Regarding multiphonon coherent scattering, the general situation is again the same as in the case of long incident wavelength: in each outgoing direction the scattered neutrons have a continuous energy spectrum, with singularities resulting from two-phonon processes and occurring at energies which vary with direction.

It has been the main purpose of this paper to put in evidence the direct relationship between the energy changes of neutrons scattered by a crystal and the dispersion law of the crystal vibrations as expressed by the $\omega_j(\mathbf{q})$ and $g(\omega)$ functions. We hope to have shown that energy measurements on scattered neutrons provide a new approach to the problem of determining these functions from scattering data. While the few experimental data so far available[24,35,36] do not as yet permit an analysis along these lines, the foregoing discussion indicates that further experimental work in this field would be of considerable interest.

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[35] B. N. Brockhouse and D. G. Hurst, Phys. Rev. **88**, 542 (1952).

[36] R. D. Lowde, Proc. Phys. Soc. (London) **A65**, 857 (1952) and reference (34a).

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Calculation of the Energy Band Structures of the Diamond and Germanium Crystals by the Method of Orthogonalized Plane Waves*

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The mathematical procedure employed in recent exploratory calculations of the energy band structures of the diamond and germanium crystals is described. Some of the symmetry properties of the eigensolutions of diamond-type lattices and the construction of an approximate potential for the diamond crystal are reviewed.

The relative order of the crystal eigenvalues $E_\gamma(\mathbf{k})$ for a particular $\mathbf{k}$ was found to depend more upon the symmetry of the crystal potential than upon the detailed nature of this potential. On the other hand, the curvatures of the energy surfaces calculated by perturbation theory were found to depend in a rather critical manner upon the exact form of the crystal potential.

It would appear that more reliable estimates of the energy band structures of actual crystals can be obtained with the aid of Herring's method of orthogonalized plane waves than by means of other approximational methods requiring comparable effort provided (1) reliable crystal potentials are employed, (2) calculations are carried to the point where the eigensolutions are satisfactorily "convergent," and (3) eigensolutions for more than just the points of high symmetry in the reduced zone are investigated.

A more elaborate calculation of the energy band structure of the germanium crystal has been undertaken; the work is now in progress.

1. INTRODUCTION

RECENT developments in the field of semiconductor physics[1,2] have stimulated widespread interest in the diamond-type valence crystals. Although the general behavior of these crystals can be readily understood in terms of simple phenomenological models, a detailed knowledge of their energy band structures should prove useful in many problems.

This paper describes the mathematical procedure employed in recent exploratory calculations of the electronic structures of the diamond[3,4] and germanium[5] crystals. The method of orthogonalized plane waves (OPW), first proposed by Herring[6] and already successfully applied to metallic lithium[7,8] and beryllium,[9] is used here for the first time to study valence crystals.

The exploratory studies of diamond and germanium have revealed some hitherto unexpected features in the energy band structures of these crystals.

In particular, the lowest conduction band states at the central point of the reduced zone in each case were found to be triply degenerate, rather than nondegenerate, as earlier work on diamond,[10,11] and silicon[12,13] had suggested. Moreover, by means of perturbation-type calculations, it was found that the states normally

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* This paper is based on a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in the Faculty of Pure Science, Columbia University, January, 1953.

[1] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950).

[2] *Semi-Conducting Materials*, edited by H. K. Henish (Butterworths Scientific Publications, London, 1951).

[3] F. Herman, Phys. Rev. **88**, 1210 (1952).

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

[5] F. Herman and J. Callaway, Phys. Rev. **89**, 518 (1953).

[6] C. Herring, Phys. Rev. **57**, 1169 (1940).

[7] C. Herring, Phys. Rev. **55**, 598 (1939).

[8] R. H. Parmenter, Phys. Rev. **86**, 552 (1952).

[9] C. Herring and A. G. Hill, Phys. Rev. **58**, 132 (1940).

[10] G. E. Kimball, J. Chem. Phys. **3**, 560 (1935).

[11] A. Morita, Science Repts. Tôhoku Univ. **33**, 92 (1949). A numerical error has recently been detected in this work by J. C. Slater and G. F. Koster (see reference 18).

[12] J. F. Mullaney, Phys. Rev. **66**, 326 (1944).

[13] D. K. Holmes, Ph.D. thesis, Carnegie Institute of Technology, 1949 [Phys. Rev. **87**, 782 (1952)].

occupied by electrons, i.e., the conduction band states of lowest energy, did not occur at the central zone point but along the six (1,0,0) axes somewhere within the reduced zone.

In the neighborhood of each of these six energy minima, the surfaces of constant energy were approximately ellipsoids of revolution. Since eigensolutions associated with only a limited number of reduced wave vectors were actually determined, the exact locations along the (1,0,0) axes of these energy minima were not deduced.

The present computations also indicate that the valence states of maximum energy in both diamond and germanium occur at the central point of the reduced zone. In each case these states are triply degenerate. Unlike some earlier results,[10,14] each of the four valence bands in diamond was found to have finite width.

In view of the strong current interest in the exact shape of the energy surfaces in the diamond-type valence crystals,[15–19] a more elaborate calculation of the band structure of the germanium crystal has been undertaken. The work is now in progress.

2. CRYSTAL EIGENFUNCTIONS AND EIGENVALUES

The electronic structure of a crystal can be determined by solving the Hartree-Fock equations for all the states belonging to the core and valence bands and the low-lying conduction bands. In the ground state, a cyclic crystal of the diamond type containing M^3 unit cells must have as many occupied states as there are occupied states in the $2M^3$ atoms forming the crystal, namely, $2ZM^3$, where Z is the nuclear charge. These $2ZM^3$ states can be arranged into $Z-4$ core bands and 4 valence bands. Each energy band contains M^3 doubly degenerate states corresponding to the M^3 allowed values of the reduced wave vector $\mathbf{k}$.

In actual numerical studies, it is not possible to work with so many electronic states. Instead, one may consider a limited number of eigensolutions which correspond to a representative set of $\mathbf{k}$ uniformly distributed throughout the reduced zone. (Since the reciprocal lattice of the diamond-type crystals is body-centered cubic, the reduced zone is the truncated octahedron shown in Fig. 1.) For example, one might choose the 256 $\mathbf{k}$ forming the simple cubic lattice one octant of which is shown in Fig. 2. Only 19 of these 256 reduced wave vectors are nonequivalent because the reciprocal lattice is invariant to the symmetry operations of the crystallographic point group O_h. Thus, a reasonably detailed picture of the form of a particular energy band could be obtained by evaluating 19 crystal eigensolutions.

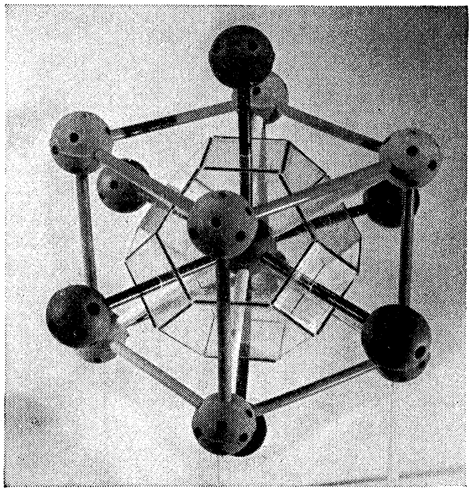

FIG. 1. Crystal model showing reduced zone.

As a further simplification, one could evaluate the energy eigenvalues and the slopes and curvatures of the energy surfaces at certain points of high symmetry in the reduced zone. The energy band structure could then be deduced from these results. Since the approach outlined in the previous paragraph represents a formidable computational task, the treatment just mentioned was utilized. In the study of the germanium crystal now under way, the eigensolutions at each ot the 19 nonequivalent points on the mesh shown in Fig. 2 and listed in Table I are being determined.

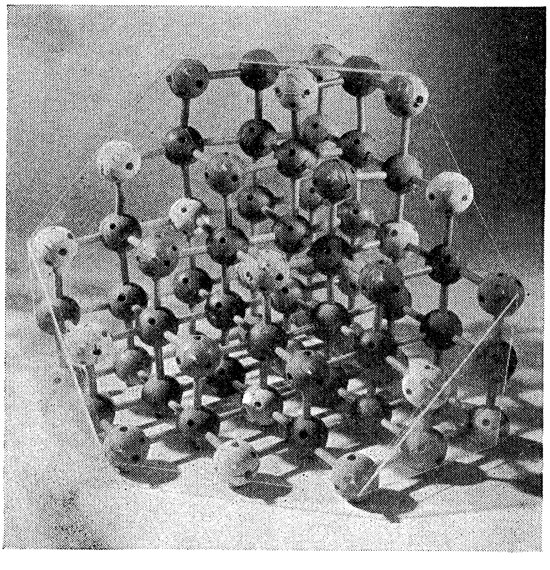

FIG. 2. Crystal model of one octant of a 256-point mesh representing the reduced zone.

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[14] G. G. Hall, Phil. Mag. 43, 338 (1952).

[15] W. Shockley, Phys. Rev. 78, 173 (1950); 90, 491 (1953).

[16] Portis, Kip, and Kittel, Phys. Rev. 90, 988 (1953).

[17] E. N. Adams II, Phys. Rev. 92, 1063 (1953); E. M. Conwell, Phys. Rev. (to be published).

[18] J. C. Slater and G. F. Koster, Quarterly Progress Report, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, July 15, 1953 (unpublished), pp. 6–10.

[19] J. C. Slater, Technical Report No. 4, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, July 15, 1953 (unpublished), pp. 76–89.

The diamond lattice is formed from two interpenetrating face-centered cubic lattices. As shown in Figs. 3 and 4, each lattice site is surrounded by four others situated at the vertices of a regular tetrahedron having the first site as center. The outlines of the unit cell are indicated, though not in full, in Fig. 4.

The symmetry operations which transform the diamond lattice into itself form a group known as the space group O_h^7.[20] One of the invariant subgroups of O_h^7 is the (infinite) translation group defined by the displacements

$$\mathbf{d}=d_1\mathbf{a}_1+d_2\mathbf{a}_2+d_3\mathbf{a}_3, \tag{2.1}$$

where d_1, d_2, and d_3 are integers and $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are the primitive translation vectors of a face-centered cubic lattice, i.e.,

$$\mathbf{a}_1=(0,\tfrac{1}{2}a,\tfrac{1}{2}a);\quad \mathbf{a}_2=(\tfrac{1}{2}a,0,\tfrac{1}{2}a);\quad \mathbf{a}_3=(\tfrac{1}{2}a,\tfrac{1}{2}a,0). \tag{2.2}$$

The Born-von Karman cyclic boundary conditions can be used to replace the infinite translation group (2.1) by a finite translation group. The cyclic crystal is assigned M^3 unit cells by restricting the integers d_i ($i=1, 2, 3$) to the range $-\frac{1}{2}M\leq d_i\leq+\frac{1}{2}M$, where M is a large integer.

Another invariant subgroup of O_h^7, known as the factor group of O_h^7, is composed of 48 operations which may be enumerated as follows. First, there are 24 pure rotations about any lattice site. These form the crystallographic point group T_d. Secondly, there are 24 compound operations each consisting of three successive operations: (a) a pure rotation of T_d about any lattice site, (b) an inversion about the same lattice site, and (c) a nonprimitive translation $\boldsymbol{\tau}=(a/4,a/4,a/4)$. All other symmetry operations transforming the diamond lattice into itself and not included in the factor group defined above can be resolved into two successive operations, the first belonging to the above factor group, and the second to the finite translation group specified by the displacements (2.1) and the large interger M.

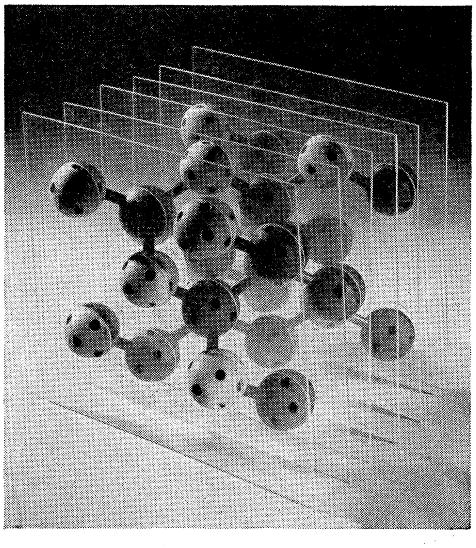

FIG. 3. Crystal model of diamond-type lattice.

Some of the symmetry properties of crystal eigensolutions of diamond-type lattices will now be reviewed.

Crystal eigenfunctions may be written in the form

$$X_\gamma(\mathbf{k},\mathbf{r})=e^{2\pi i\mathbf{k}\cdot\mathbf{r}}U_\gamma(\mathbf{k},\mathbf{r}), \tag{2.3}$$

where the functions $U_\gamma(\mathbf{k},\mathbf{r})$ are required to have the same translational symmetry as the crystal potential, i.e.,

$$U_\gamma(\mathbf{k},\mathbf{r}+\mathbf{d})=U_\gamma(\mathbf{k},\mathbf{r}), \tag{2.4}$$

where $\mathbf{d}$ is a direct lattice vector defined by (2.1). γ is a band identification index.

Crystal eigenfunctions associated with a particular reduced wave vector $\mathbf{k}$ can be arranged into mutually orthogonal sets.[21–23] The members of each set have distinctive symmetry properties. The symmetry of a crystal eigenfunction can be described in terms of the symmetry operations which transform the reduced wave vector $\mathbf{k}$ into an equivalent reduced wave vector $\mathbf{k}'$. (The reduced wave vector $\mathbf{k}'$ is said to be equivalent to $\mathbf{k}$ if $\mathbf{k}'=\mathbf{k}+\mathbf{h}$, where $\mathbf{h}$ is a reciprocal lattice vector, or if $\mathbf{k}'=R\{\mathbf{k}\}$, where R is a symmetry operation belonging to the crystallographic point group O_h.)

TABLE I. List of nonequivalent reduced wave vectors $\mathbf{k}=a^{-1}(k_1,k_2,k_3)$ belonging to 256-point mesh. $N(\mathbf{k})$ denotes the number of distinct $\mathbf{k}$ that can be generated from the listed $\mathbf{k}$ by the symmetry operations of O_h. $W(\mathbf{k})$ is a weighting factor: $\Sigma(\text{nonequiv. }\mathbf{k})N(\mathbf{k})W(\mathbf{k})=256$. The eigensolutions for $\mathbf{k}=a^{-1}(\frac{3}{4},\frac{3}{4},0)$ can be shown to be identical to those for $\mathbf{k}=a^{-1}(1,\frac{1}{4},\frac{1}{4})$.

$4k_1$	$4k_2$	$4k_3$	$N(\mathbf{k})$	$W(\mathbf{k})$	$4k_1$	$4k_2$	$4k_3$	$N(\mathbf{k})$	$W(\mathbf{k})$
0	0	0	1	1	3	1	0	24	1
1	0	0	6	1	3	1	1	24	1
1	1	0	12	1	2	2	2	8	$\frac{1}{2}$
1	1	1	8	1	3	2	0	24	1
2	0	0	6	1	3	2	1	48	$\frac{1}{2}$
2	1	0	24	1	4	0	0	6	$\frac{1}{2}$
2	1	1	24	1	4	1	0	24	$\frac{1}{2}$
2	2	0	12	1	4	1	1	24	$\frac{1}{3}$
2	2	1	24	1	3	3	0	12	$\frac{1}{3}$
3	0	0	6	1	4	2	0	24	$\frac{1}{4}$

The collection of symmetry operations transforming a wave vector $\mathbf{k}$ into an equivalent wave vector forms a group known as the group of the wave vector $\mathbf{k}$ which may be denoted by the symbol $G(\mathbf{k})$. Let the number of symmetry operations belonging to $G(\mathbf{k})$ be $g(\mathbf{k})$, the number of orthogonal sets formed by the crystal wave functions be $c(\mathbf{k})$, and the degeneracy of a member i, $i=1, 2, \cdots c(\mathbf{k})$ be f_i. In the language of group theory,[24] f_i denotes the dimensionality of the irreducible representation (IR) i.

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[20] F. Seitz, Z. Krist. **88**, 433 (1934); **90**, 289 (1935); **91**, 336 (1935); **94**, 100 (1936).

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

[22] F. C. Von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947).

[23] G. F. Koster, Phys. Rev. **89**, 67 (1953).

[24] Eyring, Walter, and Kimball, *Quantum Chemistry* (John Wiley and Sons, Inc., New York, 1944), Chap. X.

Using the notation just developed, we may now classify[25] the crystal wave functions $X_\gamma(\mathbf{k},\mathbf{r})$ according to the set of symmetry types $G_i{}^j(\mathbf{k})$, where the index $i=1, 2, 3, \cdots c(\mathbf{k})$ and the index $j=1, 2, \cdots f_{c(\mathbf{k})}$. For the general point in the reduced zone, $g(\mathbf{k})=1$, the identity operation being the only element of $G(\mathbf{k})$. The sole symmetry type is then $G_1{}^1(\mathbf{k})$. For the central point of the reduced zone, $\mathbf{k}=a^{-1}(0,0,0)$, $g(\mathbf{k})=48$, since each of the 48 members of the factor group of the space group $O_h{}^7$ transforms $\mathbf{k}=a^{-1}(0,0,0)$ into an equivalent wave vector. It can be shown[21,25] that $c(0,0,0)=10$ and that there are 4 nondegenerate, 2 doubly-degenerate, and 4 triply-degenerate irreducible representations belonging to $G(0,0,0)$.

Other typical points of high symmetry in the reduced zone are: $\mathbf{k}=a^{-1}(1,0,0)$, the midpoint of a square face, where there are 4 doubly-degenerate IR; $\mathbf{k}=a^{-1}(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, the midpoint of a hexagonal face, where there are 4 nondegenerate and 2 doubly-degenerate IR; $\mathbf{k}=a^{-1}(1,\frac{1}{2},0)$, a corner point on the zone surface, where there are 2 doubly-degenerate IR; $\mathbf{k}=a^{-1}(\frac{3}{4},\frac{3}{4},0)$ and $a^{-1}(1,\frac{1}{4},\frac{1}{4})$, the midpoints of edges on the zone surface, where there are 4 nondegenerate IR.

Symmetry classification is also possible if $\mathbf{k}$ lies on lines or planes of symmetry in the reduced zone. Thus, for $\mathbf{k}=a^{-1}(k,0,0)$, $0<k<1$, there are 4 nondegenerate and 1 doubly-degenerate IR; for $\mathbf{k}=a^{-1}(k,k,k)$, $0<k<\frac{1}{2}$, there are 2 nondegenerate and 1 doubly-degenerate IR; for $\mathbf{k}=a^{-1}(k,k,0)$, $0<k<\frac{3}{4}$, there are 4 nondegenerate IR; for $\mathbf{k}=a^{-1}(1,k,0)$, $0<k<\frac{1}{2}$, there is 1 doubly-degenerate IR; for $\mathbf{k}=a^{-1}(1,k,k)$, $0<k<\frac{1}{4}$, there are 4 nondegenerate IR; for $\mathbf{k}=a^{-1}(k_x,\frac{1}{2},k_z)$, $k_x+k_z=1$, $\frac{1}{2}<k_x<1$, $0<k_z<\frac{1}{2}$, there are 2 nondegenerate IR; finally, for $\mathbf{k}$ lying on the plane $k_z=0$ or on the plane $k_x=k_y$, there are 2 nondegenerate IR.

The energy $E_\gamma(\mathbf{k})$ possesses certain important symmetry properties. $E_\gamma(\mathbf{k})$ is invariant to any symmetry operation which transforms the reciprocal lattice into itself. Thus, $E_\gamma(\mathbf{k}+\mathbf{h})=E_\gamma(\mathbf{k})$ and $E_\gamma[R\{\mathbf{k}\}]=E_\gamma(\mathbf{k})$, where R is an operation belonging to the group O_h. The energy is a continuous function of $\mathbf{k}$ within the reduced zone. If discontinuities in $E_\gamma(\mathbf{k})$ *vs* (unreduced) $\mathbf{k}$ occur at all, they occur at the boundaries of a Brillouin zone in the extended reciprocal lattice.[26] Since the four valence bands are fully occupied in the ground state and the lowest conduction band is separated from each of these valence bands by a finite energy gap for all values of the reduced wave vector, the diamond-type crystals are insulators (diamond) or semiconductors (silicon, germanium, grey tin).[1]

The principal objective of the present study is to determine the form of the valence and conduction bands, in particular, to find where in the reduced zone the band limits occur. On the basis of symmetry considerations alone, it is not possible to predict the values of $\mathbf{k}$ for which the valence states of maximum energy and the conduction band states of minimum energy occur. Rather, it is necessary to solve the Hartree-Fock equations, as will be described more fully in later sections.

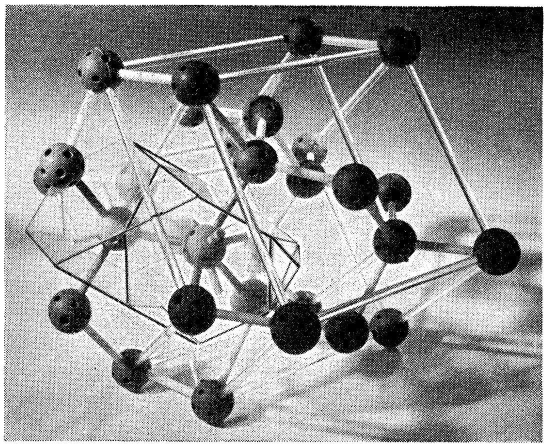

FIG. 4. Another model of diamond-type lattice. The transparent rods indicate two interpenetrating unit cubes. All the hexagonal and only a few of the triangular faces of the unit cell are shown.

It is instructive, however, to consider the energy band structure of an "empty" diamond-type lattice, i.e., the eigensolutions of a crystal having zero potential but retaining its symmetry properties in ghost form. These eigensolutions are the free-electron eigensolutions

$$X(\mathbf{h},\mathbf{k},\mathbf{r})=\exp[2\pi i(\mathbf{h}+\mathbf{k})\cdot\mathbf{r}];\quad E(\mathbf{h},\mathbf{k})=(2\pi)^2|\mathbf{h}+\mathbf{k}|^2, \tag{2.6}$$

where the energy bands are denoted by $\mathbf{h}$ instead of γ and $\mathbf{k}$ represents the reduced wave vector.

For the empty lattice, the energy profiles are parabolic, as indicated in Fig. 5. The "crystal" symmetry introduces considerable degeneracy at $\mathbf{k}$ occupying positions of high symmetry in the reduced zone. Since various energy bands overlap, some accidental degeneracies also arise.

If a perturbing potential having the symmetry of the diamond lattice is introduced, producing a "nearly-empty" lattice, many but not all the energy degeneracies are resolved. For example, the eightfold degeneracy at $\mathbf{h}=a^{-1}(1,1,1)$ is decomposed into two nondegenerate states and two triply-degenerate states. In the notation of references 21, 22, and 25, these correspond to symmetry types Γ_1, $\Gamma_{2'}$ and $\Gamma_{25'}$, Γ_{15}, respectively. The symmetry properties of the eigensolutions for the "nearly-empty" lattice, including the degeneracies, can be deduced by standard group-theoretical methods from the character tables given in references 21 and 25.

As the perturbing potential is increased in strength, so that it approaches the actual crystal potential, the four valence bands are fully separated from the remaining (conduction) bands. That the band limits do not necessarily occur at the central point of the reduced zone is suggested by the complicated structure of the energy bands for the "empty" and the "nearly-empty" lattices.

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[25] The following discussion is based on the work of C. Herring, J. Franklin Inst. **233**, 525 (1942). Table XI of that paper is in error. A corrected form of this table is available from Dr. C. Herring. Dr. Herring has kindly called to the author's attention a useful but unpublished manuscript by T. Sugita entitled "On the representation of crystallographic space-group diamond-type lattice."

[26] L. Brillouin, *Wave Propagation in Periodic Structures* (McGraw-Hill Book Company, Inc., New York, 1946).

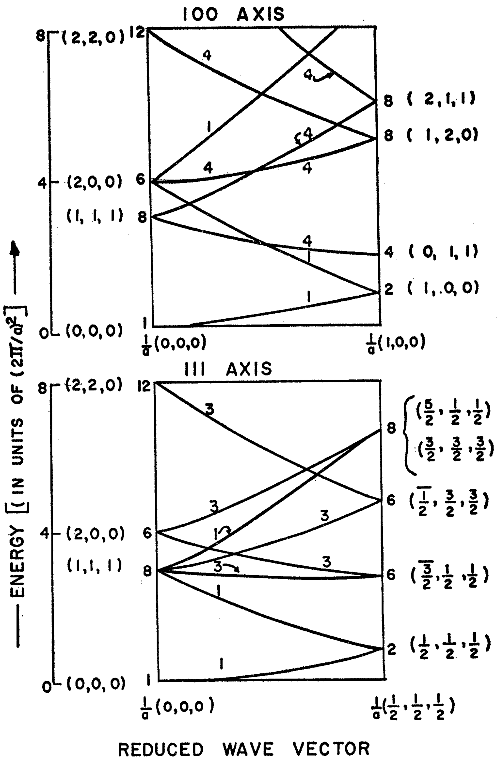

FIG. 5. Energy profiles for "empty" diamond-type lattice. The integers shown in and immediately alongside the diagrams give the degeneracies of the various eigensolutions. Typical crystal eigensolutions [see Eq. (2.6)] are listed in the abbreviated form $(h_1+k_1, h_2+k_2, h_3+k_3)$.

In the case of the "nearly-empty" lattice, the four degenerate states marked (0,1,1) are resolved into two doubly-degenerate sets, one belonging to the valence bands, the other, to the conduction bands. Similarly, the six degenerate states marked $(\bar{3}/2,1/2,1/2)$ separate into a doubly-degenerate set of valence band states, a doubly-degenerate set of conduction band states, and two nondegenerate conduction band states.

3. CONSTRUCTION OF AN APPROXIMATE CRYSTAL POTENTIAL

In the calculation of the electronic structure of a crystal, there are two main problems. The first, the determination of a suitable crystal potential, is treated in this section; the second, the numerical solution of the crystal wave equations, is discussed in the next section.

As recently emphasized by Slater[27] and earlier pointed out by Brillouin,[28] the Hartree-Fock equations for a crystal may be written in the form

$$[-\nabla^2 - V_{\text{crystal}}{}^{\gamma}(\mathbf{k},\mathbf{r})]X_\gamma(\mathbf{k},\mathbf{r}) = E_\gamma(\mathbf{k})X_\gamma(\mathbf{k},\mathbf{r}), \quad (3.1)$$

where the crystal potential appropriate to the state $(\mathbf{k},\gamma)$, $V_{\text{crystal}}{}^{\gamma}(\mathbf{k},\mathbf{r})$, is assumed to contain all Coulomb and exchange terms. The crystal eigenfunctions of (3.1) will be assumed normalized in the volume of the cyclic crystal, i.e.,

$$\int_{M^3\Omega} |X_\gamma(\mathbf{k},\mathbf{r})|^2 d\mathbf{r} = 1, \quad (3.2)$$

where Ω denotes the volume of the unit cell $(=a^3/4)$ and $M^3\Omega$ indicates the region of integration.

At the first stage of a self-consistent calculation, it is necessary to construct a suitable crystal potential. Similarly, in a less ambitious undertaking, where no attempt is made to obtain a self-consistent set of eigensolutions, an assumed crystal potential must be employed. The physical reliability of investigations of the second type depends in large measure upon how successfully the actual crystal potential can be approximated at the outset.

We now describe how the crystal potential used in the exploratory study of diamond[3,4] was devised. In the study of the germanium crystal,[5] a similar procedure was followed; however, an approximate exchange potential was not included in the crystal potential for Ge.

In the study of diamond, a crystal model was constructed by arranging neutral carbon atoms in the form of a diamond lattice having the experimental lattice constant ($a=3.5597$A[29]). Each constituent atom was assumed to be in the valence state, i.e., in the $(1s)^2(2s)^1(2p)^3\ {}^5S$ state. This is the lowest state of the free atom for which the four valence orbitals can be hybridized into four tetrahedrally equivalent directed orbitals.

The crystal charge density was then set equal to the sum of the charge densities of each of the $2M^3$ atoms forming the cyclic crystal

$$\rho_{\text{crystal}}{}^{\text{elec}}(\mathbf{r}) = \sum_{\mathbf{d}}^{M^3} \sum_{\omega=1}^{2} \rho_{\text{atom}}{}^{\text{elec}}(\mathbf{r}-\mathbf{d}-\mathbf{t}_\omega), \quad (3.3)$$

where the electronic charge density of a free carbon atom was assumed to be

$$\rho_{\text{atom}}{}^{\text{elec}}(\mathbf{r}) = 2[R_{1s}(r)]^2 + [R_{2s}(r)]^2 + 3[R_{2p}(r)]^2. \quad (3.4)$$

In (3.3), the summation on $\mathbf{d}$ is taken over the M^3 direct lattice vectors of the cyclic crystal, the summation on ω, over the two basis vectors $\mathbf{t}_1=(a/8,a/8,a/8)$ and $\mathbf{t}_2=(-a/8,-a/8,-a/8)$ locating the two atoms in the unit cell. (In what follows, the origin of coordinates is chosen at the midpoint of the unit cell.) The $R_{nl}(r)$ appearing in (3.4) are normalized radial wave functions, i.e.,

$$\int_0^\infty [R_{nl}(r)]^2 r^2 dr = 1; \quad nl = 1s,\ 2s,\ 2p.$$

These were obtained from Jucys' self-consistent field calculations for the valence state of the free carbon atom.[30]

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

[28] L. Brillouin, J. phys. **5**, 413 (1934).

[29] *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1943), twenty-seventh edition.

[30] A. Jucys, J. Phys. (U.S.S.R.) **11**, 49 (1947).

Since the tightly bound (1*s*) electrons are probably not strongly affected by crystal formation, the core contribution to the crystal charge density is undoubtedly given quite reliably by the approximation (3.3). On the other hand, the valence contribution should be somewhat different from that estimated by (3.3) because the valence states are modified by the bonding associated with crystal formation. For the sake of mathematical simplicity, no attempt to improve upon (3.3) was made. Recent work by McWeeny[31] and by Schmid[32] describes methods for obtaining improved estimates of the charge densities of atoms in bonded systems.

The crystal Coulomb potential (including the self-Coulomb potential of the state under consideration) is a periodic function and thus can be represented by a three-dimensional Fourier series:

$$V_{\text{crystal}}{}^{\text{coul}}(\mathbf{r})=\sum_{\mathbf{h}} v(\mathbf{h})^{\text{coul}}\exp(2\pi i\mathbf{h}\cdot\mathbf{r}). \tag{3.5}$$

It is easily shown, by expanding the crystal charge density in a similar form and applying Poisson's equation, that the Fourier coefficients of the crystal Coulomb potential are given by the following relations:[33]

$$v(000)^{\text{coul}}=A\int_0^\infty \rho_{\text{atom}}{}^{\text{elec}}(r)r^4dr\ \text{ry}; \tag{3.6}$$

$$v(\mathbf{h})^{\text{coul}}=\frac{B[Z-f(\mathbf{h})]\cos(2\pi\mathbf{h}\cdot\mathbf{t}_1)}{h_1^2+h_2^2+h_3^2}\ \text{ry}. \tag{3.7}$$

For diamond, $A=1.3832$, $B=0.7576$; for germanium, $A=0.3446$, $B=0.4767$. Z is the nuclear charge and $f(\mathbf{h})$ the atomic scattering factor:

$$f(\mathbf{h})=\int_\infty \rho_{\text{atom}}{}^{\text{elec}}(\mathbf{r})\exp(-2\pi i\mathbf{h}\cdot\mathbf{r})d\mathbf{r}. \tag{3.8}$$

As before, $\mathbf{h}=a^{-1}(h_1,h_2,h_3)$ is a reciprocal lattice vector. Since the reciprocal lattice is body-centered cubic, the three indices h_1, h_2, h_3 must be chosen either all even or all odd. According to the approximation (3.4), the atomic charge density is spherically symmetrical. Therefore, the following simplification may be made:

$$f(\mathbf{h})=4\pi\int_0^\infty \rho_{\text{atom}}{}^{\text{elec}}(r)\frac{\sin(2\pi|h|r)}{(2\pi|h|r)}r^2dr. \tag{3.9}$$

In writing Eqs. (3.6) and (3.7), it has been assumed that the charge density per atom is spherically symmetrical. Even though experimental evidence[34] suggests that this is not exactly the case, we elected to work with Eqs. (3.6) and (3.7) since our numerical results for $f(\mathbf{h})$ obtained from Eq. (3.9) agree reasonably well with Brill's experimental results[34] as well as with the $f(\mathbf{h})$ computed by McWeeny[35] using an atomic model similar to our own.

Since the core charge density per atom is more localized in the atomic cell than the valence charge density, the core contribution to the Fourier coefficients (3.7) decreases more slowly with increasing $|\mathbf{h}|$ than the valence contribution. In fact, the valence charge density plays a significant role in determining the numerical values of the coefficients $v(000)^{\text{coul}}$, $v(111)^{\text{coul}}$, and $v(220)^{\text{coul}}$ only.

If $v(000)^{\text{coul}}$ is not known exactly, as is certainly the case, the energy separation between the core band eigenvalues and the valence and conduction band eigenvalues will be incorrectly predicted. Since the separation between the core states and the lowest valence states is about 20 rydbergs in diamond, an incorrect value for $v(000)^{\text{coul}}$ would have a negligible effect upon the calculated energy band structure itself. [Because the top-most core states lie quite close to the bottom-most valence states in germanium, the choice of $v(000)^{\text{coul}}$ in this case is more critical.]

If the assumed crystal charge density leads to a significant error in $v(111)^{\text{coul}}$, the calculated energy band structure for diamond or germanium would be seriously affected. According to our estimates, the probable error in $v(111)^{\text{coul}}$ in each case is small enough not to be troublesome but large enough not to be entirely ignored. Finally, it would appear that the probable error in $v(220)^{\text{coul}}$ is so small that it need not be considered further.

In summary, then, we have obtained the Fourier coefficients of the crystal Coulomb potential on the basis of our crystal model. The need for such computations would disappear if very precise x-ray work could be performed to yield unambiguous numerical values for the atomic scattering factors, for then the $v(\mathbf{h})^{\text{coul}}$ could be obtained directly from the experimental $f(\mathbf{h})$.[36]

We must now attempt to devise some method for estimating the potential acting upon a valence or conduction band electron due to exchange effects. Although general treatments of the exchange terms in the Hartree-Fock equations for crystals have been given, rigorous solutions have been obtained to date only for the case of a free-electron gas.[27,28,37,38] In studies of actual crystals, exchange effects have been taken into account by various forms of the free-electron approximation.[39]

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[31] R. McWeeny, Acta Cryst. **5**, 463 (1952).

[32] L. A. Schmid, Ph.D. thesis, Princeton University, July, 1953 (unpublished); Phys. Rev. **92**, 1373 (1953).

[33] H. Fröhlich, *Electronen Theorie der Metalle* (J. Springer, Berlin, 1936).

[34] R. Brill, Acta Cryst. **3**, 333 (1950).

[35] R. McWeeny, Acta Cryst. **4**, 513 (1951). In this reference, McWeeny does not include the effect of bonding as he does in his later papers (see reference 31).

[36] The author wishes to acknowledge an illuminating conversation with Professor Brill on this point.

[37] P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930).

[38] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Sec. 75.

[39] G. V. Raynor, Repts. Progr. in Phys. **15**, 173 (1952). This excellent review article contains a very comprehensive survey of energy band calculations for actual crystals.

In our study of diamond, we have employed a technique recently discussed by Slater[27] and already applied to a numerical study of the singly ionized copper atom by Pratt.[40] According to Slater, the exchange potential for an actual crystal can be represented to a good degree of approximation by the exchange potential appropriate to a free electron gas having the same local charge density at all points in space as the actual crystal. Slater's expression for the (approximate) exchange potential is

$$V_{\text{crystal}}^{\text{exch}}(\mathbf{r})=6\left\{\frac{3}{4\pi}\cdot\frac{1}{2}\rho_{\text{crystal}}^{\text{elec}}(\mathbf{r})\right\}^{\frac{1}{3}}\text{ ry.}\qquad(3.10)$$

The factor of $\frac{1}{2}$ appears in front of $\rho_{\text{crystal}}^{\text{elec}}(\mathbf{r})$ because only half the electrons in the crystal have the same spin as the state under consideration.

The free electron exchange potential (3.10) is the same for each state. Thus, the total crystal potential,

$$V_{\text{crystal}}^{\gamma}(\mathbf{k},\mathbf{r})=V_{\text{crystal}}^{\text{coul}}(\mathbf{r})+V_{\text{crystal}}^{\text{exch}}(\mathbf{r}),\qquad(3.11)$$

is independent of $\mathbf{k}$ and γ. In what follows, we will replace the symbol $V_{\text{crystal}}^{\gamma}(\mathbf{k},\mathbf{r})$ by the more appropriate symbol $V_{\text{crystal}}(\mathbf{r})$.

The numerical methods employed in calculating the Fourier coefficients of the total crystal potential, defined by the relation

$$V_{\text{crystal}}(\mathbf{r})=\sum_{\mathbf{h}}v(\mathbf{h})\exp(2\pi i\mathbf{h}\cdot\mathbf{r}),\qquad(3.12)$$

are discussed in detail in reference 4. To conserve space, they will not be described here. The results indicate that the exchange terms contribute to all the important $v(\mathbf{h})$ to the extent of about 10 percent of the respective numerical values of the various $v(\mathbf{h})$.

It is difficult to estimate the reliability of the Slater approximation for the crystal exchange potential. According to Pratt's study of the Cu^+ ion,[40] the free-electron approximation (3.10) leads to eigensolutions about as good as one could obtain by solving Hartree's equations except in the case of the $1s$ and the $3d$ states. For these states, Pratt's eigensolutions based on (3.10) are somewhat poorer and better, respectively, than the solutions based on Hartree's equations.

In their work on beryllium,[9] Herring and Hill estimated that use of the free-electron approximation led to a result for the total exchange energy correct to within about 6 percent. In his recent work on diamond, Schmid[32] concludes that use of the same approximation yields results having a still smaller uncertainty.

It would appear that further work is required in order to establish on a firm quantitative basis the precision with which the free-electron exchange potential can represent the exchange potential appropriate to the exact Hartree-Fock equations.[41] Also, the concept of a unipotential,[42] such as (3.11), assumed to be the same for all states, deserves serious study.

For the present, however, we will make use of our assumed crystal potential. Although this potential can certainly be improved upon, we believe that it represents a reasonable approximation to the true crystal potential.

4. NUMERICAL SOLUTION OF THE CRYSTAL WAVE EQUATIONS BY THE OPW METHOD

A wide variety of numerical methods has been proposed for determining the eigensolutions for a periodic potential. Many of these have already been applied to studies of actual crystals.[39] The method of orthogonalized plane waves[6] was selected as the most suitable for the investigations of the diamond and germanium crystals for the following reasons:

(a) In studies based on the Wigner-Seitz-Slater cellular method,[43] Slater's modified cellular method,[44] and certain forms of the scattering matrix method,[45,46] the potential within all or part of an atomic cell must be assumed spherically symmetric. Since in diamond-type crystals each atom has only four nearest neighbors, it is desirable to avoid what may in fact be unrealistic approximations. In the method of orthogonalized plane waves, as in other methods employing Fourier series representations of the crystal potential,[26] the cellular potential may have any symmetry properties whatever.

(b) In calculations based on various forms of the cellular method[43,44] and on methods utilizing difference and integral equation formulations (see Appendix I), special attention must be paid to boundary conditions. On the other hand, since orthogonalized plane waves automatically satisfy all the periodicity conditions required by crystal symmetry, the numerical work associated with the OPW method is considerably simplified.

(c) It is difficult to estimate the mathematical and physical reliability of the results of energy band structure studies not carried to the point where the eigensolutions are self-consistent in the Hartree-Fock sense. However, by standard perturbation theory techniques, it is possible (1) to estimate the truncation errors associated with nearly convergent eigensolutions and (2) to estimate the dependence of the results upon the exact form of the assumed crystal potential. Such calculations are particularly easy to execute in conjunction with the OPW method.

(d) The computational labor required for the determination of a fixed number of crystal eigensolutions would appear to be about the same whether the Wigner-Seitz-Slater cellular method or the OPW method is employed. On the other hand, the difference and

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[40] G. W. Pratt, Jr., Phys. Rev. **88**, 1217 (1952).

[41] E. P. Wohlfarth, Phil. Mag. **44**, 281 (1953).

[42] G. K. Horton and R. T. Sharp, Phys. Rev. **89**, 885 (1953).

[43] J. C. Slater, Phys. Rev. **45**, 794 (1934).

[44] J. C. Slater, Phys. Rev. **51**, 846 (1937).

[45] J. Korringa, Physica **13**, 392 (1947).

[46] R. J. Harrison, Phys. Rev. **84**, 377 (1951).

integral equations cited in Appendix I require considerably more calculational effort. For practical numerical computations, the OPW method appears to offer greater convenience than localized orbital treatments[10,14,23] in their present states of development.

We now describe how the problem of determining the electronic structure of a diamond-type crystal is formulated according to Herring's orthogonalized plane wave method. We assume that a crystal potential has been determined, for example, in the manner described in the previous section, and that $V_{\text{crystal}}(\mathbf{r})$ has been expanded as a three-dimensional Fourier series [see Eq. (3.12)]. In what follows, the band index for core states will be represented by β and the band index for valence and conduction band states by α.

According to the OPW method, crystal wave functions for core states are expressed as linear combinations of suitably chosen atomic orbitals, i.e.,

$$X_\beta(\mathbf{k},\mathbf{r})=M^{-\frac{3}{2}}\sum_{\mathbf{d}}^{M^3}\epsilon^{2\pi i\mathbf{k}\cdot\mathbf{d}}\sum_{\omega=1}^{2}b_\beta(\mathbf{k},\omega)\psi_\beta(\mathbf{k},\mathbf{r}-\mathbf{d}-\mathbf{t}_\omega). \quad (4.1)$$

In (4.1), $\psi_\beta(\mathbf{k},\mathbf{r}-\mathbf{d}-\mathbf{t}_\omega)$ is a localized orbital centered at the lattice site specified by the direct lattice vector $\mathbf{d}$ and the basis vector $\mathbf{t}_\omega$; $b_\beta(\mathbf{k},\omega)$ is a phase factor. It will be assumed that the $\psi_\beta(\mathbf{k},\mathbf{r})$ form an orthonormal set and that the $\mathbf{k}$ dependence of the $\psi_\beta(\mathbf{k},\mathbf{r})$ may be neglected. Thus, $\psi_\beta(\mathbf{k},\mathbf{r})=\psi_\beta(\mathbf{r})$ and

$$\int_\infty \psi_{\beta'}^*(\mathbf{r}-\mathbf{d}'-\mathbf{t}_{\omega'})\psi_\beta(\mathbf{r}-\mathbf{d}-\mathbf{t}_\omega)d\mathbf{r} =\delta(\beta',\beta)\delta(\mathbf{d}',\mathbf{d})\delta(\omega',\omega). \quad (4.2)$$

In addition, it is assumed that the phase factors are so chosen that the eigenfunctions (4.1) are normalized to unity in the following sense

$$\int_{M^3\Omega} X_\beta^*(\mathbf{k},\mathbf{r})X_\beta(\mathbf{k},\mathbf{r})d\mathbf{r}=1. \quad (4.3)$$

Since there are two atoms per unit cell, (4.3) is satisfied provided we set $|b_\beta(\mathbf{k},\omega)|^2=\frac{1}{2}$ for all β, $\mathbf{k}$, and ω.

Crystal wave functions for valence and conduction band states are represented by linear combinations of plane waves each of which has been orthogonalized to all core wave functions (4.1) by the Schmidt process. Writing the valence and conduction band wave functions in the form

$$X_\alpha(\mathbf{k},\mathbf{r})=\sum_{\mathbf{h}}a^\alpha(\mathbf{h},\mathbf{k})\Big[(M^3\Omega)^{-\frac{1}{2}}\exp\{2\pi i(\mathbf{h}+\mathbf{k})\cdot\mathbf{r}\} -\sum_{\beta}^{\text{core}}A_\beta(\mathbf{h}+\mathbf{k})X_\beta(\mathbf{k},\mathbf{r})\Big], \quad (4.4)$$

the orthogonality coefficients $A_\beta(\mathbf{h}+\mathbf{k})$ are determined by imposing the orthogonality conditions

$$\int_{M^3\Omega} X_\beta^*(\mathbf{k},\mathbf{r})X_\alpha(\mathbf{k},\mathbf{r})d\mathbf{r}=0 \quad (\text{for all } \beta \text{ and } \alpha), \quad (4.5)$$

whence

$$A_\beta(\mathbf{h}+\mathbf{k})=\sum_{\omega=1}^{2}b_\beta^*(\mathbf{k},\omega)\exp[2\pi i(\mathbf{h}+\mathbf{k})\cdot\mathbf{t}_\omega] \times\int\psi_\beta^*(\mathbf{r})\exp[2\pi i(\mathbf{h}+\mathbf{k})\cdot\mathbf{r}]\Omega^{-\frac{1}{2}}d\mathbf{r}. \quad (4.6)$$

In the OPW expansion (4.4), the $a^\alpha(\mathbf{h},\mathbf{k})$ are (as yet) undetermined linear coefficients; the summation on β is taken over all core bands whose spin assignment is the same as that of the state under consideration; the summation on $\mathbf{h}$ ranges from $\mathbf{h}=(0,0,0)$ over all reciprocal lattice vectors $\mathbf{h}$ having moduli less than some $|\mathbf{h}|_{\max}$. Finally, let us denote by N the number of orthogonalized plane wave terms admitted to the expansion (4.4).

To obtain approximate core eigenfunctions, the atomic orbitals $\psi_\beta(\mathbf{k},\mathbf{r})$ may be replaced by the corresponding (normalized) free atomic orbitals $\varphi_{nlm}(\mathbf{r})$. For the core states, the band index β may now be replaced by the four indices n, l, m, p, where p is a parity index which may have the values $+1$ and -1. If negligible overlapping occurs between atomic orbitals centered on different lattice sites, as is actually the case, the phase factors $b_\beta(\mathbf{k},\omega)$ may be set equal to $\pm 1/\sqrt{2}$, the choice of sign depending upon the indices l, p, and ω. For a particular choice of the set n, l, m, two nonequivalent crystal wave functions may be formed using the relation (4.1), these being distinguished by the parity index p. For the special case $\mathbf{k}=(0,0,0)$, the crystal wave functions corresponding to $p=+1$, -1 are even and odd, respectively, with respect to inversion about the midpoint of any unit cell.

To this degree of approximation, each of the states belonging to a particular core band has the same energy eigenvalue. In addition, core states constructed from different indices m and p but from the same indices n and l are degenerate. Denoting the crystal potential appropriate to the core band β by $V_{\text{crystal}}{}^\beta(\mathbf{r})$, we may write

$$E_\beta=E_{nlmp} =\int_{\substack{\text{atomic}\\\text{cell}}}\varphi_{nlm}^*(\mathbf{r})[-\nabla^2-V_{\text{crystal}}{}^\beta(\mathbf{r})]\varphi_{nlm}(\mathbf{r})d\mathbf{r}. \quad (4.7)$$

As a rough approximation, $E_\beta=E_{nl}$, where E_{nl}, the free atomic energy eigenvalue, is defined by

$$E_{nl}=\int_\infty\varphi_{nlm}^*(\mathbf{r})[-\nabla^2-V_{\substack{\text{free}\\\text{atom}}}{}^{nlm}(\mathbf{r})]\varphi_{nlm}(\mathbf{r})d\mathbf{r}. \quad (4.8)$$

On the second cycle of a calculation employing self-consistent iteration, the approximation that $E_\beta=E_{nl}$ must be abandoned in favor of more reliable values for $E_\beta(\mathbf{k})$. Although it is reasonable to expect that the most tightly bound electrons give rise to energy bands having zero width, it is likewise to be expected that the least tightly bound core electrons in a crystal, such as the (3*d*) electrons in germanium, produce energy bands having finite width. Recent work by Fletcher[47] on the (3*d*) bands in nickel indicates a possible approach to the problem of obtaining an accurate representation of the eigenstates of the loosely bound core states. In the present work, such refinements were not attempted.

As first shown by Herring,[6] the energy eigenvalues $E(\mathbf{k})$ and the components of the eigenvectors $X_\alpha(\mathbf{k},\mathbf{r})$ can be determined by evaluating the Nth order determinantal equation:

$$|H(\mathbf{h}',\mathbf{h};\mathbf{k})-E(\mathbf{k})J(\mathbf{h}',\mathbf{h};\mathbf{k})|=0, \tag{4.9}$$

where the matrix elements are defined as follows:

$$H(\mathbf{h}',\mathbf{h};\mathbf{k})=(2\pi)^2|\mathbf{h}+\mathbf{k}|^2\delta(\mathbf{h}',\mathbf{h})-v(\mathbf{h}-\mathbf{h}') + \sum_{\beta}^{\text{core}} |E_\beta(\mathbf{k})|A_\beta^*(\mathbf{h}'+\mathbf{k})A_\beta(\mathbf{h}+\mathbf{k}); \tag{4.10}$$

$$J(\mathbf{h}',\mathbf{h};\mathbf{k})=\delta(\mathbf{h}',\mathbf{h})-\sum_{\beta}^{\text{core}} A_\beta^*(\mathbf{h}'+\mathbf{k})A_\beta(\mathbf{h}+\mathbf{k}). \tag{4.11}$$

In these expressions, $\mathbf{h}'$ denotes the row and $\mathbf{h}$ the column of the matrix elements of $H(\mathbf{k})$ and $J(\mathbf{k})$. $\delta(\mathbf{h}',\mathbf{h})$ is the usual Kronecker delta function.

Because orthogonalized plane waves do not form an orthonormal set, the energy parameter $E(\mathbf{k})$ appears on the off-diagonal matrix elements of the secular determinant (4.9), as may be seen from the relation (4.11). In actual numerical calculations, one may reduce (4.9) to the canonical form [$E(\mathbf{k})$ appearing only on main diagonal] by finding the inverse matrix $J^{-1}(\mathbf{k})$ and then premultiplying the matrix equation (4.9) by $J^{-1}(\mathbf{k})$. In setting up a calculation in this manner, about as much computational labor is required to obtain the inverse matrix $J^{-1}(\mathbf{k})$ as to evaluate the eigensolutions of the canonical form of (4.9). We will not discuss computational details here except to say that the actual work was carried out with the aid of the IBM Calculating Punch 602A using iterative matrix multiplication schemes.[48–50]

In the matrix element (4.10), $(2\pi)^2|\mathbf{h}+\mathbf{k}|^2$ is the (repulsive) kinetic energy term, $v(\mathbf{h}-\mathbf{h}')$, the (attractive) potential energy term. The remaining terms represent a (repulsive) pseudopotential arising from the orthogonalization.

In general, it is found in actual studies[3–5] that the orthogonality terms nearly cancel the potential energy terms. Consequently, the off-diagonal matrix elements in (4.10) are considerably reduced in absolute magnitude by the orthogonality process. It is thus possible to represent a crystal wave function by considerably fewer orthogonalized plane waves than by ordinary plane waves. In the latter case, there are no orthogonality terms present. Thus, extremely high order secular determinants must be solved before satisfactorily convergent eigensolutions are obtained.

From another viewpoint,[6,8] the atomic orbitals appearing in the OPW's (4.4) account for most of the atomic-like behavior which a crystal wave function exhibits in the neighborhood of the crystal nuclei. The remaining portion of the crystal wave function, being relatively smooth, can be represented by a reasonably small number of plane wave terms.

The partial cancellation of the potential energy terms by the orthogonality terms has its disadvantages. Unless both the crystal potential and the core eigensolutions are known with considerable precision, the off-diagonal matrix elements cannot be accurately determined. In the work on diamond[3,4] and germanium,[5] it was found that one significant figure was lost in the off-diagonal matrix elements as a consequence of this partial cancellation. Because there are more core states in the germanium crystal than in the diamond crystal, there are also more orthogonality terms. For this reason, the cancellation was more complete in germanium than in diamond. However, this is not necessarily the general rule.

Even though the OPW method converges more rapidly than the straightforward Fourier series method,[26] very high order secular determinants must be evaluated if reliable results are to be obtained. It is therefore essential to simplify the problem by taking full advantage of the symmetry properties of the crystal eigensolutions.

We now focus our attention on the eigensolutions corresponding to those reduced wave vectors which occupy positions of high symmetry in the reduced zone. These eigensolutions may be arranged in mutually orthogonal sets, as noted earlier. The $N\times N$ secular determinant for a particular $\mathbf{k}$ may then be factored into $c(\mathbf{k})$ separate secular determinants, one for each irreducible representation in the wave vector group $G(\mathbf{k})$. If a certain IR is f-fold degenerate, the corresponding (separated) secular determinant may be additionally factored into f identical and separate secular determinants. Thus, instead of solving one very high order secular determinant for each $\mathbf{k}$ investigated, it is necessary only to evaluate several relatively low order secular determinants.

To factor the Nth order secular determinant for a particular $\mathbf{k}$, the linear combinations of orthogonalized plane waves belonging to the various symmetry types $G_i{}^j(\mathbf{k})$ must be found. This is accomplished by applying standard group-theoretical methods.[24] Some typical "symmetrized" orthogonalized plane waves are listed in Table II.

It is easily shown that the core wave functions

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[47] G. C. Fletcher, Proc. Phys. Soc. (London) **A65**, 192 (1952).

[48] W. M. Kincaid, Quart. Appl. Math. **5**, 320 (1947).

[49] H. E. Fettis, Quart. Appl. Math. **8**, 206 (1950).

[50] P. S. Dwyer, *Linear Combinations* (John Wiley and Sons, Inc., New York, 1951), Chap. 15.

arising from *s*, *p*, and *d* atomic orbitals belong to the irreducible representations $(\Gamma_1,\Gamma_{2'})$, $(\Gamma_{25'},\Gamma_{15})$, and $(\Gamma_{25'},\Gamma_{15},\Gamma_{12},\Gamma_{12'})$, respectively, at $\mathbf{k}=a^{-1}(0,0,0)$. Consequently, the triply-degenerate valence band state $\Gamma_{25'}$ and the lowest triply-degenerate conduction band state Γ_{15} are automatically orthogonal to all the core states in the case of diamond but not in the case of germanium.

For states automatically orthogonal to all core states, all the orthogonality terms in the symmetrized OPW's vanish identically and the OPW method becomes fully equivalent to the ordinary Fourier series method.[26]

As suggested to the author by Herring,[51] it is possible to treat such cases as follows. To the symmetrized (ordinary) plane wave expansion, a suitable set of atomic orbitals is added. Each atomic orbital is required to behave properly near the nucleus, have the appropriate symmetry properties in the atomic cell, and vanish within half an interatomic spacing of its center. Since both the atomic part and the plane wave part are separately orthogonal to all core wave functions, the augmented plane wave expansion is itself orthogonal to all core wave functions.

In the study of diamond,[3,4] augmented plane wave expansions were not employed since it was thought worthwhile to study the convergence of the ordinary plane wave expansions for these special states and then compare this behavior to the convergence of the OPW expansions for the remaining states. In retrospect, it appears that use of the augmented plane wave expansions would have been desirable since the ordinary plane wave expansions converged very slowly. On the other hand, as already noted in the earlier announcement,[3] the convergence of the OPW expansions containing nonvanishing orthogonality terms was quite rapid.

After determining the crystal eigensolutions for **k** occupying positions of high symmetry in the reduced zone, the slope and curvature of the energy surfaces passing through these points were calculated by a well-known perturbation method.[41,52,53] The effect of the 4 valence bands and the 10 lowest conduction bands was included in the calculation leading to the curvatures of the various energy surfaces at the central point of the reduced zone. The apparent discrepancy between the form of our estimated energy bands and those recently obtained by Slater[19] might arise from the fact that Slater considers an energy band system containing four valence bands and only four conduction bands.

TABLE II. Typical linear combinations of orthogonalized plane waves belonging to some of the symmetry types of $G(0,0,0)$ and $G(1,0,0)$. The column headings of the form Γ_i and X_i denote irreducible representations in the notation of references 21 and 25. The various symmetry types are also expressed in the form $G_i{}^j$. In this table, each row corresponds to a particular orthogonalized plane wave. Each orthogonalized plane wave [see the bracketed quantity in Eq. (4.4)] is shown in the abbreviated form $[h_1+k_1\ h_2+k_2\ h_3+k_3]$. To illustrate the notation, we write out in full the three leading terms of the crystal wave functions belonging to symmetry type $G_1{}^1(1,0,0)$:

$$X_1{}^1(100,\mathbf{r})=a_1{}^1(100)[100]+a_1{}^1(011)\{[011]-[0\bar{1}\bar{1}]+[0\bar{1}1]+[01\bar{1}]\}+a_1{}^1(120)\{[\bar{1}20]-[\bar{1}\bar{2}0]+[\bar{1}02]-[\bar{1}0\bar{2}]\}.$$

In this expression, the $a_1{}^1(\mathbf{h}+\mathbf{k})$ are undetermined linear coefficients.

	Γ_1	$\Gamma_{2'}$	$\Gamma_{25'}$			Γ_{15}			$\Gamma_{12'}$	
$(\mathbf{h}+\mathbf{k}]$	$G_1{}^1$	$G_2{}^1$	$G_3{}^1$	$G_3{}^2$	$G_3{}^3$	$G_4{}^1$	$G_4{}^2$	$G_4{}^3$	$G_5{}^1$	$G_5{}^2$
$[0\ 0\ 0]$	+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	0	0	+1				+2	0
$[0\ 2\ 0]$		+1	0	+1	0				−1	+1
$[0\ 0\ 2]$		+1	+1	0	0				−1	−1
$[\bar{2}\ 0\ 0]$		−1	0	0	−1				−2	0
$[0\ \bar{2}\ 0]$		−1	0	−1	0				+1	−1
$[0\ 0\ \bar{2}]$		−1	−1	0	0				+1	+1

	X_1		X_2		X_3		X_4	
$[\mathbf{h}+\mathbf{k}]$	$G_1{}^1$	$G_1{}^2$	$G_2{}^1$	$G_2{}^2$	$G_3{}^1$	$G_3{}^2$	$G_4{}^1$	$G_4{}^2$
$[1\ 0\ 0]$	+1	0						
$[\bar{1}\ 0\ 0]$	0	+1						
$[0\ 1\ 1]$	+1	+1					+1	0
$[0\ \bar{1}\ \bar{1}]$	−1	−1					+1	0
$[0\ \bar{1}\ 1]$	+1	−1					0	+1
$[0\ 1\ \bar{1}]$	+1	−1					0	−1
$[1\ 2\ 0]$	0	+1	+1	0	0	+1	+1	+1
$[1\ \bar{2}\ 0]$	0	−1	−1	0	0	+1	+1	+1
$[\bar{1}\ 2\ 0]$	+1	0	0	+1	−1	0	+1	+1
$[\bar{1}\ \bar{2}\ 0]$	−1	0	0	−1	−1	0	+1	+1
$[1\ 0\ 2]$	0	+1	−1	0	+1	0	+1	−1
$[1\ 0\ \bar{2}]$	0	−1	+1	0	+1	0	+1	−1
$[\bar{1}\ 0\ 2]$	+1	0	0	−1	0	−1	+1	−1
$[\bar{1}\ 0\ \bar{2}]$	−1	0	0	+1	0	−1	+1	−1

5. DISCUSSION OF RESULTS

In judging the reliability of the results,[3–5] three factors must be kept in mind. First, the calculations were based on assumed crystal potentials. Secondly, the eigensolutions obtained were nearly but not fully "convergent." Finally, the energy band structures were deduced from the energy eigenvalues, the estimated slopes and the estimated curvatures of the energy surfaces at a limited number of points in the reduced zone.

Since it does not appear possible to determine in any simple manner how closely the assumed crystal potentials approximate the actual crystal potentials, certain auxiliary calculations were performed. In these, the assumed potentials were modified slightly and new sets of crystal eigensolutions determined by perturbation theory. The range of allowed variation of the

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[51] C. Herring (private communication).
[52] F. Seitz, Phys. Rev. **47**, 400 (1935).
[53] W. Shockley, Phys. Rev. **78**, 173 (1950).

crystal potential was $\pm 0.1 v_{111}$, a reasonable measure of the major uncertainty in the assumed potentials.

It was found that these changes in the assumed value of v_{111} altered the various energy eigenvalues considerably. The magnitude and direction of these shifts of $E_\alpha(\mathbf{k})$ depended upon the symmetry type of the eigensolution in question as well as upon the order of the secular determinant from which $E_\alpha(\mathbf{k})$ was obtained. Fortunately, the relative order of sufficiently convergent eigenvalues at $\mathbf{k}=(0,0,0)$ did not change as a result of these arbitrary modifications of v_{111}. It appears safe to conclude, therefore, that the lowest conduction band states at the central zone point in diamond and germanium are the triply degenerate states $\Gamma_{25'}$ rather than the nondegenerate state $\Gamma_{2'}$ even if our assumed crystal potentials are slightly in error. The recent work of Slater and Koster,[18] reported in detail by Slater,[19] offers additional support to our conclusion in the case of diamond.

On the other hand, the curvatures of the energy surfaces at $\mathbf{k}=(0,0,0)$ were found to change only under large modifications of the assumed potential in diamond but under relatively small modifications in germanium. Thus, it appears that the predicted energy band structure of germanium is much more sensitive to the physical assumptions than that of diamond.

The convergence of the crystal eigensolutions was rapid for all eigenstates in germanium and for the eigenstates in diamond which were not automatically orthogonal to all core states. Thus, the eigenvalues for these states could be obtained to at least two significant figures by solving eighth-order secular determinants.

The valence state $\Gamma_{25'}$ and the conduction band state Γ_{15} in diamond required special attention because these symmetry types were not represented among the core states. The eigensolutions of 16th-order secular determinants for these states were nearly but not fully convergent. The secular determinants for these symmetry types were set up to 24th and even higher orders and solved by perturbation theory using the 16th-order eigensolutions as the "unperturbed" eigensolutions. In this manner, the truncation errors for the 16th-order eigensolutions were found to be not more than a few percent.

The present work indicates that the estimated curvatures depend critically upon the numerical values of the crystal eigensolutions and thus in turn upon the exact form of the assumed crystal potentials. Although the use of slope and curvature information to predict the shape of the energy bands reduces the magnitude of a computation considerably, the results are not to be trusted to the same extent as those leading, for example, to the relative order of the eigensolutions at a particular $\mathbf{k}$.

A more detailed investigation of the energy band structure of the germanium crystal has been undertaken. In the study now in progress, an approximate exchange potential is included in the assumed crystal potential in addition to an approximate Coulomb potential. Some refinements have been introduced in order to improve the initial choice of the crystal Coulomb potential. Considerable pains are being taken to insure that the initial set of core eigenstates approximate the actual state of affairs closely. Instead of relying upon curvature calculations, the energy band structure will be deduced in the new work by determining the eigensolutions at each of the reduced wave vectors listed in Table I.

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APPENDIX I. DIFFERENCE AND INTEGRAL EQUATION METHODS

The unit cell of the direct lattice can be represented by a set of points $\mathbf{u}$ arranged in some convenient array. All physically interesting quantities such as the crystal potential and the crystal wave functions are defined only at these points $\mathbf{u}$. Let us assume that the crystal potential is known. Then, with the aid of the variational principle, we seek to determine the set of values $X_\gamma(\mathbf{k},\mathbf{u})$, one for each $\mathbf{u}$, for which the energy

$$E_\gamma(\mathbf{k})=\frac{\sum_{\mathbf{u}} X_\gamma^*(\mathbf{k},\mathbf{u})[-\nabla^2-V_{\text{crystal}}{}^\gamma(\mathbf{k},\mathbf{u})]X_\gamma(\mathbf{k},\mathbf{u})}{\sum_{\mathbf{u}} X_\gamma^*(\mathbf{k},\mathbf{u})X_\gamma(\mathbf{k},\mathbf{u})} \tag{1.1}$$

is a minimum, subject to two conditions: First, the crystal wave function must satisfy the periodicity properties imposed by crystal symmetry, and secondly, the crystal wave function must be orthogonal to all crystal eigenfunctions having lower energies and the same reduced wave vector $\mathbf{k}$.

The crystal eigenvalue problem thus formulated can be solved, in principle, by difference equation methods exemplified by systematic iteration,[54,55] relaxation,[55,56] or dynamical analogs[57] or by various iterative integral equation techniques.[58] Unfortunately, even if the crystal symmetry properties are fully exploited, reliable results can be obtained only if extremely fine meshes are employed.

A rough estimate of the number of nonequivalent mesh points **u** required for satisfactory convergent eigensolutions may be made as follows. First, assume that the crystal eigenfunctions for the valence and low-lying conduction band states resemble atomic $(2s)$ orbitals in any atomic cell. Secondly, assume that the interval of a suitable mesh at a distance r from the nucleus is approximately equal to the corresponding interval used in tabulating the $(2s)$ radial wave functions in Hartree-Fock computations. The number of nonequivalent **u** of a mesh thus constructed is found to be so large that calculations by the methods just described appear to require the aid of the largest automatic computing machines now available.

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A Variational Calculation of the Elastic Scattering of Electrons by Hydrogen Atoms*

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The Schwinger variational method for three-body collisions is applied to the calculation of elastic scattering of electrons by hydrogen atoms in the energy range 0–10 volts. When a Born trial field is used, the contributions of the ground state and all the excited states including the continuum can be calculated. The former contribution is equivalent to the static field approximation and the latter contributions give the corrections to it. When these are included, the results do not agree with those of Massey and Moiseiwitsch who use a different approximation. We conclude that the Schwinger variational method with a Born trial field is unsatisfactory in this energy range.

I. INTRODUCTION

PROBLEMS involving elastic three-body collisions present two complications not encountered in two-particle scattering problems. The first is the polarization of the charge distribution of the scatterer by the incoming particle. The second is the phenomenon of exchange scattering, in which the incoming particle and one of the particles of the scatterer exchange roles after scattering. This is especially complicated when these two particles are identical, and thus, by the Pauli principle, there are interference terms in the scattering cross section between the direct and the exchange scattered wave.

Heretofore, three-particle scattering problems have been treated by the Born approximation,[1] by a static-field approximation,[1] and by a generalization of the Hulthén[2] variational method which is due to Kohn.[3] The first of these methods is not likely to be very accurate at low energies. The static-field approximation, by its very nature, cannot treat the complications mentioned above. In using the last method, one can include the effect of polarization and exchange by suitable choice of trial function.

Recently, the Schwinger variational method has been extended to cover three-particle collisions.[4] In principle this method has the advantage that cruder trial functions could be used, since some of the features of the problem (polarization effects, for example) are automatically taken into account when one iterates the trial solution with the Green's function of the unperturbed problem. This advantage is part of the limitation of the method, since the integrations involving the Green's function are extremely difficult to carry out.

In the present paper, we shall apply this last method to the elastic scattering of slow electrons by hydrogen atoms. This particular problem has already been treated by several different approaches. It has been solved approximately by the Kohn-Hulthén method.[5] It has been

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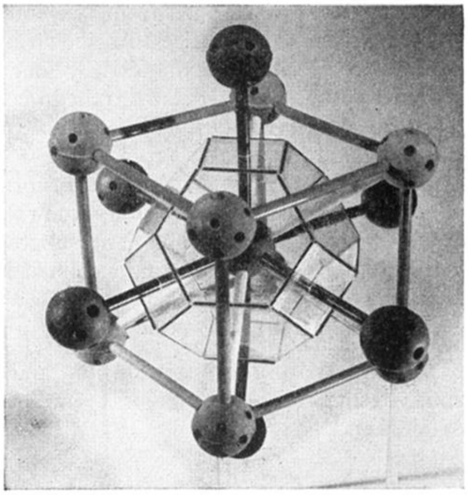

FIG. 1. Crystal model showing reduced zone.

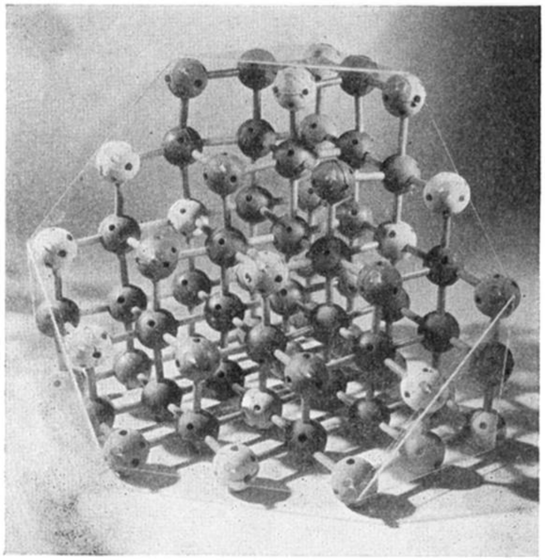

FIG. 2. Crystal model of one octant of a 256-point mesh representing the reduced zone.

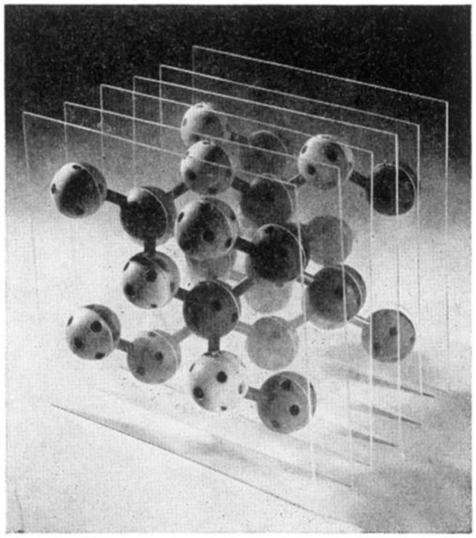

FIG. 3. Crystal model of diamond-type lattice.

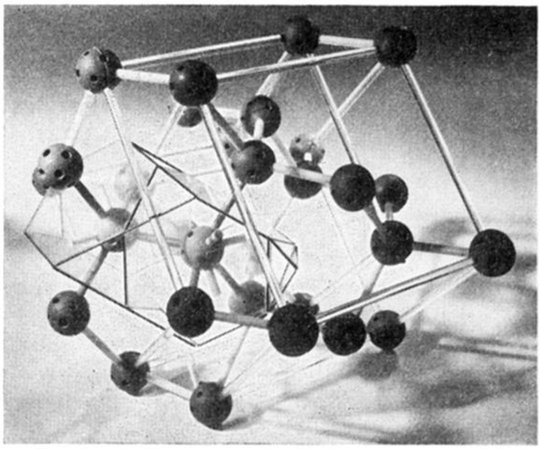

FIG. 4. Another model of diamond-type lattice. The transparent rods indicate two interpenetrating unit cubes. All the hexagonal and only a few of the triangular faces of the unit cell are shown.