

that there is as much shift as was observed at only 7% polarization. The only explanation one can give is that from Eq. (1) the actual energy shift in W_0 through changing θ_0 does not depend on the degree of polarization but only on the orientation; thus the shifts should be independent of the degree of polarization. However, there is so much integration over different planes with only 7% polarization that the curves must be smoothed out to a large degree. This, in fact, explains why no differences in structure intensity were observed at different orientations. These results, giving energy shifts at D and beyond, imply that Kronig's theory holds pretty well for electrons of 75-ev energy or greater and that the structure D to ζ is true extended structure determined by the crystal lattice. Germanium is not a simple cubic crystal and does not have 90° symmetry in general; thus, shifts in fine structure for 90° rotation of the absorber are not inconsistent with the crystal structure.

Turning now to a comparison of the results for Ge and the Ge-Si alloy, one would expect to find differences

in the positions of the structure such as that observed for α' and β' because the conduction band structure of the two crystals should be different.⁷ The shift in the K -edge for the Ge-Si alloy of 1.2 volts to lower energy, if real, would indicate that the absolute energy value of the first conduction band for the alloy lies lower than for the pure metal. Since the energy gap between the valence band and the first conduction band for 7% Si in Ge is slightly greater than for pure Ge,⁷ our result would mean that the top of the valence band would shift slightly more than 1.2 volts to lower energies in the alloy. However, we cannot be sure of the true value of the shift of the K -edge. Certainly it is no more than 1.2 ev. However, it is to be noted that the alloy sample was thicker than the sample of pure Ge by 15 to 20% and this increased thickness makes it difficult to speak with certainty concerning the relative location of the edges.⁸ The shifts in position for α' and β' are certainly larger than would be expected from a thickness effect alone, indicating real differences in the conduction bands for Ge and the Ge-Si alloy.

Energy-Band Structure of a Hypothetical Carbon Metal*

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Energy bands are derived for a hypothetical crystal composed of carbon atoms arrayed in a single face-centered-cubic lattice by the method of orthogonalized plane waves (OPW). The bands are compared with those of diamond which have been obtained by Herman. It is shown that the hypothetical crystal is an almost perfect metal. A potential for atomic carbon in the 3P ground-state is computed within the framework of Slater's free-electron-exchange approximation. An analytical approximation to this potential is provided. Results of a general symmetry analysis, appropriate for application of the OPW method to any f.c.c. lattice, are given. The cohesive energy of the metallic crystal relative to that of diamond is discussed within the approximation employed.

I. INTRODUCTION

A GENERAL discussion of cohesion in solids has been given by Wigner and Seitz.¹ As these writers have noted, the cohesive energy of diamond relative to that of its neighboring group III and group V elements is far too large in comparison with the corresponding relation of the other group IV elements to their respective neighbors to be explained on the basis of the qualitative picture they present. When the work described here was begun, it was hoped that by studying the energy-band structure of a hypothetical crystal composed of carbon atoms arrayed on a "suitably chosen" lattice and comparing the results with

those obtained by Herman²⁻⁴ for diamond, one might somehow be able to gain insight into the reasons behind this circumstance.⁵ The crystal we have selected is one in which the atoms are situated on a single face-centered-cubic lattice. The f.c.c. symmetry was chosen because it is one of the simplest types exhibited by metals and its reciprocal lattice is the same as that for diamond within a scale factor. The last feature facilitates comparison of the energy eigenvalues at points of relatively high symmetry in the Brillouin zone. The lattice constant was chosen in such a way that the mean

² F. Herman, Phys. Rev. **88**, 1210 (1952).

³ F. Herman, Phys. Rev. **93**, 1214 (1954).

⁴ F. Herman, Ph.D. thesis, Columbia University, 1953 (unpublished), available on microfilm through University Microfilms, University of Michigan, Ann Arbor, Michigan.

⁵ The cohesive energy of diamond has been calculated by Schmid who has used an approach based upon the concept of molecular bonds rather than energy bands. [L. A. Schmid, Phys. Rev. **92**, 1373 (1953).]

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¹ E. P. Wigner and F. Seitz, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 97.

electron density of the metallic structure is the same as in diamond. The procedure has the following advantage: Many of the terms which appear in the Hartree-Fock expression for the total energy of a solid, in addition to a sum of the one-electron energies, depend only on the average electron density in first approximation.⁶ Hence, the difference between the total energies of the two lattices can be estimated qualitatively by comparison of the energy bands which are occupied by electrons at $T=0^\circ\text{K}$. Since the f.c.c. lattice has only one atom per unit cell, whereas diamond has two, the condition imposed leads to a lattice constant for the metal which is smaller than that for diamond by a factor, $2^{-1/3}$. Correspondingly, the metal has a larger reciprocal lattice. Thus, simply by considering the energies associated with the empty lattices⁷ of both systems, one expects the energy bands of the f.c.c. structure to be wider than the bands of diamond. The results of the detailed analysis show that this condition actually obtains.

Herring's method⁸ of orthogonalized plane waves (OPW) has been employed since it is the same procedure which Herman has used in the case of diamond. Thus, inaccuracies in the results obtained for the two structures are expected to cancel more nearly than would be the case had we used some other technique such as the cellular approximation. As will be shown, however, our detailed procedure, which is outlined in Sec. II, differs sufficiently from Herman's that we are unable to draw rigid quantitative conclusions about the relative stability of the two lattices. We are able to demonstrate only that if the f.c.c. structure were stable for our choice of lattice constant, it would be a nearly perfect metal. That the pseudostructure is metallic cannot be considered surprising, although the result could not have been predicted with complete confidence prior to carrying out the analysis. Additional comments concerning the conclusions to be drawn from the analysis will be given in Sec. V.

II. CRYSTAL POTENTIAL AND ASSOCIATED OPW PARAMETERS

Unless explicitly stated otherwise, atomic units are assumed. (Unit of energy = 1 rydberg.) A one-electron crystal potential is constructed from atomic wave functions given by Jucys⁹ for carbon in the 3P ground-state configuration, $(2s)^2(2p)^2$. The free-electron-exchange approximation of Slater¹⁰ is employed throughout the analysis. The atomic potential for carbon is denoted by $V_a(r)$, where r is the radial coordinate. A numerical tabulation of the function, $-rV_a(r)$ is obtained by substituting values of the radial charge

density and the quantity, $2Z_p(r)$ in an expression for $V_a(r)$ which is derived readily from Slater's results. The radial charge density is computed easily from Jucys' wave functions. The function, $2Z_p(r)$, which is equal to the Coulomb potential for the atom multiplied by $-r$, has been tabulated by Freeman.¹¹ The tabulation of $-rV_a(r)$ is approximated to within 5% by the following analytical expression¹²:

$$-rV_a(r) = 1.741e^{-4.829r} + 4.522e^{-2.047r} + 5.737e^{-0.468r}. \quad (1)$$

It should be remarked that the procedure described does not represent a self-consistent solution for the field of atomic carbon in the approximation of Slater. With one exception, the crystal potential $V_c(\mathbf{r})$ is approximated by the relation

$$V_c(\mathbf{r}) = \sum_{\mu} V_a(|\mathbf{r} - \mathbf{R}_{\mu}|), \quad (2)$$

where \mathbf{R}_{μ} denotes the position of an atom in the lattice. Equation (2) represents a further approximation within the framework of the free-electron-exchange method since it contains the implicit assumption that the exchange term in the crystal potential can be obtained by superposing atomic exchange potentials. The nature of the approximation has been discussed by Woodruff.^{13,14} He has given arguments which indicate that, except for a single case, Eq. (2) represents a reasonably good approximation when one is interested in computing the Fourier coefficients of potential, $v(\mathbf{K})$, which constitute one of three types of parameters involved in the OPW method. \mathbf{K} represents a principal vector in the reciprocal lattice. The exceptional case occurs when $\mathbf{K} = (0,0,0)$. When \mathbf{K} differs from the null vector, Eq. (2) can be employed to express $v(\mathbf{K})$ in the form

$$v(\mathbf{K}) = (1/\Omega_0) \int_{\infty}^{\infty} d\tau V_a(r) e^{-i\mathbf{K}\cdot\mathbf{r}}, \quad (3)$$

where Ω_0 is the volume of a unit cell and the symbol $\int_{\infty}^{\infty} d\tau$ implies an integration over all of space. Equation (3) is valid for crystals having only one atom per unit cell, but can be generalized easily to include lattices with diamond-like symmetry. From Eq. (1) and Eq. (3) the Fourier coefficients can be expressed by a relatively simple relation of the form,

$$V(\mathbf{K}) = -(4\pi/\Omega_0) \sum_{i=1}^3 B_i / (b_i^2 + \mathbf{K}^2), \quad \mathbf{K} \neq (0,0,0), \quad (4)$$

¹¹ A. J. Freeman, Phys. Rev. **91**, 1410 (1953).

¹² The method outlined has also been employed by the writer to approximate the Slater potential for atomic argon. [R. C. Casella, Phys. Rev. **104**, 1260 (1956).]

¹³ T. O. Woodruff, Phys. Rev. **103**, 1159 (1956).

¹⁴ T. O. Woodruff, Ph.D. thesis, California Institute of Technology, 1955 (unpublished). Portions of this work are described in a review article by T. O. Woodruff, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4 (to appear shortly). The writer is grateful to Dr. Woodruff for access to his manuscript prior to publication.

⁶ See, for example, the discussion presented in the book by F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. X.

⁷ Empty-lattice energies are illustrated in Fig. 5 of reference 3.

⁸ C. Herring, Phys. Rev. **57**, 1169 (1940).

⁹ A. Jucys, Proc. Roy. Soc. (London) **A173**, 59 (1939).

¹⁰ J. C. Slater, Phys. Rev. **81**, 385 (1951).

where B_i are the constants multiplying the exponentials in Eq. (1) and b_i are the constants occurring in the exponents of the same expression.

When $\mathbf{K}=(0,0,0)$, Eqs. (2), (3), and (4) are no longer valid. Following Herman³ and Woodruff,¹³ the (additive) Coulomb and exchange contributions to $v(0,0,0)$ are treated separately. Since the Coulomb portion of the atomic potentials, $-2Z_p(|\mathbf{r}-\mathbf{R}_\mu|)/|\mathbf{r}-\mathbf{R}_\mu|$ can be superposed in constructing the corresponding portion of the crystal potential, the Coulomb contribution, $v^{(c)}(0,0,0)$ obeys a relation similar to Eq. (3) in which $V_a(r)$ is replaced by $-2Z_p(r)/r$. That is,

$$V^{(c)}(0,0,0) = -(4\pi/\Omega_0) \int_0^\infty dr r^2 [2Z_p(r)/r]. \quad (5)$$

Equation (5) has been integrated numerically, yielding $v^{(c)}(0,0,0) = -1.5156$. An expression for the exchange contribution $v^{(e)}(0,0,0)$ is derived by noting that $v(\mathbf{K})$ can always be written in the form

$$v(\mathbf{K}) = (1/\Omega_0) \int_{\text{cell}} d\tau V_c(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}}. \quad (6)$$

By replacing $V_c(r)$ in Eq. (6) with Slater's exchange correction, as applied directly to the crystal potential, and adopting Woodruff's assumption that the valence charge density may be considered constant in determining an approximate value of $v^{(e)}(0,0,0)$, one obtains the expression

$$v^{(e)}(0,0,0) = -(4\pi C/\Omega_0) \int_0^{r_0} dr \times r^2 [U_c(r)/r^2 + 4\pi X/\Omega_0]^{\frac{1}{2}}. \quad (7)$$

In Eq. (7), $C=6[3/(32\pi^2)]^{\frac{1}{2}}$, $U_c(r)$ is the radial charge density due to the core electrons, X is the number of valence electrons per atom, and r_0 is the radius of a sphere having a volume equal to Ω_0 . By numerical integration of Eq. (7), $v^{(e)}(0,0,0) = -1.4398$. It is

TABLE I. Fourier coefficients of potential, $v(\mathbf{K})$, for the metallic-carbon and diamond lattices. Comparison with Herman's results³ for diamond. \mathbf{K} denotes a principal vector in the reciprocal lattice. $2a$ equals the edge length of the basic cube (i.e., a denotes the lattice constant). Unit of energy = 1 rydberg.

\mathbf{K} (in units of π/a)	\mathbf{K}^2 [in units of $(\pi/a)^2$]	$v(\mathbf{K})$ (metallic lattice)	$ v(\mathbf{K}) $ (diamond)	$ v(\mathbf{K}) $ (diamond) (after Herman)
0 0 0	0	-2.9554	2.9554	2.8686
1 1 1	3	-0.63588	0.6454	0.6400
2 0 0	4	-0.50501	0	0
2 2 0	8	-0.28409	0.4183	0.4188
3 1 1	11	-0.21590	0.2269	0.2013
2 2 2	12	-0.20007	0	0.0016
4 0 0	16	-0.15503	0.2329	0.2272
3 3 1	19	-0.13282	0.1418	0.1256
4 2 0	20	-0.12678	0	0
4 2 2	24	-0.10734	0.1631	0.1532

* See reference 4.

easily demonstrated that application of the method to diamond-like crystals yields results which may be obtained formally by replacing Ω_0 with Ω_a and r_0 with r_a wherever they occur in Eq. (5) and Eq. (7). Ω_a denotes the volume per atom in the crystal and r_a is the radius of a sphere having a volume equal to Ω_a . Aside from notational differences, the resulting expression for $v^{(e)}(0,0,0)$ is identical with Woodruff's. The agreement is not unexpected since his assumption of uniformly distributed valence charge underlies the method employed in deriving Eq. (7).¹⁵ Since Ω_0 is equal to Ω_a for the metallic lattice and since the lattice constant has been chosen in such a way that the volume per atom is the same as in diamond, the foregoing implies that $v(0,0,0)$ is the same for both lattices in the approximation employed. The results of the present treatment are summarized in Table I, which contains numerical values of several of the Fourier coefficients associated with both the metallic and diamond lattices. The latter are compared with Herman's values⁴ of $v(\mathbf{K})$, which were determined from Jucys' wave functions¹⁶ for atomic carbon in the $5S$ bonding configuration $(2s)(2p)^3$.

In addition to the Fourier coefficients two other types of parameters must be determined in order to ascertain the energy bands by the OPW method. They are the atomic eigenvalues, E_{nl} associated with the core states and orthogonality coefficients, $A_{nl}(\mathbf{k}+\mathbf{K})$, where \mathbf{k} is the reduced wave vector. Since the orthogonality coefficients are introduced in the process of orthogonalizing plane waves to core states, they are determined by the core orbitals.¹⁷ For carbon the parameters reduce to E_{1s} and $A_{1s}(\mathbf{k}+\mathbf{K})$. Following Parmenter¹⁸ and Woodruff,¹³ new values of E_{1s} and the $1s$ atomic orbital φ_{1s} are determined instead of using the quantities obtained originally by Jucys.⁹ The mean value of a trial wave function, $C(\alpha)e^{-\alpha r}$ with respect to an atomic Hamiltonian containing $V_a(r)$, as given by Eq. (1), is computed and α is varied so as to obtain an extremum. $C(\alpha)$ is determined by the condition that φ_{1s} be normalized. From the variational procedure, $\varphi_{1s} = 7.6434 \exp(-5.683r)$ and $E_{1s} = -21.448$, whereas Jucys has obtained $E_{1s} = -22.658$. Although his value is presumably the more accurate one, it is believed more consistent to employ quantities which are derived from the same atomic potential that is used to construct the crystal potential. The argument is weakened, however, by the fact that the exchange contribution to $v(0,0,0)$ is treated in a manner which is inconsistent with the procedure employed in determining the other Fourier coefficients of potential. Values of the orthogonality coefficients are presented in Table II.

¹⁵ See reference 13, p. 1164.

¹⁶ A. Jucys, J. Phys. (U.S.S.R.) **11**, 49 (1947).

¹⁷ For a mathematical definition of the orthogonality coefficients see, for example, Eq. (4.1), reference 13.

¹⁸ R. H. Parmenter, Phys. Rev. **86**, 552 (1952).

TABLE II. Orthogonality coefficients, $A_{1s}(\mathbf{k}+\mathbf{K})$. \mathbf{k} is the reduced wave vector and \mathbf{K} is a principal vector in the reciprocal lattice. a denotes the lattice constant. Values are presented for the metallic lattice at the symmetry points, $\Gamma[\mathbf{k}=(0,0,0)]$, $X[\mathbf{k}=(\pi/a)(1,0,0)]$, and $L[\mathbf{k}=(\pi/a)(\frac{1}{2},\frac{1}{2},\frac{1}{2})]$ and at the point, $\mathbf{k}=(\pi/a)(\frac{1}{2},0,0)$, which lies along the symmetry axis, Δ in the Brillouin zone. For diamond, values are given at Γ . Notation is after Bouckaert *et al.*^a In the table, $\mathbf{k}+\mathbf{K}$ is given in units of π/a .

$\mathbf{k}+\mathbf{K}$ at Γ	$A_{1s}(\mathbf{k}+\mathbf{K})$ at Γ	A_{1s} at Γ (diamond)	$\mathbf{k}+\mathbf{K}$ at X	$A_{1s}(\mathbf{k}+\mathbf{K})$ at X
0 0 0	0.16915	0.11961	1 0 0	0.15558
1 1 1	0.13291	0.10241	0 1 1	0.14358
2 0 0	0.12339	0.097495	1 2 0	0.11486
2 2 0	0.093973	0.080993	2 1 1	0.10719
3 1 1	0.078305	0.071219	1 2 2	0.088265
2 2 2	0.073946	0.068352	3 0 0	0.088265

$\mathbf{k}+\mathbf{K}$ at L	$A_{1s}(\mathbf{k}+\mathbf{K})$ at L	$\mathbf{k}+\mathbf{K}$ along Δ	$A_{1s}(\mathbf{k}+\mathbf{K})$ along Δ
1 0 0	0.15881	0 0 0	0.16559
1 1 1	0.13546	1 1 1	0.14079
1 1 1	0.11691	0 0 0	0.14079
1 1 1	0.10192	1 1 1	0.12117
1 1 1	0.10192	2 0 0	0.12117
1 1 1	0.089643	0 0 0	0.10539
1 1 1		2 0 0	0.10539

^a See reference 21.

III. SYMMETRY ANALYSIS

As is well known, advantage can be taken of the lattice symmetry to simplify the secular equations which result when stationary mean values of a crystal Hamiltonian are computed with respect to trial functions expanded in a finite number of OPW. Since the technique is described adequately elsewhere,¹⁹ details are omitted. Briefly, one first constructs symmetry combinations (SC) of plane waves (PW) which are degenerate in the empty lattice. The SCPW transform according to irreducible representations of the group of the wave vector. Then the SCPW are orthogonalized to the core states to obtain orthogonalized SCPW (OSCPW). Finally, the trial functions are expanded in terms of the OSCPW. It can easily be shown that OSCPW can be constructed by formally replacing each PW in a given SCPW by its corresponding OPW.

Since, to the writer's knowledge, SCPW for f.c.c. lattices do not occur elsewhere in the literature,²⁰ several are presented in an Appendix for PW belonging to low-lying levels in the empty lattice and having reduced wave vectors located at the points Γ , X , and L in the Brillouin zone. The notation is that of Bouckaert *et al.*²¹

¹⁹ See reference 3, 4, and 14. The method appears in a particularly convenient form in Woodruff's thesis, reference 14. A similar procedure oriented toward the Wigner-Seitz method is given by F. C. Von der Lage and H. Bethe [Phys. Rev. 71, 612 (1947)].

²⁰ Recently Heine has determined the energy bands of aluminum. [V. Heine, Proc. Roy. Soc. (London) A240, 340, 354, 361 (1957).] An earlier application of the OPW method involving an f.c.c. lattice (copper) was made by M. Fukuchi, Progr. Theoret. Phys. (Japan) 16, 222 (1956). Since there is only one valence electron per atom in copper vs three in aluminum and four in the carbon metal, it may be presumed that the earlier work required a less extensive symmetry analysis.

²¹ Bouckaert, Smoluchowski, and Wigner, Phys. Rev. 50, 58 (1936).

From the information in the Appendix, one can construct explicit representation matrices and thus obtain SCPW associated with other levels in the empty lattice. Of course, the SCPW presented are not unique and one could equally well start with an equivalent set belonging to equivalent irreducible representations.

Generally, the plane waves in a set which are degenerate in the empty lattice transform reducibly into each other under the operations of the group of the wave vector. It is convenient to know which irreducible representations are contained in the reducible representations associated with each set of plane waves which have relatively low empty-lattice energy. The information for f.c.c. lattices is presented in Table III.²²

IV. RESULTS

The secular equations which result from the symmetrized OPW method have been factored to obtain the one-electron energies of the crystal with the aid of the Illiac digital computer at the University of Illinois.

TABLE III. Occurrence of irreducible representations (i.r.) of the group of the wave vector in the empty lattice spectrum. The table is divided into three parts, each of which may be regarded as a matrix. Rows are labeled by the wave vector, $\mathbf{k}+\mathbf{K}$, of a typical plane wave in a degenerate set having the same reduced wave vector, \mathbf{k} , and empty lattice energy, $|\mathbf{k}+\mathbf{K}|^2$. [\mathbf{K} is a principal vector in the reciprocal lattice.] Columns are labeled by the i.r. belonging to the group of \mathbf{k} . The m th entry gives the number of times the i.r., " n ," is contained in the reducible representation having plane waves in the set " m " as a basis. Omission of an entry implies the omitted entry is zero. The three parts correspond to \mathbf{k} at Γ , X , and L respectively in the reduced zone. Notation is after Bouckaert *et al.*^a $\mathbf{k}+\mathbf{K}$ is given in units of π/a , where a is the lattice constant.

$\mathbf{k}+\mathbf{K}$	Γ_1	Γ_{15}	$\Gamma_{25'}$	$\Gamma_{2'}$	Γ_{12}	Γ_{25}	$\Gamma_{15'}$	$\Gamma_{12'}$	$\Gamma_{1'}$	Γ_2
0 0 0	1									
1 1 1	1	1	1	1						
2 0 0	1	1			1					
2 2 0	1	1	1			1				
3 1 1	1	2	2	1	1	1	1	1		
2 2 2	1	1	1	1						
4 0 0	1	1			1					
1 3 3	1	2	2	1	1	1	1	1		

$\mathbf{k}+\mathbf{K}$	X_1	$X_{4'}$	$X_{6'}$	X_3	X_5	X_2	$X_{2'}$	$X_{2''}$	X_4	$X_{1'}$
0 0 0	1	1								
0 1 1	1		1	1						
1 2 0	1	1	1		1	1	1			
2 1 1	1	1	1	1	1				1	
1 2 2	1	1	1	1	1					1
3 0 0	1	1								
0 1 3	1		2	1		1				1
3 2 0	1	1	1		1	1	1			

$\mathbf{k}+\mathbf{K}$	L_1	$L_{2'}$	$L_{3'}$	L_3	L_2	$L_{1'}$
1 1 1	1	1				
1 1 1	1	1	1	1		
1 1 1	1	1	1	1		
1 1 1	1	1				
1 1 1	1	1	1	1		
1 1 1	1	1	2	2	1	1
1 1 1	1	1	1	1		

^a See reference 21.

²² A corresponding table for diamond-type lattices is given by Herman. (Table VIII, reference 4.)

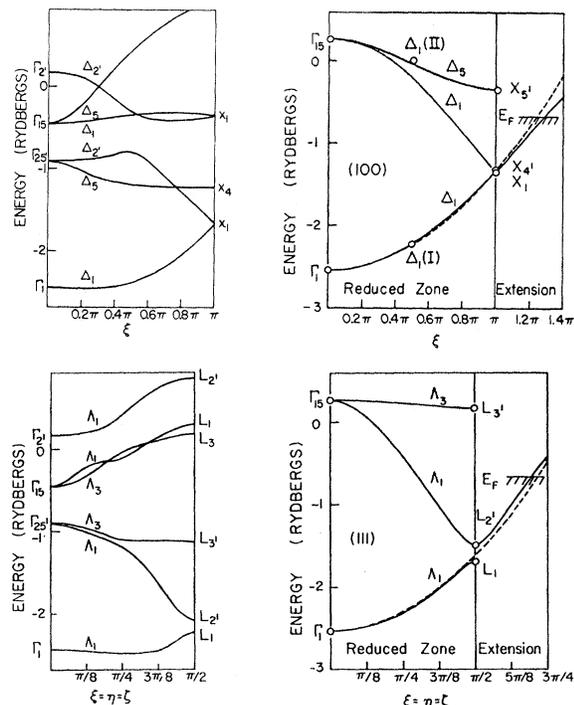


FIG. 1. Energy bands of the metallic-carbon and diamond lattices. Above, the reduced wave vector, \mathbf{k} lies along the [100] direction. Below, \mathbf{k} lies along the [111] direction. The curves for diamond (after Slater and Koster²³) appear to the left of those for the metal. They have been redrawn in the same scale employed in the diagrams associated with the metal. The origins in the energy scales of the two systems are displaced relative to each other in order to demonstrate the results of the "procedural differences" discussed in Sec. V. The small circles appearing in the illustration of the bands of the metal designate energy values determined by the OPW method (cf. Table IV). Continuous curves represent the results of interpolation with the LCAO procedure. The curves labeled Δ_1 must approach the zone boundary ($\xi = \pi$) with zero slope in the case of the metal. The curvature is sufficiently rapid near the boundary, however, that the bands appear to have finite slopes in the diagram. Portions of the interpolated curves are repeated in the extended zones to facilitate comparison with the energies (broken curves) of effectively free electrons having an effective mass equal to 1.13. The Fermi energy is denoted by E_F . $\xi = k_x$, $\eta = k_y a$, and $\zeta = k_z a$, where k_x , k_y , and k_z are the x , y , and z components of \mathbf{k} and a is the lattice constant.

The results are displayed in Table IV, which illustrates the degree of convergence attained, and in Fig. 1 where the energy bands are shown as functions of \mathbf{k} for values of \mathbf{k} lying along the [100] and [111] directions. The energy bands are obtained by interpolating with the LCAO method, as proposed by Slater and Koster,²³ between nine OPW-determined solutions at points of relatively high symmetry. Portions of the extended zones are included and the interpolated results are compared with a parabola (broken curve) corresponding to the energies of effectively free electrons having an effective mass, m^* , equal to 1.13 in units of the free-electron mass. This effective mass m^* is determined by the relation $1/m^* = \langle 1/m^* \rangle$, where $\langle 1/m^* \rangle$ is the average

²³ J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

TABLE IV. Convergence of eigensolutions. E_i denotes an energy eigenvalue obtained by factorization of a secular determinant of rank i . Generally, only the lowest root is presented for each symmetry type considered. When two roots having the same symmetry are given, symbols (I) and (II), designating the lower and higher roots respectively, are attached to the symmetry symbols heading the columns. When two symmetry combinations belonging to the same irreducible representation are degenerate in the empty lattice, the rank of the associated secular determinant, increases from i to $i+2$ (see Table III). Notation is after Bouckaert *et al.*^a Unit of energy = 1 rydberg.

	Γ_1 (I)	Γ_{15}	$\Gamma_{25'}$	Γ_1 (II)	$\Gamma_{2'}$	Δ_1 (I)
E_1	-2.4107	1.1612	1.7710		2.0448	-2.0795
E_2	-2.5063	0.7941	1.7364	1.9431	2.0402	
E_3	-2.5363	0.5854		1.8768	2.0325	-2.1424
E_4	-2.5370		1.7175	1.8743		
E_5	-2.5372	0.3635	1.7007	1.8703		-2.2137
E_6	-2.5373	0.2835		1.8699		
E_7		0.2592				-2.2206
	Δ_1 (II)	X_1 (I)	$X_{4'}$	$X_{5'}$	X_1 (II)	X_3
E_1		-1.0962	-1.0713	0.0869		0.5288
E_2		-1.2941	-1.1077	-0.0980	0.4320	0.5220
E_3	0.1733	-1.3134	-1.2577	-0.1566	0.4003	0.4949
E_4		-1.3376		-0.2509	0.3959	0.4852
E_5	0.1147		-1.2964			
E_6		-1.3387	-1.3254	-0.3383	0.3860	
E_7	0.0146					
	L_1 (I)	$L_{2'}$	$L_{3'}$	L_1 (II)	L_3	
E_1	-1.5535	-1.2852	0.7013		1.5413	
E_2	-1.6546	-1.3020	0.5399	1.3163	1.5358	
E_3	-1.6837	-1.3789	0.4720	1.3126	1.5211	
E_4						
E_5	-1.6952	-1.4841	0.2599	1.3001	1.4943	
E_6	-1.6952	-1.4950	0.1728	1.2897	1.4816	

^a See reference 21.

value of the quantity $(E - E_{\Gamma_1})/(\mathbf{k} + \mathbf{K})^2$ as obtained directly from the OPW-determined values of E at four points in the extended zones: $\mathbf{k} + \mathbf{K} = (\pi/a)(\frac{1}{2}, 0, 0)$, $(\pi/a)(1, 0, 0)$, $(\pi/a)(\frac{3}{2}, 0, 0)$, and $(\pi/a)(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The quantity $2a$ equals the edge length of the basic cube in the f.c.c. lattice.

The Fermi level, E_F , is determined by the relation²⁴

$$E_F - E_{\Gamma_1} = (1/m^*) (5/3) (2.21/r_s^2), \quad (8)$$

where r_s is defined by the condition that $(4\pi/3)r_s^3$ equal $\Omega_a/4$, the mean volume per valence electron. From the foregoing, $r_s = 1.32$ and $E_F = -0.66$. From Fig. 1, it is seen that the deviation from free-electron behavior is small for values of $E(\mathbf{k} + \mathbf{K})$ which do not exceed E_F . That is, the f.c.c. carbon lattice may be considered a nearly perfect metal with $m^* = 1.13$, if one ignores the relatively small energy discontinuities at the boundaries of the first zone and assumes that the behavior of the energy bands for arbitrary directions of \mathbf{k} is typified by their behavior for \mathbf{k} along the [100] and [111] directions as long as E does not exceed E_F . The assumption is plausible for two reasons. First, the behavior for \mathbf{k} along the [100] and [111] directions is nearly the same. Second, the bands Δ_1 and Λ_1 do not split as \mathbf{k} is allowed to leave the symmetry axes, Δ and

²⁴ See reference 6, Eq. (23), Chap. X.

Λ respectively. As E approaches E_F , however, the assumption is probably no longer valid since the band labeled Δ_5 and Λ_3 in Fig. 1, splits into two bands for general values of \mathbf{k} .²¹ For some values of \mathbf{k} one of the "split-off" bands probably extends below E_F . That is, for E less than but nearly equal to E_F , deviations from effectively free-electron behavior are expected to be somewhat greater than is indicated in Fig. 1. Spin-orbital effects are neglected throughout the analysis.

V. COMPARISON WITH DIAMOND

Herman's solutions for the one-electron energies in diamond at the points Γ , X , and L in the Brillouin zone have been interpolated with the LCAO method by Slater and Koster. The illustration of their results is reproduced²⁵ in Fig. 1 to facilitate comparison with the results of the present study. Recently, Bassani²⁶ has extended Woodruff's results¹³ for the energy bands in silicon at $\mathbf{k}=(0,0,0)$ to the point $\mathbf{k}=(\pi/a)(1,0,0)$ and has interpolated between the two sets of energy values with the LCAO method. In contrast with the differences between the diamond and metallic-carbon lattices, his results show that the bands of silicon and diamond exhibit remarkable similarities.

From Table IV, the value of E_{Γ_1} , the lowest level in the bands of the metallic lattice, is approximately equal to -2.54 , whereas Herman has obtained the value, -2.44 , for the corresponding level in diamond.²⁷ The near coincidence of the levels mainly results from the condition imposed in selecting the lattice constant of the metal, but partly arises from differences between the method employed by Herman and that described in Sec. II. A measure of the extent to which the procedural differences affect the results has been ascertained by redetermining the solution E_{Γ_1} for the case of diamond, using values of $v(\mathbf{K})$, $A_{1s}(\mathbf{k}+\mathbf{K})$, and the value of $E_{1s}(-21.448)$ determined in exactly the same way as are the corresponding quantities for the metallic lattice.²⁸ From solution of a secular equation of third order, $E_{\Gamma_1}=-2.76$. Since eigenvalues belonging to Γ_1 converge with relative rapidity, it is believed that the value of E_{Γ_1} would not be altered appreciably if one were to extend the calculation by including a larger number of OSCPW in the trial function. A similar investigation of the energies, $E_{\Gamma_{25'}}$, $E_{\Gamma_{15}}$, and $E_{\Gamma_{2'}}$, which converge more slowly, indicates that if the bands were determined more accurately by the procedure given in Sec. II, the results would probably be about the same

as those obtained by Herman, except for a general lowering of the levels by approximately 0.3 rydberg. This result is indicated in Fig. 1, where the origin of the energy scale for the diamond bands is displaced by -0.32 relative to that for the metal. Part of the discrepancy obviously results from the fact that in the present analysis E_{1s} , φ_{1s} , and the radial atomic charge density are derived from a field associated with the ground state of atomic carbon, whereas Herman has used corresponding quantities arising from the 5S bonding state. It is believed that the deviations resulting from this circumstance generally lie within those which result from different treatments of the Fourier coefficients of potential, particularly $v(0,0,0)$, and of the core parameters.

The mean one-electron energy per electron in the metallic lattice, $\langle E_M \rangle$, has been obtained from a modified form of Eq. (8) in which E_F is replaced by $\langle E_M \rangle$ and the factor, $5/3$, appearing in the right side of the equation, is omitted. It is found that $\langle E_M \rangle = -1.42$. Since the electrons in the valence band of diamond are far from free, a procedure analogous to that employed in determining $\langle E_M \rangle$ does not seem an appropriate way to obtain the corresponding quantity, $\langle E_D \rangle$. $\langle E_D \rangle$ is estimated in the following rather crude manner: The density-of-states function, $g(E)$ is calculated by considering the valence band to be composed of three overlapping sub-bands. The density of states, $g_i(E)$ associated with the i th sub-band is assumed to be a constant for values of E lying within the sub-band and to vanish elsewhere. The first sub-band is considered to extend from E_{Γ_1} to E_{X_1} and the second, from $E_{L_{2'}}$ to an energy lying about 0.1 rydberg above $E_{\Gamma_{25'}}$. (See Fig. 1.) The third, which contains twice as many electrons as either of the other two, extends from E_{X_4} to $E_{\Gamma_{25'}}$. The value of g_i within the i th sub-band is determined by requiring that it contain the proper number of electrons per unit volume of the crystal. $g(E)$ is constructed by summing the quantities $g_i(E)$ which do not vanish in a given range of E . Then $\langle E_D \rangle$ is computed, in the usual way, by averaging E with respect to the weighting function, $g(E)$. When the edges of the sub-bands are determined from the values obtained by Herman, it is found that $\langle E_D \rangle = -1.4$. That is, it is not possible to determine which of the two systems has a lower mean value of one-electron energies in the approximation employed. If the procedural differences described earlier are taken into account, one might argue that $\langle E_D \rangle - \langle E_M \rangle \sim -0.3$, which would imply that the diamond lattice is more stable. On a purely theoretical basis, however, this argument clearly is open to question. A qualitative investigation of the differences between the other terms appearing in the expressions for the cohesive energy of the metallic lattice and of diamond indicates that their inclusion would lower the total energy of diamond relative to the metal. It appears difficult to determine the extent of the

²⁵ From Fig. 5, reference 23. (The curves have been redrawn in the same scale used in illustrating the bands of the metallic lattice.)

²⁶ F. Bassani, Phys. Rev. **108**, 263 (1957). The writer is grateful to Dr. Bassani for access to his results prior to publication.

²⁷ Herman's results may be obtained approximately from values of the interpolation constants for diamond which are quoted by Slater and Koster, reference 23.

²⁸ See Tables I and II, Sec. II. Expressions for the matrix elements have been obtained from those for silicon at the origin of the Brillouin zone, as given in Woodruff's thesis, reference 14.

lowering without a more accurate calculation than seems feasible at present.

Although we are forced to conclude that the band approximation is not capable of dealing in a quantitative way with the difference in the cohesive energy of diamond and a metallic form of carbon—a result which is scarcely surprising—it seems safe to close with a few speculative comments. The analysis presented here indicates clearly that a lattice of carbon having a close-packed lattice would behave as an ideal metal. Thus, it seems reasonable to suppose that the cohesive energy of such a metal would fit in a contiguous manner into the cohesive energies of the sequence Li (36.5 kcal/mole), Be (76.6 kcal/mole), B (96 kcal/mole) and lie near 120 kcal/mole at largest. Such behavior would be consistent with the behavior of the quadrivalent solids in the other rows of the periodic system (see Fig. 2 of reference 1). This conclusion implies, in turn, that the unusually large cohesive energy of diamond, namely 170 kcal/mole, is the result of an unusual matching of the lattice structure and electronic properties which is not achieved again among similar monatomic solids although it is achieved in the tungsten group. When viewed from the standpoint of the band diagrams, one presumably can say that the extra cohesive energy of diamond is associated with an unusual lowering of the center of gravity of the four occupied bands relative to the position of the occupied levels in the metallic form.

VI. ACKNOWLEDGMENTS

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APPENDIX. SYMMETRY COMBINATIONS OF PLANE WAVES FOR F.C.C. LATTICES

A PW, normalized²⁹ in a periodic crystal and having wave vector, $\mathbf{k} + \mathbf{K}$, is designated by $W(\mathbf{k} + \mathbf{K})$. A set of PW having the same empty-lattice energy, $|\mathbf{k} + \mathbf{K}|^2$, is denoted by $\{\mathbf{k} + \mathbf{K}\}$. A SCPW belonging to the ν th row of the j th irreducible representation of the group of \mathbf{k} is designated by $S_{\nu}^{(j)}(\{\mathbf{k} + \mathbf{K}\})$. It may be written in the form

$$S_{\nu}^{(j)}(\{\mathbf{k} + \mathbf{K}\}) = \sum_{\mathbf{k} + \mathbf{K}} b_{\nu}^{(j)}(\mathbf{K}) W(\mathbf{k} + \mathbf{K}). \quad (9)$$

The summation indicated in Eq. (9) extends over all \mathbf{K} in the set $\{\mathbf{k} + \mathbf{K}\}$. The expansion coefficients, $b_{\nu}^{(j)}(\mathbf{K})$

²⁹ The notation follows that employed in Sec. III.

TABLE V. Expansion coefficients, $b_{\nu}^{(j)}(\mathbf{K})$, occurring in symmetry combinations of plane waves appropriate for the application of the OPW method to f.c.c. lattices. [See Eq. (9).] The table is divided into three parts corresponding to the values of \mathbf{k} at the points Γ , X , and L in the Brillouin zone. Notation is after Bouckaert *et al.*^a In the table rows are labeled by the wave vector, $\mathbf{k} + \mathbf{K}$, of the plane wave, $W(\mathbf{k} + \mathbf{K})$. Columns are headed by two symbols which are separated by a comma: The first denotes the irreducible representation, j , and the second designates the value of ν . The entry in the j , ν th column and $(\mathbf{k} + \mathbf{K})$ th row is the value of $b_{\nu}^{(j)}(\mathbf{K})$ which is multiplied by $W(\mathbf{k} + \mathbf{K})$ in the process of constructing $S_{\nu}^{(j)}(\{\mathbf{k} + \mathbf{K}\})$ in accordance with Eq. (9). Omission of an entry implies the omitted entry is zero. $\mathbf{k} + \mathbf{K}$ is given in units of π/a , where a is the lattice constant. A negative component of $\mathbf{k} + \mathbf{K}$ is written with a minus sign over the absolute value of the component.

$\mathbf{k} + \mathbf{K}$	$\Gamma_{1,1}$	$\Gamma_{16,1}$	$\Gamma_{16,2}$	$\Gamma_{16,3}$	$\Gamma_{25',1}$	$\Gamma_{25',2}$	$\Gamma_{25',3}$	$\Gamma_{2',1}$
0 0 0	+1							
1 1 1	+1	+1	-1	+1	+1	-1	+1	+1
1 $\bar{1}$ $\bar{1}$	+1	+1	+1	-1	+1	+1	-1	+1
$\bar{1}$ 1 $\bar{1}$	+1	-1	+1	+1	-1	+1	+1	+1
$\bar{1}$ $\bar{1}$ 1	+1	-1	-1	-1	-1	-1	-1	+1
$\bar{1}$ $\bar{1}$ $\bar{1}$	+1	-1	+1	-1	+1	-1	+1	-1
$\bar{1}$ 1 1	+1	-1	-1	+1	+1	+1	-1	-1
1 $\bar{1}$ 1	+1	+1	-1	-1	-1	+1	+1	-1
1 1 $\bar{1}$	+1	+1	+1	+1	-1	-1	-1	-1
2 0 0	+1	+1						
0 2 0	+1			+1				
0 0 2	+1		-1					
$\bar{2}$ 0 0	+1	-1						
0 $\bar{2}$ 0	+1			-1				
0 0 $\bar{2}$	+1		+1					

$\mathbf{k} + \mathbf{K}$	$X_{1,1}$	$X_{4',1}$	$X_{6',1}$	$X_{6',2}$	$X_{8,1}$	$X_{6,1}$	$X_{6,2}$
1 0 0	+1	+1					
$\bar{1}$ 0 0	+1	-1					
0 1 1	+1		+1	+1	+1		
0 1 $\bar{1}$	+1		+1	-1	-1		
0 $\bar{1}$ $\bar{1}$	+1		-1	-1	+1		
0 $\bar{1}$ 1	+1		-1	+1	-1		
1 2 0	+1	+1	+1			+1	
1 0 2	+1	+1		+1			+1
1 $\bar{2}$ 0	+1	+1	-1			-1	
1 0 $\bar{2}$	+1	+1		-1			-1
$\bar{1}$ $\bar{2}$ 0	+1	-1	-1			+1	
$\bar{1}$ 0 $\bar{2}$	+1	-1		-1			+1
$\bar{1}$ 2 0	+1	-1	+1			-1	
$\bar{1}$ 0 2	+1	-1		+1			-1

$\mathbf{k} + \mathbf{K}$	$L_{1,1}$	$L_{2',1}$	$L_{3',1}$	$L_{3',2}$	$L_{3,1}$	$L_{3,2}$
$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$	+1	+1				
$-\frac{1}{2}$ $-\frac{1}{2}$ $-\frac{1}{2}$	+1	-1				
$\frac{3}{2}$ $-\frac{1}{2}$ $-\frac{1}{2}$	+1	+1	+1	+1	+1	-1
$-\frac{3}{2}$ $\frac{1}{2}$ $-\frac{1}{2}$	+1	+1	-1	-2	-2	
$-\frac{1}{2}$ $-\frac{3}{2}$ $\frac{1}{2}$	+1	+1	-1	+1	+1	+1
$-\frac{3}{2}$ $\frac{3}{2}$ $\frac{1}{2}$	+1	-1	-1	-1	+1	-1
$\frac{1}{2}$ $-\frac{3}{2}$ $\frac{3}{2}$	+1	-1	+2	-2		
$\frac{3}{2}$ $\frac{1}{2}$ $-\frac{3}{2}$	+1	-1	+1	-1	+1	+1

^a See reference 21.

occurring in several SCPW associated with low-lying levels in the empty lattice are presented in Table V. Generally, SCPW constructed directly from the information given in the table do not appear in normalized form.