Electronic Band Structure of Group IV Elements and of III-V Compounds*

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The orthogonalized plane wave method is applied to the zincblende lattice. Crystal symmetrized combinations of plane waves are constructed for the zincblende lattice and the secular equations for the electronic levels at symmetry points of the reduced zone are derived as explicit functions of parameters depending on the crystal potential and on the core eigenstates. Calculations of valence and conduction eigenvalues and eigenfunctions are carried out on a number of group IV elements and of III-V compounds starting from the Hartree-Fock atomic core states and a model crystal potential constructed as a sum of atomic potentials in which the Slater approximation is used for the exchange contribution. The resulting band structures are very similar for all the semiconductors considered and the sequence of electronic levels confirms previous qualitative analyses. A comparison with experiments reveals, however, that those s-like conduction states which are most sensitive to the crystal potential are too high with respect to the other conduction states in the present approximation. An analysis of the approximation used indicates that the largest error in the calculations comes from the use of the Slater exchange in the model potential. Ways of improving on the accuracy of the calculations are suggested; one way is to use Hartree-Fock-Slater atomic results as a starting point. It is shown for the case of germanium that this improvement brings the results for the s-like conduction states into a closer agreement with experiment.

I. INTRODUCTION

THE work of Herman[1] on diamond and subsequent work by a number of authors[2] on silicon and germanium has shown that the orthogonalized plane wave (OPW) method of Herring[3] is quite appropriate to computation of the electronic energy levels in covalent semiconductors. The OPW method consists in expanding the valence and conduction wave functions in combinations of plane waves whose symmetry is compatible with the state under consideration and imposing the condition that such wave functions be orthogonal to the inner electronic states of the crystal (core states). The coefficients of this expansion and the eigenvalues are then obtained from the variational principle by solving secular equations of order equal to the number of symmetrized combinations of plane waves used in expanding the valance and conduction wave functions.

In the case of valence crystals such as metals and semiconductors a relatively small number of plane waves is needed to obtain satisfactory convergence on the energies and wave functions. This is because the valence electron distribution from a given atom overlaps appreciably that from other atoms and the resulting density of valence electrons is nearly constant over most of the volume of the unit cell. Furthermore, the correct behavior of the valence and conduction wave functions near the nuclei is imitated by the condition of orthogonality to the core states. This condition results in additional terms in the matrix elements of the

secular equation besides those originating from the crystal potential. As pointed out by Phillips and Kleinman[4] these additional terms can be considered as originating from a nonlocal eigenvalue-dependent repulsive potential whose main effect is that of nearly cancelling the crystal potential in the core region thus making the results rather similar to those for an "empty lattice."[5] This cancellation effect is not limited to the case of energy bands in crystals and has been discussed in general by Cohen and Heine.[6] Besides accounting for the convergence of the OPW method, the above considerations clarify the approach to the band structure developed by Bassani and Celli[7,8] from a perturbation on the empty lattice and the semi-empirical pseudopotential scheme introduced by Phillips[9] and refined by Bassani and Celli.[8]

A great deal of progress has been made in the past few years in detecting and interpreting interband transitions and this has greatly increased our knowledge of the band structure in a large number of semiconductors. We refer to a few relevant papers[10] to point out that the theoretical progress in this field, though greatly stimulated by the existing energy band calculations has mostly come from qualitative analyses and from the semiempirical pseudopotential scheme. A detailed com-

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[1] F. Herman, Phys. Rev. 88, 1210 (1952).
[2] F. Herman and J. Callaway, Phys. Rev. 89, 518 (1953); F. Herman, Physica 20, 801 (1954); T. O. Woodruff, Phys. Rev. 103, 1159 (1956); F. Bassani, *ibid*. 108, 263 (1957); Nuovo Cimento 13, 244 (1959); L. Kleinman and J. C. Phillips, Phys. Rev. 118, 1153 (1960).
[3] C. Herring, Phys. Rev. 57, 1169 (1940). T. O. Woodruff, in *Solid State Physics*, edited by E. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, p. 367.

[4] J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959).
[5] W. Shockley, Phys. Rev. 52, 866 (1937).
[6] M. H. Cohen and V. Heine, Phys. Rev. 122, 1821 (1961).
[7] F. Bassani and V. Celli, Studia Ghisleriana II, 157 (1959); see also Nuovo Cimento 11, 805 (1959).
[8] F. Bassani and V. Celli, J. Phys. Chem. Solids 20, 64 (1961).
[9] J. C. Phillips, Phys. Rev. 112, 685 (1958).
[10] H. R. Philipp and E. A. Taft, Phys. Rev. 113, 1002 (1959); 120, 37 (1960); M. Cardona and H. S. Sommers, Jr., *ibid*. 122, 1382 (1961); J. Tauc and A. Abraham, J. Phys. Chem. Solids 20, 190 (1961); J. C. Phillips, Phys. Rev. 125, 1931 (1962); H. Ehrenreich, H. R. Philipp, and J. C. Phillips, Phys. Rev. Letters 8, 59 (1962); M. Cardona and D. L. Greenway, Phys. Rev. 125, 1231 (1962); H. R. Philipp and E. A. Taft, *ibid*. 127, 159 (1962); D. Brust, J. C. Phillips, and F. Bassani, Phys. Rev. Letters 9, 94 (1962).

FIG. 1. "Empty lattice" analysis of the symmetry points Γ, L, and X and of the symmetry directions Λ and Δ of the reduced zone in the zincblende structure. The eigenvalues of the "empty lattice" $E = (4\pi^2/a^2)(|\mathbf{k}+\mathbf{h}|)^2$ are plotted as functions of $\mathbf{k}$ in arbitrary units. Eigenvalues corresponding to sets of plane waves which are degenerate at symmetry points are indicated by angular brackets. The number of plane waves in the set and the irreducible representations belonging to every set are also indicated. The states below the horizontal dashed line become the valence states and the lowest conduction states of the crystal under the effect of the crystal potential and of the repulsive-like potential due to the core states.

$$k = \tfrac{2\pi}{a}(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}) \qquad k = (0,0,0) \qquad k = \tfrac{2\pi}{a}(1,0,0)$$
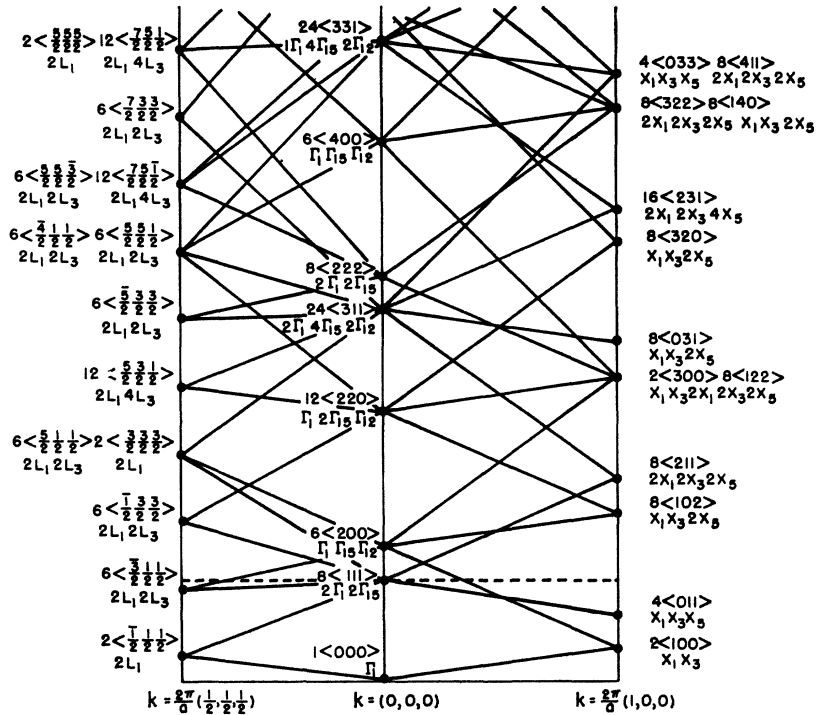
parison between theory and experiments however must ultimately come from *a priori* energy band calculations systematically performed on a large number of solids with an accuracy of 0.01 Ry.

In this paper we have attempted a systematic calculation of the band structure of group IV elements and of a number of III–V compounds. Though a detailed comparison with experiments on interband transitions is beyond the accuracy of the present calculations we feel that an analysis of the results for a large number of solids of the same symmetry can be of value in providing a better understanding of their band structures and in assessing the significance of the approximations which have been made.

In Sec. II we describe the construction of the symmetrized combinations of plane waves (S.C.P.W.) at the symmetry points $\Gamma(\mathbf{k}=0)$, $L[\mathbf{k}=(2\pi/a)(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})]$, and $X[\mathbf{k}=(2\pi/a)(1,0,0)]$ for the zincblende lattice and show how they are related to the S.C.P.W.'s for the diamond lattice. The matrix elements of the secular equations are then derived as functions of the lattice potential and of the core states. In Sec. III we compute the parameters which enter the matrix elements for a number of solids which crystallize in the zincblende and diamond structures using the approximations described by Herman[11] and Woodruff.[2,3] In Sec. IV we give and discuss the results for the energy band structure of SiC, C, BN, Si, AlP, Ge, and GaAs. In Sec. V we investigate the effect of the approximations used on the resulting band structures. It is indicated that the relative positions of the conduction states are affected

principally by the approximation used for the exchange contribution to the crystal potential. A detailed calculation is done on Ge using atomic wave functions which are consistent with the crystal potential considered and it is shown that this improves the agreement with experiment. In Sec. VI we present some conclusions to be derived from the present work.

II. OPW METHOD APPLIED TO THE ZINCBLENDE AND DIAMOND STRUCTURES

The zincblende structure consists of two fcc sublattices whose points are occupied by different types of atoms, displaced with respect to each other by the vector $a(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4})$, where a is the edge of the cube. When the two types of atoms are the same the structure reduces to the diamond structure. The group of the zincblende lattice has 24 symmetry operations and is a subgroup of the diamond lattice such that its product by the group formed by inversion and identity gives the group of the diamond lattice. The symmetry analysis of the Brillouin zone has been given by Parmenter.[12] We make use of his character tables to obtain the S.C.P.W.'s which are partner functions in the irreducible representations of the small groups of $\mathbf{k}^{11,13}$ at the symmetry points Γ, L, and X of the reduced zone. In Fig. 1 we indicate the plane waves used in the calculation by giving the "empty lattice" eigenvalues along the symmetry direction Λ and Δ and at the symmetry points together with the irreducible representations to which

[11] F. Herman, Phys. Rev. **93**, 1214 (1954).

[12] R. H. Parmenter, Phys. Rev. **100**, 573 (1955).
[13] L. P. Bouckaert, R. Smoluchowski and E. Wigner, Phys. Rev. **50**, 58 (1936).

TABLE I. Some crystal symmetrized combinations of plane waves in the zincblende lattice at the symmetry points $\Gamma(\mathbf{k}=0)$, $L[\mathbf{k}=(2\pi/a)(\frac{1}{2},\frac{1}{2},\frac{1}{2})]$ and $X[\mathbf{k}=(2\pi/a)(1,0,0)]$ of the reduced zone. In the first row the irreducible representations are indicated using the symbols of Parmenter (reference 12). The superscript on the left indicates the dimension of the irreducible representation; for the irreducible representations of dimension greater than one, only the combinations belonging to the first row are given. In the case of the irreducible representations X_1 and X_3, the origin has been chosen to be a lattice point; in the case of all other irreducible representations, the origin has been chosen to be the midpoint between two nearest atoms.

$\frac{a}{2\pi}(\mathbf{k}+\mathbf{h})$	$^1\Gamma_1$	$^1\Gamma_1$	$^3\Gamma_{15}^{(1)}$	$^3\Gamma_{15}^{(1)}$	$^2\Gamma_{12}^{(1)}$
$(0,0,0)$	1				
$(1,1,1)$	1	i	1	i	
$(1,1,\bar{1})$	-1	$-i$	1	i	
$(\bar{1},1,\bar{1})$	-1	$-i$	1	i	
$(\bar{1},\bar{1},1)$	-1	$-i$	-1	$-i$	
$(\bar{1},\bar{1},\bar{1})$	1	$-i$	1	$-i$	
$(\bar{1},1,1)$	-1	i	1	$-i$	
$(1,\bar{1},1)$	-1	i	1	$-i$	
$(1,1,\bar{1})$	-1	i	-1	i	
$(2,0,0)$		i	0		0
$(0,2,0)$		i	0		i
$(0,0,2)$		i	1		$-i$
$(\bar{2},0,0)$		$-i$	0		0
$(0,\bar{2},0)$		$-i$	0		$-i$
$(0,0,\bar{2})$		$-i$	1		i
$(2,2,0)$	1	1	0		1
$(2,0,2)$	1	0	i		-1
$(0,2,2)$	1	0	i		0
$(2,\bar{2},0)$	-1	1	0		-1
$(2,0,\bar{2})$	-1	0	i		1
$(0,2,\bar{2})$	-1	0	i		0
$(\bar{2},\bar{2},0)$	1	1	0		1
$(\bar{2},0,\bar{2})$	1	0	$-i$		-1
$(0,\bar{2},\bar{2})$	1	0	$-i$		0
$(\bar{2},2,0)$	-1	1	0		-1
$(\bar{2},0,2)$	-1	0	$-i$		1
$(0,\bar{2},2)$	-1	0	$-i$		0

Conventional origin

$\frac{a}{2\pi}(\mathbf{k}+\mathbf{h})$	$^1L_1$	$^1L_1$	$^2L_3^{(1)}$	$^2L_3^{(1)}$
$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	1	i		
$(-\frac{1}{2},-\frac{1}{2},-\frac{1}{2})$	1	$-i$		
$(-\frac{3}{2},\frac{1}{2},\frac{1}{2})$	1	i	1	i
$(\frac{1}{2},-\frac{3}{2},\frac{1}{2})$	1	i	-1	$-i$
$(\frac{1}{2},\frac{1}{2},-\frac{3}{2})$	1	i	0	0
$(\frac{3}{2},-\frac{1}{2},-\frac{1}{2})$	1	$-i$	1	$-i$
$(-\frac{1}{2},\frac{3}{2},-\frac{1}{2})$	1	$-i$	-1	i
$(-\frac{1}{2},-\frac{1}{2},\frac{3}{2})$	1	$-i$	0	0
$(-\frac{1}{2},\frac{3}{2},\frac{3}{2})$	1	i	1	i
$(\frac{3}{2},-\frac{1}{2},\frac{3}{2})$	1	i	-1	$-i$
$(\frac{3}{2},\frac{3}{2},-\frac{1}{2})$	1	i	0	0
$(\frac{1}{2},-\frac{3}{2},-\frac{3}{2})$	1	$-i$	1	$-i$
$(-\frac{3}{2},\frac{1}{2},-\frac{3}{2})$	1	$-i$	-1	i
$(-\frac{3}{2},-\frac{3}{2},\frac{1}{2})$	1	$-i$	0	0
$(\frac{3}{2},\frac{3}{2},\frac{3}{2})$	1	i		
$(-\frac{3}{2},-\frac{3}{2},-\frac{3}{2})$	1	$-i$		
$(\frac{5}{2},\frac{1}{2},\frac{1}{2})$	1	i	1	i
$(\frac{1}{2},\frac{5}{2},\frac{1}{2})$	1	i	-1	$-i$
$(\frac{1}{2},\frac{1}{2},\frac{5}{2})$	1	i	0	0
$(-\frac{5}{2},-\frac{1}{2},-\frac{1}{2})$	1	$-i$	1	$-i$
$(-\frac{1}{2},-\frac{5}{2},-\frac{1}{2})$	1	$-i$	-1	i
$(-\frac{1}{2},-\frac{1}{2},-\frac{5}{2})$	1	$-i$	0	0

$\frac{a}{2\pi}(\mathbf{k}+\mathbf{h})$	$^1X_1$	$^1X_1$	$^1X_3$	$^1X_3$	$^2X_5^{(1)}$	$^2X_5^{(1)}$
$(1,0,0)$	1		i			
$(\bar{1},0,0)$	1		$-i$			
$(0,1,1)$	1		1		1	
$(0,1,\bar{1})$	1		-1		0	
$(0,\bar{1},\bar{1})$	1		1		1	
$(0,\bar{1},1)$	1		-1		0	
$(1,0,2)$	1		i		1	i
$(1,2,0)$	1		i		1	i
$(1,0,\bar{2})$	1		i		1	i
$(1,\bar{2},0)$	1		i		1	i
$(\bar{1},0,\bar{2})$	1		$-i$		1	$-i$
$(\bar{1},\bar{2},0)$	1		$-i$		1	$-i$
$(\bar{1},0,2)$	1		$-i$		1	$-i$
$(\bar{1},2,0)$	1		$-i$		1	$-i$
$(2,1,1)$	1	i	1	i	1	i
$(2,1,\bar{1})$	1	$-i$	-1	i	0	0
$(2,\bar{1},1)$	1	$-i$	-1	i	0	0
$(2,\bar{1},\bar{1})$	1	i	1	i	1	i
$(\bar{2},1,\bar{1})$	1	$-i$	1	$-i$	1	$-i$
$(\bar{2},\bar{1},1)$	1	i	-1	$-i$	0	0
$(\bar{2},1,\bar{1})$	1	i	-1	$-i$	0	0
$(\bar{2},1,1)$	1	$-i$	1	$-i$	1	$-i$
$(3,0,0)$	1		i			
$(\bar{3},0,0)$	1		$-i$			
$(1,2,2)$	1	i	1	i	1	i
$(1,2,\bar{2})$	1	$-i$	-1	i	0	0
$(1,\bar{2},2)$	1	$-i$	-1	i	0	0
$(1,\bar{2},\bar{2})$	1	i	1	i	-1	$-i$
$(\bar{1},\bar{2},\bar{2})$	1	$-i$	1	$-i$	1	$-i$
$(\bar{1},\bar{2},2)$	1	i	-1	$-i$	0	0
$(\bar{1},2,\bar{2})$	1	i	-1	$-i$	0	0
$(\bar{1},2,2)$	1	$-i$	1	$-i$	-1	i

Point origin   Conventional origin

they belong. The S.C.P.W.'s formed from the plane waves of lowest energy are presented in Table I. They are related to those given by Herman[11] for the diamond structure but have been chosen in such a way as to give real matrix elements in the zincblende lattice. At the points Γ and L the conventional origin at the midpoint between two nearest atoms is chosen. The S.C.P.W.'s belonging to a row of a given irreducible representation are chosen to be even or odd with respect to inversion, and all the odd combinations are multiplied by the imaginary factor i. In the diamond lattice, the odd and the even combinations of plane waves belong to dif-

ferent irreducible representations, consequently the combinations belonging to Γ_1 in the zincblende lattice contain all the combinations belonging to Γ_1 and $\Gamma_{2'}$ in the diamond lattice. In the same sense Γ_{15} splits into $\Gamma_{25'}$ and Γ_{15}, L_1 into $L_{2'}$ and L_1, L_3 into L_3 and $L_{3'}$. The situation is not so simple at the point X because in the diamond structure the small group of $\mathbf{k}$ at the point X contains also translations.[14] In order to make full use of the symmetry and to obtain real matrix elements, we have found it convenient to choose a lattice point as

[14] C. Herring, J. Franklin Inst. 233, 525 (1942); see also W. Döring and V. Zehler: Ann. Physik 13, 214 (1953).

the origin for the S.C.P.W.'s belonging to X_1 and X_3. Also, at the point X the combinations which are anti-symmetric under inversion have been multiplied by the imaginary factor i. In the case of the diamond lattice, the combinations belonging to X_1 and X_3 become partner functions of the two-dimensional representation X_1 and give degenerate eigenvalues. The combinations belonging to X_5 include in a nontrivial way contributions belonging to the irreducible representations X_4 and X_3 of the diamond structure. In practice we use the S.C.P.W.'s of the type indicated in Table I for both the zincblende structure and the diamond structure.

The jth S.C.P.W. belonging to the first row of the αth irreducible representation and constructed from the set $\langle \mathbf{k}+\mathbf{h}\rangle$ of all vectors having the same magnitude will be denoted by

$$S_j{}^\alpha(|\mathbf{k}+\mathbf{h}|, \mathbf{r}) = \sum_s a_s{}^{\alpha,j}(\Omega N)^{-1/2}\exp[i(\mathbf{k}+\mathbf{h}_s)\cdot\mathbf{r}]. \quad (1)$$

In Eq. (1), Ω is the volume of the unit cell, N the number of cells, $\mathbf{h}_s$ is a reciprocal lattice vector belonging to the set $\langle\mathbf{k}+\mathbf{h}\rangle$. The valence and conduction functions are:

$$\psi_v{}^\alpha(\mathbf{k},\mathbf{r}) = \sum_j c_j[S_j{}^\alpha - \sum_c (\psi_c{}^\alpha, S_j{}^\alpha)\psi_c{}^\alpha], \quad (2)$$

where $\psi_c(\mathbf{k},\mathbf{r})$ are the core wave function, whose eigenvalues E_c are known, and the sum on j is to run over all sets $\langle\mathbf{k}+\mathbf{h}\rangle$. The coefficients c_j of the expansion as well as the eigenvalues $E_V(\mathbf{k})$ are obtained by solving the secular equations:

$$\langle S_i|H - E|\psi_v\rangle = 0. \quad (3)$$

The eigenvalues are the zeroes of a secular determinant whose matrix elements are:

$$M_{ij} = \langle S_i{}^\alpha|H - E|S_j{}^\alpha\rangle$$
$$+ \sum_c (E - E_c)(S_i{}^\alpha,\psi_c)(\psi_c, S_j{}^\alpha). \quad (4)$$

The crystal Hamiltonian can be taken as the sum of the kinetic term and a crystal potential which is the sum of atomic-like potentials at the lattice sites. The atomic-like potentials are further approximated by a local expression. There are two atomic potentials and two sets of core eigenstates, referring to atoms 1 and 2 of the sublattices. For the case of the conventional origin (midpoint between the two sublattices), expression 4 becomes:

$$M_{ij} = \sum_{rs} a_r{}^{\alpha,i*}a_s{}^{\alpha,j}\{(|\mathbf{k}+\mathbf{h}_r|^2 - E)\delta_{r,s} + [V^S(|\mathbf{h}_s - \mathbf{h}_r|)$$
$$+ \sum_{nl} P_l(\cos\omega)R_{nl}{}^S(|\mathbf{k}+\mathbf{h}_r|,|\mathbf{k}+\mathbf{h}_s|)]$$
$$\times\cos[(\mathbf{h}_s - \mathbf{h}_r)\cdot\tfrac{1}{8}a(1,1,1)] + [V^A(|\mathbf{h}_s - \mathbf{h}_r|)$$
$$+ \sum_{nl} P_l(\cos\omega)R_{nl}{}^A(|\mathbf{k}+\mathbf{h}_r|,|\mathbf{k}+\mathbf{h}_s|)]$$
$$\times i\sin[(\mathbf{h}_s - \mathbf{h}_r)\cdot\tfrac{1}{8}a(1,1,1)]. \quad (5)$$

In Eq. (5), P_l indicates the Legendre polynomial and ω is the angle between the vectors $\mathbf{k}+\mathbf{h}_r$ and $\mathbf{k}+\mathbf{h}_s$; the other symbols involve the usual Fourier coefficients of the potential of atoms 1 and 2 and the orthogonality coefficients A_{nl} of their core states in the following way:

$$V^S(|\mathbf{h}_s - \mathbf{h}_r|) = V_1(|\mathbf{h}_s - \mathbf{h}_r|) + V_2(|\mathbf{h}_s - \mathbf{h}_r|)$$
$$V^A(|\mathbf{h}_s - \mathbf{h}_r|) = V_1(|\mathbf{h}_s - \mathbf{h}_r|) - V_2(|\mathbf{h}_s - \mathbf{h}_r|)$$
$$R_{nl}{}^S(|\mathbf{k}+\mathbf{h}_r|,|\mathbf{k}+\mathbf{h}_s|)$$
$$= (E - E_{nl,1})A_{nl,1}{}^*(|\mathbf{k}+\mathbf{h}_r|)A_{nl,1}(|\mathbf{k}+\mathbf{h}_s|)$$
$$+ (E - E_{nl,2})A_{nl,2}{}^*(|\mathbf{k}+\mathbf{h}_r|)A_{nl,2}(|\mathbf{k}+\mathbf{h}_s|) \quad (5a)$$
$$R_{nl}{}^A(|\mathbf{k}+\mathbf{h}_r|,|\mathbf{k}+\mathbf{h}_s|)$$
$$= (E - E_{nl,1})A_{nl,1}{}^*(|\mathbf{k}+\mathbf{h}_r|)A_{nl,1}(|\mathbf{k}+\mathbf{h}_s|)$$
$$- (E - E_{nl,2})A_{nl,2}{}^*(|\mathbf{k}+\mathbf{h}_r|)A_{nl,2}(|\mathbf{k}+\mathbf{h}_s|).$$

When the origin is a lattice point, expression 4 becomes:

$$M_{ij}{}^\alpha = \sum_{rs} a_r{}^{\alpha,i*}a_s{}^{\alpha,j}\Big\{(|\mathbf{k}+\mathbf{h}_r|^2 - E)\delta_{rs} + [V^S(|\mathbf{h}_s - \mathbf{h}_r|)$$
$$+ \sum_{nl} P_l(\cos\omega)R_{nl}{}^S(|\mathbf{k}+\mathbf{h}_r|,|\mathbf{k}+\mathbf{h}_s|)]\frac{1+\exp[i(\mathbf{h}_r - \mathbf{h}_s)\cdot\tfrac{1}{4}a(1,1,1)]}{2}$$
$$+ [V^A(\mathbf{h}_r - \mathbf{h}_s) + \sum_{nl} P_l(\cos\omega)R_{nl}{}^A(|\mathbf{k}+\mathbf{h}_r|,|\mathbf{k}+\mathbf{h}_s|)]\frac{1-\exp[i(\mathbf{h}_r - \mathbf{h}_s)\cdot\tfrac{1}{4}a(1,1,1)]}{2}\Big\}. \quad (6)$$

The matrix elements of the secular equation for the eigenstates of the zincblende lattice have been constructed as functions of the parameters (5a) at the symmetry points Γ, L, and X with the plane waves indicated in Fig. 1 by using combinations of the type given in Table I. If the two atoms of the sublattices are identical V^A and R^A vanish and we are left with the secular equations for the diamond structure.

III. CALCULATION OF THE PARAMETERS

The basic parameters which appear in the secular equations of the OPW method can be easily computed

from the results of atomic Hartree-Fock calculations in the way indicated by Herman[11] and Woodruff.[3]

The core eigenvalues are assumed to be the same in the crystal as in the free atom. The wave functions for the core states are Bloch wave functions of atomic orbitals with the neglect of overlap between different atoms. The orthogonality coefficients of formula (5a) have been computed for the atoms of interest from:

$$A_{nl}(|\mathbf{k}+\mathbf{h}|) = \left[\frac{4\pi(2l+1)}{\Omega}\right]^{1/2} i^l \int_0^\infty P_{nl}(r)j_l(kr)r\,dr, \quad (7)$$

TABLE II. Fourier coefficients of the crystal potential as defined in Sec. II, corresponding to the smallest reciprocal lattice vectors for a number of group IV and III–V semiconductors. The lattice parameters used (in atomic units) are the following: $C(a=6.728)$, $BN(a=6.832)$, $SiC(a=8.217)$, $Si(a=10.26)$, $AlP(a=10.337)$, $Ge(a=10.671)$, $GaAs(a=10.649)$. The atomic wave functions used are the same as indicated in Table III.

$V\left(\left\|\dfrac{a}{2\pi}\mathbf{h}\right\|^2\right)$	C	BN	SiC	Si	AlP	Ge	GaAs
$V^S(3)$	−0.908	−0.868	−0.865	−0.727	−0.727	−0.959	−0.962
$V^S(8)$	−0.416	−0.404	−0.432	−0.380	−0.377	−0.584	−0.587
$V^S(11)$	−0.318	−0.311	−0.343	−0.306	−0.305	−0.492	−0.495
$V^S(16)$	−0.230	−0.227	−0.259	−0.237	−0.236	−0.400	−0.402
$V^S(19)$	−0.199	−0.195	−0.226	−0.211	−0.209	−0.362	−0.363
$V^S(24)$	−0.162	−0.160	−0.188	−0.179	−0.177	−0.314	−0.315
$V^A(3)$		0.099	0.191		0.099		0.042
$V^A(4)$		0.089	0.165		0.070		0.033
$V^A(8)$		0.060	0.116		0.032		0.017
$V^A(11)$		0.047	0.098		0.022		0.012
$V^A(12)$		0.043	0.094		0.020		0.011
$V^A(16)$		0.033	0.080		0.014		0.008
$V^A(19)$		0.027	0.073		0.012		0.007
$V^A(24)$		0.022	0.063		0.010		0.006

where Ω is the volume of the unit cell j_l the spherical Bessel function and $P_{nl}(r)$ the radial part of the atomic orbital.

The atomic-like potentials which make up the crystal potential are each the sum of a Coulomb contribution and an exchange contribution. The Coulomb contribution can be easily computed from the density of electrons, as obtained from the Hartree-Fock calculation by using the well-known formula:

$$V_{\text{Coul}}(r)=-\frac{2Z}{r}+\frac{2}{r}\int_0^r \rho_r(r')dr'+2\int_r^\infty \frac{1}{r'}\rho_r(r')dr', \quad (8)$$

where Z is the nuclear charge and ρ_r is the radial density of electrons, $\rho_r(r)=\rho(r)/4\pi r^2$. The exchange contribution is approximated by the Slater formula[15]

$$V_{\text{exch}}(r)=-6[(3/8\pi)\rho(r)]^{1/3}, \quad (9)$$

where $\rho(r)$ is the density of electrons. We use for $\rho(r)$ the atomic local density and compute the remaining parameters (5a) from

$$V(|\mathbf{h}|)=\frac{4\pi}{\Omega}\int_0^\infty [V_{\text{Coul}}(r)+V_{\text{exch}}(r)]\frac{\sin|\mathbf{h}|r}{|\mathbf{h}|r}r^2 dr. \quad (10)$$

Rydberg units have been consistently used in formulas 8, 9, and 10. The Fourier coefficients of the potential $V^S(|\mathbf{h}|)$ and $V^A(|\mathbf{h}|)$ and the orthogonality coefficients have been computed for C, BN, Si, AlP, SiC, Ge, and GaAs from the available Hartree-Fock atomic calculations.[16] In Tables II and III we list some of these parameters for the above substances together with the core state eigenvalues.

As remarked by several authors,[2,3] the space average $V(0)$ of the crystal potential is not reliably computed

in the present approximation because it is extremely sensitive to the behavior of the atomic-like potentials far from the nuclei, just where the relative error is largest. Calculation by Eq. (10) would give an exchange contribution to $V(0)$ too large by a factor greater than two. Woodruff[3] and Herman[11] have suggested remedies for this difficulty. We follow Woodruff's prescription of assuming a uniform density of valence electrons in computing the exchange part of $V(0)$, but we allow the $V(0)$ actually used to deviate slightly from the value so computed. The value of $V^S(0)$ used in each calculation will be explicitly stated.

Some latitude in the choice of $V(0)$ for valence and conduction state calculations exists independently of the sensitivity just discussed. As suggested by Herman,[17] the core state eigenvalues might be shifted from the atomic orbital energies, all by the same amount, by the potentials of the other atoms in the lattice. If such a "core shift" is accompanied by an equal change in $V(0)$ all valence and conduction states will be shifted by the same amount and no change in the band structure will occur. This can be easily seen by direct substitution in the secular determinant whose matrix elements are given by Eq. (4). It can also be seen from Eq. (4) that a "core shift" without a corresponding change in $V(0)$ produces the same effect on the band structure as a change in $V(0)$ by the opposite amount in the absence of "core shifts." It is not possible to distinguish in their effects between shifts of the core eigenvalues or changes of $V(0)$ and therefore it is sufficient to study the valence and conduction band structure as a function of $V(0)$. The value of $V^S(0)$ used in a calculation with atomic core eigenvalues can be defined as the space average of the potential minus a "core shift" when such a shift exists. As pointed out by Herman in a private communication to the authors, in the III–V

[15] J. C. Slater, Phys. Rev. 81, 385 (1951).

[16] R. E. Watson and A. J. Freeman, Phys. Rev. 123, 521 (1961); 124, 1117 (1961).

[17] F. Herman and S. Skillman, in Proceedings of the International Conference on Semiconductor Physics, Prague, 1960 (Czechoslovakian Academy of Sciences, Prague, 1961), p. 20.

TABLE III. Eigenvalues (in Ry) and orthogonality coefficients of the core states corresponding to the smallest values of $|k+h|^2$ at the point $\Gamma(k=0)$ for a number of Group IV and III–V compounds. The atomic wave functions used are taken from reference 16 and from the following self-consistent Hartree-Fock calculations on atoms in their ground state configuration: A Jucys, Proc. Roy. Soc. (London) A173, 59 (1939) (carbon); D. R. Hartree and W. Hartree, *ibid*. A193, 299 (1948) (nitrogen); Glembatski, Kibartas and Iutsis, Zh. Eksperim. i Teor. Fiz. 23, 617 (1955) [translation: Soviet Phys.—JETP 2, 476 (1956)] (boron).

	C	BN		SiC		Si	AlP		Ge	GaAs	
	C	B	N	C	Si	Si	Al	P	Ge	Ga	As
$E1s$	−22.658	−15.386	−31.400	−22.658	−137.591	−137.591	−116.976	−159.911	−810.470	−757.622	−865.156
$E2s$					−12.300	−12.300	−9.814	−15.012	−104.290	−96.330	−112.612
$E2p$					−8.500	−8.500	−6.429	−10.793	−92.462	−84.980	−100.300
$E3s$									−14.378	−12.788	−16.058
$E3p$									−10.320	−8.964	−11.760
$E3d$									−3.266	−2.384	−4.224
$A1s(0)$	0.127	0.166	0.097	0.942	0.026	0.018	0.020	0.016	0.005	0.005	0.005
$A1s(3)$	0.106	0.130	0.086	0.083	0.025	0.018	0.020	0.016	0.005	0.005	0.004
$A1s(4)$	0.101	0.121	0.082	0.080	0.024	0.018	0.020	0.016	0.005	0.005	0.004
$A1s(8)$	0.082	0.092	0.071	0.069	0.024	0.017	0.019	0.016	0.005	0.005	0.004
$A2s(0)$					−0.219	−0.157	−0.180	−0.135	−0.033	−0.035	−0.031
$A2s(3)$					−0.162	−0.129	−0.143	−0.115	−0.032	−0.034	−0.031
$A2s(4)$					−0.148	−0.121	−0.133	−0.109	−0.032	−0.034	−0.030
$A2s(8)$					−0.104	−0.096	−0.100	−0.090	−0.031	−0.032	−0.029
$-iA2p(3)$					0.124	0.080	0.102	0.063	0.006	0.006	0.005
$-iA2p(4)$					0.130	0.086	0.108	0.068	0.006	0.007	0.006
$-iA2p(8)$					0.129	0.095	0.112	0.079	0.009	0.010	0.008
$A3s(0)$									0.156	0.170	0.146
$A3s(3)$									0.127	0.135	0.121
$A3s(4)$									0.120	0.126	0.114
$A3s(8)$									0.094	0.096	0.091
$-iA3p(3)$									−0.088	−0.099	−0.078
$-iA3p(4)$									−0.095	−0.106	−0.086
$-iA3p(8)$									−0.105	−0.114	−0.097
$A3d(3)$									−0.066	−0.088	−0.050
$A3d(4)$									−0.077	−0.100	−0.060
$A3d(8)$									−0.097	−0.117	−0.081

compounds there is the further possibility that the core state eigenvalues of the two sublattices may be shifted by different amounts with respect to their atomic values. When Woodruff's prescription is used to compute the space average of the potential it turns out that the "core shifts" are always very small and their antisymmetric parts can be neglected in the absence of ionicity.

The general nature of the approximation described above has been discussed in detail by Woodruff.[2,3] The major advantage of constructing the crystal potential as a sum of atomic potentials and using the Slater approximation for the exchange contribution lies in the great simplification it introduces. The validity of the approximation depends on the validity of the Slater approximation to exchange and on the extent to which the densities of electrons on different atoms overlap. We have undertaken the present calculations with the confidence that the band structure is not too sensitive to details in the crystal potential; we will come back to this point in discussing the results.

IV. ENERGY BANDS IN A NUMBER OF SEMICONDUCTORS

The band structures of a number of III–V compounds and Group IV elements have been obtained by solving the secular equations described in Sec. II with the parameters computed in Sec. III. The calculations have been programmed and carried out on the IBM 704 electronic computer.

We present as an example detailed results for SiC. We list in Table IV the eigenvalues and corresponding eigenfunctions of the valence states and of the lowest conduction states for SiC; the value $V^s(0)=-2.44$ Ry, the average of the two values obtained for Si by Woodruff[2] and for C by Herman[1] has been used. In Fig. 2 we plot the dependence of the eigenvalues on the number of plane waves used in the expansion of the wave functions; it can be noted that the convergence is, in general, satisfactory and the plane waves shown in Fig. 1 appear to be sufficient to establish the relative position of the electronic eigenvalues. The valence state Γ_{15} of p-like symmetry converges, however, more slowly than the other states and this happens every time the C atom is involved because it has only the $1s$ core state. Kleinman and Phillips[18] have shown in diamond that adding 380 more plane waves does not decrease the energy by more than 0.1 Ry and we assume the same to be true in this case. The energy-band profiles for SiC in the symmetry directions [100] and [111] are plotted in Fig. 3 using the eigenvalues of Table IV. The computed points are indicated by circles and are joined by smooth curves $E(k)$ along the symmetry lines taking into account the compatibility relations[18]

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[18] L. Kleinman and J. C. Phillips, Phys. Rev. 116, 880 (1959).

TABLE IV. Eigenvalues (in Ry) and eigenvector coefficients for the valence states and the lowest conduction states in SiC at the symmetry points Γ, X, and L. The coefficients correspond to the symmetrized combinations of plane waves listed in Table II; the coefficients of the other combinations of plane waves indicated in Fig. 1 are generally smaller; they are available from the authors upon request.

Irr. repr.	$\Gamma_1(1)$	$L_1(1)$	$X_1(1)$	$L_1(2)$	$X_3(1)$	$^2L_3(1)$	$^2X_5(1)$	$^3\Gamma_{15}(1)$	$X_1(2)$	$X_3(2)$	$L_1(3)$	$\Gamma_1(2)$	$^2L_3(2)$	$^3\Gamma_{15}(2)$
Energies	-1.939	-1.738	-1.667	-1.344	-1.282	-1.007	-0.994	-0.771	-0.568	-0.334	-0.275	-0.273	-0.230	-0.140
c_1	0.948	-0.322	0.852	0.868	0.937	-0.293	0.919	0.684	-0.546	-0.093	-0.243	0.353	0.843	0.490
c_2	-0.295	0.881	0.564	0.359	0.151	0.818	0.338	-0.453	0.815	0.975	0.315	0.594	0.474	0.869
c_3	-0.202	-0.363	-0.142	0.145	-0.206	0.215	-0.133	0.487	-0.222	0.064	0.889	0.673	-0.246	0.243
c_4	-0.185	-0.193	-0.123	-0.060	-0.006	-0.165	0.038	0.093	0.048	-0.215	0.146	0.380	-0.065	0.052
c_5	-0.011	0.017	0.083	0.274	0.261	-0.010	-0.102	-0.203	-0.109	-0.064	-0.108	0.176	-0.077	0.169
c_6	.	0.148	-0.001	-0.063	-0.093	0.167	-0.136	.	-0.002	-0.064	-0.234	.	0.045	.
c_7	.	0.065	0.035	0.101	0.000	.	0.064	.	0.080	-0.030	0.044	.	.	.
c_8	.	-0.008	0.041	-0.116	0.017	.	.	.	0.034	0.077	-0.086	.	.	.
c_9	.	0.043	.	-0.051	.	.	.	.	.	.	0.116	.	.	.
c_{10}	.	-0.060	.	-0.079	.	.	.	.	.	.	-0.007	.	.	.
	.	.	.	.	.	.	.	.	.	.	.	.	.	.
	.	.	.	.	.	.	.	.	.	.	.	.	.	.

between various eigenstates and the noncrossing rule.[19] These curves could have been obtained quite accurately by the pseudopotential interpolation procedure[8,9] but the purpose of the present paper is to use them only to visualize the band structure as determined from the calculations at the symmetry points. The results in
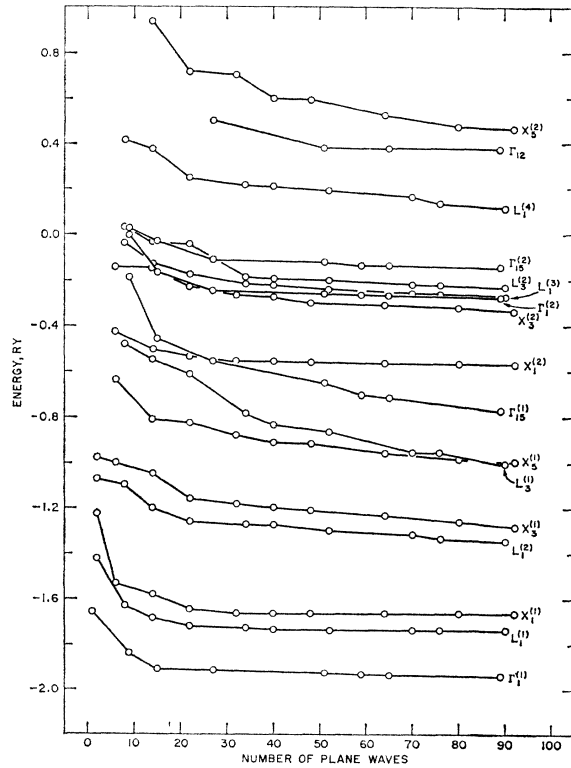

FIG. 2. Convergence of the energy eigenvalues in SiC. The eigenvalues of the valence states and of the lowest conduction states (in Ry) are plotted as functions of the number of plane waves used in the expansion of the wave functions up to the total number included in Fig. 1.

SiC indicate that the maximum of the valence band is the eigenvalue Γ_{15} at the center of the reduced zone, the minimum of the conduction band is the eigenvalue $X_1(2)$ at the point $(2\pi/a)(1,0,0)$ of the reduced zone, the indirect energy gap is 0.21 Ry, a value consistent with experiment.[20] The splittings between the valence states X_1 and X_3 and between the conduction states $X_1(2)$ and $X_3(2)$ are rather large, 0.38 and 0.24 Ry, respectively. This arises from the fact that the two atoms have different sizes and different numbers of core states, resulting in large antisymmetric terms $V^A + R^A$ in the matrix elements. The only difference between the secular equations for X_1 and X_3 is in the signs of the antisymmetric terms so that their being large results in large splittings of X_1 and X_3. Results qualitatively similar to the ones reported in Table IV and Fig. 3 were previously obtained for SiC by Kobayashi[21] by using a much smaller number of plane
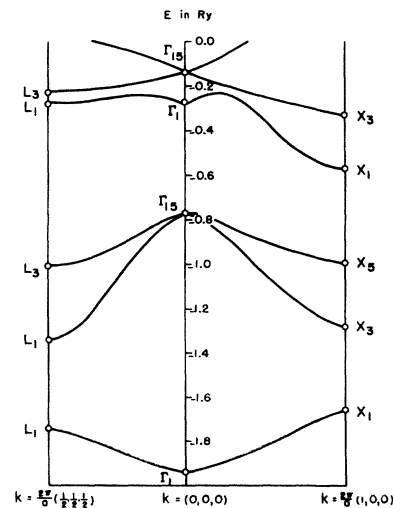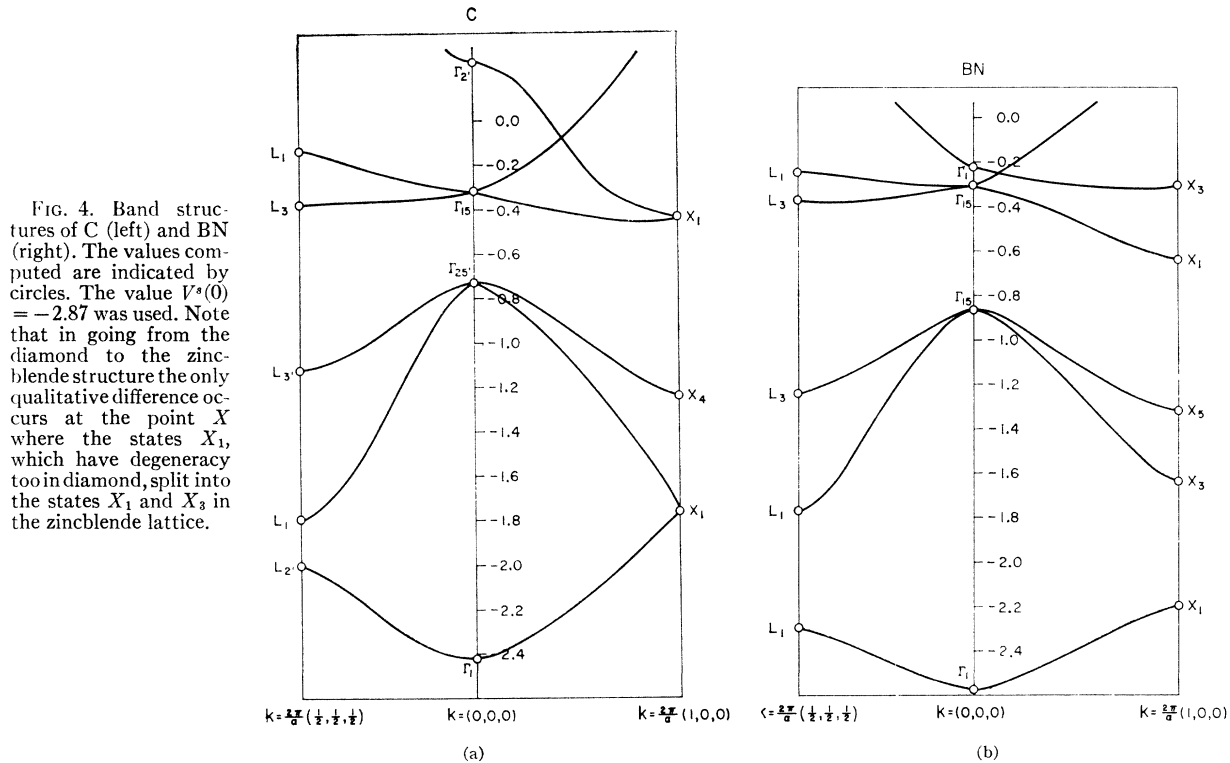

FIG. 3. Band structure of SiC. The computed values (in Ry) for the electronic states at the symmetry points Γ, L, and X are indicated by circles. The lines indicate the expected band profiles in the directions Λ and Δ.

[19] J. Von Neuman and E. Wigner, Physik Z. 30, 467 (1929).

[20] H. R. Philipp, Phys. Rev. 111, 440 (1958).
[21] S. Kobayashi, J. Phys. Soc. Japan 13, 261 (1958).

FIG. 4. Band structures of C (left) and BN (right). The values computed are indicated by circles. The value $V^s(0) = -2.87$ was used. Note that in going from the diamond to the zincblende structure the only qualitative difference occurs at the point X where the states X_1, which have degeneracy too in diamond, split into the states X_1 and X_3 in the zincblende lattice.

(a)   (b)

waves and estimating the parameters in a rather crude manner. The qualitative agreement between our results and that previous calculation is further evidence of the fact that the basic features of the band structure are a consequence principally of the lattice symmetry and are already displayed in a low-order approximation to the OPW method. This has been discussed in a number of papers[7,8,12,22] and seems to be true in all covalent crystals where the OPW method is applicable. To finish with SiC we wish to mention that it is experimentally accepted that the C atom has an excess negative charge of about 0.9,[22] and this effect is not explicitly included in our calculation.[23] We think however that this will have a small effect on the band structure of valence and conduction states for reasons to be discussed in the next section.

Calculations analogous to the one described for SiC have been done for C, BN, Si, AlP, Ge, and GaAs and the resulting band structures are similarly plotted in Figs. 4, 5, and 6. We have verified that the convergence of the results is generally satisfactory with the number of plane waves shown in Fig. 1. The only exceptions occur for diamond and boron nitride where the states which have p-like symmetry are automatically orthogonal to the core states. This was previously pointed out by Herman.[1,2] As mentioned before Kleinman and

Phillips have computed the eigenvalue of the state $\Gamma_{25'}$ in C using 434 plane waves and have shown that this has the effect of lowering this eigenvalue by less than 0.1 Ry with respect to the result obtained using 89 plane waves. Consequently we expect that our result for the energy gap in diamond is too small by about 0.1 Ry, and in BN is too small by a probably larger amount. The results of Figs. 4, 5, and 6 essentially confirm the qualitative considerations on the band structure of the zincblende lattice of Herman[24] and Callaway[25] based on a perturbation on the diamond lattice and of Bassani and Celli[8] based on a perturbation on the empty lattice. As expected, similarity exists both in the band structures of all III–V compounds studied and also in the relationships of the band structure of each compound to that of the Group IV element which has the same number of core electrons. The highest valence state is $\Gamma_{25'}$ in the diamond lattice, Γ_{15} in the zincblende lattice, and the latter is lower. The III–V valence states L_3 and X_5 are also somewhat lower than their IV correspondents $L_{3'}$ and X_4. The conduction states L_3 and Γ_{15} lie only very slightly higher in III–V than in IV. The state which appears to be most sensitive to the change from diamond to zincblende structure is $\Gamma_{2'}$ (Γ_1 in the zincblende structure), which is also very sensitive to any change in the potential within a given structure. This is because for this particular symmetry the states $\langle 111 \rangle$ and $\langle 200 \rangle$ of the "empty

[22] W. G. Spitzer, D. A. Kleinman, and C. J. Frosch, Phys. Rev. 113, 133 (1959); W. G. Spitzer, D. Kleinman, and D. Walsh, ibid. 113, 127 (1959).

[23] The authors are grateful to Dr. Patrick for bringing this point to their attention.

[24] F. Herman, J. Electronics 1, 103 (1955).

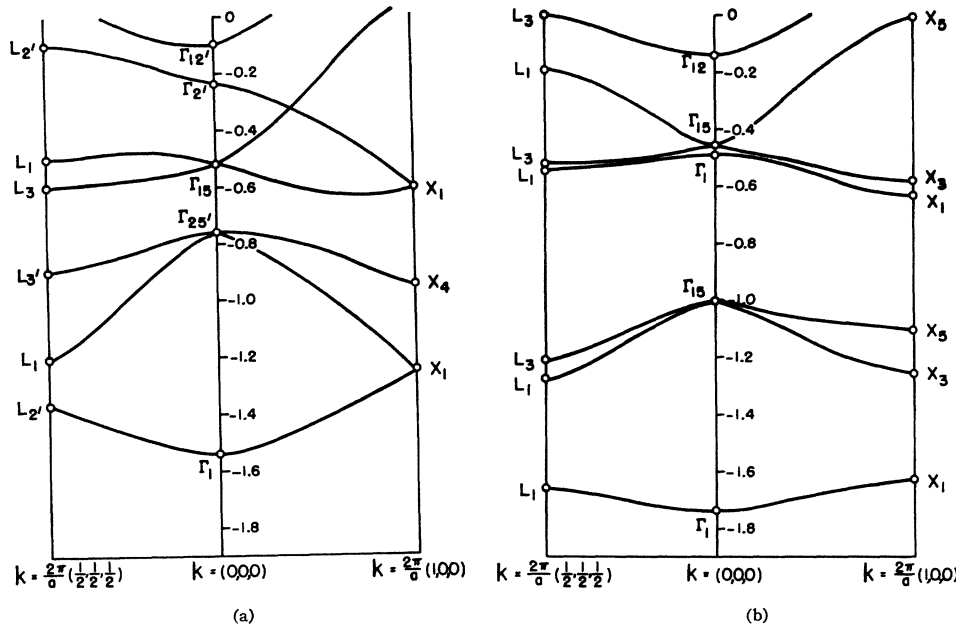[25] J. Callaway, J. Electronics 2, 230 (1957).

Fig. 5. Band structures of Si (left) and AlP (right). The values computed are indicated by circles. The value $V^S(0)$ = −2.0 was used.

lattice" are coupled by a large off diagonal matrix element. A qualitative difference between the band structure of the diamond lattice and of the zincblende lattice occurs at the point X, where the valence and conduction states X_1 of the diamond lattice which have degeneracy two split into the nondegenerate states X_1 and X_3 when the antisymmetric potential is introduced. This splitting produces a gap in the valence band of the zincblende type compounds and introduces two critical points $[\nabla_k E(k) = 0]$ into the conduction bands at $\mathbf{k} = (2\pi/a)(1,0,0)$. The splitting $X_1 - X_3$ seems to decrease with increasing atomic number of the elements which form the compound.

The band structures of diamond and boron nitride computed with the value of $V(0)$ obtained by Herman for diamond are plotted in Fig. 4. The minimum of the conduction band is in the [100] direction in C and at the point $(2\pi/a)(1,0,0)$ in BN. The indirect energy gap is ∼0.3 Ry in diamond, a value which is smaller by about 0.1 Ry than the experimental value.[26] The direct transitions $\Gamma_{25'} - \Gamma_{15}$, $X_4 - X_1$, and $L_{3'} - L_3$ occur at energies which are not inconsistent with interpreting the reflectivity peaks observed by Philipp and Taft[26] at 7, 12.5, and ∼9 eV as due to such transitions. In BN the indirect energy gap comes out to be 0.22 Ry; definite experimental evidence is lacking on this point but the result is somewhat surprising in view of the fact that, in general, the gap increases going from the Group IV to the corresponding III–V compounds. The onset of direct transitions corresponding to $\Gamma_{15}(1) \rightarrow \Gamma_{15}(2)$ in BN occurs instead at larger energies than in diamond in agreement with the preliminary observations of Phillip and Taft.[26] The reason why the calcu-

lated indirect gap is smaller in BN than in C is the large splitting of the conduction states $X_1(2)$ and $X_3(2)$ (0.35 Ry) compared with the decrease in the top valence state obtained going from C to BN (0.14 Ry). Our results on diamond are essentially in agreement with the previous calculations of Herman[1] and of Kleinman and Phillips[17] except for the position of the conduction state $X_1(2)$ (they have −0.27 Ry compared with our −0.44 Ry). We have been unable to find the origin of this disagreement. Our results on BN are also remarkably different from those obtained by Phillips and Kleinman with a first-order perturbation on diamond. They obtain a band gap of 0.7 Ry and a small splitting of the conduction states X_1 and X_3 (0.1 Ry). The difference in the parameters does not account for the disagreement so that we are lead to believe that a perturbation on the diamond structure is not quantitatively accurate when the antisymmetric Fourier coefficients of the potential are relatively large even for large reciprocal lattice vectors. Another calculation on BN, performed by using perturbation on the "empty lattice"[8] with the parameters of Phillips and Kleinman, gave a splitting of the conduction states X_1 and X_3 of 0.28 Ry.

The band structures of Si and AlP are shown in Fig. 5. For both, the value of $V^S(0) = -2$ Ry has been used. The band structure of Si is in reasonable agreement with the accepted experimental results; the minimum of the conduction band is in the [100] direction and the indirect energy gap is about 0.1 Ry. The value for the direct gap $\Gamma_{25'} - \Gamma_{15}$ is also consistent with experiment. Two previous calculations on Si had been performed in the past by Woodruff and Bassani[2] and by Phillips and Kleinman[2] using core eigenstates computed from a constructed Hamiltonian. While the

[26] C. D. Clark, J. Phys. Chem. Solids 8, 481 (1959); H. R. Philipp and E. A. Taft, Phys. Rev. 127, 159 (1962).

FIG. 6. Band structures of Ge (left) and GaAs (right). The values computed are indicated by circles. The value $V^S(0) = -2.0$ was used.
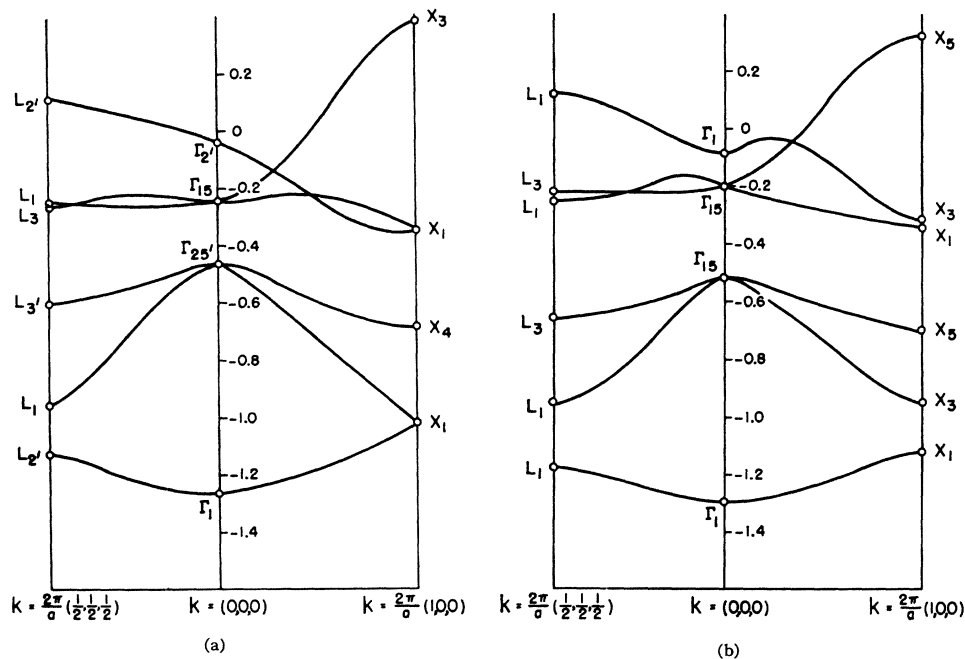
present band structure is qualitatively the same as obtained in both previous calculations, there are differences in the relative position of the conduction states L_1 and $\Gamma_{2'}$ with respect to other states. The position of these two states is lower in our calculation than in Phillips and Kleinman calculations and then would have been found in Woodruff and Bassani's calculations had they been carried to the same convergence, but the relative order of the conduction levels remains the same; in particular the conduction state L_1 is higher than the conduction state L_3 and $\Gamma_{2'}$ is about 0.5 Ry above Γ_{15}. Herman and Skillman have first noticed, in their calculations on Ge,[17] that those two conduction states are particularly sensitive to a constant shift in the energies of the core states, which has the same effect on the band structure as a change in $V(0)$. Phillips[10] has used this fact to suggest the possibility that L_1 is lower than L_3 in silicon and $\Gamma_{2'}$ is very close to Γ_{15}. On this assumption, he has interpreted the experiments of Tauc and Abraham[10] on ultraviolet reflectivity of Si-Ge alloys. We have verified that a change in $V(0)$ would not be enough to produce this effect, but we believe that the assumption is correct for reasons to be discussed later. The band structure obtained for AlP is also shown in Fig. 5 and compares to that of Si much in the same way as the band structure for BN compares to that for C. The energy gap, however, is increased to three times the energy gap in Si; experimentally the energy gap is only twice that in Si.[27] The reason for the large calculated energy gap increase from Si to AlP is due to the fact that the splitting of the conduction states X_1 and X_3 in AlP is now very

small (0.05 Ry) while the valence state Γ_{15} in AlP is considerably lower than the state $\Gamma_{25'}$ in Si (by 0.25 Ry).

The band structures computed for Ge and GaAs are shown in Fig. 6 and are very similar to the ones previously discussed for Si and AlP. The presence of the d core states seems to be of very little importance because the orthogonality coefficients of the d core functions are very small (see Table III). The fact that the presence of a filled $3d$ core shell does not effect the d-like valence states has also been noted by Ham[28] in his calculations on Rb by the Green's function method. In comparing the band structure of Fig. 6 with experiments we notice unsatisfactory features in the conduction bands associated with the states of s-like symmetry. In Ge at the center of the zone the lowest conduction state should be $\Gamma_{2'}$ while our calculation gives $\Gamma_{15} < \Gamma_{2'}$; the minimum of the conduction band should be at the state L_1 while we find the minimum to correspond to the state X_1. The disagreement with experiment appears also in GaAs where we find the minimum of the conduction band to be the state X_1 while we expect from Ehrenreich's[29] analysis of the experimental information on GaAs that the minimum be the state Γ_1 at the center of the zone. As we suspected for the case of Si and AlP, this comparison with experiments shows that the approximations used in computing the parameters of Sec. III affect the results in giving too high a value for the s-like conduction states $\Gamma_{2'}$ and L_1 relative to the other conduction states. We may remark that a previous calculation on Ge by Herman and Callaway[2] which consistently neglected exchange suffered the same defect, while a calculation by Herman[2]

[27] H. G. Grimmeiss, W. Kischio and A. Rabenau, J. Phys. Chem. Solids 16, 302 (1960).

[28] F. Ham, Phys. Rev. 128, 82 (1962).
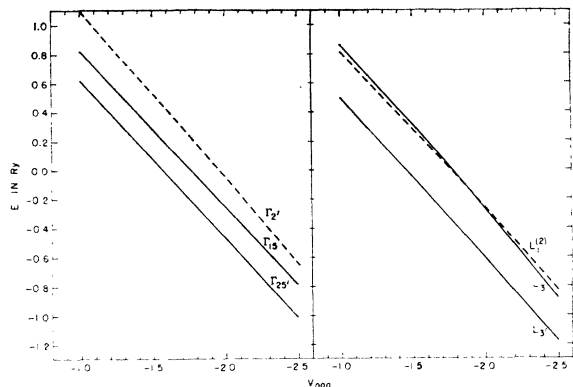[29] H. Ehrenreich, Phys. Rev. 120, 1951 (1960).

FIG. 7. Dependence of some energy eigenvalues on $V^S(0)$ for the case of Ge. As in the results of Fig. 6 the Hartree-Fock atomic solutions of Freeman and Watson (reference 16) have been used.

which included exchange in the crystal potential but made use of core eigenstates computed without exchange gave results in better agreement with the experiment. We will show in the next section the reason for these results in connection with a general discussion of the approximation used. Another calculation with neglect of exchange has been carried out on Ge and GaAs by Gashimzade and Khartsiev.[30] They use the simplified approach to the OPW method proposed by Antoncick[31] and based on replacing the condition of orthogonality to the core wave function by Gombás[32] statistical repulsive potential. Although, as the authors point out, the number of plane waves used in this calculation is to small to obtain satisfactory convergence on the eigenvalues, their preliminary results indicate the potency of the OPW method for calculating the band structure of complex semiconductors.

V. DISCUSSION OF THE APPROXIMATIONS

We have remarked that, in general, the computed band structures of Figs. 3, 4, 5, and 6 show qualitative agreement with experiment but reveal a number of unsatisfactory features in a quantitative comparison; consequently an analysis of the various approximations used is in order.

We first consider the dependence of the valence and conduction eigenvalues on $V^S(0)$. Such a dependence must be considered in detail for the reasons discussed in Sec. III. We have investigated the dependence of our calculated band structure on $V^S(0)$ and we find that a variation of this quantity within 1 Ry does not change significantly the band structure in the calculations so far discussed. Sensitivity to $V^S(0)$ is greatest for Ge and we present in Fig. 7 the variation of the Ge

[30] F. M. Gashimzade and V. E. Khartsiev, Fiz. Tverd. Tela 3, 1453 (1961) [translation: Soviet Phys.—Solid State 3, 1054 (1961)].
[31] E. Antoncick, Czechoslov. J. Phys. 4, 439 (1954); see also R. Gáspár, Acta Phys. Acad. Sci. Hung. 9, 79 (1958).
[32] P. Gombás, in Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 36.

valence and conduction eigenvalues of interest as functions of $V^S(0)$.

Secondly, our calculations do not take into account the fact that the III–V compounds have a certain degree of ionicity. Ionicity in compounds which have the zinc-blende structure means only that the atomic volume contains a fraction of valence electrons different from that supplied by the atom in question and does *not* imply that the density of electrons goes through a sharp minimum at some point between the two different atoms as is the case in the purely ionic crystals. Accordingly, we think that the OPW method can still be applied to the valence and conduction states of III–V compounds and probably also to those of the II–VI compounds. The main effects of ionicity in the OPW calculation is to produce a change in the crystal potential and a shift in the core eigenvalues which will be different for the two sublattices. A rigorous treatment of ionicity requires a completely self-consistent calculation for both the core and the valence states. Such a calculation is beyond the scope of the present work but we may consider the extreme case of ionicity one to show that even in that case the effect on the OPW results is expected to be very small. Let us suppose that the ionicity is 1 and we apply the OPW method to a crystal made of ions instead of starting with atomic solutions. With respect to their eigenvalues in the neutral atoms, the core states in an isolated positive (negative) ion are shifted to lower (higher) energy and all by nearly the same amount.[16] The ions which now constitute the crystal produce a Madelung potential which is practically constant in the core

TABLE V. Comparison of some crystal eigenvalues (in Ry) and some OPW parameters for boron nitride computed for different ionicities. The results of column 2 have been obtained starting with atomic functions and core eigenvalues appropriate to the neutral atoms. The results of column 3 have been obtained from atomic orbitals and core eigenvalues appropriate to B^- and N^+, in this case $E_{1s, B} = E_{1s, B^-} - \alpha_m e^2/a$ and $E_{1s, N} = E_{1s, N^+} + \alpha_m e^2/a$. The results of column 4 have been obtained from atomic orbitals and core eigenvalues appropriate to B^+ and N^-, in this case $E_{1s, B} = E_{1s, B^+} + \alpha_m e^2/a$ and $E_{1s, N} = E_{1s, N^-} - \alpha_m e^2/a$.[a]

	BN	B⁻N⁺	B⁺N⁻
$E_{1s, B}$	−15.391	−15.964	−15.260
$E_{1s, N}$	−31.258	−31.457	−31.596
$V^S(3)$	−0.868	−0.896	−0.875
$V^A(3)$	0.097	0.132	0.083
$V^A(4)$	0.088	0.103	0.086
$A_{1s, B}(3)$	0.130	0.130	0.129
$A_{1s, N}(3)$	0.086	0.086	0.086
$\Gamma_{15}(1)$	−0.863	−0.978	−0.857
$\Gamma_{15}(2)$	−0.305	−0.290	−0.325
$\Gamma_1(2)$	−0.243	−0.298	−0.226
$X_5(1)$	−1.316	−1.382	−1.317
$X_1(2)$	−0.654	−0.640	−0.657
$L_3(1)$	−1.240	−1.362	−1.234
$L_3(2)$	−0.369	−0.366	−0.391
$L_1(3)$	−0.257	−0.259	−0.266

[a] Orbital energies and wave functions for B and N atoms and their ions are computed by the atomic SCF program ANL SSS SCF No. 5B written by C. C. J. Roothaan and P. Bagus. The value of the Madelung constant for the zincblende structure is 3.7829.

TABLE VI. Crystal eigenvalues (in Ry) for diamond obtained with two different values of the largest Fourier coefficients of the potential $V(3)$. In the second column we report the results obtained by using the valence contribution to the Coulomb potential computed from the atomic potentials. In the third column we report the results obtained by using, for the valence contributions to $V(3)$, the value consistently computed from the crystal wave functions.

	Atomic densities	Self-consistency in valence Coulomb
$V_{\mathrm{val}}(3)$	0.282	0.345
$\rho_{\mathrm{val}}(3)$	0.791	0.968
Γ_1	-2.418	-2.357
$\Gamma_{25'}$	-0.730	-0.616
Γ_{15}	-0.316	-0.250
$\Gamma_{2'}$	0.269	0.396
$X_1(1)$	-1.767	-1.682
X_4	-1.254	-1.173
$X_1(2)$	-0.427	-0.420
$L_{2'}$	-1.992	-1.899
$L_1(1)$	-1.792	-1.747
$L_{3'}$	-1.118	-1.000
L_3	-0.367	-0.278
$L_1(2)$	-0.120	-0.029

region[33] and whose effect on the core states is that of shifting to higher (lower) energy the eigenvalues of positive (negative) ions. These two effects nearly cancel and consequently the contribution to the matrix elements arising from the core states would be very little changed. The Fourier coefficients of the potential would be also very little changed because going from the atom to the ion produces a significant change in the potential only far from the nucleus and the oscillating factor in the Fourier transform greatly reduces the contribution from that region of space. We have studied in detail the effect of ionicity on BN and report in Table V a comparison of a few parameters and some crystal eigenvalues for the three cases of a crystal constructed from neutral atoms, from B^- and N^+ and from B^+ and N^-. The ionicity produces differences in the results which do not basically change the band structure.

The major source of error in the calculations is certainly associated with the model crystal potential used. An initial error comes from the fact that the crystal potential is constructed as a sum of atomic potentials. The error associated with this approximation in the Coulomb part of the potential has been investigated by Kleinman and Phillips[18] by recomputing the Fourier coefficients of the density of valence electrons from the valence crystal wave functions rather than from the atomic densities. They find reasonable agreement between the results of the two ways of computing the crystal potential. We have used their procedure of sampling the Brillouin zone to recompute the valence part of the Fourier coefficients of the Coulomb potential and have noticed that at least in the diamond structure

self-consistency can be achieved in the Coulomb part of the valence potential after a few iterations without significant changes in the energy band structure. The results of this calculation for diamond are given in Table VI. The final values of the Fourier coefficients of the charge density due to the valence electrons can be compared with the results from x-ray scattering as explained by Kleinman and Phillips.[34] Our result for $\rho(3)$ is in good agreement with the experimental data, the higher Fourier coefficients are probably too small to be reliably computed in the present scheme and they have not been varied in our calculation.

A more serious source of error is that we have constructed the crystal potential as the sum of atomic-like potentials whose exchange contribution has been replaced by the Slater approximation. The exchange operator is really nonlocal and should be used as such in the crystal Hartree-Fock equations to obtain self-consistent solutions. Such a formidable calculation has never been attempted. Many authors have pointed out the inaccuracy associated with using the same average exchange potential for all valence and conduction states and have given various prescriptions for constructing an l-dependent potential particularly suited for calculations on metals.[35] We think a very promising and general approach to be that of separating core-valence exchange and valence-valence exchange and adding to this last term the valence-valence correlation contribution. Such an approach has recently been developed[36] by using the Green's function method of many-body theory. Numerical calculations with this method will require nontrivial modifications of our program. Another way of improving our calculations is to retain the Slater exchange potential but to use core states consistent with the approximation. The importance of using eigenvalues and eigenfunctions for the core states which are self-consistent solutions of the model crystal Hamiltonian has been particularly emphasized by Quelle,[37] who has discovered by preliminary calculations in Ge and Si that this has the effect of decreasing the conduction states $\Gamma_{2'}$ and L_1 with respect to the other states. Recently, Herman and Skillman[38] have completed a series of atomic self-consistent calculations by using the Slater approximation to exchange so that it appears that this improvement is now possible. Through the courtesy of Herman we have been furnished the results of the Hartree-Fock Slater calculations on Ge prior to publication and we have used

[33] V. Takahashi and Y. Sakamoto, J. Sci. Hiroshima University 24, 117 (1960). The authors are indebted to Dr. M. Tosi for showing them how the results of this paper can be used to compute the Madelung potential in the zincblende lattice near a lattice point and to prove that the potential is nearly a constant in the core region.

[34] L. Kleinman and J. C. Phillips, Phys. Rev. 116, 880 (1959); 125, 819 (1962).

[35] J. Callaway, Phys. Rev. 97, 933 (1955); 103, 1219 (1956); V. Heine, Proc. Roy. Soc. (London) 240, 361 (1957); B. Segall, Phys. Rev. 125, 109 (1962).

[36] F. Bassani, J. Robinson, B. Goodman, and J. R. Schrieffer, Phys. Rev. 127, 1969 (1962).

[37] F. Quelle, Massachusetts Institute of Technology Progress Report No. 43, 77 (unpublished); Bull. Am. Phys. Soc. 7, 214 (1962).

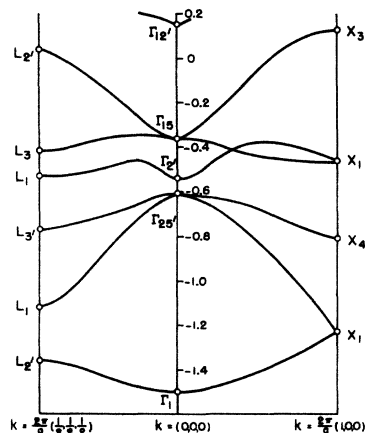[38] F. Herman and S. Skillman, Bull. Am. Phys. Soc. 7, 214 (1962).

FIG. 8. Band structure of Ge computed by using Hartree-Fock Slater atomic eigenstates. The values computed are indicated by circles. The value $V^S(0) = -2.0$ was used.

them to compute the band structure. The results obtained are displayed in Fig. 8 and are in much closer agreement with experiment than the results of Fig. 6 on Ge. The energies of the conduction states $\Gamma_{2'}$ and L_1 have now decreased with respect to the other states and the energy gap is about 0.06 Ry with $V^S(0) = -2.0$ Ry. The minimum of the conduction band is at $\Gamma_{2'}$ but the position of the state L_1 is so cloase to it (differing by 0.005 Ry) that a small change in the potential or just in $V(0)$ may shift the minimum to L_1.

The source of the difference in the band structure produced by using the Herman-Skillman core states is that the Slater exchange potential changes the core state eigenvalues by amounts which differ and depend on the quantum numbers of the state, while the orthogonality coefficients change hardly at all. The eigenvalues of the core states with the Slater potential are now closer to the Hartree-eigenvalues obtained neglecting exchange than to the true Hartree-Fock eigenvalues, and this explains why Herman[2] obtained the right order of states in Ge by using the Hartree atomic results. The situation is illustrated in Table VII where the eigenvalues of the core states are listed together with the eigenvalues of valence and conduction states for different approximations to exchange in Ge. In Fig. 9, we have plotted the dependence of the sensitive eigenvalues on $V^S(0)$ and we note that in this case the choice of $V^S(0)$ is rather critical, as already pointed out by Herman[17] who has also carried out such a calculation on Ge. The value of $V^S(0)$ computed with the prescription of Woodruff is -2.17 Ry. The core shift one would obtain by summing the Coulomb potential of the other atoms of the crystal is ~ -0.08 so that we would have a calculated $V(0)$ of -2.1 Ry, very close to the value required to obtain agreement with experiment. The values one would obtain for the space average of the potential and for the "core shifts" would be much greater than the ones here indicated if we used the same potential to compute $V(0)$ as we used to compute the other Fourier coefficients of the potential. In this case, however, a large error would be involved

TABLE VII. Comparison of the eigenvalues of Ge obtained from different approximations, in Ry. The second column lists the core eigenvalues and the valence eigenvalues in order of increasing energy obtained in the approximation used by Herman (reference 2), i.e., Hartree results without exchange for the atomic states and Slater exchange in the crystal potential. The third column lists the energies obtained by using the approximations of Sec. III, Hartree-Fock results with exchange for the atomic states and Slater exchange in the crystal potential. The fourth column lists the energies obtained by using the Hartree-Fock Slater approximation for the atomic states as well as for the crystal potential. The value $V(0) = -2.0$ Ry was used.

	H.S.	F.W.	H.F.S.
E_{1s}	−810.800	−810.470	−801.954
E_{2s}	−100.800	−104.290	−100.625
E_{2P}	−91.000	−92.462	−90.172
E_{3s}	−13.260	−14.378	−12.888
E_{3P}	−9.750	−10.320	−9.323
E_{3d}	−2.440	−3.266	−3.013
Γ_1	−1.394	−1.271	−1.500
$L_{2'}$	−1.249	−1.133	−1.357
$X_1^{(1)}$	−1.117	−1.017	−1.228
$L_1^{(1)}$	−1.009	−0.958	−1.121
X_4	−0.691	−0.686	−0.805
L_3	−0.643	−0.603	−0.766
$\Gamma_{25'}$	−0.500	−0.468	−0.612
$\Gamma_{2'}$	−0.397	−0.038	−0.549
$L_1^{(2)}$	−0.386	−0.262	−0.525
$X_1^{(2)}$	−0.334	−0.344	−0.464
L_3	−0.264	−0.263	−0.423
Γ_{15}	−0.230	−0.248	−0.369

by taking the crystal potential as a sum of atomic potentials because the Slater approximation to exchange is proportional to the cube root of the crystal density and we would substitute for it the sum of the cube roots of atomic densities. The error would probably become very small and the procedure may become possible if one modifies the expression for the average exchange potential by including the correlation screening in the way suggested by Robinson, Bassani, Knox, and Schrieffer.[39] In this case, however, the Herman and Skillman core states would no longer be consistent with the potential.
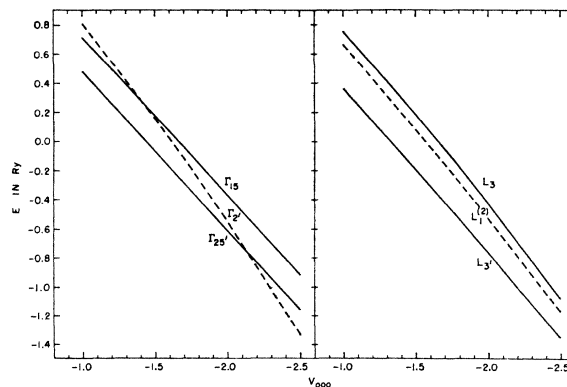

FIG. 9. Dependence on $V^S(0)$ of some energy eigenvalues in Ge. As in the results reported in Fig. 8 the Hartree-Fock Slater atomic eigenstates of Herman and Skillman for Ge in the valence state $4s^1 4p^3$ have been used.

[39] J. Robinson, F. Bassani, R. S. Knox, and J. R. Schrieffer, Phys. Rev. Letters 9, 215 (1962).

VI. CONCLUSION

We have applied the formalism of the OPW method to derive the secular equations for the electronic energy levels at symmetry points in the reduced zone of a zincblende lattice as explicit functions of the Fourier coefficients of the crystal potential and of the core eigenstates. The secular equations reduce automatically to the ones for the diamond lattice when only one type of atom is present.

Calculations have been carried out on a large number of semiconductors with simplifying approximations in the core states and the exchange potential. The results displayed in Figs. 3, 4, 5, and 6 indicate that all the substances considered are semiconductors or insulators. The structure of the valence band is nearly the same in all the semiconductors considered and its width decreases with increasing atomic number, in agreement with experiment. In the zincblende structure, the valence band is split into two bands separated by a rather large energy gap. The conduction states are generally more sensitive to the approximations in the crystal potential and to the core state eigenvalues so that a quantitative comparison with experiments is not always satisfactory. From the comparison between different calculations on Ge shown in Figs. 7 and 8 and from the experimental data we infer that the L_1 and the Γ_1 ($\Gamma_{2'}$ in diamond structure) conduction states are consistently too high in our calculations. At the point X, the results are much less sensitive to the approximation used and the fact that the splitting of the conduction states X_1 and X_3 in the zincblende structure decreases with increasing atomic number is probably a reliable result. The calculation performed in Ge with the atomic wave functions of Herman and Skillman yield a band structure which is remarkably close to the experimental band structure in spite of the Slater approximation to exchange and of the neglect of correlation. This indicates that it would be desirable to recompute the band structure using the Herman and Skillman atomic functions. Spin-orbit effects have not been included in the present calculations because we are concerned with light atoms; for the case of Ge our wave functions have been successfully used by Liu[40] to compute the spin-orbit splitting, effective masses and g tensors. In the band structure of compounds of elements with larger atomic number than the ones considered here, spin-orbit effects will play an essential role.

[40] L. Liu, Phys. Rev. **126**, 1317 (1962).