The total wave function of a state is the product of the space-wave function and the spin wave function. The spin-orbit or the relativistic perturbation matrices are being set up in this representation in which the non-relativistic Hamiltonian H_0 is diagonal. We shall discuss these matrices separately at the symmetry points Γ, X, and L in the reduced zone in the remainder of this chapter.

At the Symmetry Point $\Gamma[k=(0,0,0)]$

At the center of the Brillouin zone in the zincblende structure, the irreducible representation Γ_1 is s like, nondegenerate when excluding spin and doubly degenerate when spin is included. The irreducible representation Γ_{15} is p like, triply degenerate without spin and sixfold degenerate when spin is included. Since Γ_{15} is p like, it will be split under the spin-orbit interaction into two levels, Γ_7 and Γ_8, which are twofold and fourfold degenerate, respectively; while the s-like state Γ_1 is not expected to be effected by this interaction but to be shifted by the relativistic shifts.

The valence band edges for the III-V and the IV-IV compound semiconductors are at Γ_{15} which is split by the spin-orbit interaction. Since the perturbation Hamiltonian only connects the state in the irreducible representation Γ_{15} with another degenerate Γ_{15} state, we only need to evaluate the 6×6 matrix on the basis of the six degenerate functions of Γ_{15} if the influence of the other Γ_{15} can be neglected. Its nonvanishing spin-orbit matrix elements are

$$\langle\Gamma_{15}{}^{zx}\pm|H_{so}|\Gamma_{15}{}^{xy}\mp\rangle$$
$$=\sum_s\sum_{n,n'}\ (b^s{}_{\Gamma_{15},np}{}^*b^s{}_{\Gamma_{15},n'p}\langle X^s{}_{ny}|h_x|X^s{}_{n'z}\rangle$$
$$+b^s{}_{\Gamma_{15},nyz}{}^*b^s{}_{\Gamma_{15},n'yz}\langle X^s{}_{nzx}|h_x|X^s{}_{n'xy}\rangle$$
$$\equiv-iS,\quad\text{(III.9a)}$$

$$\langle\Gamma_{15}{}^{yz}\pm|H_{so}|\Gamma_{15}{}^{xy}\mp\rangle$$
$$\equiv\pm S,\quad\text{(III.9b)}$$

$$\langle\Gamma_{15}{}^{yz}\pm|H_{so}|\Gamma_{15}{}^{zx}\pm\rangle$$
$$\equiv\mp iS,\quad\text{(III.9c)}$$

and their complex conjugates, where h_x is the x component of the operator $\mathbf{h}$ defined in (II.8c) and $|+\rangle$ and $|-\rangle$ are used to denote the usual spin-up and spin-down wave functions. The phases of the wave functions can be so chosen as to make S a real quantity.

By means of a unitary transformation this 6×6 matrix can be brought into the form of having two equivalent 3×3 submatrices on the diagonal. So the problem is further reduced to a 3×3 matrix,

$$\begin{bmatrix} 0 & -iS & S \\ iS & 0 & -iS \\ S & iS & 0 \end{bmatrix}.$$

The equivalence of the two submatrices implies that the split-off levels from the Γ_{15} state are at least doubly degenerate. This submatrix can be readily diagonalized to yield the eigenvalues S, S and $-2S$, and the splitting of the Γ_{15} level becomes

$$\Delta_{so}(\Gamma_{15}) = 3S.$$

The spin-orbit matrix element between two atomic-core functions χ_{nl} contained in S has the explicit form

$$\langle \chi_{nl} | h_x | \chi_{n'l} \rangle = -i \frac{\hbar^2}{4m^2c^2} \int_0^\infty dr P_{nl} P_{n'l} \frac{1}{r} \frac{dV}{dr}$$

$$\equiv -\frac{i}{2l+1} \Delta_{nl,n'l}. \quad (III.10)$$

For $n=n'$, the spin-orbit overlap integral $\Delta_{nl,n'l}$ defined in the above becomes the spin-orbit splitting of the atomic-core state. This relation enables us to express the spin-orbit splitting of the crystal valence state in terms of that of the atomic-core states and their overlap integrals. Finally, we can write

$$\Delta_{so}(\Gamma_{15}) = \sum_s \sum_{n,n'} (b^s_{\Gamma_{15},np}{}^* b^s_{\Gamma_{15},n'p} \Delta^s_{np,n'p}$$
$$-\tfrac{3}{5} b^s_{\Gamma_{15},nyz}{}^* b^s_{\Gamma_{15},n'yz} \Delta^s_{nd,n'd}), \quad (III.11)$$

where s denotes the two different atoms.

The spin-orbit perturbation Hamiltonian also connects two different Γ_{15} states. However, in the compounds under investigation in this work, the two levels $\Gamma_{15}{}^{valence}$ and $\Gamma_{15}{}^{conduction}$ are far apart as compared with the spin-orbit splitting itself. Therefore, we should expect these interband connections to be very small and the above consideration based on a 3×3 matrix alone is sufficient.

In contrast to the fact that the diagonal matrix elements of the spin-orbit matrix vanish, the relativistic matrix (the mass-velocity correction plus the Darwin correction) is diagonal, i.e., the matrix elements between states belonging to different irreducible representations or to different columns in the same irreducible representation vanish. This is due to the fact that the two relativistic correction terms have the same symmetry as that of the nonrelativistic (unperturbed) Hamiltonian H_0. Consequently, the perturbations to the energy levels due to these two relativistic corrections in the perturbing Hamiltonian are just solid shifts by an amount equal to the corresponding diagonal matrix elements.

As in the spin-orbit splitting, these relativistic shifts of the energy levels in crystals, ΔE_{rel}, can also be expressed in terms of the relativistic shifts of the atomic-core states in the corresponding isolated atoms, $R^s_{nl,n'l}$. The relativistic shifts of the crystal energy levels Γ_{15} and Γ_1 are now:

$$\Delta E_{rel}(\Gamma_{15}) = \sum_s \sum_{n,n'} (b^s_{\Gamma_{15},np}{}^* b^s_{\Gamma_{15},n'p} R^s_{np,n'p}$$
$$+ b^s_{\Gamma_{15},nyz}{}^* b^s_{\Gamma_{15},n'yz} R^s_{nd,n'd}), \quad (III.12a)$$

$$\Delta E_{rel}(\Gamma_1) = \sum_s \sum_{n,n'} b^s_{\Gamma_1,ns}{}^* b^s_{\Gamma_1,n's} R^s_{ns,n's}, \quad (III.12b)$$

where

$$R^s_{nl,n'l} = \langle \chi^s_{nl} | H_{mv} + H_d | \chi^s_{n'l} \rangle,$$

which can be evaluated according to (II.9) and (II.10).

Again as in the spin-orbit calculation, because of the large spacings between two different levels of the same symmetry, influences from other levels of the same symmetry are negligible to the results obtained by (III.12).

At the Symmetry Point $X[k=(2\pi/a)(1,0,0)]$

Based on the nonrelativistic calculations of Bassani and Yoshimine, the conduction-band minima of the III-V and the IV-IV compound semiconductors under investigation here are at the X point in the reduced zone. The nonvanishing spin-orbit matrix elements are found to be

$$\langle X_5{}^{y+z}\pm | H_{so} | X_5{}^{y-z}\mp \rangle$$
$$= 2 \sum_{s=1}^2 (-1)^s \sum_{n,n'} (b^s_{X_5,np}{}^* b^s_{X_5,n'p}$$
$$\times \langle \chi^s_{ny} | h_x | \chi^s_{n'z} \rangle - b^s_{X_5,nyz}{}^* b^s_{X_5,n'yz}$$
$$\times \langle \chi^s_{nzx} | h_x | \chi^s_{n'xy} \rangle)$$
$$\equiv iE \quad (III.13)$$

and their complex conjugates. The influences of the levels X_1 and X_3 on the spin-orbit splitting of the X_5 level are of second order if the energy gaps between X_5 and these levels are large. Then, a 4×4 matrix set up on the basis of the four degenerate eigenfunctions at X_5 is sufficient for the spin-orbit calculation. We further notice that a unitary transformation can reduce this 4×4 matrix into two equivalent 2×2 submatrices on the diagonal, each in the form

$$\begin{pmatrix} 0 & iE \\ -iE & 0 \end{pmatrix}.$$

This secular matrix has eigenvalues E and $-E$, which yield a spin-orbit splitting $2E$ for the level X_5. As done in the previous section, this crystal spin-orbit splitting can be expressed in terms of atomic-core spin-orbit splittings together with their overlap integrals. We have

$$\Delta_{so}(X_5) = 2 \left| \sum_{s=1}^2 \sum_{n,n'} (-1)^{s+1} \right.$$
$$\times (\tfrac{2}{3} b^s_{X_5,np}{}^* b^s_{X_5,n'p} \Delta^s_{np,n'p}$$
$$\left. - \tfrac{2}{5} b^s_{X_5,nyz}{}^* b^s_{X_5,n'yz} \Delta^s_{nd,n'd}) \right|. \quad (III.14)$$

The two relativistic correction terms cause shifts to the energy levels, which are listed below:

$$\Delta E_{rel}(X_1) = \sum_{n,n'} (b^1_{X_1,ns}{}^* b^1_{X_1,n's} R^1_{ns,n's}$$
$$+ b^2_{X_1,np}{}^* b^2_{X_1,n'p} R^2_{np,n'p}$$
$$+ b^1_{X_1,nx^2}{}^* b^1_{X_1,n'x^2} R^1_{nd,n'd}$$
$$+ b^2_{X_1,nyz}{}^* b^2_{X_1,n'yz} R^2_{nd,n'd}), \quad (III.15a)$$

$$\Delta E_{\mathrm{rel}}(X_3) = \sum_{n,n'} (b^2{}_{X_3,ns}{}^* b^2{}_{X_3,n's} R^2{}_{ns,n's}$$
$$+ b^1{}_{X_3,np}{}^* b^1{}_{X_3,n'p} R^1{}_{np,n'p}$$
$$+ b^1{}_{X_3,nyz}{}^* b^1{}_{X_3,n'yz} R^1{}_{nd,n'd}$$
$$+ b^2{}_{X_3,nx^2}{}^* b^2{}_{X_3,n'x^2} R^2{}_{nd,n'd}) , \quad \text{(III.15b)}$$

$$\Delta E_{\mathrm{rel}}(X_5) = 2\sum_{s}\sum_{n,n'} (b^s{}_{X_5,np}{}^* b^s{}_{X_5,n'p} R^s{}_{np,n'p}$$
$$+ b^s{}_{X_5,nyz}{}^* b^s{}_{X_5,n'yz} R^s{}_{nd,n'd}) . \quad \text{(III.15c)}$$

From the double group irreducible representation for the diamond structure, it can be seen that the fourfold degenerate level X_4 does not split under the spin-orbit interaction. Liu[6] has shown that for the silicon crystal the spin-orbit splitting of Δ_5 at a point near X_4 was only about 3% of the splitting of $\Gamma_{25'}$, which is the valence band edge. Since the X_5 state in the zincblende structure has the same symmetry as Δ_5 in the diamond structure, we do not anticipate the spin-orbit splitting at X_5 state in the zincblende structure to be too large as compared with that at Γ_{15} state. As can be seen from (III.14), it is essentially the difference between the atomic splittings of the two different atoms, each weighted by a weighting factor. When the two species of atoms become one common species, the difference between the two weighted atomic splittings will vanish.

At the Symmetry Point $L[k= (\pi/a)(1,1,1)]$

The spin-orbit splitting of the degenerate p-like level L_3 can be arrived at by diagonalizing a 4×4 spin-orbit matrix with nonvanishing matrix elements:

$$\langle L_3{}^{x+y-2z}\pm | H_{\mathrm{SO}} | L_3{}^{x-y}\pm \rangle$$
$$= \pm 2\sum_{s}\sum_{n,n'} (b^s{}_{L_3,np}{}^* b^s{}_{L_3,n'p}\langle \chi^s{}_{ny} | h_z | \chi^s{}_{n'x}\rangle$$
$$- b^s{}_{L_3,nyz}{}^* b^s{}_{L_3,n'yz}\langle \chi^s{}_{nyz} | h_z | \chi^s{}_{n'zx}\rangle$$
$$- 2b^s{}_{L_3,nyz}{}^* b^s{}_{L_3,n'x^2}\langle \chi^s{}_{nxy} | h_z | \chi^s{}_{n'x^2}\rangle)$$
$$\equiv \pm iA \quad \text{(III.16a)}$$

$$\langle L_3{}^{x+y-2z}\pm | H_{\mathrm{SO}} | L_3{}^{x-y}\mp \rangle$$
$$= (\pm 1 + i)A . \quad \text{(III.16b)}$$

Again, this 4×4 matrix can be transformed into two equivalent submatrices each in the form

$$\begin{pmatrix} -iA & (-1-i)A \\ (1-i)A & iA \end{pmatrix} .$$

The difference between the two eigenvalues, $2\sqrt{3}A$, is the spin-orbit splitting of the level L_3. In terms of the atomic-core splittings and their overlap integrals, it becomes

$$\Delta_{\mathrm{SO}}(L_3) = 4\sum_{s}\sum_{n,n'} (\tfrac{1}{3}b^s{}_{L_3,np}{}^* b^s{}_{L_3,n'p}\Delta^s{}_{np,n'p}$$
$$- \tfrac{1}{5}b^s{}_{L_3,nyz}{}^* b^s{}_{L_3,n'yz}\Delta^s{}_{nd,n'd}$$
$$- \frac{4}{5\sqrt{3}}b^s{}_{L_3,nyz}{}^* b^s{}_{L_3,n'x^2}\Delta^s{}_{nd,n'd}) . \quad \text{(III.17)}$$

If we assume that the quantity $\sqrt{3}A$ is roughly equal to the quantity S from the spin-orbit matrix for Γ_{15}, we will see that the splitting of the level L_3 is about two-thirds of that of the level Γ_{15}.

Similar to the relativistic shifts to the energy levels at Γ and X, the energy shifts to the levels at L are the diagonal matrix elements, which are being presented as follows:

$$\Delta E_{\mathrm{rel}}(L_3) = 2\sum_{s}\sum_{n,n'} (b^s{}_{L_3,np}{}^* b^s{}_{L_3,n'p} R^s{}_{np,n'p}$$
$$+ b^s{}_{L_3,nyz}{}^* b^s{}_{L_3,n'yz} R^s{}_{nd,n'd}$$
$$+ \tfrac{2}{3}b^s{}_{L_3,nx^2}{}^* b^s{}_{L_3,n'x^2} R^s{}_{nd,n'd}), \quad \text{(III.18a)}$$

$$\Delta E_{\mathrm{rel}}(L_1) = \sum_{s}\sum_{n,n'} (b^s{}_{L_1,ns}{}^* b^s{}_{L_1,n's} R^s{}_{ns,n's}$$
$$+ 3b^s{}_{L_1,np}{}^* b^s{}_{L_1,n'p} R^s{}_{np,n'p}$$
$$+ 3b^s{}_{L_1,nyz}{}^* b^s{}_{L_1,n'yz} R^s{}_{nd,n'd}) . \quad \text{(III.18b)}$$

As mentioned earlier, in heavy elements where the energy levels are close together, influences from other levels may become important. A larger matrix including all these connections must be constructed to handle the problem. Although this is not necessary for the present investigation, such consideration has been incorporated into the computor programs for future investigations.

IV. RESULTS OF CALCULATION

The method developed in this work can be applied to semiconductors of diamond and zincblende structures. However, owing to the unavailability of the OPW crystal wave functions, only four compound semiconductors having zincblende structure, namely BN, SiC, AlP, and GaAs, have been selected for the investigation of the relativistic effects in their energy-band structures. The crystal wave functions of the OPW type obtained by Bassani and Yoshimine[9] have been used for constructing the perturbation matrices. As mentioned previously, only the core part of each OPW was used in our calculations except in the case of BN where the core part of an OPW contains only s orbitals, which do not contribute to the spin-orbit splittings.

In the OPW's the coefficients, $b^{\alpha,s}{}_{\mathbf{k},nlm}$, associated with the core orbitals $\phi^s{}_{nlm}$ at some symmetry points in the Brillouin zone are calculated according to Eqs. (II.4) and (II.5),[10] summing over 88 plane waves at the symmetry points Γ and X, and summing over 120 plane waves at L. The parameters used in these calculations, i.e., $A_{nl}(\mathbf{k})$, $a_\alpha(\mathbf{k})$, and $F^\alpha(\mathbf{k})$, are taken from the work of Bassani and Yoshimine.[9]

It has been shown that the crystal spin-orbit splittings can be expressed in terms of the atomic-core splittings and their overlap integrals. Similarly the relativistic shifts of crystal states can be expressed in terms of the atomic relativistic shifts and their overlap inte-

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[10] Slight modification is needed for (II 5) because of the use of cubic harmonics instead of spherical harmonics.

TABLE I. Atomic spin-orbit splittings and relativistic shifts (energy in eV). Δ(so)exp is the experimental one-electron spin-orbit splitting. Those of the electrons in closed shells are taken from the x-ray data given in Ref. 12 and those of the valence electrons are derived from the spectroscopy data given in Ref. 13.

Core		B	C	N	Al	Si	P	Ga	As
1S	R(vel)	−0.4258	−0.9176	−1.7463	−22.487	−30.458	−40.381	−769.48	−990.32
	R(dar)	0.3864	0.8178	1.5373	19.054	25.723	34.006	635.77	817.42
2S	R(vel)	−0.0255	−0.0602	−0.1229	−1.9487	−2.7577	−3.7963	−94.495	−123.39
	R(dar)	0.0189	0.0436	0.0855	1.3200	1.8581	2.5459	61.057	79.542
2P	R(vel)	−0.0011	−0.0032	−0.0083	−0.1960	−0.2921	−0.4196	−13.834	−18.339
	R(dar)	−0.0002	−0.0005	−0.0010	−0.0147	−0.0200	−0.0266	−0.3971	−0.4947
	Δ(so)calc	0.0033	0.0093	0.0204	0.4596	0.6698	0.9440	27.150	35.706
	Δ(so)exp	0.002	0.0061	0.013	0.40	0.72	1.1	27.0	35.8
3S	R(vel)				−0.1438	−0.2422	−0.3726	−14.915	−20.174
	R(dar)				0.0948	0.1585	0.2420	9.1943	12.395
3P	R(vel)				−0.0087	−0.0183	−0.0323	−2.3891	−3.3378
	R(dar)				−0.0005	−0.0010	−0.0015	−0.0526	−0.0691
	Δ(so)calc				0.0170	0.0347	0.0593	3.5909	4.9593
	Δ(so)exp				0.014	0.029	0.056	3.9	5.7
3D	R(vel)							−0.3270	−0.5205
	R(dar)							−0.0193	−0.0283
	Δ(so)calc							0.4950	0.7709
	Δ(so)exp							0.41	0.55
4S	R(vel)							−1.1385	−2.0163
	R(dar)							0.6957	1.2269
4P	R(vel)							−0.0846	−0.2126
	R(dar)							−0.0017	−0.0041
	Δ(so)calc							0.1223	0.3024
	Δ(so)exp							0.10	0.28
1S2S	R(vel)				−6.5659	−9.0897	−12.279	−267.04	−346.13
	R(dar)				5.0360	6.9410	9.3402	197.48	255.55
1S3S	R(vel)							−105.22	−138.77
	R(dar)							76.649	100.90
2S3S	R(vel)							−37.460	−49.781
	R(dar)							23.718	31.432
2P3P	R(vel)							−5.7022	−7.7550
	R(dar)							−0.1167	−0.1478
	Δ(so)calc							9.5421	12.8465

grals. These atomic values are calculated according to (II.9), (II.10), and (III.10) using the atomic wave functions and atomic energy eigenvalues obtained by Herman and Skillman.[11] The results of these atomic values are presented in Table I together with the corresponding experimental spin-orbit splittings of the core states obtained from x-ray data[12] and of the valence states from optical data.[13] In the present calculations, the experimental atomic-core values and the calculated overlap integrals have been used.

The spin-orbit splittings of the crystal states in AlP and GaAs are calculated according to (III.11), (III.14), and (III.17). For BN and also for the contributions due to C in SiC, the spin-orbit matrix elements are calculated according to (II.11) and then the spin-orbit matrices are diagonalized in the same manner as stated in the previous section. The calculated results for the spin-orbit splittings are listed in Table II. The relativistic shifts for all the above listed semiconductors are calculated according to (III.12), (III.15), and (III.18). The results are given in Table III. With these relativistic corrections applied to the energy levels calculated by Bassani and Yoshimine, we arrived at the values for various direct and indirect energy gaps which are listed in Table IV.

In order to see whether enough orthogonalized plane waves had been used in these calculations, a convergence study has been carried out for the spin-orbit splittings of the four semiconductors under investigation. When only the core part of an OPW is used to approximate the electron wave function, the convergence is quite satisfactory. For instance, in the case

[11] F. Herman and S. Skillman, Atomic Structure Calculations (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).
[12] A. E. Sandstrom, Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 30, p. 224.
[13] C. E. Moore, Natl. Bur. Std. Circ. No. 467, 1949.

of the splitting of the valence Γ_{15} state in GaAs, after applying 58 plane waves, adding 30 extra plane waves to the calculation only increases the result by 4%. When the OPW is represented only by the plane-wave part, however, as in the case of BN, the convergence is not as rapid as in the previous case. We have found that the calculation of the spin-orbit splitting of the valence Γ_{15} level in BN increases 18% in the range between 58 and 88 plane waves. This rather poor convergence is inherited from the poor convergence in the original OPW function calculation because occupied core states, to which the wave function must be orthogonalized, are missing in BN.

V. COMPARISON WITH EXPERIMENTS AND DISCUSSIONS

In the next step, we would like to compare the calculations with physical observations. Some available optical transitions and the spin-orbit splittings deduced from these transitions are listed in Tables II and IV next to their corresponding calculated values. The majority of these data quoted have been obtained from analyzing the reflectivity spectra in optical experiments. Among the four compounds under investigation, GaAs contains the heaviest elements. Therefore, this crystal would have the largest spin-orbit splittings and relativistic shifts in comparison with the other three crystals. Conversely, the spin-orbit splittings and the relativistic shifts in the crystals having very light elements such as BN would be small and difficult to be detected experimentally.

TABLE II. Crystal spin-orbit splittings (in eV) at Γ, X, L for BN, SiC, AlP, and GaAs. "Atom A" designates the contribution to the calculated splitting from the atom belonging to the third column in the periodic table or the first appearing atom in the chemical formula of a IV-IV compound; "Atom B" designates the contribution from the atom belonging to the fifth column or the second atom in a IV-IV compound.

		BN	SiC	AlP	GaAs
Γ_{15}val	Atom A	0.0037	0.119	0.0550	0.263
	Atom B	0.0027	0.001	0.0015	0.031
	Calculated	0.0064d	0.120	0.0565b	0.294b
	Experimental				0.33a
Γ_{15}cond	Atom A		0.00284	0.0017	0.026
	Atom B		0.00003	0.0233	0.136
	Calculated		0.00287	0.0250b	0.162b
X_5val	Atom A	0.000084	0.058	0.0301	0.123
	Atom B	−0.000051	−0.00006	−0.0045	−0.042
	Calculated	0.000033d	0.058	0.0256b	0.081b
X_5cond	Atom A		0.044	0.0154	0.118
	Atom B			−0.0170	−0.102
	Calculated		0.044	0.0016b	0.016b
L_3val	Atom A	0.007	0.097	0.049	0.211
	Atom B	0.0049	0.0031	0.001	0.024
	Calculated	0.0119d	0.100	0.050b	0.235b
	Experimental				0.26c

a R. Braunstein, J. Phys. Chem. Solids **8**, 280 (1959).
b Experimental spin-orbit splittings from x-ray data (Ref. 12) and calculated atomic spin-orbit overlap integrals have been used.
c J. Tauc and A. Abraham, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Publishing House of Czechoslovak Academy of Sciences, Prague, 1961), p. 375.
d Calculated from matrix elements between two sets of plane waves.

TABLE III. Crystal relativistic shifts (in eV) at Γ, X, L for BN, SiC, AlP, and GaAs.

ΔE_{rel}	BN	SiC	AlP	GaAs
$\Gamma_1$val	−0.0062	−0.077	−0.066	−0.235
$\Gamma_1$cond	−0.010	−0.090	−0.69	−0.403
Γ_{15}val		−0.052	−0.030	−0.192
Γ_{15}cond		−0.0012	−0.010	−0.105
X_1val	−0.0055	−0.011	−0.082	−0.306
X_1cond	0.0000	−0.0017	−0.010	−0.080
X_3val	−0.0041	−0.066	−0.028	−0.185
X_3cond	−0.0028	−0.055	−0.016	−0.105
X_5val		−0.038	−0.027	−0.153
X_5cond		−0.029	−0.023	−0.202
L_1val	−0.0019	−0.020	−0.023	−0.283
L_1cond	−0.0075	−0.036	−0.030	−0.146
L_3val		−0.063	−0.040	−0.223
L_3cond		−0.0025	−0.014	−0.130

In Table II, we see that the discrepancy between the experimental and the calculated values of the spin-orbit splittings of the valence Γ_{15} state in GaAs is only 11%. The calculated result is 0.29 eV and the corresponding experimental value is 0.33 eV. In view of the uncertainties involved in the crystal wave functions used, which were, above all, not obtained self-consistently, this agreement is rather striking.

We further remark that at the Γ and L points of the Brillouin zone, the contributions to a total spin-orbit splitting from two different atoms do not exhibit any simple relation to their atomic number as we might have expected at first thought. We notice in Table II, that the dominant contribution in a spin-orbit splitting shifts from one atom to the other as we move from a lower p-like state to a higher p-like state. This shift can be understood qualitatively by considering the zinc-blende structure as the result of applying a perturbation of an antisymmetric potential V^a to the diamond structure.

TABLE IV. Energy Gaps (in eV) for BN, SiC, AlP, and GaAs.

		BN	SiC	AlP	GaAs
Indirect gap (Γ_{15}val → X_1cond)	Exptl.		2.8f	2.4c	
	N.R.a Calc.	2.949	2.74	5.080	2.393
	R.b Calc.	2.947	2.77	5.061	2.313
Direct gap At Γ	Exptl.				1.5d
	N.R. Calc.	7.663	6.773	6.995	4.300
	R. Calc.	7.660	6.695	6.937	4.182
Direct gap At X	Exptl.				5.0e
	N.R. Calc.	9.088	5.789	6.482	4.891
	R. Calc.	9.087	5.795	6.486	4.924
Direct gap At L	Exptl.				3.1e
	N.R. Calc.	11.905	9.955	9.095	5.517
	R. Calc.	11.900	9.934	9.080	5.409

a Nonrelativistic.
b Relativistic.
c G. H. Grimmeiss, W. Kischio, and A. Rabenau, J. Phys. Chem. Solids **16**, 302 (1960).
d M. D. Sturge, Phys. Rev. **127**, 768 (1962).
e H. Ehrenreich, H. R. Philipp, and J. C. Phillips, Phys. Rev. Letters **8**, 59 (1962).
f J. A. Lely and F. A. Kroger, *Proceedings of the International Coll. 1956, Garmisch-Partenkirchen* (Friedrich Vieweg and Sohn, Berlin, 1958), p. 514

As an example, let us consider the lower and the higher Γ_{15} states. The valence Γ_{15} state in the zinc-blende structure evolves from the bonding (anti-symmetric with respect to the interchanging of the two atoms) valence state $\Gamma_{25'}$ in the diamond structure as V^a is gradually turned on, while the lowest conduction Γ_{15} state in the zincblende structure evolves from the antibonding (symmetric) conduction state Γ_{15} in the diamond structure. These two levels in the diamond structure can be written as follows:

$$\Gamma_{25'}{}^{\mathrm{val,dia}} \propto \phi_1 - \phi_2, \qquad (\mathrm{V.1a})$$

$$\Gamma_{25'}{}^{\mathrm{cond,dia}} \propto \phi_1 + \phi_2. \qquad (\mathrm{V.1b})$$

In the above expressions we have used the notations ϕ_1 and ϕ_2 to represent the two core parts in (II.3) separately centered around the two sublattices. If we take into account only the matrix element between the concerned state and its nearest-neighboring state, and assume that atomic cores do not overlap, in the first-order perturbation theory the two Γ_{15} states in the zinc-blende structure become:

$$\Gamma_{15}{}^{\mathrm{val,zb}} \simeq \Gamma_{25'}{}^{\mathrm{val,dia}} + \epsilon \Gamma_{15}{}^{\mathrm{val,dia}}$$

$$\simeq (\phi_1 - \phi_2) + \epsilon (\phi_1 + \phi_2), \qquad (\mathrm{V.2a})$$

$$\Gamma_{15}{}^{\mathrm{cond,zb}} \simeq \Gamma_{15}{}^{\mathrm{cond,dia}} - \epsilon \Gamma_{25'}{}^{\mathrm{val,dia}}$$

$$\simeq (\phi_1 + \phi_2) - \epsilon (\phi_1 - \phi_2), \qquad (\mathrm{V.2b})$$

where

$$\epsilon = \frac{\langle \Gamma_{15}{}^{\mathrm{cond}} | V^a | \Gamma_{25'}{}^{\mathrm{val}} \rangle}{E(\Gamma_{25'}) - E(\Gamma_{15})}.$$

It can be shown from the time-reversal symmetry of the crystal wave functions that ϵ is a real quantity. We notice, then, that if the first order term in ϵ is additive to the contribution of an atom at energy level, say $\Gamma_{15}{}^{\mathrm{val,zb}}$, it must be subtractive to the contribution of the same atom at the other level, say $\Gamma_{15}{}^{\mathrm{cond,zb}}$. In other words, if at one level the contribution from one atom plays the dominant role, then at the other level, the other atom must take over this role.

This effect is particularly evident in silicon carbide with a spin-orbit splitting of 0.12 eV for the valence Γ_{15} state, which is even larger than the corresponding value[6] of 0.042 eV in crystalline silicon. This enhancement may be attributed to the strong antisymmetric potential V^a. At valence Γ_{15}, the antisymmetric potential pulls the electron very close to the silicon atom causing the contribution from that atom to the spin-orbit splitting to be very large. At conduction Γ_{15}, the electron is pushed away from the silicon atom, and therefore, the contribution from that atom decreases.

It is interesting to compare the spin-orbit splittings of the crystal states with an average of the corresponding values in the two isolated atoms. As seen in Tables I and II the former is usually enhanced from the latter. Physically, the enhancement means that the wave function in the crystal is contracted in the core region of each atomic site. Thus one cannot just use the atomic values for a quantitative evaluation of the crystal splitting. Therefore, it is particularly significant to learn that our presently available crystal wave functions give meaningful results in the spin-orbit calculations.

In summary, the results from our relativistic band calculations of BN, SiC, AlP, and GaAs show that apart from spin-orbit splittings the relativistic corrections are only of secondary importance to the energy states. In crystals of heavier elements where the relativistic shifts are comparable to the energy gaps themselves, however, the band structures calculated relativistically would look quite different from those calculated nonrelativistically, and our present formalism can be applied to these substances once the OPW wave functions are available.

ACKNOWLEDGMENTS