

Crystal Symmetry, Group Theory, and Band Structure Calculations

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I. Introduction

The central problem of quantum mechanics is to solve the Schrödinger equation, which has the form

$$(-\hbar^2/2m)\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}). \quad (\text{I.1})$$

In the particular case of a single crystal, the solution is made easier because

the potential energy $V(r)$ conforms to the *symmetry* of the lattice, and this property can be divided into two categories.

Translational symmetry is responsible for the existence of energy bands, and the *point symmetries*—*rotation*, *reflection*, and *inversion*—determine the nature of these bands. This latter type has associated with it the feature of *degeneracy*, which we would expect intuitively to arise in the following fashion: when a crystal is subjected to a symmetry operation, its structure is unaffected. From this, it follows that the energy associated with the formation of this structure from a group of isolated atoms is the same for any one of the set of equivalent configurations. In terms of the Schrödinger equation, there is a single eigenvalue for a set of eigenfunctions corresponding to the various equivalent positions, which is precisely what we mean by degeneracy. A decrease in the amount of symmetry in a system should then have a corresponding effect on the degree of degeneracy, and we shall show that this is indeed the case.

As an example of the connection between symmetry and degeneracy, consider the one-dimensional harmonic oscillator. The Schrödinger equation is

$$(d^2\psi/dx^2) + (2m/\hbar^2)[E - (\kappa x^2/2)]\psi = 0, \quad (I.2)$$

where κ is the Hooke's law constant. Using $\alpha = 2mE/\hbar^2$ and $\beta^2 = m\kappa/\hbar^2$, Eq. (I.2) becomes

$$(d^2\psi/dx^2) + (\alpha - \beta^2 x)\psi = 0. \quad (I.3)$$

The solutions of (I.3) are the Hermite functions

$$\psi_n = \exp(-\alpha x^2/2) H_n(x) \quad (I.4)$$

and the eigenvalues are

$$E_n = (n + \frac{1}{2})h\nu \quad (I.5)$$

where $n = 0, 1, 2, \dots$, and $\nu = 2\pi(\kappa/m)^{1/2}$. There is a distinct solution $\psi_n(x)$ for each value of n and the system is therefore nondegenerate.

The three-dimensional Schrödinger equations (I.1) when applied to an oscillator with unequal constants κ_x , κ_y , κ_z along the three coordinate axes can be solved by the separation of variables, which results in three ordinary differential equations having the same form as Eq. (I.2). The eigenvalues are

$$E_{n_x, n_y, n_z} = [(n_x + \frac{1}{2})h\nu_x + (n_y + \frac{1}{2})h\nu_y + (n_z + \frac{1}{2})h\nu_z] \quad (I.6)$$

where $n_x = 0, 1, 2, \dots$ and $\nu_x = 2\pi(\kappa_x/m)^{1/2}$, etc. For the special case of the isotropic oscillator, defined by

$$\kappa_x = \kappa_y = \kappa_z = \kappa$$

the energy levels become

$$\begin{aligned} E &= (n_x + n_y + n_z + \tfrac{3}{2})h\nu \\ &= (n + \tfrac{3}{2})h\nu, \end{aligned} \quad (\text{I.7})$$

where $n = n_x + n_y + n_z$. The total energy E now depends only on n , and for a given value of n , there are $(n + 1)$ choices for n_x , namely,

$$n_x = 0, 1, 2, \dots, n.$$

Then, for $n_x = 0$, there are $(n + 1)$ choices of n_y ; for $n_x = 1$, there are n choices of n_y ; for $n_x = n$, there is 1 choice of n_y . The degree of degeneracy is thus

$$\tfrac{1}{2}[(n + 1) + 1](n + 1) = \tfrac{1}{2}(n + 1)(n + 2) \quad (\text{I.8})$$

and this degeneracy is a consequence of the symmetry.

It has been pointed out by McIntosh¹ that this result is somewhat surprising, since the inherent degeneracy of the system is only threefold; that is, the x , y , and z directions are physically equivalent for an isotropic oscillator. The extra degrees of degeneracy are termed *accidental*, and arise from the fact that it is possible for the sum $n_x + n_y + n_z$ to be equal to a given integer n in more than three ways.

The nature of the wave functions is also affected by the symmetry. For example, let the potential energy $V(x)$ be symmetrical about the y -axis, so that $V(x) = V(-x)$. The one-dimensional Schrödinger equation satisfied by $\psi(x)$,

$$[-\hbar^2/2m)(d^2/dx^2) + V(x)]\psi(x) = E\psi(x),$$

will be the same as that satisfied by $\psi(-x)$. If the solution is nondegenerate, then $\psi(-x)$ must be related to $\psi(x)$ by

$$\psi(-x) = c\psi(x),$$

where c is a constant. If the wave functions are normalized, then $c = \pm 1$, and $\psi(x)$ is either an even or an odd function. Hence, the simple symmetry for this example has imposed conditions on the solution, and we shall see in the more complicated cases to be discussed that the linear combinations of functions taken as solutions have symmetry properties consistent with the lattice to which they apply.

The analytical method by which we take advantage of the crystalline symmetries, and which also permits a simple determination of the degeneracies, is based on a branch of algebra known as *group theory*. Because our main purpose here is to make the results of a group theory acces-

¹ H. V. McIntosh, *Am. J. Phys.* **27**, 620 (1959).

sible to experimental physicists, we shall introduce only those concepts which are necessary for the systems to be discussed. Further, all formal proofs will be omitted and the various theorems quoted will be made plausible by citing examples. For those interested in the analytical foundations of group theory, a more profound treatment and an excellent bibliography are given in Hamermesh.²

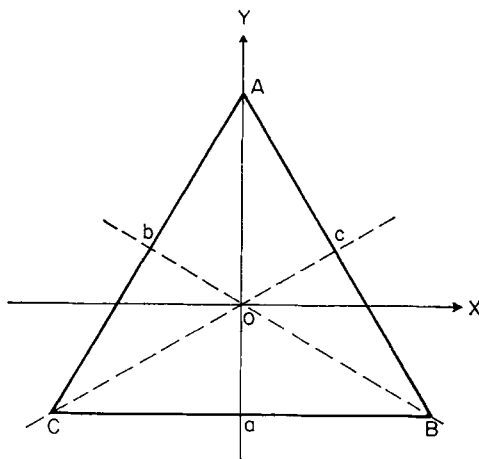


FIG. 1. An equilateral triangle and associated symmetry elements.

II. The Algebra of Groups

1. THE FUNDAMENTAL CONCEPTS OF GROUP THEORY

A *group* is defined³ as a collection of elements A, B, C, \dots which obey the following combinatory laws:

- (1) The product of any two elements in the collection is also a member of the collection.
- (2) The collection contains an identity or unit operation E (from the German *einheit*, unity) such that $EA = AE = A$ for every element.
- (3) The associative law of multiplication holds: $(AB)C = A(BC)$.
- (4) Every element A has a unique inverse A^{-1} which is a member of the collection. That is, $AA^{-1} = A^{-1}A = E$.

As an example, consider the equilateral triangle of Fig. 1. Regarding the

² M. Hamermesh, "Group Theory and its Applications to Physical Problems." Addison-Wesley, Reading, Massachusetts, 1962.

³ H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry." Wiley, New York, 1944.

lines Aa , Bb , and Cc as fixed in the plane, the operations which leave this triangle congruent to its original position are:

- (1) E , the identity
- (2) A , a reflection in line Aa
- (3) B , a reflection in line Bb
- (4) C , a reflection in line Cc
- (5) D , a 120° clockwise rotation
- (6) F , a 120° counterclockwise (or a 240° clockwise) rotation.

It is easily seen that

$$AD = B,$$

where the convention is used that operation D is followed by operation A . We note that

$$DA = C \neq B.$$

All such products are summarized in Table I, the *group multiplication* or *Cayley* table. The total number of elements g is called the *order* of the group, so that $g = 6$.

A *subgroup* is a portion of a group which obeys the combinatory laws. Table I shows that some subgroups of the group E, A, B, C, D, F are (a) E , (b) E, A , and (c) E, D, F . Note that the order of the subgroups is a factor of the order of the group.

TABLE I. MULTIPLICATION OR CAYLEY TABLE
FOR THE SYMMETRY OPERATIONS OF AN EQUILATERAL TRIANGLE (THE GROUP C_{3v})

		First operation					
		E	A	B	C	D	F
Second operation	E	E	A	B	C	D	F
	A	A	E	D	F	B	C
	B	B	F	E	D	C	A
	C	C	D	F	E	A	B
	D	D	C	A	B	F	E
	F	F	B	C	A	E	D

Groups can also be divided into *classes*, which are collections of related operations. Two elements P and Q belong to the same class if

$$Q = X^{-1}PX, \quad (1.1)$$

where X is any member of the group. For example,

$$\begin{aligned} A^{-1}DA &= A^{-1}C = AC = F \\ A^{-1}FA &= AB = D, \end{aligned}$$

so that D and F constitute a class. Similarly, A , B , and C are another class, and E forms a third one. Hence the group is completely broken down into three mutually exclusive classes: reflections, rotations, and the identity. For this simple example, intuition would have sufficed to divide the elements of the group into classes, but in most cases, it is necessary to apply Eq. (1.1). We note that this equation corresponds to a *similarity transformation* which converts an operator P into the corresponding operator Q expressed in a different coordinate system. We can see this by letting \mathbf{r}_1 be an arbitrary vector and \mathbf{r}_2 be the result of operating on \mathbf{r}_1 with one of the members (for example, A) of the group under consideration. Then

$$\mathbf{r}_2 = A\mathbf{r}_1. \quad (1.2)$$

Now let us transform the coordinate system XOY of Fig. 1 into a new system $X'OY'$. This can be accomplished by using a transformation matrix P , whose definition we shall take as⁴

$$\mathbf{r}_1 = P\mathbf{r}_1'. \quad (1.3)$$

Similarly

$$\mathbf{r}_2 = P\mathbf{r}_2'. \quad (1.4)$$

Inserting (1.3) and (1.4) into (1.2),

$$\mathbf{r}_2' = P^{-1}AP\mathbf{r}_1'. \quad (1.5)$$

However, in the new coordinate system, (1.2) becomes

$$\mathbf{r}_2' = A'\mathbf{r}_1' \quad (1.6)$$

so that

$$A' = P^{-1}AP. \quad (1.7)$$

This verifies the assertion that the members of a given class may be obtained from one another by coordinate transformations. We note from (1.1), however, that these transformations must be those which are generated by members of the group in question.

⁴ R. S. Burington and C. C. Torrance, "Higher Mathematics." McGraw-Hill, New York, 1939.

2. AN INTRODUCTION TO GROUP REPRESENTATIONS

A *representation* of a group is any collection of elements which obey the group multiplication table. For example, a representation can be obtained by considering the matrices associated with rotations and reflections in a plane. Figure 2a shows the rotation of a vector \mathbf{r} through an angle θ , where the two sets of coordinates of the vector are related by

$$\begin{Bmatrix} x_2 \\ y_2 \end{Bmatrix} = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \begin{Bmatrix} x_1 \\ y_1 \end{Bmatrix}. \quad (2.1)$$

This relation follows from the identities

$$\cos(\theta + \psi) = \cos \theta \cos \psi - \sin \theta \sin \psi$$

$$\sin(\theta + \psi) = \sin \theta \cos \psi + \cos \theta \sin \psi$$

where ψ is the angle between $\mathbf{r}(x_1, y_1)$ and the x axis. Multiplying each of these equations by r gives a set equivalent to (2.1). Figure 2b shows the reflection of a point (x_1, y_1) in a line making an angle ϕ with the x axis to

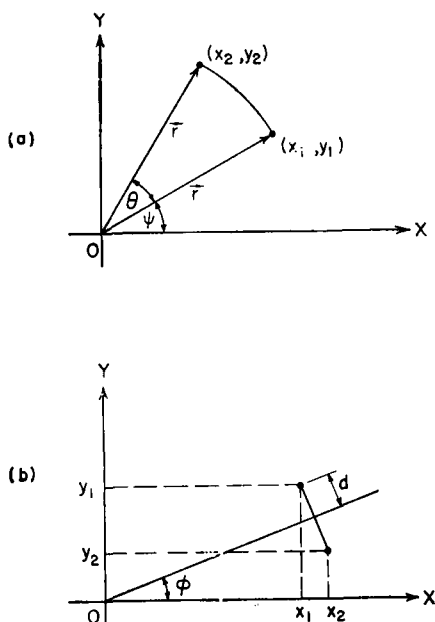


FIG. 2. Method of determining the matrix for (a) a rotation and (b) a reflection.

TABLE II. IRREDUCIBLE REPRESENTATIONS FOR THE GROUP OF TABLE I

	<i>E</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>F</i>
Γ_1	1	1	1	1	1	1
Γ_2	1	-1	-1	-1	1	1
Γ_3	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \sqrt{3}/2 \\ \sqrt{3}/2 & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \sqrt{3}/2 \\ -\sqrt{3}/2 & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\sqrt{3}/2 \\ \sqrt{3}/2 & -\frac{1}{2} \end{pmatrix}$

TABLE III. A REDUCIBLE REPRESENTATION FOR THE GROUP OF TABLE I

	<i>E</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>F</i>
Γ_4	$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix}$

produce a point (x_2, y_2) . The coordinates are related by

$$\begin{aligned}x_2 &= x_1 + 2d \sin \phi, \\y_2 &= y_1 - 2d \cos \phi,\end{aligned}$$

from which

$$\begin{Bmatrix} x_2 \\ y_2 \end{Bmatrix} = \begin{bmatrix} \cos 2\phi & \sin 2\phi \\ \sin 2\phi & -\cos 2\phi \end{bmatrix} \begin{Bmatrix} x_1 \\ y_1 \end{Bmatrix}. \quad (2.2)$$

Using the matrices given in (2.1) and (2.2), we can obtain the representation denoted by Γ_3 in Table II (it is customary to use the symbol Γ to denote some representations). It is easy to verify that the six matrices of Γ_3 multiply as required by Table I. Note that the matrices belonging to Γ_3 are based on the axes XOY having the orientation shown in Fig. 1.

The representation Γ_3 is two dimensional; that is, it consists of 2×2 matrices. Every group also has a one-dimensional representation of the form $E = A = B = C = D = F = 1$, denoted by Γ_1 in Table II. This representation is said to be *unfaithful*; it leads to all the entries of Table I, plus many others which violate the table. Another one-dimensional representation, denoted Γ_2 in Table II, is also unfaithful.

It is also possible to find representations of higher dimensions. Suppose we specify the position of the corners of the equilateral triangle by the set of six coordinates $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \alpha_1, \alpha_2, \alpha_3$ of Fig. 3. The symmetry operations above can be then represented as 6×6 matrices, and the coordinates \mathbf{r}_i and α_i are said to form a *basis* for this representation. For example, the effect of C (a reflection in the line OC) can be denoted by

$$\begin{bmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix} \begin{Bmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \mathbf{r}_3 \\ \alpha_1 \\ \alpha_2 \\ \alpha_3 \end{Bmatrix} = \begin{Bmatrix} \mathbf{r}_3 \\ \mathbf{r}_2 \\ \mathbf{r}_1 \\ \alpha_3 \\ \alpha_2 \\ \alpha_1 \end{Bmatrix}. \quad (2.3)$$

A similar 6×6 matrix can be obtained for the other five operations of the group, and it will be found that these six matrices obey the group multiplication table and hence form a representation Γ_4 . We shall denote the matrices in Γ_4 by $\Gamma_4(C)$, etc., and these six matrices are listed in Table III.

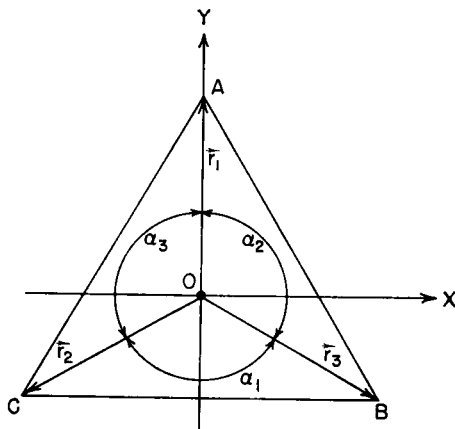


FIG. 3. The equilateral triangle and the basis elements of a reducible group.

If we now perform a similarity transformation on the matrix $\Gamma_4(C)$,

$$\Gamma'_4(C) = P^{-1}\Gamma_4(C)P \quad (2.4)$$

where

$$P = \begin{bmatrix} 1/\sqrt{3} & 0 & -\sqrt{2}/\sqrt{3} & 0 & 0 & 0 \\ 1/\sqrt{3} & 1/\sqrt{2} & 1/\sqrt{6} & 0 & 0 & 0 \\ 1/\sqrt{3} & -1/\sqrt{2} & 1/\sqrt{6} & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/\sqrt{3} & 0 & -\sqrt{2}/\sqrt{3} \\ 0 & 0 & 0 & 1/\sqrt{3} & 1/\sqrt{2} & 1/\sqrt{6} \\ 0 & 0 & 0 & 1/\sqrt{3} & -1/\sqrt{2} & 1/\sqrt{6} \end{bmatrix} \quad (2.5)$$

we find that

$$\Gamma'_4(C) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1/2 & \sqrt{3}/2 & 0 & 0 & 0 \\ 0 & \sqrt{3}/2 & -1/2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/2 & \sqrt{3}/2 \\ 0 & 0 & 0 & 0 & \sqrt{3}/2 & -1/2 \end{bmatrix} \quad (2.6)$$

This matrix will be recognized from Table II as having the form

$$\Gamma_4'(C) = \begin{bmatrix} \boxed{\Gamma_1(C)} & 0 & 0 & 0 & 0 & 0 \\ 0 & & & 0 & 0 & 0 \\ 0 & \boxed{\Gamma_3(C)} & & 0 & 0 & 0 \\ 0 & 0 & 0 & \boxed{\Gamma_1(C)} & 0 & 0 \\ 0 & 0 & 0 & 0 & & \\ 0 & 0 & 0 & 0 & \boxed{\Gamma_3(C)} & \end{bmatrix} \quad (2.7)$$

where $\Gamma_1(C)$ is a 1×1 block appearing twice on the main diagonal, and $\Gamma_3(C)$ is a 2×2 block.

The matrix $\Gamma_4(C)$ is said to be *reduced* (in group theory treatises, the term *completely reduced* is used) and a reduced matrix is one for which the part above and below the main diagonal consists entirely of zeros. We then say that the representation Γ_4 is *reducible*. It is easy to verify that the same matrix P and its inverse P^{-1} will convert all the $6 \times$ matrices of Table III into the corresponding reduced form. On the other hand, it is not possible to find a similarity transformation which will simultaneously convert *all* the

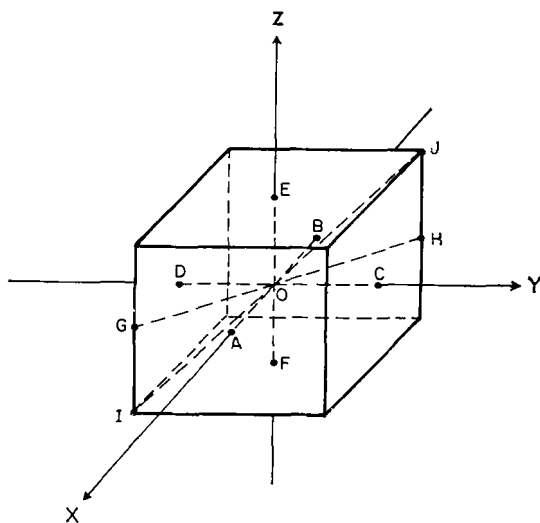


FIG. 4. The symmetry elements for a cube.

matrices of Γ_3 to diagonal form, so that Γ_3 is an *irreducible* representation. Since any one-dimensional representation is inherently irreducible, Table II lists only irreducible ones. As a consequence of Eq. (2.7), we say that the reducible representation Γ_4 *contains* the irreducible representations Γ_1 and Γ_3 twice each. (We shall not discuss the procedure for determining the reduction matrix P , since it will not be needed for the applications to energy band theory.)

In anticipation of the significance of the reduction process, we may point out that matrices of the form of $\Gamma_4'(C)$ in (2.7) have the important property of *nonmixing*, which means that when two matrices of the same block form are multiplied together, the product also possesses this form and further, the blocks in the product matrix are simply the products of the individual diagonal submatrices. For example, if we multiply $\Gamma_4'(C)$ by $\Gamma_4'(A)$, we obtain

$$\Gamma_4'(F) = \Gamma_4'(A)\Gamma_4'(C)$$

$$= \begin{bmatrix} \boxed{\Gamma_1(A)\Gamma_1(C)} & & & 0 \\ & \boxed{\Gamma_3(A)\Gamma_3(C)} & & \\ & & \boxed{\Gamma_1(A)\Gamma_1(C)} & \\ & & & \boxed{\Gamma_3(A)\Gamma_3(C)} \\ 0 & & & \end{bmatrix}.$$

3. THE CRYSTALLOGRAPHIC POINT GROUPS

To review the properties and notation associated with the three-dimensional groups encountered in crystal physics, let us consider as an example the symmetry group of a cube. We can study the behavior of a cube under the operations (the *covering* operations) which leave it coincident with

TABLE IV. THE OCTAHEDRAL GROUP O

Symbol	Multiplicity	Definition
E	1	The identity
C_4	6	$\pm 90^\circ$ rotation about cube axes
C_4^2	3	180° rotation about cube axes
C_2	6	180° rotation about axes parallel to face diagonals
C_3	8	$\pm 120^\circ$ rotation about body diagonals

its original position by labeling the centers of the six faces (Fig. 4) as A through F . It is easy to see that rotations of the cube about the principal axes (OX , OY , OZ), about axes such as GH parallel to face diagonals, or about axes such as IJ (the body diagonals) can be symmetry operations. There are a total of twenty-four such operations, as listed in Table IV. Note that the symbol C_n indicates the nature of the rotation. For example, C_3 denotes a 120° rotation; i.e., a rotation of value $(2\pi/3)$. The multiplicity column tells how many distinct ways there are of performing a given operation. For the example of C_3 , there are four body diagonals in a cube and hence eight rotations of $\pm 120^\circ$ which leave the cube congruent to its original position.

Now consider the axis AB . We can set up a *cyclic* subgroup consisting of the following four operations:

$$90^\circ \text{ rotation,} \quad 180^\circ \text{ rotation,} \quad 270^\circ \text{ rotation,} \quad 360^\circ \text{ rotation.}$$

That is, a cyclic group is one which repeats itself after a finite number of operations—in this case, four. The members are thus C_4 , C_4^2 , C_4^3 , and E . Let us denote A and B as *invariant points* under the operations of the cyclic subgroup. We shall now give an argument of Weyl⁵ to calculate the number of possible sets composed of a symmetry operation and an associated invariant point for the cubic group of twenty-four operations (but excluding E , for which every point on the surface of the cube is invariant). Each of the twenty-three axes has two invariant points, so that there are a total of $2(g - 1)$ such sets, where g is the number of elements or the order of the group.

Now A and B are invariant under the operations of the cyclic subgroup, but the other twenty operations of the cubic group convert them into C , D , E , and F , and we shall call A through F *equivalent points* corresponding to the cyclic subgroup. If we let ν be the order of the cyclic subgroup, and n the number of equivalent points, we see that

$$n = g/\nu \tag{3.1}$$

since $g = 24$, $\nu = 4$, and $n = 6$ (Weyl gives a simple argument to establish this relation in general). Each pair of points (A, B) , (C, D) , and (E, F) corresponds to a cyclic subgroup containing three operations (again excluding E) out of the total group of twenty-three. Hence, if we multiply (g/ν) by $(\nu - 1)$ and sum this product over the other collections of equivalent points (one corresponds to body diagonal axes and the other to those parallel to face diagonals), we again obtain all possible sets of an

⁵ H. Weyl, "Symmetry." Princeton Univ. Press, Princeton, New Jersey, 1952.

operation and an invariant point. Equating the two ways of enumerating these gives

$$2(g-1) = \sum (g/\nu)(\nu-1)$$

or

$$2 - 2/g = \sum (1 - 1/\nu) \quad (3.2)$$

where the sum is taken over the three different kinds of symmetry axes.

To interpret this equation, we first assume that $g \geq 2$, since a one-element group is trivial. Hence, the left-hand side of Eq. (3.2) is at least 1 but less than 2, and the sum must have at least two terms, but not more than three. For each subgroup must have at least two members to be cyclic, so that $\nu \geq 2$, and $(1 - 1/\nu) \geq \frac{1}{2}$. Then four or more terms in the sum makes it at least as large as 2, so that Eq. (3.2) becomes either

$$2/g = 1/\nu_1 + 1/\nu_2 \quad (3.3)$$

or

$$1 + 2/g = 1/\nu_1 + 1/\nu_2 + 1/\nu_3. \quad (3.4)$$

Considering first (3.3), we write it as

$$2 = g/\nu_1 + g/\nu_2$$

and the two positive integers (g/ν_1) and (g/ν_2) can have a sum of 2 only if both are 1, or

$$\nu_1 = \nu_2 = g.$$

This means that the entire group is cyclic with respect to a given axis; there are no other symmetry elements. Such groups are denoted by C_n , where $n = 1, 2, 3, \dots$.

For Eq. (3.4), arrange the multiplicities ν in ascending order,

$$\nu_1 \leq \nu_2 \leq \nu_3.$$

Not all three ν_i can be greater than 2, for then the left-hand side would become at least $\frac{1}{3} + \frac{1}{3} + \frac{1}{3}$, which does not satisfy (3.4). Hence the smallest one, ν_1 , is 2 and (3.4) becomes

$$1/\nu_2 + 1/\nu_3 = 1/2 + 2/g.$$

Next, ν_2 and ν_3 cannot both be as large as 4, for the left side is then at least $\frac{1}{2} + \frac{1}{2}$, which again is not possible. Hence $\nu_2 = 2$ or 3.

For the combination $\nu_1 = 2, \nu_2 = 2$, (3.4) then gives

$$\nu_3 = g/2. \quad (3.5)$$

The groups defined by the set of numbers $\nu_1 = 2, \nu_2 = 2, \nu_3 = g/2$ are called *dihedral* groups, denoted by D_n . As an example, consider the right prism

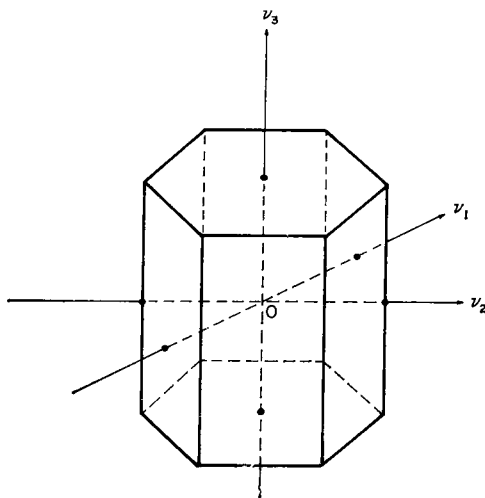


FIG. 5. The symmetry elements of a hexagonal prism.

of Fig. 5. The vertical sixfold axis is labeled ν_3 since it corresponds to a cyclic subgroup of order 6. The operations of this subgroup are defined as indicated in Table V (the first four entries), which shows that $g = 12$.

There are three each of two kinds of horizontal axes, labeled ν_1 and ν_2 respectively. These are twofold axes and the corresponding operations, three of each kind for the three pairs of faces and vertices, are denoted C_2' and C_2'' , respectively. Hence, this group D_6 consists of a sixfold cyclic subgroup, and there are six possible 180° rotations about axes normal to the sixfold axis. The values $\nu_1 = 2$, $\nu_2 = 2$, and $\nu_3 = g/2 = 6$ agree with the results obtained above. The dihedral groups in general have a principal axis of symmetry plus the proper number of perpendicular twofold axes, and are denoted by D_2, D_3, D_4, \dots .

TABLE V. THE SYMMETRY GROUP D_3 FOR THE HEXAGONAL PRISM

Symbol	Multiplicity	Definition
E	1	The identity
C_6	2	$\pm 60^\circ$
C_3	2	$\pm 120^\circ$
C_2	1	180°
C_2'	3	180° about axis perpendicular to prism faces
C_2''	3	180° about axis through prism edges

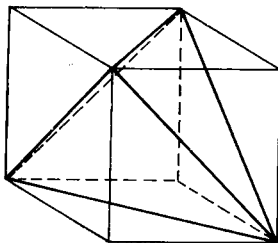


FIG. 6. The relation of the regular tetrahedron to the cube.

For the combination $\nu_1 = 2$, $\nu_2 = 3$, Eq. (3.4) reduces to

$$1/6 + 2/g = 1/\nu_3$$

or

$$\nu_3 = 6g/(g + 12). \quad (3.6)$$

The only finite values of g which give an integral solution are $g = 12$, $\nu_3 = 3$; $g = 24$, $\nu_3 = 4$; $g = 60$, $\nu_3 = 5$. The group for $\nu_3 = 3$ is called the *tetrahedral* group T , and it represents the symmetry operations of a regular four-sided pyramid. The tetrahedral group is actually a subgroup of the cubic group of Table IV, and the geometric relation between the tetrahedron and the cube is shown in Fig. 6. The group for $\nu_3 = 4$ is the *octahedral* group O , and thus is just the group of Table IV, since the symmetry properties of the cube can be expressed in terms of those of the vertices of the octahedron. For $\nu_3 = 5$, we have the *dodecahedral* group, exemplified by the regular figure formed from twelve identical pentagons.

Let us now introduce the *inversion operator* J into this discussion. This is the operator which converts a given point into its reflection with respect to the origin. That is, a point with coordinates (x, y, z) is transformed into $(-x, -y, -z)$, and we shall denote this as $(\bar{x}, \bar{y}, \bar{z})$. The effect of J on the coordinate system $OXYZ$ is then to produce the set of axes $O\bar{X}\bar{Y}\bar{Z}$, which are left-handed, so that J is an *improper* operation. Now J by itself is a symmetry operation, and it may also be combined with the rotations con-

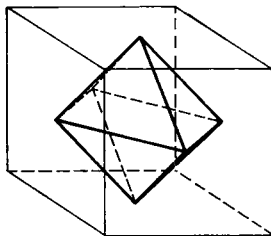


FIG. 7. The relation of the regular octahedron to the cube.

sidered above to produce new symmetry operations. For example, the cube of Fig. 4 is congruent to itself when every point is inverted through O , and the same is true for the operations JC_4 , JC_4^2 , JC_2 , and JC_3 . Hence, the *full cubic group* O_h consists of forty-eight elements of ten classes—the five classes of Table IV and the ones just listed. This group is also called the *holohedral* symmetry group of the cube, and the groups O and T are subgroups. The notation O_h is based on the fact that this forty-eight-element group may be obtained in an alternate way. We start with the twelve-member group T and add an improper symmetry element in the form of a diagonal reflection plane, denoted σ_d (reflection planes are customarily indicated by σ , with a subscript h, v, or d to denote that they are horizontal, vertical, or diagonal with respect to the coordinate system). An example of such a plane is one determined by GH and the z -axis of Fig. 4. There are a total of six such operations σ_d , and in addition, a reflection σ and a rotation C_n can be combined to obtain an *alternating* operation S_n . For the cube of Fig. 4, a rotation C_2 about GH followed by a reflection σ_d in the diagonal plane normal to GH produces a new arrangement of the equivalent points. These additional six operations S_2 plus the σ_d operations when combined with σ_h in planes like OXY gives the full forty-eight-member group O_h . We may also start with T and add σ_h to obtain a different twenty-four-element group T_h . Hence, there are five cubic groups all told: T , T_d , T_h , O , and O_h .

The final point to consider in this review of point groups is the fact that restrictions are imposed on the index n for groups such as C_n and D_n when we take into account the translational symmetry properties of crystals. One way of visualizing these limitations is through a diophantine equation derived from Fig. 8. If symmetrical figures are arranged in a

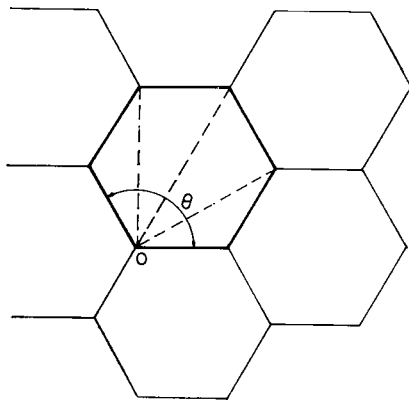


FIG. 8. Determination of the allowed rotational symmetries in a plane pattern.

periodic array, then an intersection point such as O must have the property that the figures meet without overlap or gaps. Hence, the angle θ must equal $2\pi/m$, where m is an integer. Now if the regular figures have n sides, the value of θ is also given by $(n - 2)\pi/n$, so that

$$[1 - (2/n)]\pi = 2\pi/m$$

or

$$1/m + 1/n = 1/2. \quad (3.7)$$

The only integers which satisfy this relation are $m = 3, n = 6$; $m = 4, n = 4$; $m = 6, n = 3$. Hence, only threefold, fourfold, and sixfold symmetry are permitted in crystalline point groups.

4. THE CHARACTER SYSTEM OF A GROUP

In applying group theory, it is seldom necessary to specify the matrices which form a representation or those which reduce one. Generally, all that is needed is the *trace* or *character* of each matrix (the trace of a matrix is the sum of the elements on the main diagonal). The set of characters for the representations of a given group is called the *character system* and Table IV shows this system for the group of the equilateral triangle. If we consider a regular triangular prism, the symmetry operations are the same, but we denote them by E , C_3 (a rotation of $\pm 120^\circ$ about the threefold axis), and σ_v (a reflection in a vertical plane passing through the threefold axis). This group is then denoted C_{3v} , i.e., the cyclic group C_3 combined with three equivalent reflections. We note that the characters for any element in a given class are the same, and hence the table can be condensed into the form shown in Table VII.

Using the symbol χ to denote a character, Table VI illustrates the following very important relation between the characters of a reducible

TABLE VI. CHARACTERS OF THE REPRESENTATIONS FOR THE GROUP C_{3v} OF TABLE I

	E	A	B	C	D	F
Γ_1	1	1	1	1	1	1
Γ_2	1	-1	-1	-1	1	1
Γ_3	2	0	0	0	-1	-1
Γ_4	6	2	2	2	0	0

TABLE VII. CHARACTER SYSTEM FOR C_{3v}

	E	σ_v	C_3
Γ_1	1	1	1
Γ_2	1	-1	1
Γ_3	2	0	-1
Γ_4	6	2	0

representation and of the irreducible representations which it contains:

$$n_k = [\sum_R \chi(R) \chi_k(R)]/d, \quad (4.1)$$

where n_k is the number of times the k th irreducible representation is contained in the reducible one, $\chi(R)$ the character of the matrix of R for the reducible representation, $\chi_k(R)$ the character of k th irreducible representation, and d the dimension of the reducible representation. As mentioned in the introduction, we shall not prove theorems of this type, but merely establish their plausibility by the use of examples. For the group C_{3v} , $d = 6$, and for Γ_1 , (4.1) becomes

$$n_1 = [\chi(E)\chi_1(E) + \chi(A)\chi_1(A) + \chi(B)\chi_1(B) + \chi(C)\chi_1(C) + \chi(D)\chi_1(D) + \chi(F)\chi_1(F)]/6$$

or

$$n_1 = [6(1) + 2(1) + 2(1) + 2(1) + 0(1) + 0(1)]/6 = 2. \quad (4.2)$$

Similarly,

$$n_2 = 0, \quad n_3 = 2,$$

which means that Γ_1 and Γ_3 are each contained in Γ_4 twice, whereas Γ_2 is not contained at all. This agrees with Eq. (2.7) and shows that Eq. (4.1) eliminates the necessity for finding the matrix which reduces a representation.

Next, we notice from Eq. (2.7) that

$$\sum_k d_k^2 = g \quad (4.3)$$

where d_k is the dimensional of k th irreducible representation, and g the order of the group. For the present example, we see that the relation

$$1^2 + 1^2 + 2^2 = 6 \quad (4.4)$$

gives one possible combination of squares which satisfies (4.3). Another possibility is

$$1^2 + 1^2 + 1^2 + 1^2 + 1^2 + 1^2 = 6,$$

but this means that the group must have six one-dimensional representations. It can be seen, however, that the only sets of six numbers (real or complex) which satisfy the group multiplication table are Γ_1 and Γ_2 . Hence, the only combination of squares satisfying (4.3) is given by Eq. (4.4), and we have the corollary that the number of irreducible representations of a group equals the number of classes in the group.

We conclude this brief introduction to group algebra by discussing the method of obtaining the character system for the irreducible representations of a group, using a method due to Bethe.⁶ Denote the three classes of C_{3v} by

$$K_1 = E; \quad K_2 = A, B, C; \quad K_3 = D, F.$$

Then we see, for example, that

$$\begin{aligned} K_2 K_3 &= (A, B, C)(D, F) \\ &= (B, C, A, C, A, B) = 2K_2. \end{aligned} \quad (4.5)$$

Similarly,

$$\begin{aligned} K_2^2 &= 3K_1 + 3K_3 \\ K_3^2 &= 2K_1 + K_3 \end{aligned}$$

or, in general,

$$K_i K_j = K_j K_i = \sum_k c_{ijk} K_k \quad (4.6)$$

where typical values are

$$c_{221} = 3, \quad c_{222} = 0, \quad c_{223} = 3.$$

Now let χ_k be a character associated with class k and let r_k be the number of elements in this class. Then it can be seen from Table VI that

$$r_i r_j \chi_i \chi_j = \chi_1 \sum_k c_{ijk} r_k \chi_k \quad (4.7)$$

so that

$$\begin{aligned} 3 \cdot 3 \chi_2^2 &= \chi_1 [3 \cdot 1 \cdot \chi_1 + 3 \cdot 2 \cdot \chi_3] \\ 4 \chi_3^2 &= \chi_1 [2 \chi_1 + 2 \chi_3] \\ 6 \chi_2 \chi_3 &= 6 \chi_1 \chi_2. \end{aligned} \quad (4.8)$$

⁶ H. A. Bethe, *Ann. Physik* [5] **3**, 133 (1929). Our present example comes from H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry." Van Nostrand, Princeton, New Jersey, 1943; a proof is given in Hamermesh.²

The characters of K_1 are automatically determined by a combination of Eq. (4.3) and the requirement that the number of irreducible representations be equal to the number of classes. This means that the characters of K_1 must be three numbers whose squares have a sum of 6, or

$$\chi_1 = 1, 1, 2.$$

Putting each of these in turn in (4.8) produces Table VI.

III. The LCAO or Tight-Binding Approximation

5. A REVIEW OF THE FUNDAMENTAL PRINCIPLES

The *tight-binding* or *linear combination of atomic orbitals* (LCAO) approximation is discussed in several references,⁷ so that we shall merely restate here some of the basic principles. The Schrödinger equation for a multielectron atom cannot be separated because of the presence in the Hamiltonian of terms of the form e^2/r_{ij} , where r_{ij} is the coordinate of the j th electron with respect to the i th one. If we neglect these terms as a first approximation and further assume that each electron sees a spherically symmetric effective potential energy $V(r_i)$, then the Schrödinger equation is separable in spherical coordinates (r, θ, ϕ) and the angular parts of the solutions will be of the same form as those for the hydrogen atom. These solutions are called *atomic orbitals* and the normalized angular part of the first nine orbitals may be expressed as

$$\begin{aligned} l = 0, \quad m_l = 0 & \quad s = 1/2\sqrt{\pi} \\ l = 1, \quad m_l = 1 & \quad p_{+1} = [\sqrt{3/2}\sqrt{(2\pi)}] \sin \theta e^{i\phi} \\ l = 1, \quad m_l = 0 & \quad p_0 = (\sqrt{3/2}\sqrt{\pi}) \cos \theta \\ l = 1, \quad m_l = -1 & \quad p_{-1} = [\sqrt{3/2}\sqrt{(2\pi)}] \sin \theta e^{-i\phi} \\ l = 2, \quad m_l = 2 & \quad d_{+2} = [\sqrt{(15)/4}\sqrt{(2\pi)}] \sin^2 \theta e^{2i\phi} \\ l = 2, \quad m_l = 1 & \quad d_{+1} = [\sqrt{(15)/2}\sqrt{(2\pi)}] \sin \theta \cos \theta e^{i\phi} \\ l = 2, \quad m_l = 0 & \quad d_0 = (\sqrt{5/4}\sqrt{\pi}) (3 \cos^2 \theta - 1) \\ l = 2, \quad m_l = -1 & \quad d_{-1} = [\sqrt{(15)/2}\sqrt{(2\pi)}] \sin \theta \cos \theta e^{-i\phi} \\ l = 2, \quad m_l = -2 & \quad d_{-2} = [\sqrt{(15)/4}\sqrt{(2\pi)}] \sin^2 \theta e^{-2i\phi} \end{aligned} \quad (5.1a)$$

where l is the quantum number associated with the coordinate θ and m_l goes with the coordinate ϕ . For ease in visualizing these eigenfunctions, it is convenient to use the following linear combinations, which incorporate

⁷ A. J. Dekker, "Solid State Physics." Prentice-Hall, Englewood Cliffs, New Jersey, 1957.

an additional normalizing factor $1/\sqrt{2}$:

$$\begin{aligned}
 s &= 1/2\sqrt{\pi} \\
 p_x &= \frac{1}{2}[p_{+1} + p_{-1}] = (\sqrt{3}/2\sqrt{\pi}) \sin \theta \cos \phi \\
 p_y &= \frac{1}{2}[-i(p_{+1} - p_{-1})] = (\sqrt{3}/2\sqrt{\pi}) \sin \theta \sin \phi \\
 p_z &= p_0 = (\sqrt{3}/2\sqrt{\pi}) \cos \theta \\
 d_{x^2-y^2} &= \frac{1}{2}[d_{+2} + d_{-2}] = [\sqrt{(15)}/4\sqrt{\pi}] \sin^2 \theta \cos 2\phi \\
 &= [\sqrt{15}/4\sqrt{\pi}] \sin^2 \theta (\cos^2 \phi - \sin^2 \phi) \quad (5.1b) \\
 d_{xy} &= \frac{1}{2}[-i(d_{+2} - d_{-2})] = [\sqrt{(15)}/4\sqrt{\pi}] \sin^2 \theta \sin 2\phi \\
 &= (\sqrt{(15)}/2\sqrt{\pi}) \sin^2 \theta \cos \phi \sin \phi \\
 d_{xz} &= \frac{1}{2}(d_{+1} + d_{-1}) = (\sqrt{(15)}/2\sqrt{\pi}) \sin \theta \cos \theta \cos \phi \\
 d_{yz} &= \frac{1}{2}[-i(d_{+1} - d_{-1})] = (\sqrt{(15)}/2\sqrt{\pi}) \sin \theta \cos \theta \sin \phi \\
 d_{z^2} &= d_0 = (\sqrt{5}/4\sqrt{\pi}) (3 \cos^2 \theta - 1).
 \end{aligned}$$

These functions are plotted in Fig. 9, which provides an indication of

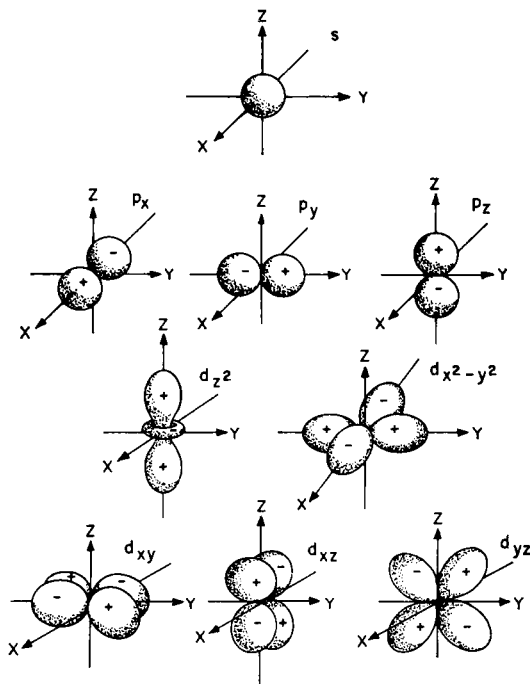


FIG. 9. The atomic orbitals for $l = 0, 1$, and 2 .

their directional characteristics. The significance of the subscripts comes from the defining equations for spherical coordinates, which are

$$x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi, \quad z = r \cos \theta.$$

Under a symmetry operation, r is invariant, so we can say that

$$p_x \propto \sin \theta \cos \phi \quad (5.1c)$$

or

$$p_x \propto x$$

and

$$d_{xy} \propto xy.$$

Turning now to the approximate solution of the Schrödinger equation, let us consider an atom with position-vector \mathbf{R}_j . An electron at \mathbf{r} will have a coordinate $(\mathbf{r} - \mathbf{R}_j)$ with respect to this atom, and we will denote the atomic orbitals for this electron by $\phi(\mathbf{r} - \mathbf{R}_j)$. We then try a solution

$$\psi_{\mathbf{k}} = \sum_j \exp(i\mathbf{k} \cdot \mathbf{R}_j) \phi(\mathbf{r} - \mathbf{R}_j) \quad (5.2)$$

where the sum is taken over all the atoms in the crystal. To show that this solution is in Bloch form, we let \mathbf{r}_a denote the position-vector of a lattice point (which is not necessarily the same as an atomic position \mathbf{R}_j). Substituting $\mathbf{r} + \mathbf{r}_a$ for \mathbf{r} in Eq. (5.2) and multiplying the right-hand side by $\exp(i\mathbf{k} \cdot \mathbf{r}_a)$ $\exp(-i\mathbf{k} \cdot \mathbf{r}_a)$ gives

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{r}_a) = \exp(i\mathbf{k} \cdot \mathbf{r}_a) \sum_j \exp[i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{r}_a)] \phi[\mathbf{r} - (\mathbf{R}_j - \mathbf{r}_a)]$$

or

$$\psi(\mathbf{r} + \mathbf{r}_a) = \exp(i\mathbf{k} \cdot \mathbf{r}_a) \psi(\mathbf{r}).$$

Now multiply the Schrödinger equation (I.1) for $\psi_{\mathbf{k}}$ by $\psi_{\mathbf{k}}^*$ and then integrate over all of space, obtaining

$$\iint \psi_{\mathbf{k}}^* [-(\hbar^2/2m) \nabla^2 + V] \psi_{\mathbf{k}} d\tau - E \iint \psi_{\mathbf{k}}^* \psi_{\mathbf{k}} d\tau = 0. \quad (5.3)$$

It is convenient to decompose V into two terms, as follows:

$$V(\mathbf{r}) = V_a(\mathbf{r} - \mathbf{R}_j) + V'(\mathbf{r} - \mathbf{R}_j) \quad (5.4)$$

where V_a is the potential energy which an electron would have in a single, isolated atom and V' is the additional potential energy it would acquire when the atom is incorporated into the crystal. Substituting this into Eq. (5.3) gives

$$\iint \psi_{\mathbf{k}}^* [-(\hbar^2/2m) \nabla^2 + V_a + V'] \psi_{\mathbf{k}} d\tau - E \iint \psi_{\mathbf{k}}^* \psi_{\mathbf{k}} d\tau = 0. \quad (5.5)$$

The second integral on the left we will evaluate by substituting Eq. (5.2).

This results in a sum of products of atomic orbitals, and if we use the assumption that the atoms are widely spaced, then integrals involving functions centered around two different atoms will vanish.

Integrals of the form $\int \psi(\mathbf{r} - \mathbf{R}_j) \psi(\mathbf{r} - \mathbf{R}_j) d\tau$ reduce to unity for normalized functions. Since there are N such integrals, where N is the number of atoms, the second integral becomes EN .

The first term in (5.5) can be broken up into two parts, one of which is chosen as

$$\int \psi_k^* [-(\hbar^2/2m) \nabla^2 + V_a] \psi_k d\tau = NE_a \quad (5.6)$$

where E_a is the energy of the electron in the free atom. This leaves only the term involving V' to be considered. We shall neglect all terms in the summations except those involving immediate neighbors. Define

$$\alpha = -N \int \phi^*(\mathbf{r} - \mathbf{R}_j) V' \phi(\mathbf{r} - \mathbf{R}_j) d\tau \quad (5.7)$$

$$\beta = -N \int \phi^*(\mathbf{r} - \mathbf{R}_m) V' \phi(\mathbf{r} - \mathbf{R}_j) d\tau$$

where j and m are neighbors and where the negative signs are used to make α and β positive. If we assume for the moment that ϕ is spherically symmetric, corresponding to the s function of Fig. 9, then the β integrals are the same for all nearest neighbors. Using (5.6) and (5.7), (5.5) becomes

$$E = E_a - \alpha - \beta \sum_m \exp [i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_m)] \quad (5.8)$$

where the sum is over the nearest neighbors of atom j .

The nearest neighbors of an atom in the three types of cubic lattices are specified by

Simple cubic: $(\pm a, 0, 0), (0, \pm a, 0), (0, 0, \pm a)$

Body-centered cubic: $(\pm a/2, \pm a/2, \pm a/2)$

Face-centered cubic: $(0, \pm a, \pm a), (\pm a, 0, \pm a), (\pm a, \pm a, 0)$

and these positions, when substituted into (5.8), give the following expressions for the energy:

Simple cubic:

$$E = E_a - \alpha - 2\beta(\cos k_x a + \cos k_y a + \cos k_z a) \quad (5.9)$$

Body-centered cubic:

$$E = E_a - \alpha - 8\beta \cos(k_x a) \cos(k_y a) \cos(k_z a) \quad (5.10)$$

Face-centered cubic:

$$E = E_a - \alpha - 4\beta [\cos(k_x a) \cos(k_y a) + \cos(k_x a) \cos(k_z a) + \cos(k_y a) \cos(k_z a)]. \quad (5.11)$$

To interpret these results, consider a two-dimensional square lattice. Putting $k_z = 0$ into (5.9) gives:

$$E - E_a + \alpha = -2\beta (\cos k_x a + \cos k_y a)$$

where E_a , α , and β are unknown constants. Since these constants do not affect the form of the relation between E and k , we can replace E by a *reduced energy* E_r , defined as

$$E_r = (E - E_a + \alpha)/2\beta = -(\cos k_x a + \cos k_y a).$$

Curves of k_x versus k_y for various values of E_r are shown in Fig. 10.

Next, we shall consider the tight-binding approximation in the simple cubic lattice when the functions $\phi(r - R_j)$ are taken as one of the p functions of Fig. 9. The integrals of Eq. (5.7) are different for p functions from those for s functions, and further, the integrals are not the same for all

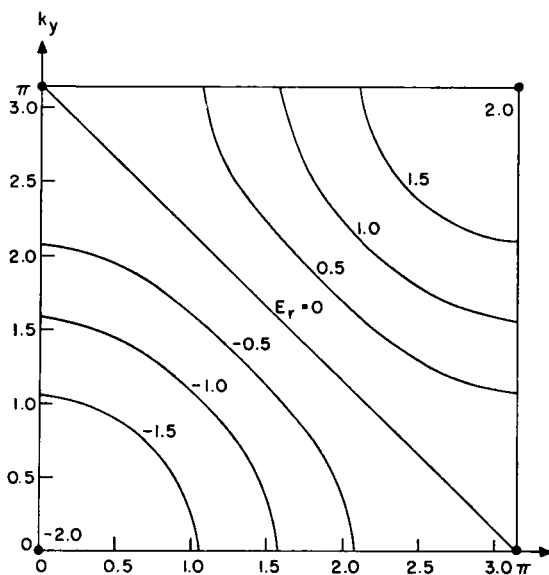


FIG. 10. A two-dimensional tight-binding calculation.

nearest neighbors because of the directional properties of p_x , p_y , and p_z . For convenience, consider just the p_x function, and denote the integral corresponding to α by α_p . There will be a function p_x located at the origin, and six more located at each of six nearest neighbors in a simple cubic lattice. Then there are two kinds of integrals of the form of β in Eq. (5.7), denoted by β_{p1} and β_{p2} , respectively, and we have

$$E = E_{ap} - \alpha_p - 2\beta_{p1} \cos k_x a - 2\beta_{p2} (\cos k_y a + \cos k_z a)$$

where

$$\alpha_p = -N \int \phi^*(0) V' \phi(0) d\tau$$

$$\beta_{p1} = -N \int \phi^*(a, 0, 0) V' \phi(0) d\tau$$

$$\beta_{p2} = -N \int \phi^*(0, a, 0) V' \phi(0) d\tau$$

and in addition, $\phi(0)$ is a function located at the origin, $\phi(a, 0, 0)$ is located at $x = a$, and $\phi(0, a, 0)$ is located at $y = a$ (moving this function to $y = -a$ or to $z = \pm a$ gives the same integral).

Now let us extend these results to a crystal with several nonequivalent atoms per unit cell, and express ϕ_k as a linear combination of all three p functions. Then there will be an expression of the form (5.1) for each atom in the unit cell; that is

$$\phi_{nk} = \sum_j \exp(i\mathbf{k} \cdot \mathbf{R}_j) \phi_n(\mathbf{r} - \mathbf{R}_j) \quad (5.12)$$

where we have used the convention

$$\phi_1 = p_x, \quad \phi_2 = p_y, \quad \phi_3 = p_z$$

in order to utilize the summation notation. The general solution to the Schrödinger equation is then

$$\phi_k(r) = \sum_{j,n,s} B_{ns} \exp(i\mathbf{k} \cdot \mathbf{R}_{js}) \phi_n(\mathbf{r} - \mathbf{R}_{js}) \quad (5.13)$$

where the B_{ns} are constants to be determined, and the subscript s refers to the nonequivalent atoms. Again writing V as $V_a + V'$, introducing this $\phi_k(r)$ into the Schrödinger equation, and multiplying by each of the ϕ_{nk}^* in turn, followed by an integration, we obtain a series of homogeneous equations in the unknowns B_{ns} . Requiring the determinant of these co-

efficients to vanish leads to the *secular equation*, for which examples will be given shortly.

Finally, for a crystal of arbitrary complexity, and making use of combinations of *s*, *p*, and *d* functions, we would expect the resulting calculations to involve a large number of integrals of the form of (5.13), which we shall denote by the symbol

$$(\phi_n^* | V' | \phi_m) = N \int \phi_n^* V' \phi_m d\tau. \quad (5.14)$$

Further, we shall show in what follows that the tight-binding method leads to high-order secular equations involving these integrals, and one of the key applications of group theory to solid state physics concerns itself with the choice of linear combinations of atomic orbitals which automatically reduce the degree of the secular determinant.

6. THE METHOD OF SLATER AND KOSTER

Slater and Koster⁸ have shown how to conveniently handle the geometrical considerations involved in the tight-binding method. Before discussing their approach, however, it will be worthwhile to examine briefly

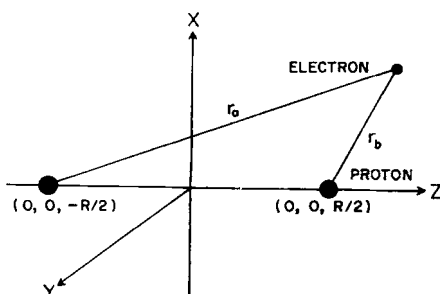


FIG. 11. The geometry used for H_2^+ .

the question of notation, and this, in turn, requires a consideration of the solution of the Schrödinger equation for the singly ionized hydrogen molecule. This system is illustrated in Fig. 11, where we show two protons lying on the *z*-axis and separated by a distance *R* (taken as fixed). Following Eyring *et al.*,³ the operator ∇^2 is expressed in confocal elliptic coordinates μ , ν , and ϕ , where

$$\mu = (r_a + r_b)/R, \quad \nu = (r_a - r_b)/R \quad (6.1)$$

⁸ J. C. Slater and G. F. Koster, *Phys. Rev.* **94**, 1498 (1954).

and ϕ is the azimuthal angle about the z -axis with respect to the XOY -plane. This choice of ϕ makes it identical to the ϕ used in the spherical coordinate system (r, θ, ϕ) if the two protons become coincident at the origin. The surfaces $\mu = \text{constant}$ are confocal ellipsoids with the two protons at the foci, and the surfaces $\nu = \text{constant}$ are confocal hyperboloids which are orthogonal to the ellipsoids. The Laplacian in this coordinate system is then

$$\nabla^2 = \frac{4}{R^2(\mu^2 - \nu^2)} \left[\frac{\partial}{\partial \mu} \left\{ (\mu^2 - 1) \frac{\partial}{\partial \nu} \right\} \right] + \frac{\partial}{\partial \nu} \left\{ (1 - \nu^2) \frac{\partial}{\partial \mu} \right\} + \frac{\mu^2 - \nu^2}{(\mu^2 - 1)(1 - \nu^2)} \frac{\partial^2}{\partial \phi^2} \right]. \quad (6.2)$$

If we try a solution of the form

$$\psi(\mu, \nu, \phi) = M(\mu)N(\nu)\Phi(\phi) \quad (6.3)$$

then the fact that ϕ enters (6.2) only as $\partial^2/\partial\phi^2$ results in the ordinary differential equation

$$d^2\Phi/d\phi^2 = -\lambda^2\Phi \quad (6.4)$$

where $-\lambda^2$ is taken as the separation constant. The resulting equation in μ and ν can also be separated, but the individual equations must be solved numerically and will not be considered here. Equation (6.4), like the corresponding equation involving the magnetic quantum number m_l , has eigenvalues $\lambda = 0, \pm 1, \pm 2, \dots$. The complete solutions $\psi(\mu, \nu, \phi)$ are called *molecular orbitals* and they are designated like the corresponding atomic orbitals which would result if the two protons were united at the origin. In addition, each value $|\lambda|$ of the magnitude of λ corresponds to a different state, unlike the atomic case, where the values

$$m_l = l, l - 1, \dots, 0, \dots, -l$$

all belong to the same energy; that is, they are degenerate (in the absence of a magnetic field). In analogy with s, p, d, \dots , the values $|\lambda| = 0, 1, 2, \dots$ are designated $\sigma, \pi, \delta, \dots$, and the possible molecular orbitals are then $1s\sigma, 2s\sigma, 2p\sigma, 2p\pi, 3s\sigma, 3p\sigma, 3p\pi, 3d\sigma, 3d\pi, 3d\delta, \dots$.

To introduce the geometrical results of Slater and Koster, we choose some atom in a crystal as the origin O of a spherical coordinate system and consider the vector \mathbf{r} determined by any one of its neighbors located at the point P (Fig. 12). The direction cosines l, m , and n of r with respect to the rectangular coordinates are given by

$$l = x/r = \cos \phi \sin \theta, \quad m = y/r = \sin \phi \sin \theta, \quad n = z/r = \cos \theta. \quad (6.5)$$

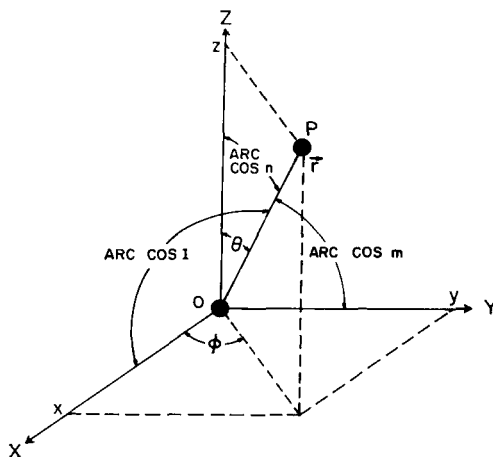


FIG. 12. Coordinates used for two-center integrals.

We wish to set up a second coordinate system $OX'Y'Z'$ with the same origin at $OXYZ$ and with the OZ' axis lying along OP . The transformation matrix will be designated by

$$\begin{array}{l} OX \\ OY \\ OZ \end{array} \begin{array}{l} OX' \\ OY' \\ OZ' \end{array} \begin{array}{l} a_{11} \quad a_{12} \quad a_{13} \\ a_{21} \quad a_{22} \quad a_{23} \\ a_{31} \quad a_{32} \quad a_{33} \end{array}$$

so that

$$a_{13} = l, \quad a_{23} = m, \quad a_{33} = n. \quad (6.6)$$

Consider now an integral of the form (5.14) with ϕ_n^* and ϕ_m both taken, for example, as p_x' . Let us write p_x' simply as x' , in accordance with Eq. (5.1a). Then, again from (5.1a), the transformed functions can be obtained as follows:

$$\begin{Bmatrix} x' \\ y' \\ z' \end{Bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{Bmatrix} (\sqrt{3}/2\sqrt{\pi}) \sin \theta \cos \phi \\ (\sqrt{3}/2\sqrt{\pi}) \sin \theta \sin \phi \\ (\sqrt{3}/2\sqrt{\pi}) \cos \theta \end{Bmatrix}. \quad (6.7)$$

However, it is more convenient for purposes of manipulation to use the functions of (5.1) although the linear combinations of (5.1a) are easier

to interpret physically. To reintroduce these functions, we take the three equations of the form:

$$x' = a_{11}x + a_{12}y + a_{13}z$$

and rewrite them as

$$\begin{aligned} x' &= \frac{1}{2}[(a_{11} + ia_{12})(x - iy)] + \frac{1}{2}[(a_{11} - ia_{12})(x + iy)] + a_{13}z \\ y' &= \frac{1}{2}[(a_{21} + ia_{22})(x - iy)] + \frac{1}{2}[(a_{21} - ia_{22})(x + iy)] + a_{23}z \end{aligned} \quad (6.8)$$

(with a similar expression for z'). We note that

$$\begin{aligned} x + iy &= \sqrt{2}p_{+1} \propto \sin \theta e^{i\phi} \\ x - iy &= \sqrt{2}p_{-1} \propto \sin \theta e^{-i\phi} \\ z &= p_0 \propto \cos \theta. \end{aligned} \quad (6.9)$$

The integral we are interested in is then

$$\begin{aligned} (x'^* | V' | x') &= (\{\frac{1}{2}[(a_{11} - ia_{12})(x + iy)] + \frac{1}{2}[(a_{11} + ia_{12})(x - iy)] \\ &\quad + a_{13}z\} | V' | \{\frac{1}{2}[(a_{11} + ia_{12})(x - iy)] \\ &\quad + \frac{1}{2}[(a_{11} - ia_{12})(x + iy)] + a_{13}z\}) \end{aligned} \quad (6.10)$$

If we expand this expression and work out each of the nine integrals we find that some of them will immediately vanish, since

$$\int_0^{2\pi} \exp(im_l\phi) d\phi = 0 \quad (6.11)$$

when $m_l = \pm 1, \pm 2, \dots$. The nonvanishing integrals in this example are of two types, and the following special symbols are used for them:

$$\begin{aligned} (p_0^* | V' | p_0) &= (3/4\pi) (\cos \theta | V' | \cos \theta) = (pp\sigma) \\ (p_{+1}^* | V' | p_{+1}) &= (3/8\pi) (\sin \theta e^{\mp i\phi} | V' | \sin \theta e^{\pm i\phi}) \\ &= (3/8\pi) (\sin \theta | V' | \sin \theta) = (pp\pi) \end{aligned} \quad (6.12)$$

where σ and π refer to $m_l = 0$ and $m_l = \pm 1$, respectively, in accordance with the convention already mentioned. Using (6.9), (6.11), and (6.12), Eq. (6.10) becomes

$$\begin{aligned} (x'^* | V' | x) &= \frac{1}{2}(a_{11}^2 + a_{12}^2)(\sqrt{2}p_{+1} | V' | \sqrt{2}p_{-1}) + a_{13}^2(p_0 | V' | p_0) \\ &= (1 - l^2)(pp\pi) + l^2(pp\sigma). \end{aligned} \quad (6.13)$$

where we have used the well-known property of an orthogonal matrix:

$$a_{11}^2 + a_{12}^2 + a_{13}^2 = 1. \quad (6.14)$$

A somewhat more involved example is the integral $(x'^* | V' | x'y')$, since the normalization constants must be considered. We shall need the additional symbols:

$$(p_0^* | V' | d_0) = [\sqrt{(15)/8\pi}](\cos \theta | V' | 3 \cos^2 \theta - 1) = (pd\sigma) \quad (6.15)$$

$$(p_{+1}^* | V' | d_{+1}) = [\sqrt{(45)/8\pi}](\sin \theta | V' | \sin \theta \cos \theta) = (pd\pi)$$

From (6.8), we have that

$$\begin{aligned} x'y' = & \frac{1}{2}[(a_{11}a_{21} + a_{12}a_{22})] + \frac{1}{2}[(a_{11} + ia_{12})(x - iy)a_{23}z] \\ & + \frac{1}{2}[(a_{11} - ia_{12})(x + iy)a_{23}z] + \frac{1}{2}[(a_{21} + ia_{22})(x - iy)a_{13}z] \\ & + \frac{1}{2}[(a_{21} - ia_{22})(x + iy)a_{13}z] + a_{13}a_{23}z^2. \end{aligned} \quad (6.16)$$

The first and last terms of (6.16) can be combined to give:

$$\begin{aligned} -(lm/2)(x^2 + y^2) + lmz^2 &= lm[z^2 - \frac{1}{2}(x^2 + y^2)] \\ &= (lm/2)[3z^2 - r^2] \end{aligned} \quad (6.17)$$

since:

$$x^2 + y^2 + z^2 = r^2.$$

This term is the sole contributor to the σ integral, since all other terms in (6.16) involve $e^{\pm i\phi}$. The π contribution comes from the remaining terms of (6.8) and multiplying by x'^* and integrating gives

$$\begin{aligned} \frac{1}{2}[(a_{11}^2 + a_{12}^2)a_{23} + (a_{11}a_{21} + a_{12}a_{22})a_{13}(x + iy | V' | \{x - iy\}z)] \\ = \frac{1}{2}[(1 - 2l^2)m](x + iy | V' | \{x - iy\}z). \end{aligned} \quad (6.18)$$

The complete integral is then

$$\begin{aligned} (x'^* | V' | x'y') &= (l^2m/2)(z | V' | 3z^2 - r^2) \\ &+ \frac{1}{2}[(1 - 2l^2)m](x + iy | V' | \{x - iy\}z) \\ &= (l^2m/2)(\cos \theta | V' | 3 \cos^2 \theta - 1) \\ &+ \frac{1}{2}[(1 - 2l^2)m](\sin \theta | V' | \sin \theta \cos \theta). \end{aligned} \quad (6.19)$$

This can be written in terms of symbols as

$$(x'^* | V' | x'y') = \sqrt{3}l^2m(pd\sigma) + (1 - 2l^2)(pd\pi) \quad (6.20)$$

Similar expressions have been worked out in the Slater and Koster⁷ paper for all combinations of s , p , and d functions, and the results are given in Table VIII. In this table, the simpler notation

$$(x'^* | V' | x'y') = (x, xy) \quad (6.21)$$

TABLE VIII. TWO-CENTER INTEGRALS IN TERMS OF ATOMIC-ORBITAL INTEGRALS^a

$E_{s,s}$	$(ss\sigma)$
$E_{s,x}$	$l(sp\sigma)$
$E_{x,x}$	$l^2(pp\sigma) + (1 - l^2)(pp\pi)$
$E_{x,y}$	$lm(pp\sigma) - lm(pp\pi)$
$E_{x,z}$	$ln(pp\sigma) - ln(pp\pi)$
$E_{s,xy}$	$\sqrt{3}lm(sd\sigma)$
E_{s,x^2-y^2}	$\frac{1}{2}\sqrt{3}(l^2 - m^2)(sd\sigma)$
$E_{s,3z^2-r^2}$	$[n^2 - \frac{1}{2}(l^2 + m^2)](sd\sigma)$
$E_{x,xy}$	$\sqrt{3}l^2m(pd\sigma) + m(1 - 2l^2)(pd\pi)$
$E_{x,yx}$	$\sqrt{3}lmn(pd\sigma) - 2lmn(pd\pi)$
$E_{x,zx}$	$\sqrt{3}l^2n(pd\sigma) + n(1 - 2l^2)(pd\pi)$
E_{x,x^2-y^2}	$\frac{1}{2}\sqrt{3}l(l^2 - m^2)(pd\sigma) + l(1 - l^2 + m^2)(pd\pi)$
E_{y,x^2-y^2}	$\frac{1}{2}\sqrt{3}m(l^2 - m^2)(pd\sigma) - m(1 + l^2 - m^2)(pd\pi)$
E_{z,x^2-y^2}	$\frac{1}{2}\sqrt{3}n(l^2 - m^2)(pd\sigma) - n(l^2 - m^2)(pd\pi)$
$E_{x,3z^2-r^2}$	$l[n^2 - \frac{1}{2}(l^2 + m^2)](pd\sigma) - \sqrt{3}ln^2(pd\pi)$
$E_{y,3z^2-r^2}$	$m[n^2 - \frac{1}{2}(l^2 + m^2)](pd\sigma) - \sqrt{3}mn^2(pd\pi)$
$E_{z,3z^2-r^2}$	$n[n^2 - \frac{1}{2}(l^2 + m^2)](pd\sigma) + \sqrt{3}n(l^2 + m^2)(pd\pi)$
$E_{xy,xy}$	$3l^2m^2(dd\sigma) + (l^2 + m^2 - 4l^2m^2)(dd\pi) + (n^2 + l^2m^2)(dd\delta)$
$E_{xy,yx}$	$3lm^2n(dd\sigma) + ln(1 - 4m^2)(dd\pi) + ln(m^2 - 1)(dd\delta)$
$E_{xy,zz}$	$3l^2mn(dd\sigma) + mn(1 - 4l^2)(dd\pi) + mn(l^2 - 1)(dd\delta)$
E_{xy,x^2-y^2}	$\frac{3}{2}lm(l^2 - m^2)(dd\sigma) + 2lm(m^2 - l^2)(dd\pi) + \frac{1}{2}lm(l^2 - m^2)(dd\delta)$
E_{yx,x^2-y^2}	$\frac{3}{2}mn(l^2 - m^2)(dd\sigma) - mn[1 + 2(l^2 - m^2)](dd\pi) + mn[1 + \frac{1}{2}(l^2 - m^2)](dd\delta)$
E_{zx,x^2-y^2}	$\frac{3}{2}nl(l^2 - m^2)(dd\sigma) + nl[1 - 2(l^2 - m^2)](dd\pi) - nl[1 - \frac{1}{2}(l^2 - m^2)](dd\delta)$
$E_{xy,3z^2-r^2}$	$\sqrt{3}lm[n^2 - \frac{1}{2}(l^2 + m^2)](dd\sigma) - 2\sqrt{3}lmn^2(dd\pi) + \frac{1}{2}\sqrt{3}lm(1 + n^2)(dd\delta)$
$E_{yz,3z^2-r^2}$	$\sqrt{3}mn[n^2 - \frac{1}{2}(l^2 + m^2)](dd\sigma) + \sqrt{3}mn(l^2 + m^2 - n^2)(dd\pi) - \frac{1}{2}\sqrt{3}mn(l^2 + m^2)(dd\delta)$
$E_{zx,3z^2-r^2}$	$\sqrt{3}ln[n^2 - \frac{1}{2}(l^2 + m^2)](dd\sigma) + \sqrt{3}ln(l^2 + m^2 - n^2)(dd\pi) - \frac{1}{2}\sqrt{3}ln(l^2 + m^2)(dd\delta)$
$E_{x^2-y^2,x^2-y^2}$	$\frac{3}{4}(l^2 - m^2)^2(dd\sigma) + [l^2 + m^2 - (l^2 - m^2)^2](dd\pi) + [n^2 + \frac{1}{4}(l^2 - m^2)^2](dd\delta)$
$E_{x^2-y^2,3z^2-r^2}$	$\frac{1}{2}\sqrt{3}(l^2 - m^2)[n^2 - \frac{1}{2}(l^2 + m^2)](dd\sigma) + \sqrt{3}n^2(m^2 - l^2)(dd\pi) + \frac{1}{4}\sqrt{3}(1 + n^2)(l^2 - m^2)(dd\delta)$
$E_{3z^2-r^2,3z^2-r^2}$	$[n^2 - \frac{1}{2}(l^2 + m^2)]^2(dd\sigma) + 3n^2(l^2 + m^2)(dd\pi) + \frac{3}{4}(l^2 + m^2)^2(dd\delta)$

^a To agree with text, change notation from $E_{s,s}$ to (s, s) , $E_{s,x}$ to (s, x) , etc.

is used, and any entries not given can be found by simple permutation of the coordinates and direction cosines.

The formulas of Table VIII can now be applied to actual lattices and one example which we shall use shortly is the simple cubic. The nearest neighbors have already been stated to have coordinates $(\pm a, 0, 0)$, $(0, \pm a, 0)$, and $(0, 0, \pm a)$, and we are interested in evaluating terms corresponding to the last term on the right of (5.8). As we have already shown, for nearest neighbors, this gives

$$(ss\sigma)_1 \sum \exp [i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_m)] = 2(ss\sigma)_1(\cos \xi + \cos \eta + \cos \zeta) \quad (6.22)$$

where the subscript 1 denotes first-nearest neighbors, $(ss\sigma)_1$ corresponds to what we have previously called β , and we use the abbreviations

$$\xi = k_x a, \quad \eta = k_y a, \quad \zeta = k_z a. \quad (6.23)$$

There are twelve second-nearest neighbors in a simple cubic lattice, located at points like $(a, a, 0)$ and the summation term is

$$\begin{aligned} (ss\sigma)_2 [\exp [i(k_x + k_y)a] + \exp [i(k_x - k_y)a] + (\text{similar combinations})] \\ = 2(ss\sigma)_2 [\cos (\xi + \eta) + \cos (\xi - \eta) + \cos (\eta + \zeta) \\ + \cos (\eta - \zeta) + \cos (\zeta + \xi) + \cos (\zeta - \xi)] \\ = 4(ss\sigma)_2 [\cos \xi \cos \eta + \cos \eta \cos \zeta + \cos \zeta \cos \xi]. \end{aligned} \quad (6.24)$$

Similarly, for eight third-nearest neighbors, located at the points $(\pm a, \pm a, \pm a)$, the corresponding term is

$$\begin{aligned} 2(ss\sigma)_3 [\cos (\xi + \eta + \zeta) + \cos (\xi - \eta - \zeta) + \cos (-\xi + \eta - \zeta) \\ + \cos (-\xi - \eta + \zeta)] = 9(ss\sigma)_3 [\cos \xi \cos \eta \cos \zeta]. \end{aligned} \quad (6.25)$$

This process for the p -states is somewhat more involved since we have integrals of both the σ -type and π -type to consider, corresponding respectively to β_{p1} and β_{p2} of Section 5. To indicate how the entry (x/x) of Table IX is calculated, we realize from Fig. 13 that a function p_x located at O will give rise to two σ -integrals with its first-nearest neighbors on the y - and z -axes. The summation term for first-nearest neighbors is then

$$\begin{aligned} (pp\sigma)_1 [\exp (ik_x a) + \exp (-ik_x a)] + (pp\pi)_1 [\exp (ik_y a) + \exp (-ik_y a) \\ + \exp (ik_z a) + \exp (-k_z a)] = 2(pp\sigma)_1 \cos \xi \\ + 2(pp\pi)_1 (\cos \eta + \cos \zeta). \end{aligned} \quad (6.26)$$

The geometrical arrangement for second-nearest neighbors is indicated by Fig. 14, where we have sketched the p_x orbitals for the four neighbors lying in the x, y -plane. These orbits do not form simple σ -integrals and

TABLE IX. NEAREST-NEIGHOR INTEGRALS IN TERMS OF TWO-CENTER INTEGRALS

(s/s)	$s_0 + 2(ss\sigma)_1 (\cos \xi + \cos \eta + \cos \zeta)$ $+ 4(ss\sigma)_2 (\cos \xi \cos \eta + \cos \xi \cos \zeta + \cos \eta \cos \zeta)$ $+ 8(ss\sigma)_3 \cos \xi \cos \eta \cos \zeta$
(s/x)	$2i(sp\sigma)_1 \sin \xi + 2\sqrt{2}i(sp\sigma)_2 (\sin \xi \cos \eta + \sin \xi \cos \zeta)$ $+ (8/\sqrt{3})i(sp\sigma)_3 \sin \xi \cos \eta \cos \zeta$
(s/xy)	$- 2\sqrt{3} (sp\sigma)_2 \sin \xi \sin \eta - (8/\sqrt{3}) (sd\sigma)_3 \sin \xi \sin \eta \cos \zeta$
$(s/x - y)$	$\sqrt{3}(sd\sigma)_1 (\cos \xi - \cos \eta) + \sqrt{3}(sd\sigma)_2 (\cos \xi \cos \zeta - \cos \eta \cos \zeta)$
$(s/3z^2 - r^2)$	$(sd\sigma)_1 (-\cos \xi - \cos \eta + 2 \cos \zeta)$ $+ (sd\sigma)_2 (-2 \cos \xi \cos \eta + \cos \xi \cos \zeta + \cos \eta \cos \zeta)$
(x/x)	$p_0 + 2(pp\sigma)_1 \cos \xi + 2(pp\pi)_1 (\cos \eta + \cos \zeta)$ $+ 2(pp\sigma)_2 (\cos \xi \cos \eta + \cos \xi \cos \zeta)$ $+ 2(pp\pi)_2 (\cos \xi \cos \eta + \cos \xi \cos \zeta + 2 \cos \eta \cos \zeta)$ $+ [(8/3)(pp\sigma)_3 + (16/3)(pp\pi)_3] \cos \xi \cos \eta \cos \zeta$
(x/y)	$- 2[(pp\sigma)_2 - (pp\pi)_2] \sin \xi \sin \eta$ $- (8/3)[(pp\sigma)_3 - (pp\pi)_3] \sin \xi \sin \eta \cos \zeta$
(x/xy)	$2i(pd\pi)_1 \sin \eta + (\sqrt{6})i(pd\sigma)_2 \cos \xi \sin \eta + 2\sqrt{2}i(pd\pi)_2 \sin \eta \cos \zeta$ $+ [(8/3)(pd\sigma)_3 + (8/3\sqrt{3})(pd\pi)_3]i \cos \xi \sin \eta \cos \zeta$
(x/yz)	$[-(8/3)(pd\sigma)_3 + (16/3\sqrt{3})(pd\pi)_3]i \sin \xi \sin \eta \sin \zeta$
$(x/x^2 - y^2)$	$\sqrt{3}(pd\sigma)_1 \sin \xi - (3/2)i(pd\sigma)_{xi} \sin \xi \cos \zeta$ $+ 2\sqrt{2}(pd\pi)_{xi} [\sin \xi \cos \eta + \frac{1}{2} \sin \xi \cos \zeta] + (8/\sqrt{3})(pd\pi)_{xi}$ $\times \sin \xi \cos \eta \cos \zeta$
$(x/3z^2 - r^2)$	$-(pd\sigma)_{xi} \sin \xi + \sqrt{2}(pd\sigma)_{xi} [\sin \xi \cos \eta - \frac{1}{2} \sin \xi \cos \zeta]$ $- (\sqrt{6})(pd\pi)_{xi} \sin \xi \cos \zeta - (8/3)(pd\pi)_{xi} \sin \xi \cos \eta \cos \zeta$
$(z/3z^2 - r^2)$	$2i(pd\sigma)_1 \sin \zeta + [(1/\sqrt{2})(pd\sigma)_2 + (\sqrt{6})(pd\pi)_2]i$ $\times [\cos \xi \sin \zeta + \cos \eta \sin \zeta] + (16/3)(pd\pi)_{xi} \cos \xi \cos \eta \sin \zeta$
(xy/xy)	$d_0 + 2(dd\pi)_1 (\cos \xi + \cos \eta) + 2(dd\delta)_1 \cos \zeta + 3(dd\sigma)_2 \cos \xi \cos \eta$ $+ 2(dd\pi)_2 (\cos \xi \cos \zeta + \cos \eta \cos \zeta) + (dd\delta)_2$ $\times (\cos \xi \cos \eta + 2 \cos \xi \cos \zeta + 2 \cos \eta \cos \zeta)$ $+ [(8/3)(dd\sigma)_3 + (16/9)(dd\pi)_3 + (32/9)(dd\delta)_3] \cos \xi \cos \eta \cos \zeta$
(xy/xz)	$2[-(dd\pi)_2 + (dd\delta)_2] \sin \eta \sin \zeta$ $+ [-(8/3)(dd\sigma)_3 + (8/9)(dd\pi)_3 + (16/9)(dd\delta)_3] \cos \xi \sin \eta \sin \zeta$
$(xy/x^2 - y^2)$	zero
$(xy/3z^2 - r^2)$	$\sqrt{3}[(dd\sigma)_2 - (dd\delta)_2] \sin \xi \sin \eta + (16/3\sqrt{3})[(dd\pi)_3 - (dd\delta)_3]$ $\sin \xi \sin \eta \cos \zeta$
$(xz/x^2 - y^2)$	$-\frac{3}{2}[(dd\sigma)_2 - (dd\delta)_2] \sin \xi \sin \zeta - (8/3)[(dd\pi)_3 - (dd\delta)_3]$ $\times \sin \xi \cos \eta \sin \zeta$

TABLE IX—Continued.

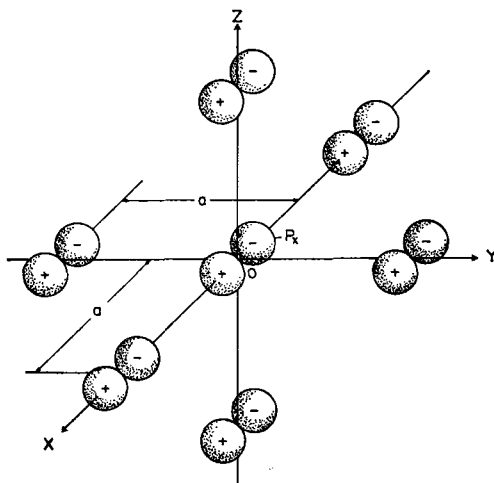
$(xz/3z^2 - r^2)$	$\frac{1}{2}\sqrt{3}[-(dd\sigma)_2 + (dd\delta)_2]\sin\xi\sin\zeta - (8/3\sqrt{3})[(dd\pi)_3 - (dd\delta)_3]\times\sin\xi\cos\eta\sin\zeta$
$(x^2 - y^2/x^2 - y^2)$	$d_0 + \frac{3}{2}(dd\sigma)_1(\cos\xi + \cos\eta) + (dd\delta)_1(\frac{1}{2}\cos\xi + \frac{1}{2}\cos\eta + 2\cos\zeta) + 4(dd\pi)_2\cos\xi\cos\eta + [\frac{3}{2}(dd\sigma)_2 + (dd\pi)_2 + (9/4)(dd\delta)_2]\times(\cos\xi\cos\zeta + \cos\eta\cos\zeta) + [(16/3)(dd\pi)_3 + (8/3)(dd\delta)_3]\cos\xi\cos\eta\cos\zeta$
$(3z^2 - r^2/3z^2 - r^2)$	$d_0 + (dd\sigma)_1(\frac{1}{2}\cos\xi + \frac{1}{2}\cos\eta + 2\cos\zeta) + \frac{3}{2}(dd\delta)_1\times(\cos\xi + \cos\eta) + (dd\sigma)\times(\cos\xi\cos\eta + \frac{1}{4}\cos\xi\cos\zeta + \frac{1}{4}\cos\eta\cos\zeta) + 3(dd\pi)_2\times(\cos\xi\cos\zeta + \cos\eta\cos\zeta) + 3(dd\delta)_2\times(\cos\xi\cos\eta + \frac{1}{4}\cos\xi\cos\zeta + \frac{1}{4}\cos\eta\cos\zeta) + [(16/3)(dd\pi)_3 + (8/3)(dd\delta)_3]\cos\xi\cos\eta\cos\zeta$
$(x^2 - y^2/3z^2 - r^2)$	$\frac{1}{2}\sqrt{3}[-(dd\sigma)_1 + (dd\delta)_1](\cos\xi - \cos\eta) + [\frac{1}{4}\sqrt{3}(dd\sigma)_2 - \sqrt{3}(dd\pi)_2 + \frac{3}{4}\sqrt{3}(dd\delta)_2](\cos\xi\cos\zeta - \cos\eta\cos\zeta)$

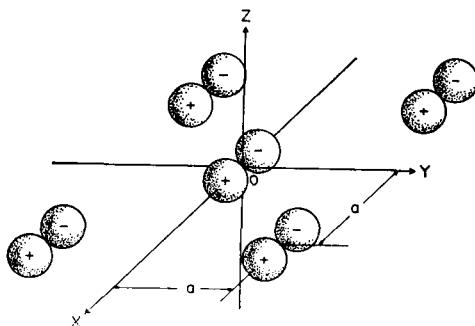
π -integrals, as for nearest neighbors, but instead, we must go back to Table VIII, using the entry

$$(x, x) = l^2(pp\sigma) + (1 - l^2)(pp\pi) \quad (6.27)$$

which becomes

$$(x, x)_2 = \frac{1}{2}[(pp\sigma)_2 + (pp\pi)_2] \quad (6.28)$$

FIG. 13. Arrangement of nearest-neighbor p_x functions.

FIG. 14. Arrangement of second-nearest p_z functions.

where $l = \sqrt{2}/2$ for a 45° angle. The summation in (5.8) is

$$\begin{aligned} \exp[i(\xi + \eta)] + \exp[i(-\xi + \eta)] + \exp[i(-\xi - \eta)] \\ + \exp[i(\xi - \eta)] = 4 \cos \xi \cos \eta \quad (6.29) \end{aligned}$$

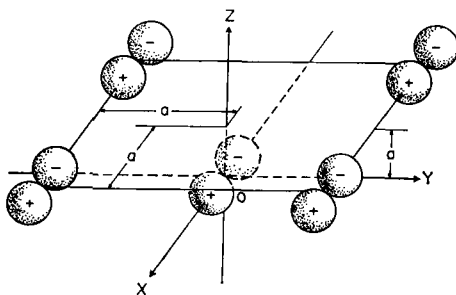
so that the x, y -plane gives a contribution $2 \cos \xi \cos \eta [(pp\sigma)_2 + (pp\pi)_2]$ to the complete integral. The x, z -plane has a similar contribution but the y, z -plane produces pure π -integrals, giving a contribution $4 \cos \eta \cos \xi (pp\pi)_2$. The total result gives the second-nearest neighbor term in the table.

The third-nearest neighbors are shown in Fig. 15, and all eight integrals involve σ and π terms. By Table VIII,

$$(x, x)_3 = \frac{1}{3}(pp\sigma)_3 + \frac{2}{3}(pp\pi)_3$$

and combining this with the summation as previously evaluated in (6.25) gives the last term of the (x, x) entry in Table IX.

In this discussion, we have stressed primarily the manipulative features

FIG. 15. Arrangement of third-nearest p_z functions.

of the Slater-Koster method. Our subsequent considerations will involve some of the applications.

IV. The Band Structure of Beta-Brass

7. A GENERAL DESCRIPTION OF BETA-BRASS

An example which illustrates the usefulness of group theory as applied to the LCAO method is the study of beta-brass made by Amsterdam.⁹ This alloy in its ideal form consists of equal numbers of copper and zinc atoms, with a unit cell as shown in Fig. 16. This unit cell contains one zinc

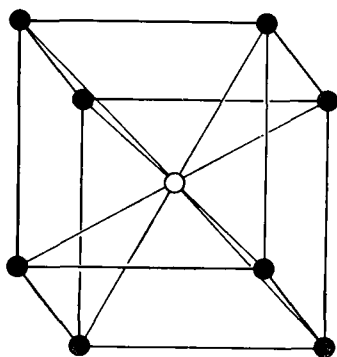


FIG. 16. The unit cell of beta-brass; ●, Cu; ○, Zn.

atom and the equivalent of one copper atom, and the lattice is simple cubic, with an atom of each kind assigned to each lattice point.

The electron configuration of copper is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ and zinc has the outer subshell $3d^{10} 4s^2$. Amsterdam's calculation is then based on consideration of these twenty-three valence electrons. According to Pauling,¹⁰ Cu has an ionic radius of 0.96 Å and Zn has a radius of 0.74 Å. It seems reasonable, therefore, to base a tight-binding approximation on interactions between Zn nearest neighbors and Cu next-nearest neighbors of Cu atoms. If we take the edge of the cubic unit cell all as $2a$, then the Cu-Zn interaction corresponds to third-nearest neighbor interaction in a simple cubic lattice with edge a , and the Cu-Cu interaction corresponds to nearest neighbor interaction in a simple cubic lattice of edge $2a$. Hence, we can use the results of Slater and Koster already presented in Table IX.

⁹ M. F. Amsterdam, "The Band Structure of Beta-Brass," Ph.D. dissertation, Temple University, Philadelphia, Pennsylvania, 1958.

¹⁰ L. Pauling, "Nature of the Chemical Bond." Cornell Univ. Press, Ithaca, New York, 1945.

8. CHARACTER SYSTEM FOR THE HOLOHEDRAL CUBIC GROUP O_h

The character table for the group O_h is easily obtained by combining the concepts of Section 4 with the symmetry properties of the cube. Table X lists the forty-eight operations comprising ten classes of this group and Table XI shows the character system. To establish this table, we first

TABLE X. SYMMETRY OPERATIONS FOR THE CUBIC GROUP O_h

Operation	Multiplicity	Description
E	1	The identity
C_4	6	$\pm 90^\circ$ rotation about a coordinate axis
C_4^2	3	$\pm 180^\circ$ rotation about a coordinate axis
C_2	6	$\pm 180^\circ$ rotation about an axis of the type $x = y, z = 0$
C_3	8	$\pm 120^\circ$ rotation about a cube diagonal
J	1	Inversion through the center
JC_4	6	} Combination of J and the rotations above
JC_4^2	3	
JC_2	6	
JC_3	8	

obtain the values for χ_1 from the requirement that we need ten numbers whose squares have a sum of 48. Empirically, this is satisfied by

$$1^2 + 1^2 + 1^2 + 1^2 + 2^2 + 2^2 + 3^2 + 3^2 + 3^2 + 3^2 = 48 \quad (8.1)$$

and Bethe's procedure (which is considerably more tedious now) results in the character table given. This table is taken from Bouckaert *et al.*¹¹ who are responsible for the peculiar designations of the representations (and for which an explanation will be offered in a later section). An interesting feature of a character table involving the inversion operator is that if it is divided into four blocks as shown by the dotted lines, three are identical and the fourth one is the negative of the others. This considerably simplifies the computation of the characters.

Some of these representations can have atomic orbitals associated with them. To see how this comes about, we use a line of reasoning by Jones,¹² and consider the effects of the cubic symmetry operations on an arbitrary point with coordinates x, y, z . For C_4 , for example, a 90° rotation about

¹¹ L. P. Bouckaert, R. Smoluchowski, and E. Wigner, *Phys. Rev.* **50**, 58 (1936). We shall refer to this paper as BSW.

¹² H. Jones, "The Theory of Brillouin Zones and Electronic States in Crystals," North-Holland Publ., Amsterdam, 1960.

TABLE XI. CHARACTER SYSTEM FOR THE CUBIC GROUP O_h

	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	J	$3JC_4^2$	$6JC_4$	$6JC_2$	$8JC_3$	Associated functions
Γ_1	1	1	1	1	1	1	1	1	1	1	s
Γ_2	1	1	-1	-1	1	1	1	-1	-1	1	$d_x^2, d_x^2 - y^2$
Γ_{12}	2	2	0	0	-1	2	2	0	0	-1	
Γ_{16}'	3	-1	1	-1	0	3	-1	1	-1	0	
Γ_{25}'	3	-1	-1	1	0	3	-1	-1	1	0	d_{xy}, d_{yz}, d_{zx}
Γ_1'	1	1	1	1	1	-1	-1	-1	-1	-1	p_x, p_y, p_z
Γ_2'	1	1	-1	-1	1	-1	-1	1	1	-1	
Γ_{12}'	2	2	0	0	-1	-2	-2	0	0	1	
Γ_{16}	3	-1	1	-1	0	-3	1	-1	1	0	
Γ_{25}	3	-1	-1	1	0	-3	1	1	-1	0	

the OZ axis will convert x, y, z into either $-y, x, z$ (which we denote by $\bar{y}xz$) or into $y\bar{x}z$, and the inversion J on xyz gives $\bar{x}\bar{y}\bar{z}$. The results for the group O are given in Table XII and the additional twenty-four entries for O_h can be obtained by simply reversing all three signs.

A representation can be generated in terms of xyz , similar to the procedure associated with Eq. (2.3). Referring back to this equation, we

TABLE XII. SYMMETRY OPERATIONS OF THE CUBIC GROUP O

E	xyz
$3C_4^2$	$\bar{x}\bar{y}z, \quad x\bar{y}\bar{z}, \quad \bar{x}y\bar{z}$
$6C_4$	$\bar{y}xz, \quad y\bar{x}z, \quad x\bar{z}y, \quad xz\bar{y}, \quad zy\bar{x}, \quad \bar{z}yx$
$6C_2$	$yx\bar{z}, \quad z\bar{y}x, \quad \bar{x}zy, \quad \bar{y}\bar{x}\bar{z}, \quad \bar{z}\bar{y}\bar{x}, \quad \bar{x}\bar{z}\bar{y}$
$8C_3$	$zxy, \quad yzx, \quad z\bar{x}\bar{y}, \quad \bar{y}\bar{z}x, \quad \bar{z}\bar{x}y, \quad \bar{y}z\bar{x}, \quad \bar{z}x\bar{y}, \quad y\bar{z}\bar{x}$

realize that E has the form

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{Bmatrix} x \\ y \\ z \end{Bmatrix} = \begin{Bmatrix} x \\ y \\ z \end{Bmatrix} \quad (8.2)$$

with a character of 3 and that one matrix for C_4^2 , for example, is

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{Bmatrix} x \\ y \\ z \end{Bmatrix} = \begin{Bmatrix} x \\ \bar{y} \\ \bar{z} \end{Bmatrix}$$

with a character of -1 . The full set of characters is then $3, -1, 1, -1, 0, -3, 1, -1, 1, 0$, which we see is identical to the representation Γ_{15} of Table XII. Since the orbitals p_x, p_y, p_z are proportional to x, y, z , respectively, we say that the set of triply degenerate p functions *belongs* to the representation Γ_{15} . Using the same arguments, the completely symmetric s orbital belongs to Γ_1 , and by considering the behavior of the products, we can show that d_{xy}, d_{yz}, d_{zx} belong to $\Gamma_{2'5}$ and $d_{z^2}, d_{x^2-y^2}$ belong to Γ_{12} . This information is summarized in Table XII. The d functions bring up another interesting point: in the free atom they correspond to a fivefold degenerate level, but in a cubic crystal, the d state has been split into a twofold and a threefold state. This phenomenon is known as *crystal field splitting*, and it illustrates the remark made in Part I about the connection between symmetry and degeneracy. An extensive discussion of this topic will be found in another article in this series.¹³ In addition, character tables for the thirty-two crystallographic point groups will be found in an earlier article of this series.¹⁴

9. THE FREE-ELECTRON APPROXIMATION

The LCAO or tight-binding approximation is based on the assumption that nearest-neighbor interactions are of primary importance in determining the band structure of a solid, and the appropriate wave functions are then linear combinations of free-atom functions. We can go to the opposite extreme, and assume that the electron wave functions are plane waves which extend throughout the crystal and that the lattice potential is everywhere constant. That is, we assume that $V = 0$ in the Schrödinger

¹³ C. M. Herzfeld and P. H. E. Meijer, *Solid State Phys.* **12**, 1 (1961).

¹⁴ G. F. Koster, *Solid State Phys.* **5**, 174 (1957).

equation, obtaining what is called the *free electron* or *empty lattice* approximation. The solution of the wave equation under these conditions is a simple matter and it would appear at first glance that the approximation would be so unrealistic as to be useless. It turns out, however, that the information obtained in this way is a great deal of help in interpreting data obtained by more elaborate methods, and we shall show how this comes about by using the development of Jones.¹²

Returning to Eq. (I.1), we try a solution of Bloch form:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})u(\mathbf{r}) \quad (9.1)$$

where \mathbf{k} is the wave vector or propagation constant. Substitution of (9.1) into (I.1) gives

$$\nabla^2 u + 2i\mathbf{k} \cdot \nabla u + (2m/\hbar^2)[E - (\hbar^2 k^2/2m) - V]u = 0 \quad (9.2)$$

and for $V(\mathbf{r}) = 0$, this equation reduces to one of second order with constant coefficients, so that it has exponential solutions.

A convenient form for these solutions comes by considering the geometry of the crystal lattice. If \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 are three noncoplanar vectors connecting lattice points and if n_1 , n_2 , n_3 are an arbitrary set of integers (positive, negative, or zero), then the direct lattice is mapped out by the points $(n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3)$. If the nine components of the three vectors \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 are considered as a matrix \mathbf{A} , the lattice points are determined by the relations

$$\mathbf{A}\mathbf{n} = \begin{bmatrix} a_{1x} & a_{2x} & a_{3x} \\ a_{1y} & a_{2y} & a_{3y} \\ a_{1z} & a_{2z} & a_{3z} \end{bmatrix} \begin{Bmatrix} n_1 \\ n_2 \\ n_3 \end{Bmatrix}. \quad (9.3)$$

The reciprocal lattice is determined by a set of vectors \mathbf{b}_1 , \mathbf{b}_2 , \mathbf{b}_3 defined by

$$\mathbf{a}_i \cdot \mathbf{b}_j = \delta_{ij} \quad [i, j = 1, 2, 3] \quad (9.4)$$

where δ_{ij} is the Kronecker delta. From (9.3) and (9.4), it then follows that the reciprocal lattice can also be specified by a matrix \mathbf{B} , analogous to \mathbf{A} , such that

$$\mathbf{1B} = (l_1, l_2, l_3) \begin{bmatrix} b_{1x} & b_{1y} & b_{1z} \\ b_{2x} & b_{2y} & b_{2z} \\ b_{3x} & b_{3y} & b_{3z} \end{bmatrix} \quad (9.5)$$

where

$$\mathbf{1} = (l_1, l_2, l_3) \quad (9.6)$$

is a row matrix. That is, a vector can be expressed as a matrix of either a single column (like n , above) or a single row, depending upon its position in equations like (9.3) or (9.5). The direct and reciprocal matrices are related by

$$\mathbf{B}\mathbf{A} = \mathbf{I} \quad (9.7)$$

where \mathbf{I} is the unit matrix.

If $V = 0$, (9.2) has a solution

$$u = \exp [-2\pi i(\mathbf{1B}) \cdot \mathbf{r}] \quad (9.8)$$

since

$$\mathbf{grad} u = -2\pi i(\mathbf{1B})u$$

and

$$\text{div } \mathbf{grad} u = -(2\pi \mathbf{1B})^2 u.$$

Substituting these into (9.2) with $V = 0$ then leads to the eigenvalues

$$E = (\hbar^2/2m)(\mathbf{k} - 2\pi \mathbf{1B})^2. \quad (9.9)$$

Combining (9.1) and (9.8) shows that the wave functions for any V are

$$\psi_{\mathbf{k}} = \exp [i(\mathbf{k} - 2\pi \mathbf{1B}) \cdot \mathbf{r}]. \quad (9.10)$$

The eigenvalues given by Eq. (9.9) represent E versus \mathbf{k} curves as plotted within the first Brillouin zone of the lattice in question. For a simple cubic lattice, the reciprocal lattice is also simple cubic and the points and lines of high symmetry in the Brillouin zone have been labeled as shown in Fig. 17 by BSW.¹¹ Using the notation of Eq. (6.23), we can write \mathbf{k} as

$$\mathbf{k} = (1/a)(\xi, \eta, \zeta) \quad (9.11)$$

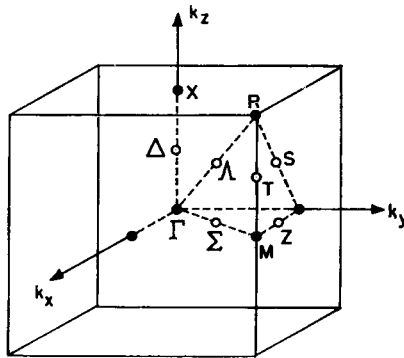


FIG. 17. The Brillouin zone of the simple cubic lattice.

where a is the direct-lattice constant. Also

$$\mathbf{lB} = (l_1, l_2, l_3)(1/a)$$

so that

$$E = (\hbar^2/2ma^2)[(\xi - 2\pi l_1)^2 + (\eta - 2\pi l_2)^2 + (\zeta - 2\pi l_3)^2] \quad (9.12)$$

and

$$\psi_{\mathbf{k}} = \exp \{i[(\xi - 2\pi l_1)x + (\eta - 2\pi l_2)y + (\zeta - 2\pi l_3)z]/a\}. \quad (9.13)$$

To plot E as a function of \mathbf{k} using (9.12) on a two-dimensional graph, we select various directions in the Brillouin zone. For example, along the Δ -axis of Fig. 17 we have $\xi = \eta = 0$ and

$$E = (\hbar^2/2ma^2)[l_1^2 + l_2^2 + (\zeta - l_3)^2] \quad (9.14)$$

$$\psi_{\mathbf{k}} = \exp \{2\pi i[-l_1x - l_2y + (\zeta - l_3)]/a\} \quad (9.15)$$

where $\zeta = \zeta/2\pi$, using a common convention. The curves of E versus ζ are shown in Fig. 18, each curve being labeled with the values of (l_1, l_2, l_3) to which it corresponds. Note that two of these curves are fourfold de-

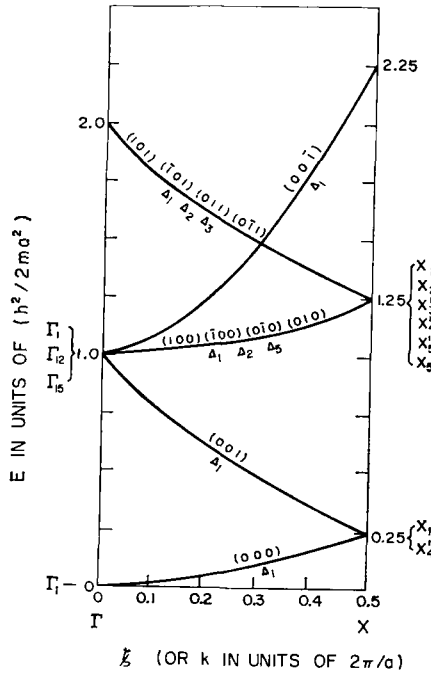


FIG. 18. Free electron energy bands along the Δ -axis of the simple cubic lattice.

TABLE XIII. CHARACTER SYSTEM FOR THE Δ -AXIS OF A SIMPLE CUBIC LATTICE

	E	C_4^2	$2C_4$	$2JC_4^2$	$2JC_2$	
Δ_1	1	1	1	1	1	z^2
Δ_2	1	1	-1	1	-1	$x^2 - y^2$
Δ_2'	1	1	-1	-1	1	xy
Δ_1'	1	1	1	-1	-1	
Δ_6	2	-2	0	0	0	xz, yz
	xyz	$\bar{x}\bar{y}z$	$y\bar{x}z$	$x\bar{y}z$	$\bar{y}\bar{x}z$	
			$\bar{y}xz$	$\bar{x}yz$	yxz	

generate, since the wave functions of Eq. (9.15) are distinct for each triplet (l_1, l_2, l_3) shown.

Since the Brillouin zone, like the direct lattice, is simple cubic, its symmetry properties can be derived from that of the group O_h . We note, however, that as we proceed from Γ to X along the Δ -axis, these properties change. That is, at any point on the Δ -axis except Γ or X , the symmetry reduces to the following five operations:

$$E, C_4^2, C_4, JC_4^2, JC_2.$$

Considering an arbitrary point on this axis, C_4 refers to a 90° rotation about the k_z -axis, whereas JC_4^2 is a 180° rotation about the k_x -axis or k_y -axis followed by the inversion. The associated character system is given in Table XIII as taken from BSW.¹¹ The bottom row of this table contains the eight entries from Table XII (including those involving J) which leave z invariant. We realize now that the designation of representations by Γ and Δ corresponds to the labels used for the points and lines of high symmetry in the Brillouin zone.

The situation for the point X is more involved, since a rotation about the k_x -axis or k_y -axis is not equivalent to a rotation about the k_z -axis. Using a subscript \perp for the former and \parallel for the latter, we obtain the character system of Table XIV, also due to BSW. In preparing this table, the fact that $\pm\pi/a$ are equivalent points has been used.

These character tables enable us to introduce the concept of *compatibility*, for which Jones¹² has the simplest explanation. As we go along the

TABLE XIV. CHARACTER SYSTEM FOR THE POINT X IN THE BRILLOUIN ZONE OF A SIMPLE CUBIC LATTICE

	E	$2C_4^2 \perp$	$C_4^2 \parallel$	$2C_4 \parallel$	$2C_2$	J	$2JC_4^2 \perp$	$JC_4^2 \parallel$	$2JC_4 \parallel$	$2JC_2$
X_1	1	1	1	1	1	1	1	1	1	1
X_2	1	1	1	-1	-1	1	1	1	-1	-1
X_3	1	-1	1	-1	1	1	-1	1	-1	1
X_4	1	-1	1	1	-1	1	-1	1	1	-1
X_5	2	0	-2	0	0	2	0	-2	0	0
X_1'	1	1	1	1	1	-1	-1	-1	-1	-1
X_2'	1	1	1	-1	-1	-1	-1	-1	1	1
X_3'	1	-1	1	-1	1	-1	1	-1	1	-1
X_4'	1	-1	1	1	-1	-1	1	-1	-1	1
X_5'	2	0	-2	0	0	-2	0	2	0	0
<hr/>										
	xyz	$x\bar{y}\bar{z}$	$\bar{x}\bar{y}z$	$\bar{y}xz$	$y\bar{x}\bar{z}$					
		$\bar{x}y\bar{z}$		$y\bar{x}z$	$\bar{y}\bar{x}\bar{z}$					

k_z -axis from Γ to X , we see that there is a summation relation among some of the characters. For example, the row Γ_{12} of Table XI is the sum of the rows Δ_1 and Δ_2 of Table XIII, and this is symbolized as

$$\Gamma_{12} \rightarrow \Delta_1 + \Delta_2$$

where we compare characters for only those operations which are common to both tables; that is, for the column headings of Table XIII. Similarly we have

$$\Gamma_{15}' \rightarrow \Delta_1' + \Delta_5$$

and there are also direct relations such as

$$\Gamma_1' \rightarrow \Delta_1, \quad \Gamma_2' \rightarrow \Delta_2'.$$

The complete set of compatibility relations for the path ΓX is given in

TABLE XV. COMPATIBILITY RELATIONS FOR THE Δ -AXIS OF A SIMPLE CUBIC LATTICE

$\Gamma_1 \rightarrow \Delta_1$	$\Gamma_1' \rightarrow \Delta_1'$
$\Gamma_2 \rightarrow \Delta_2$	$\Gamma_2' \rightarrow \Delta_2'$
$\Gamma_{12} \rightarrow \Delta_1 + \Delta_2$	$\Gamma_{12}' \rightarrow \Delta_1' + \Delta_2'$
$\Gamma_{15}' \rightarrow \Delta_1' + \Delta_5$	$\Gamma_{15} \rightarrow \Delta_1 + \Delta_5$
$\Gamma_{25}' \rightarrow \Delta_2' + \Delta_5$	$\Gamma_{25} \rightarrow \Delta_2 + \Delta_5$
$X_1 \rightarrow \Delta_1$	$X_1' \rightarrow \Delta_1'$
$X_2 \rightarrow \Delta_2$	$X_2' \rightarrow \Delta_2'$
$X_3 \rightarrow \Delta_2'$	$X_3' \rightarrow \Delta_2$
$X_4 \rightarrow \Delta_1'$	$X_4' \rightarrow \Delta_1$
$X_5 \rightarrow \Delta_5$	$X_5' \rightarrow \Delta_5$

Table XV; the upper section shows the logic behind the choice of subscripts for the Γ and Δ representations. In forming these relations, we note that $C_{4^2|1}$ at the point X corresponds to C_4^2 along the Δ -axis, since a 180° rotation about ΓX leaves X invariant. The same is true for $C_{4|1}$ and C_4 . However, $JC_4^2 \perp$ at X corresponds to JC_4^2 since a 180° rotation about the k_x -axis or k_y -axis (but *not* the k_z -axis) followed by the inversion leaves X invariant. The five operations of Table XIV that must match up with Table XIII are then

$$E, C_{4^2|1}, C_{4|1}, JC_4^2 \perp, JC_2.$$

The reasoning behind the compatibility relations is based on the requirement that the trace of a matrix is invariant under a similarity transformation. Consider as an example the triply degenerate representation Γ_{15} , which is irreducible at the center of the Brillouin zone. As we move out along the axis, this representation may become reducible and a single similarity transformation can convert all the 3×3 matrices into diagonal ones or to block form. In either case, the new traces add up to the original trace so that the character systems are connected by compatibility relations of the type given. Another physical way of thinking about compatibility relations comes by considering the three p -functions along some symmetry axis of a cubic crystal. At the point Γ , the functions p_x, p_y, p_z are completely equivalent in a cubic environment, and we have a threefold degeneracy in our E versus \mathbf{k} curve. Suppose we move out along the k_x -axis. Then p_x and p_y are still equivalent, but p_x in general corresponds to a different energy. Hence, the threefold degeneracy at the center of the zone has been split into a nondegenerate and a doubly degenerate energy curve. Thus, the E versus \mathbf{k} curves will touch at the center of the zone.

We next must consider the functions to be associated with the representations of Tables XI, XIII, and XIV. We have already shown the atomic

orbitals that can belong to some of the representations in Table XI, but we would now like to find the corresponding functions of the form (9.15). The lowest energy, by Fig. 18, corresponds to $\xi = 0$ and $\mathbf{l} = (000)$, giving

$$\psi = 1.$$

Following the procedure of Section 8, this completely symmetric function belongs to Γ_1 . Going along the axis, we have

$$\psi = \exp(2\pi i \xi z/a). \quad (9.16)$$

Since z is invariant, then so is ψ in (9.16) and it should therefore belong to the representation Δ_1 .

Arriving at the point X , the corresponding functions are

$$\begin{aligned} \psi &= \exp(\pi i z/a) & \text{for } l_3 = 0; \\ \psi &= \exp(-\pi i z/a) & \text{for } l_3 = 1. \end{aligned} \quad (9.17)$$

If we now attempt to determine what representations of Table XIV belong with either of these functions, we find that in fact none of them do. This is because their symmetry does not match up with the characters in any given row. The way out of this dilemma is to use those linear combinations of these two functions which do have the proper symmetry. These combinations will, of course, satisfy the free-electron Schrödinger equation. To determine them, we introduce another theorem from group theory which we justify, as usual, by citing examples. This rule states that a linear combination ϕ_i belonging to the i th irreducible representation can be found from any eigenfunction ϕ by (a) operating on ϕ with each operation R in the group, (b) multiplying the result by the character $\chi_i(R)$ in row i and column R of the character table and (c) taking the sum of all such terms. Symbolically

$$\phi_i = \sum_R \chi_i(R) R\phi. \quad (9.18)$$

To consider examples, we return to Table XI. The function p_x , or x , can be associated with the representation Γ_{15} by using (9.18) as follows:

$$\begin{array}{cccccc} E & C_4^2 & C_4^2 & C_4^2 & \cdots & JC_3 \\ \phi_1 = 1(p_x) + 1(-p_x) + 1(p_x) + 1(-p_x) + \cdots + 1(p_x) & = 0. \end{array}$$

Similarly we find that ϕ_2 , ϕ_{12} , \cdots also vanish, and the only linear combination that does not vanish is

$$\phi_{15} = 3(p_x) - 1(-p_x) - 1(p_x) - 1(-p_x) + \cdots + 0(p_x) = 8p_x.$$

We would find in the same way that p_y and p_z also belong only to Γ_{15} ,

giving the same information previously obtained but in a complicated way. Hence, the character system of a group can be used to generate solutions to the Schrödinger equation which have the symmetry of the physical system to which the equation is being applied. The operators of the form $\sum_{R\chi_i(R)} R$ which accomplish this process are known as *projection operators*, this name coming from the fact that their use to find suitably symmetric linear combinations is analogous to the process of decomposing an arbitrary vector in n -space into its components. A detailed discussion of projection operators will be found in Birman.¹⁵

Applying this method to the eigenfunctions on the Δ -axis for $l = (000)$, we obtain the following results:

(a) At Γ , ψ is a constant, and therefore application of Eq. (9.18) merely involves adding up the forty-eight characters for each row of Table XI. The only nonzero sum comes from Γ_1 as we would expect, and this function is labeled as belonging to Γ_1 on the left-hand vertical axis of Fig. 18.

(b) Since z is invariant under the five operations of Table XIII, the function $\exp \{2\pi i \xi z/a\}$ belongs to Δ_1 and to no other representation, and the curve is labeled to show this.

(c) At $\xi = 0.5$, we have

$$\psi = \exp (\pi i z/a). \quad (9.19)$$

We now construct Table XVII by extracting from Table XII all the operations which leave the point π/a invariant or convert it into the equivalent point $-\pi/a$. It is then easy to see that the function in (9.19) is converted into the linear combination

$$\phi_1 = 8[\exp (\pi i z/a) - \exp (\pi i z/a)]$$

by X_1 and into

$$\phi_4' = 8[\exp (\pi i z/a) - \exp (-\pi i z/a)]$$

by X_4' , all other representations giving zero. Hence, the function $\cos (\pi z/a)$ belongs to X_1 and $\sin (\pi z/a)$ belongs to X_4' . This has been indicated on the right-hand vertical axis of Fig. 18. We note that the transition

$$\Gamma_1 \rightarrow \Delta_1 \rightarrow X_1 \quad \text{or} \quad X_4'$$

as we go along the lowest curve of Fig. 18 is in agreement with the compatibility relations of Table XV. It is then immediately apparent by compatibility that the function along the next curve must belong to Δ_1 . This is verified by the fact that

$$\psi = \exp (-\pi i z/a)$$

for $l = (001)$.

¹⁵ J. L. Birman, "Notes on Advanced Topics in Solid-State Theory." University of Pennsylvania, Physics Department, Philadelphia, Pennsylvania, 1960.

Returning to Γ along the curve connecting $E = 0.25$ (in reduced units) and $E = 1.0$, at the left-hand end there are six values for \mathbf{l} corresponding to the same energy; namely $\mathbf{l} = (100)$, $(\bar{1}00)$, $(0\bar{1}0)$, (010) , $(00\bar{1})$, and (001) . Since this is the most complicated situation we have yet encountered, we shall work out the linear combinations for the curve connecting $E = 1.0$ with $E = 1.25$. For example,

$$\psi_{(100)} = \exp [2\pi i(x + \xi z)/a].$$

The bottom row of Table XIII shows (a) that the factor $\exp (2\pi i \xi z/a)$ is a constant (call it C) and (b) the other part of the function gives, by (9.18), the combinations

$$\begin{aligned} \Delta_1: \phi_1 &= C[1 \exp (2\pi i x/a) + 1 \exp (-2\pi i x/a) + 1 \exp (2\pi i y/a) \\ &\quad + 1 \exp (-2\pi i y/a) + 1 \exp (2\pi i x/a) + 1 \exp (-2\pi i x/a) \\ &\quad + 1 \exp (-2\pi i y/a) + 1 \exp (2\pi i y/a)] \\ &= 4C[\cos (2\pi x/a) + \cos (2\pi y/a)] \end{aligned} \quad (9.20)$$

$$\Delta_2: \phi_2 = 4C[\cos (2\pi x/a) - \cos (2\pi y/a)] \quad (9.21)$$

$$\begin{aligned} \Delta_2': \phi_2' &= C[1 \exp (2\pi i x/a) + 1 \exp (-2\pi i x/a) - 1 \exp (2\pi i y/a) \\ &\quad - 1 \exp (-2\pi i y/a) + 1 \exp (-2\pi i y/a) \\ &\quad + 1 \exp (2\pi i y/a)] = 0 \end{aligned}$$

$$\Delta_1': \phi_1' = 0$$

$$\begin{aligned} \Delta_5: \phi_5 &= C[2 \exp (2\pi i x/a) - 2 \exp (-2\pi i x/a)] \\ &= 4C \sin (2\pi x/a) \end{aligned} \quad (9.22)$$

For $\psi_{(100)} = \exp [2\pi i(-x + \xi z)/a]$ we obtain exactly the same combinations since $\cos x = \cos (-x)$. Similarly, the functions $\psi_{(010)}$ and $\psi_{(0\bar{1}0)}$ are projected out into linear combinations by Table XIII, giving again the same linear combination for Δ_1 and Δ_2 , but for Δ_5 , we obtain the new function

$$\Delta_5: \phi_5 = C[2 \exp (2\pi i y/a) - 2 \exp (-2\pi i y/a)] = 4C \sin (2\pi y/a). \quad (9.23)$$

Combining the above results, we have the set of functions

$$\begin{aligned} \Delta_1: \phi_1 &= \exp (2\pi i \xi z/a) [\cos (2\pi x/a) + \cos (2\pi y/a)] \\ \Delta_2: \phi_2 &= \exp (2\pi i \xi z/a) [\cos (2\pi x/a) - \cos (2\pi y/a)] \\ \Delta_5: \phi_5 &= \begin{cases} \exp (2\pi i \xi z/a) \sin 2\pi x/a \\ \exp (2\pi i \xi z/a) \sin 2\pi y/a. \end{cases} \end{aligned} \quad (9.24)$$

We note that Δ_5 is twofold degenerate, as indicated by the character table, and that the E versus \mathbf{k} curve in Fig. 18 is labeled to correspond with Eq. (9.24). A similar procedure at the value $E = 1.0$ gives the following associated functions:

$$\begin{aligned}\Gamma_1: \phi_1 &= \cos(2\pi x/a) + \cos(2\pi y/a) + \cos(2\pi z/a) \\ \Gamma_{12}: \phi_{12} &= \begin{cases} \cos(2\pi x/a) - \cos(2\pi y/a) \\ \cos(2\pi z/a) - \frac{1}{2}[\cos(2\pi x/a) + \cos(2\pi y/a)] \end{cases} \\ \Gamma_{15}: \phi_{15} &= \begin{cases} \sin 2\pi x/a \\ \sin 2\pi y/a \\ \sin 2\pi z/a \end{cases}\end{aligned}$$

where the degeneracies again correspond to the characters in the first column of Table XI.

Finally, for completeness—and for future use—we have given the corresponding energy band diagram (Fig. 19), character system (Table XVI),

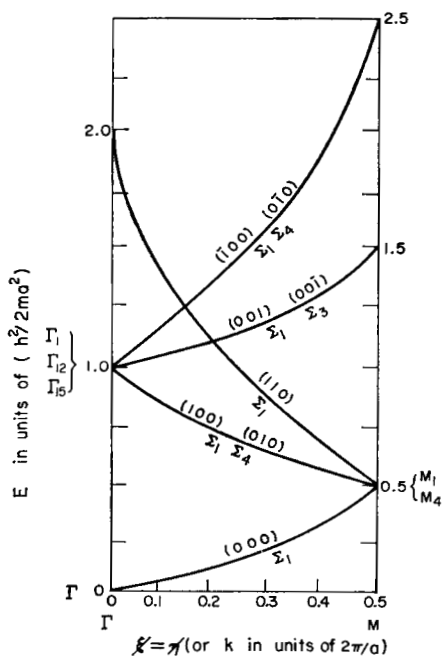


FIG. 19. Free electron energy bands along the Σ -axis of the simple cubic lattice.

TABLE XVI. CHARACTER SYSTEM FOR THE Σ -AXIS OF A SIMPLE CUBIC LATTICE

	E	C_2	JC_4^2	JC_2	Associated d functions
Σ_1	1	1	1	1	xy, z^2
Σ_2	1	1	-1	-1	$yz - xz$
Σ_3	1	-1	-1	1	$yz + xz$
Σ_4	1	-1	1	-1	$x^2 - y^2$
	xyz	$yx\bar{z}$	$xy\bar{z}$	yxz	

and compatibility relations (Table XVII) for the Σ -axis. Figures 18 and 19 have the same scale and the left-hand edges should, of course, match.

10. THE TIGHT-BINDING APPROXIMATION FOR BETA-BRASS

The tight-binding calculation on beta-brass made by Amsterdam⁹ is an excellent illustration of the power, and limitations, of group theory in the determination of energy-band structure. His treatment is based on the assumption that the conduction band arises from the ten $3d$ electrons of copper and zinc. Hence, the five d -functions are used to form the integrals $(\phi_n^* | V' | \phi_m)$. As an example of the treatment of the resulting secular determinants, consider the calculation for the Σ -axis of Fig. 17. As already stated, we shall treat the copper-zinc interactions like those of third-nearest neighbors in a simple cubic lattice of edge a and the copper-copper interactions as nearest neighbors in a lattice of edge $2a$.

TABLE XVII. COMPATIBILITY RELATIONS FOR THE Σ -AXIS OF A SIMPLE CUBIC LATTICE

$\Gamma_1 \rightarrow \Sigma_1$	$\Gamma_1' \rightarrow \Sigma_2$
$\Gamma_2 \rightarrow \Sigma_4$	$\Gamma_2' \rightarrow \Sigma_3$
$\Gamma_{12} \rightarrow \Sigma_1$	$\Gamma_{12}' \rightarrow \Sigma_2 + \Sigma_3$
$\Gamma_{15}' \rightarrow \Sigma_2 + \Sigma_3 + \Sigma_4$	$\Gamma_{15} \rightarrow \Sigma_1 + \Sigma_3 + \Sigma_4$
$\Gamma_{25}' \rightarrow \Sigma_1 + \Sigma_2 + \Sigma_3$	$\Gamma_{25} \rightarrow \Sigma_1 + \Sigma_2 + \Sigma_4$
$M_1 \rightarrow \Sigma_1$	$M_1' \rightarrow \Sigma_2$
$M_2 \rightarrow \Sigma_4$	$M_2' \rightarrow \Sigma_3$
$M_3 \rightarrow \Sigma_1$	$M_3' \rightarrow \Sigma_2$
$M_4 \rightarrow \Sigma_4$	$M_4' \rightarrow \Sigma_3$
$M_5 \rightarrow \Sigma_2 + \Sigma_3$	$M_5' \rightarrow \Sigma_1 + \Sigma_4$

Now let us establish the form of the secular equation which results from the use of the solution given in (5.13). The ϕ_n are the d -functions, denoted as ϕ_1 through ϕ_5 . We can then write (5.13) in the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{n,s} B_{ns} \psi_{n\mathbf{k}} \tag{10.1}$$

by using (5.12). The sum on the right of (10.1) involves ten terms—five each for Cu and for Zn—since the unit cell contains one copper and one zinc atom. Substituting (10.1) in the Schrödinger equation, multiplying by each of the ten complex conjugates $\psi_{m\mathbf{k}}^*$, and integrating gives

$$\sum B_{ns} \left[\int \left\{ \psi_{m\mathbf{k}}^* [(-\hbar^2/2m)\nabla^2 + V] \psi_{n\mathbf{k}} - E \int \psi_{m\mathbf{k}}^* \psi_{n\mathbf{k}} \right\} d\tau \right] = 0.$$

Equating the determinants of the coefficients of the B_{ns} to zero, this reduces to a 10×10 secular equation. A typical diagonal term in this determinant has the form $[(\phi_{1C} | V' | \phi_{1C}) - E]$, where ϕ_{1C} is one of the d functions for the Cu atom and V' is defined in Section 4. A typical off-diagonal term would be $(\phi_{1C} | V' | \phi_{2Z})$, but many of these terms vanish and the secular equation can be written as

		Cu					Zn					
		xy	yz	zx	x^2-y^2	z^2	xy	yz	zx	x^2-y^2	z^2	
Cu	xy	$G-E$	0	0	0	0	M	0	0	0	Q	}
	yz	0	$H-E$	0	0	0	0	M	P	0	0	
	zx	0	0	$H-E$	0	0	0	P	M	0	0	
	x^2-y^2	0	0	0	$K-E$	0	0	0	0	N	0	
	z^2	0	0	0	0	$L-E$	Q	0	0	0	N	
Zn	xy	M	0	0	0	Q	$D-E$	0	0	0	0	
	yz	0	M	P	0	0	0	$D-E$	0	0	0	
	zx	0	P	M	0	0	0	0	$D-E$	0	0	
	x^2-y^2	0	0	0	N	0	0	0	$D-E$	0	0	
	z^2	Q	0	0	0	N	0	0	0	0	$D-E$	

$= 0$

(10.2)

where the order of the rows and columns is arbitrary, and where the non-vanishing elements of the determinant are defined by

$$\begin{aligned}
 (xyc \mid V' \mid xyz) &= G \\
 (yzc \mid V' \mid yzc) &= (xzc \mid V' \mid xzc) = H \\
 (x^2 - yc^2 \mid V' \mid x^2 - yc^2) &= K \\
 (zc^2 \mid V' \mid zc^2) &= L \\
 (xyz \mid V' \mid xyz) &= (yzz \mid V' \mid yzz) = (zxz \mid V' \mid xzx) \\
 &= (x^2 - yz^2 \mid V' \mid x^2 - yz^2) = (zz^2 \mid V' \mid zz^2) = D \\
 (xyc \mid V' \mid xyz) &= (xyz \mid V' \mid xyc) = (yzc \mid V' \mid yxz) \\
 &= (zxc \mid V' \mid xzx) = M \\
 (x^2 - yc^2 \mid V' \mid x^2 - yz^2) &= (zc^2 \mid V' \mid zz^2) = N \\
 (yzc \mid V' \mid xzx) &= P \\
 (xyc \mid V' \mid zz^2) &= Q.
 \end{aligned} \tag{10.3}$$

To show why the determinant of Eq. (10.2) has the form indicated,

TABLE XVIII. TERMS IN THE SECULAR EQUATION FOR THE Σ -AXIS OF BETA-BRASS

Zn-Zn

$$D = d_0$$

Cu-Cu

$$(xy/xy) = G = d_0 + 4(dd\pi)_1 \cos 2\xi + 2(dd\delta)_1$$

$$(yz/yz) = (zx/zx) = H = d_0 + 2(dd\pi)_1 (1 + \cos 2\xi) + 2(dd\delta)_1 \cos 2\xi$$

$$(x^2 - y^2/x^2 - y^2) = K = d_0 + 3(dd\sigma)_1 \cos 2\xi + (dd\delta)_1 (\cos 2\xi + 2)$$

$$(3z^2 - r^2/3z^2 - r^2) = L = d_0 + (dd\sigma)_1 (\cos 2\xi + 2) + 3(dd\delta)_1 \cos 2\xi$$

Cu-Zn

$$(xy/xy) = (yz/yz) = (zx/zx) = M$$

$$= [(8/3)(dd\sigma)_3 + (16/9)(dd\pi)_3 + (32/9)(dd\delta)_2] \cos^2 \xi$$

$$(x^2 - y^2/x^2 - y^2) = (3z^2 - r^2/3z^2 - r^2) = N$$

$$= [(16/3)(dd\pi)_3 + (8/3)(dd\delta)_3] \cos^2 \xi$$

$$(yz/zx) = P = [-(8/3)(dd\sigma)_3 + (8/9)(dd\pi)_3 + (16/9)(dd\delta)_3] \sin^2 \xi$$

$$(xy/3z^2 - r^2) = Q = (16/3\sqrt{3})[(dd\pi)_3 - (dd\delta)_3] \sin^2 \xi$$

we turn to Table IX for an evaluation of the various elements. For example, the lower right-hand quadrant has only diagonal integrals D , and these are all the same. This follows from the fact that all the entries in Table IX involving the same two d functions are the sum of d_0 and terms involving $(dd\sigma)_1$, $(dd\sigma)_2$, $(dd\pi)_2$, etc. But we are neglecting Zn-Zn interactions, so that all these two-center integrals reduce to $d_0 = D$.

For the Cu-Cu terms, we use $\xi = \eta$ and $\zeta = 0$ to obtain as an example

$$G = (xy/xy) = d_0 + 2(dd\pi)_1 2 \cos 2\xi + 2(dd\delta)_1 \cos 0$$

or

$$G = d_0 + 4(dd\pi)_1 \cos 2\xi + 2(dd\delta)_1$$

where we have replaced ξ by 2ξ to incorporate the fact that the copper atoms are separated by a distance $2a$, and where only nearest-neighbor terms have been retained. Similarly,

$$H = (yz/yz) = d_0 + 2(dd\pi)_1 (\cos 2\xi + 1) + 2(dd\delta)_1 \cos 2\xi = (zx/zx).$$

Carrying on in this fashion we obtain Table XVIII, which lists all the nonvanishing elements. Note that for the Cu-Zn entries, the lattice constant is a (rather than $2a$) and all terms except those for third-nearest neighbors have been dropped.

The secular determinant can now be rearranged to get it in the block form

xyz	xyz	zc^2	zz^2	x^2-yc^2	x^2-yz^2	yzc	yzz	xzc	xzz		
$G-E$	M	0	Q								
M	$D-E$	Q	0								
0	Q	$L-E$	N								
Q	0	N	$D-E$								
				$K-E$	N						
				N	$D-E$						
				$H-E$	M					0	P
				M	$D-E$					P	0
				0	P	$H-E$	M				
				P	0	M	$D-E$				

=0

TABLE XIX. THE QUANTITIES $R\phi$ FOR d -FUNCTIONS ON THE Σ -AXIS OF A SIMPLE CUBIC LATTICE

	E	C_2	JC_4^2	JC_2
xy	xy	yx	xy	yx
yz	yz	$-xz$	$-yz$	xz
xz	xz	$-yz$	$-xz$	yz
$x^2 - y^2$	$x^2 - y^2$	$-(x^2 - y^2)$	$x^2 - y^2$	$-(x^2 - y^2)$
z^2	z^2	z^2	z^2	z^2

The labeling of the rows is the same as that of the columns and all elements not written are zero.

We can use the methods of group theory to reduce the 4×4 subdeterminant in the lower right-hand corner. Using the information at the bottom of Table XVI, we calculate the way in which the five d functions will be affected by the symmetry operations associated with the Σ -axis, and this information is summarized in Table XIX. This table lists the quantities $R\phi$ of (9.18), and using the character system of Table XVI gives for the representation Σ_1 the following linear combinations:

$$xy: 1(xy) + 1(yx) + 1(xy) + 1(yx) = 4xy$$

$$yz: 1(yz) + 1(-xz) + 1(-yz) + 1(xz) = 0$$

$$xz: 1(xz) + 1(-yz) + 1(-xz) + 1(yz) = 0$$

$$x^2 - y^2: 1(x^2 - y^2) + 1(y^2 - x^2) + 1(x^2 - y^2) + 1(y^2 - x^2) = 0$$

$$z^2: 1(z^2) + 1(z^2) + 1(z^2) + 1(z^2) = 4z^2.$$

Hence, xy and z^2 belong to Σ_1 , but this representation is *not* degenerate (this point will be clarified below). Similarly, we find the other results in the last column of Table XVI, and we note that group theory has converted our five individual d functions into five linear combinations. Further, the functions belonging to different irreducible representations do not produce any elements in the secular determinant; that is, they do not *mix*. To see this, consider for example the integral $(yz - xz_C | V' | yz + xz_C)$. Then

$$\begin{aligned} (yz - xz_C | V' | yz + xz_C) &= (yz_C | V' | yz_C) - (xz_C | V' | xz_C) \\ &\quad + (yz_C | V' | xz_C) - (xz_C | V' | yz_C) \end{aligned}$$

and by (10.3) this expression vanishes. On the other hand, by similarly

expanding, we see that

$$(yz + xz_C | V' | yz + xz_C) = 2H$$

and

$$(yz + xz_C | V' | yz + xz_C) = 2M + 2P.$$

Dropping the factors of 2, the secular equation now becomes

$$xy_C \quad xyz \quad zc^2 \quad zz^2 \quad x^2 - yc^2 \quad x^2 - yz^2 \quad xz + yzc \quad xz + yzz \quad xz - yzc \quad xz - yzz$$

$G-E \quad M \quad 0 \quad Q$					=0	
$M \quad D-E \quad Q \quad 0$						
$0 \quad Q \quad L-E \quad N$						
$Q \quad 0 \quad N \quad D-E$						
				$K-E \quad N$		
				$N \quad D-E$		
				$H-E \quad M+P$		
				$M+P \quad D-E$		
						$H-E \quad M-P$
						$M-P \quad D-E$
$\underbrace{\hspace{10em}}_{\Sigma_1}$				$\underbrace{\hspace{10em}}_{\Sigma_4}$		$\underbrace{\hspace{10em}}_{\Sigma_3}$
						$\underbrace{\hspace{10em}}_{\Sigma_2}$

(10.4)

The application of group theory has thus reduced one of the 4×4 sub-determinants into a pair of 2×2 determinants, and this is as far as the theory takes us in this direction.

We note that this example is in accord with (4.1). The five d functions form a reducible representation, with characters as follows:

E	C_2	JC_4^2	JC_2
5	1	1	1

so that

$$n_k = [\Sigma \chi \chi_k / 4]$$

and

$$n_1 = 2, \quad n_2 = 1, \quad n_3 = 1, \quad n_4 = 1.$$

Then the irreducible representation Σ_1 is contained twice in the reducible representation and the other three are contained once. Also, the character for E in any irreducible representation automatically gives the degeneracy, and in the case of Σ_1 , we must therefore have two nondegenerate states, rather than a single, doubly degenerate one.

The application of group theory to the secular equation has thus eliminated one of the 4×4 determinants, and this is as far as we can go on a purely algebraic basis. It is now necessary to introduce numerical values in order to plot the E versus \mathbf{k} curves obtained from the LCAO method, and in addition, the fourth-order irreducible determinant must be expanded. In order to discuss a simpler numerical example, let us turn to the secular equation for the Δ -axis, which has the form

Cu					Zn					
xy	yz	zx	x^2-y^2	z^2	xy	yz	zx	x^2-y^2	z^2	
$K-E$ $J-E$ $J-E$ $M-E$ $R-E$	Z Z Z W W	Z Z Z W W	$D-E$ $D-E$ $D-E$ $D-E$ $D-E$	$D-E$ $D-E$ $D-E$ $D-E$ $D-E$	$=0$					

and, upon rearrangement, becomes

$$\begin{array}{cccccccccc}
 xy_c & xyz & yzc & yzz & zxc & zxz & x^2 - yc^2 & x^2 - yz^2 & xc^2 & xz^2 \\
 \hline
 \begin{array}{|c|c|} \hline K-E & Z \\ \hline Z & D-E \\ \hline \end{array} & & & & & & & & & \\
 & & \begin{array}{|c|c|} \hline J-E & Z \\ \hline Z & D-E \\ \hline \end{array} & & & & & & & \\
 & & & & \begin{array}{|c|c|} \hline J-E & Z \\ \hline Z & D-E \\ \hline \end{array} & & & & & \\
 & & & & & & \begin{array}{|c|c|} \hline M-E & W \\ \hline W & D-E \\ \hline \end{array} & & & \\
 & & & & & & & & \begin{array}{|c|c|} \hline R-E & W \\ \hline W & D-E \\ \hline \end{array} & \\
 \hline
 \end{array} = 0$$

$$\underbrace{\hspace{10em}}_{\Delta_2'} \quad \underbrace{\hspace{10em}}_{\Delta_5} \quad \underbrace{\hspace{10em}}_{\Delta_2} \quad \underbrace{\hspace{10em}}_{\Delta_1}$$

(10.5)

The elements of this determinant are listed in Table XX and the d functions associated with the irreducible representations along the Δ -axis are given in the right-hand column of Table XIII. This information was obtained by using the bottom row of Table XIII to set up a table analogous to Table XIX and then forming the projection operators belonging to each irreducible representation.

The determinant corresponding to the representation Δ_2' in (10.5) can be expanded to give

$$2E = K + D \pm [(D - K)^2 + 4Z^2]^{1/2}, \quad (10.6)$$

and substituting the expressions of Table XX yields the relation

$$\begin{aligned}
 2E = & d_{0c} + 4(dd\pi)_1 + 2(dd\delta)_1 \cos 2\zeta + d_{0z} \\
 & \pm [\{d_{0z} - d_{0c} - 4(dd\pi)_1 - 2(dd\delta)_1 \cos 2\zeta\}^2 \\
 & + (32/3)\{(dd\delta)_3 + (2/3)(dd\pi)_3 + (4/3)(dd\delta)_3\}^2]^{1/2}.
 \end{aligned} \quad (10.7)$$

TABLE XX. TERMS IN THE SECULAR EQUATION FOR THE Δ -AXIS OF BETA-BRASS

Zn-Zn

$$D = d_0$$

Cu-Cu

$$(xy/xy) = K = d_0 + 4(dd\pi)_1 + 2(dd\delta)_1 \cos 2\zeta$$

$$(yz/yz) = J = (zx/zx) = d_0 + 2(dd\pi)_1 (1 + 2 \cos 2\zeta) + 2(dd\delta)_1$$

$$(x^2 - y^2/x^2 - y^2) = M = d_0 + d(dd\sigma)_1 + (dd\delta)_1 (1 + 2 \cos 2\zeta)$$

$$(3z^2 - r^2/3z^2 - r^2) = R = d_0 + (dd\sigma)_1 (1 + 2 \cos 2\zeta) + 3(dd\delta)_1$$

Cu-Zn

$$(xy/xy) = (yz/yz) = (xz/xz) = Z$$

$$= [(8/3)(dd\sigma)_3 + (16/9)(dd\pi)_3 + (32/9)(dd\delta)_3] \cos \zeta$$

$$(x^2 - y^2/x^2 - y^2) = W = (3z^2 - r^2/3z^2 - r^2)$$

$$= [(16/3)(dd\pi)_3 + (8/3)(dd\delta)_3] \cos \zeta$$

To assign values to the nearest-neighbor integrals in (10.7), Amsterdam⁹ refers to an argument of Slater and Koster,⁸ which in turn, is based on calculations by Howarth¹⁶ for copper and Fletcher¹⁷ for nickel. In the first place, it is assumed that $(dd\sigma)$, $(dd\pi)$, and $(dd\delta)$ bear an identical relation to one another in copper, nickel, and beta-brass, using as a justification the fact that we are dealing only with valence electrons and the specific nature of the core is not too important. Now Fletcher was able to evaluate integrals of this type by using an analytical expression for $V'(r)$ obtained from a Hartree self-consistent calculation on Cu, and Amsterdam quotes the ratios as

$$(dd\pi) = -0.54(dd\sigma), \quad (dd\delta) = 0.82(dd\sigma). \quad (10.8)$$

Substituting (10.8) into (10.7), we obtain

$$\begin{aligned} E_r = & (dd\sigma)_1(0.016 \cos 2\zeta - 2.16) \\ & \pm [(d_{0z} - d_{0c}) + (dd\sigma)_1 (2.16 - 0.016 \cos 2\zeta)^2 \\ & + 4(dd\sigma)_3 \cos \zeta]^2]^{1/2} \end{aligned} \quad (10.9)$$

where $E_r = 2E - d_{0z} - d_{0c}$ is the reduced energy for this calculation.

¹⁶ D. J. Howarth, *Proc. Roy. Soc.* **A220**, 513 (1953).

¹⁷ G. C. Fletcher, *Proc. Phys. Soc. (London)* **A65**, 192 (1952).

To estimate the term $(d_{0z} - d_{0c})$ inside the radical, we use the $3d$ atomic levels of -10.6 and -3.3 eV and work functions of 4.3 and 5.6 eV for Zn and Cu, respectively, to obtain an energy difference of

$$[-14.9 - (-8.9)] \text{ eV} = -6.0 \text{ eV} = -0.44 \text{ Ry.} \quad (10.10)$$

Assuming that the energy difference in the brass lattice is only slightly different from that for the free atoms permits us to use this value for $(d_{0z} - d_{0c})$.

Finally, to estimate $(dd\sigma)_1$ and $(dd\sigma)_3$, we use the value

$$(dd\sigma) = -0.025 \text{ Ry}$$

as determined for Ni, and then use another Slater-Koster argument; namely that these integrals for other metals should vary inversely as the distance between the ion-core "surfaces." These distances, in turn, are given as follows:

$$\text{Ni } 2.5 \text{ \AA}, \quad \text{Cu } 3.0 \text{ \AA}, \quad \text{CuZn } 2.6 \text{ \AA}.$$

Hence

$$(dd\sigma)_1 = -0.030 \text{ \AA}, \quad (dd\sigma)_3 = -0.026 \text{ \AA}. \quad (10.11)$$

The values of (10.10) and (10.11) when substituted into (10.9) show that

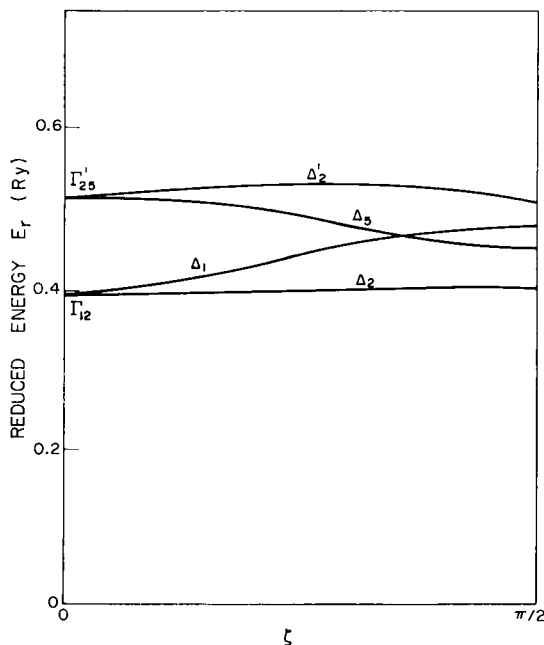


FIG. 20. Tight-binding energy bands along the Δ -axis of beta-brass.

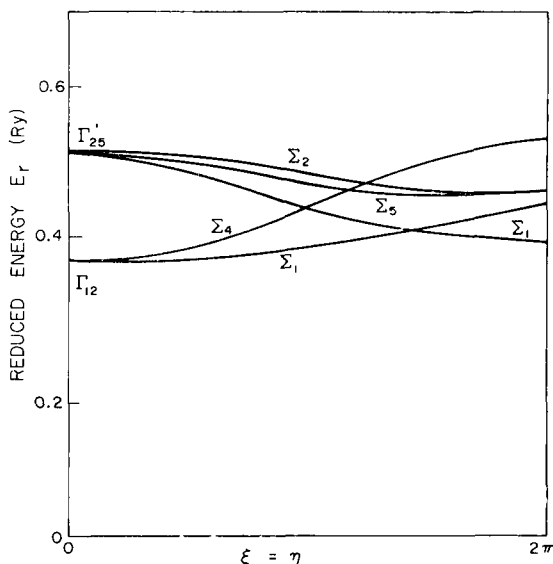


FIG. 21. Tight-binding energy bands along the Σ -axis of beta-brass.

(a) $E_r = -0.44 + 0.55$ at $\zeta = 0$ and that (b) E_r is essentially constant as ζ goes from 0 to $\pi/2$, since the terms in $\cos \zeta$ are negligible. The curve corresponding to the positive sign is plotted in Fig. 20. Going to the next determinant, the one for Δ_5 , we find in the same way that E_r starts at 0.55 but falls to about 0.41 at $\zeta = \pi/2$. The figure also shows the Δ_2 and Δ_1 curves, and we note the agreement with the compatibility relations. Figure 21 shows the corresponding results for the Σ -axis, and in this case, the fourth-order determinant was worked out on a computer.

V. The Band Structure of Tellurium

11. THE SPACE GROUP FOR TELLURIUM

Tellurium is a semiconducting element lying in column VIa of the Periodic Table. The other members of this column are the insulators oxygen and sulfur, the semiconductor selenium, and polonium, a metal. Figure 22 shows a perspective view of the tellurium crystal and Fig. 23 is a view along the c -axis of the previous figure.

The atoms are arranged in spiral chains, with three atoms to each turn, so that the fourth atom lies directly over the first, the fifth is directly over the second, and so on. The chains are arranged to form hexagons, but the symmetry of the crystal is trigonal because of the threefold nature of

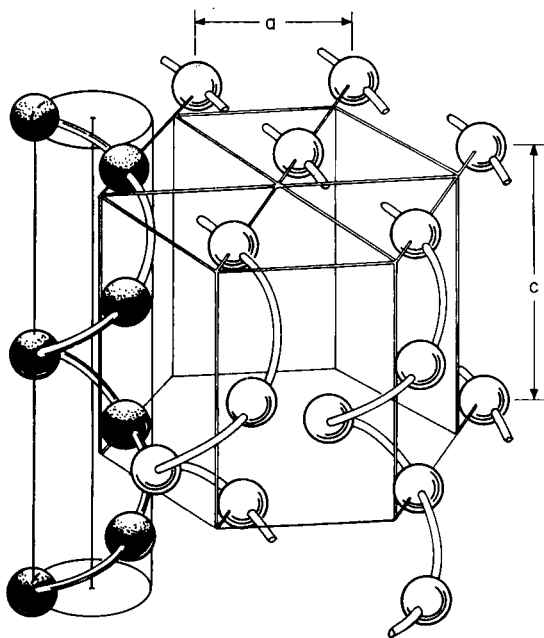


FIG. 22. The crystal structure of tellurium.

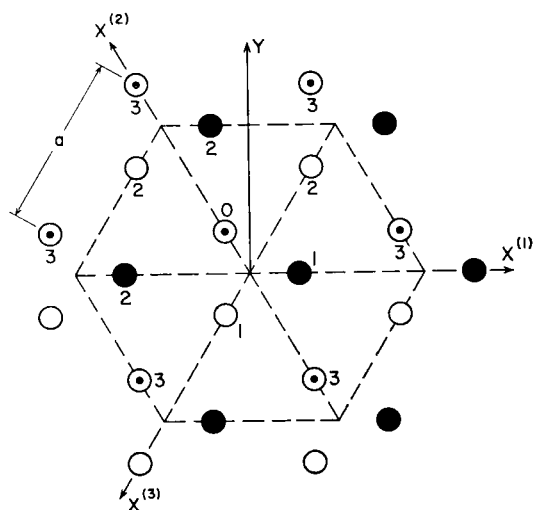


FIG. 23. The tellurium lattice viewed along the screw axis. ●, first atom in chain; ⊙, second atom in chain; ○, third atom in chain; 1, first, 2, second, 3, third nearest neighbor to 0 atom.

the chains. The spiral arrangements are called *screw axes*, since they are generated by combining a 120° rotation with a displacement of $c/3$ along the rotation axis.

The symmetry operations of the tellurium lattice are related to those of the group C_{3v} of Table I. They are

- (1) E , the identity.
- (2) C_3 , a 120° rotation about the z -axis, followed by a translation $c/3$ along the axis.
- (3) C_3^2 .
- (4) $C_2^{(1)}$, a 180° rotation about the axis $X^{(1)}$ of Fig. 23, followed by a translation $c/3$.
- (5) $C_2^{(2)}$, a 180° rotation about $X^{(2)}$, followed by a translation 0 .
- (6) $C_2^{(3)}$, a 180° rotation about $X^{(3)}$, followed by a translation $2c/3$.

These six operations do not form a group, however, because of the screw axes. For example, $C_3C_3^2$ (or $C_3^2C_3$) is equivalent to a pure translation c , which is not in the above list. We shall now show how to generate the point group for tellurium.

Let us designate a displacement of magnitude c along the z -axis by T and consider the effect of T and an operation like $C_2^{(1)}$ taken in either order. Figure 24a represents three consecutive atoms in a chain, with the three levels in the c -direction labeled 0, 1, and 2. This denotes their height above the xy -plane as 0, $c/3$ and $2c/3$, respectively. The corresponding atoms are

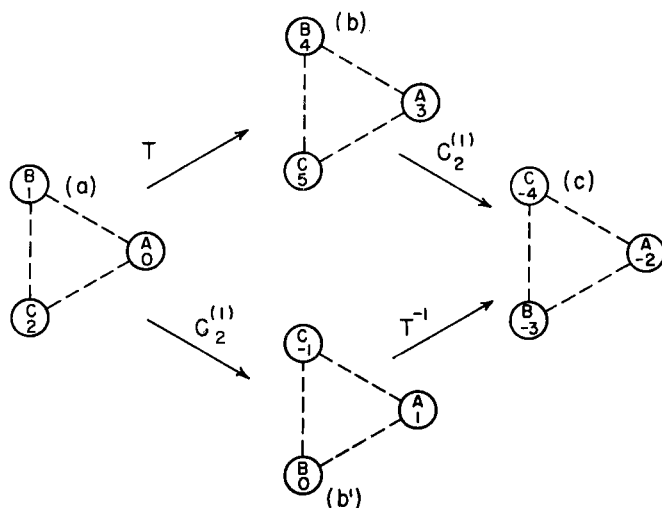


FIG. 24. A geometrical demonstration of the relation $T^2 = E$.

TABLE XXI. MULTIPLICATION TABLE FOR THE SPACE GROUP OF TELLURIUM

			First operation													
					K_1	K_2	K_3		K_4		K_5			K_6		
			E	T	C_3	TC_3^2	C_3^2	TC_3	$C_2^{(1)}$	$TC_2^{(2)}$	$TC_2^{(3)}$	$TC_2^{(1)}$	$C_2^{(2)}$	$C_2^{(3)}$		
Second operation	K_1	E	E	T	C_3	TC_3^2	C_3^2	TC_3	$C_2^{(1)}$	$TC_2^{(2)}$	$TC_2^{(3)}$	$TC_2^{(1)}$	$C_2^{(2)}$	$C_2^{(3)}$		
	K_2	T	T	E	TC_3	C_3^2	TC_3^2	C_3	$TC_2^{(1)}$	$C_2^{(3)}$	$C_2^{(3)}$	$C_2^{(1)}$	$TC_2^{(2)}$	$TC_2^{(3)}$		
	K_3	C_3	C_3	TC_3	C_3^2	E	T	TC_3^2	$C_2^{(3)}$	$TC_2^{(1)}$	$C_2^{(2)}$	$TC_2^{(3)}$	$C_2^{(1)}$	$TC_2^{(2)}$		
		TC_3^2	TC_3^2	C_3^2	E	TC_3	C_3	T	$C_2^{(2)}$	$C_2^{(3)}$	$TC_2^{(1)}$	$TC_2^{(2)}$	$TC_2^{(3)}$	$C_2^{(1)}$		
	K_4	C_3^2	C_3^2	TC_3^2	T	C_3	TC_3	E	$TC_2^{(2)}$	$TC_2^{(3)}$	$C_2^{(1)}$	$C_2^{(2)}$	$C_2^{(3)}$	$TC_2^{(1)}$		
		TC_3	TC_3	C_3	TC_3^2	T	E	C_3^2	$TC_2^{(3)}$	$C_2^{(1)}$	$TC_2^{(2)}$	$C_2^{(3)}$	$TC_2^{(1)}$	$C_2^{(2)}$		
	K_5	$C_2^{(1)}$	$C_2^{(1)}$	$TC_2^{(1)}$	$C_2^{(2)}$	$C_2^{(3)}$	$TC_2^{(3)}$	$TC_2^{(2)}$	E	TC_3	C_3^2	T	C_3	TC_3^2		
		$TC_2^{(2)}$	$TC_2^{(2)}$	$C_2^{(2)}$	$C_2^{(3)}$	$TC_2^{(1)}$	$C_2^{(1)}$	$TC_2^{(3)}$	C_3^2	E	TC_3	TC_3^2	T	C_3		
		$TC_2^{(3)}$	$TC_2^{(3)}$	$C_2^{(3)}$	$TC_2^{(1)}$	$C_2^{(2)}$	$TC_2^{(2)}$	$C_2^{(1)}$	TC_3	C_3^2	E	C_3	TC_3^2	T		
	K_6	$TC_2^{(1)}$	$TC_2^{(1)}$	$C_2^{(1)}$	$TC_2^{(2)}$	$TC_2^{(3)}$	$C_2^{(3)}$	$C_2^{(2)}$	T	C_3	TC_3^2	E	TC_3	C_3^2		
		$C_2^{(2)}$	$C_2^{(2)}$	$TC_2^{(2)}$	$TC_2^{(3)}$	$C_2^{(1)}$	$TC_2^{(1)}$	$C_2^{(3)}$	TC_3^2	T	C_3	C_3^2	E	TC_3		
		$C_2^{(3)}$	$C_2^{(3)}$	$TC_2^{(3)}$	$C_2^{(1)}$	$TC_2^{(2)}$	$C_2^{(2)}$	$TC_2^{(1)}$	C_3	TC_3^2	T	TC_3	C_3^2	E		

labeled A , B , and C . The result of T is shown in Fig. 24b, where the new levels are denoted 3, 4, and 5 to indicate that each atom has moved a distance $3c/3$ along the z -axis. Applying $C_2^{(1)}$ to this arrangement gives the result shown in Fig. 24c. Now, going in reverse order, $C_2^{(1)}$ produces Fig. 24b' and the inverse T^{-1} of T once again gives Fig. 24c, so that

$$C_2^{(1)} T = T^{-1} C_2^{(1)}.$$

From this we may easily show that

$$T C_2^{(1)} T = T^{-1} C_2^{(1)} T^{-1} \quad (11.1)$$

since

$$T C_2^{(1)} T = T T^{-1} C_2^{(1)} = C_2^{(1)}$$

and

$$C_2^{(1)} T T^{-1} = T^{-1} C_2^{(1)} T^{-1} = C_2^{(1)}.$$

But (11.1) may also be obtained from the assumption that

$$T^2 = E$$

or

$$T = T^{-1}, \quad (11.2)$$

as can be seen if we multiply (11.2) by $C_2^{(1)}$ on the right, and then by itself on the right.

Now (11.2) has an interesting physical interpretation: if we think of the tellurium chain as similar to a helical spring, we can regard it as saying that a displacement of one turn is physically the same in either direction, and this has meaning for an infinitely long structure. Equation (11.2) enables us to form a closed group of operations by combining T with C_3 and the $C_2^{(1)}$ to obtain the Cayley table, Table XXI. This table shows that the twelve operations form six classes, in accordance with the definition of Eq. (1.1).

12. THE FREE-ELECTRON BANDS AND THE COMPATIBILITY RELATIONS

The shape of the Brillouin zone for tellurium is determined from an examination of Fig. 23. We see that any given atom (a dark circle, for example) has for its nearest neighbors of the same type a hexagon in the

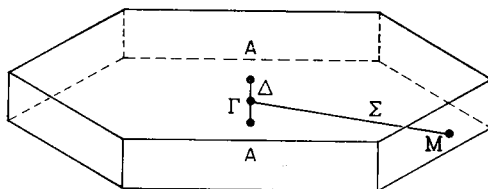


FIG. 25. The Brillouin zone for tellurium.

electron approximation. For example, along the Δ -axis of Fig. 25 $\xi = \eta = 0$ and (12.3) reduces to

$$E = (\hbar^2/2ma^2)[l_1^2 + (l_1 + 2l_2)^2/3 + (a/c)^2(\xi - l_3)^2]. \quad (12.4)$$

For tellurium, the value of (a/c) is very close to 0.75, and we can plot E versus ξ for various combinations of (l_1, l_2, l_3) , as shown in Fig. 26. Note that the curve for which $E = 4/3$ at $\xi = 0$ has six possible sets of l values, the notation $(0\bar{1}0)$ being used for $l_1 = 0, l_2 = -1, l_3 = 0$, and this energy curve is therefore sixfold degenerate. The valence electrons of tellurium have the configuration $5s^2 5p^4$, and since there are three non-equivalent atoms in a single turn of the spiral chain, this corresponds to

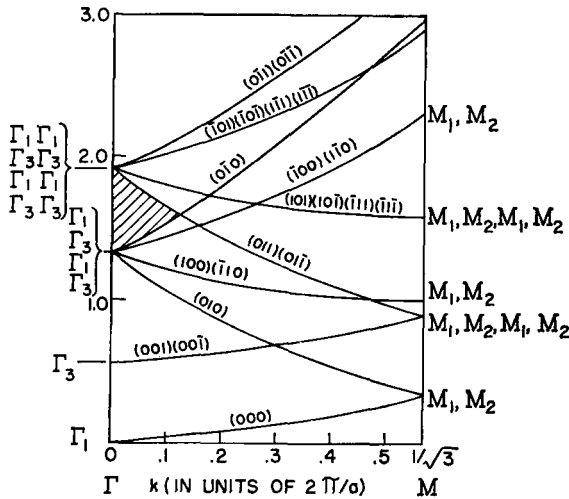


Fig. 27. Free electron energy bands along the Σ -axis for tellurium.

eighteen valence electrons. Considering spin allows two electrons per energy level so that the ninth level from the bottom represents the valence band, thus determining the position of the forbidden gap which has been shaded in. A similar calculation gives the E versus k curves along the ΓM direction, shown in Fig. 27.

Returning to Eq. (11.2), we can also give to it an interpretation based on the geometrical properties of the Brillouin zone. In our introductory discussion on symmetry, we considered the effect of various operations on the atoms which lie in direct space. In reciprocal space, however, what we are concerned with is the effect of the symmetry operations on the wave functions as well as the atoms. At the top of the Brillouin zone,

point $A(0, 0, \pi/c)$ of Fig. 25, a wave function of the form (9.1) will be

$$\psi_{\mathbf{k}}(z) = \exp(ikz)u_{\mathbf{k}}(z). \quad (12.5)$$

If we now perform the operation C_3 on this function three times, z becomes $z + c$, and

$$\psi_{\mathbf{k}} = \exp[ik(z + c)]u_{\mathbf{k}}(z) = -\psi_{\mathbf{k}}$$

since $u_{\mathbf{k}}$ is periodic with period c and

$$\exp[i\pi(z + c)/c] = -\exp(i\pi z/c).$$

A second such operation returns $\psi_{\mathbf{k}}$ to its original value, and at this point in the Brillouin zone we have an additional symmetry element T , a displacement of c along the z -axis, such that $T^2 = E$. Hence, in determining the character table by the method of Section 4, we use Table XXI in exactly the same way that we used Table I for the group C_{3v} , and there will be six irreducible representations since there are six classes. The result is shown in Table XXII, and this table also represents the character system associated with the point Γ , where (12.5) reduces to

$$\psi_0(z) = u_0(z)$$

so that the operation T has no effect on the character system. In other

TABLE XXII. CHARACTER TABLE FOR THE POINTS A AND Γ
(FOR THE POINT Γ , THE OPERATION T IS DELETED)

	$C_2^{(1)}$			$TC_2^{(1)}$		
	C_3		$TC_2^{(2)}$	TC_3	$C_2^{(2)}$	
	E	TC_3^2	$TC_2^{(1)}$	T	C_3^2	$C_2^{(1)}$
Γ_1	1	1	1	1	1	1
Γ_2	1	1	-1	1	1	-1
Γ_3	2	-1	0	2	-1	0
A_1	1	-1	1	-1	1	-1
A_2	1	-1	-1	-1	1	1
A_3	2	1	0	-2	-1	0

words, at the center of the Brillouin zone, the space group reduces to the point group, and the operation T is equivalent to E . Thus, the character system for Γ is the upper left-hand corner of Table XXII with T deleted and the three classes then become $K_1 = E$; $K_2 = C_3, C_3^2$; $K_3 = C_2^{(1)}, C_2^{(2)}, C_2^{(3)}$, as we would expect. Hence, at the point Γ , the screw axis does not enter the analysis, whereas at A it doubles the size of the group.

Now let us consider the situation at some point along the Δ -axis, excluding the end point Γ and A . Suppose for the moment that the only symmetry associated with an arbitrary point along this axis is the translational symmetry of the lattice. We can find the characters for the translational operation by considering a one-dimensional chain of N atoms bent into a circle to insure that the lattice is completely periodic. The only symmetry operation is the translation T from one atom to its neighbor, so that the group consists of $E, T, T^2, \dots, T^{N-1}$, and $T^N = E$. This group is *commutative* or *Abelian*; that is, $T^m T^n = T^n T^m$ for every m and n . It is simple to show that for such a group, every element is in a class by itself. Then all the representations are one-dimensional and there are N of them. If $D(T)$ denotes the determinants in the representations, they must obey

$$D^N(T) = 1 \quad (12.6)$$

and the solutions to this equation are

$$D(T) = 1^{1/N} = \exp(2\pi i l/N) \quad (12.7)$$

where

$$l = 0, 1, 2, \dots, N - 1.$$

The representations are

	E	T	T^2	\dots	T^{N-1}
Γ_0	1	1	1	\dots	1
Γ_1	1	$\exp[2\pi i/N]$	$\exp[4\pi i/N]$	\dots	$\exp[(N-1)2\pi i/N]$
\vdots					
\vdots					
\vdots					
Γ_{N-1}	1	$\exp[(N-1)2\pi i/N]$	$\exp[(N-1)4\pi i/N]$	\dots	$\exp[(N-1)^2 2\pi i/N]$

and this is also the character table, since all the representations are one-dimensional.

The above result shows that all the representations can be expressed in the form $\exp[2\pi i l/N]$. This can be rewritten as

$$\exp[2\pi i a(l/Na)] = \exp(ikR) \quad (12.8)$$

where a is the lattice constant and

$$k = 2\pi l/Na, \quad R = la. \quad (12.9)$$

To see the origin of (12.9), we apply the condition that the wave function (12.5) must also obey the cyclic boundary conditions, so that

$$\exp [ik(x + Na)]u(x + Na) = \exp (ikx)u(x)$$

or

$$\exp (ikNa) = 1$$

from which

$$k = 2\pi l/Na.$$

Using the definition (9.4) of the reciprocal lattice, $ab = 1$, and defining $R = la$ as a typical displacement, verifies (12.8).

Along the Δ -axis of tellurium, we have both translational and rotational symmetry. Considering first the rotational part, the symmetry operations are a 120° rotation, a 240° rotation, and a 360° rotation (equivalent to the unity operation). These three operations form a commutative group and, by the procedure outlined above, we can determine the characters to be the cube roots of unity, which are 1, ω , and ω^2 , where $\omega = \exp (2\pi i/3)$. The translational characters, from (12.8), have the form 1, δ , and δ^2 , where $\delta = \exp (ikR)$. We shall show below that the characters for the two types of operations can be combined by direct multiplication, leading to Table XXIII.

The compatibility relations for tellurium are somewhat complicated to obtain because of the dual nature of the characters. At Γ , the quantity δ in Table XXIII is unity, so that $\omega + \omega^2 = \omega^2 + \omega = 1$. It is seen then that $\Delta_2 + \Delta_3$ corresponds to Γ_3 , which we designate by

$$\Gamma_3 \rightarrow \Delta_2 + \Delta_3.$$

TABLE XXIII. CHARACTER TABLE FOR THE Δ -AXIS OF TELLURIUM^a

	E	C_3	C_3^2
Δ_1	1	δ	δ^2
Δ_2	1	$\omega\delta$	$\omega\delta^2$
Δ_3	1	$\omega^2\delta$	$\omega^2\delta^2$

^a $\omega = \exp (2\pi i/3)$; $\delta = \exp (ikR)$.

At A, we have $k = \pi/c$ and the translation R corresponds to $c/3$, so that

$$\delta = \exp [i(\pi/c)(c/3)] = e^{i2\pi/6}.$$

The character table for this particular point is then

	E	C_3	C_3^2
Δ_1	1	$\exp(2\pi i/6)$	$\exp(2\pi i/3)$
Δ_2	1	$\exp(2\pi i/2)$	$\exp(4\pi i/3)$
Δ_3	1	$\exp(5\pi i/6)$	$\exp(2\pi i)$

It is then easy to verify the compatibility relations of Table XXIV.

TABLE XXIV. COMPATIBILITY RELATIONS FOR THE Δ - AND Σ -AXIS OF TELLURIUM

$\Gamma_1 \rightarrow \Sigma_1 \rightarrow M_1$	
$\Gamma_2 \rightarrow \Sigma_2 \rightarrow M_2$	
$\Gamma_3 \rightarrow \Sigma_1 + \Sigma_2$	
$\Gamma_1 \rightarrow \Delta_1$	$\Delta_1 \rightarrow \Delta_2$
$\Gamma_2 \rightarrow \Delta_1$	$\Delta_2 \rightarrow \Delta_2$
$\Gamma_3 \rightarrow \Delta_2 + \Delta_3$	$\Delta_3 \rightarrow \Delta_1 + \Delta_3$

The functions we shall use for tellurium are those of (12.2). As an example, consider the functions at Γ for $1 = (001)$ or $(00\bar{1})$, which are

$$\psi = \exp(2\pi iz/c).$$

In computing the appropriate linear combinations at this point, we need consider only the six symmetry operations of Table I and can ignore the screw displacements, as we have already shown. However, the twofold degeneracy of Γ_3 makes it necessary to use the complete representations in Table II rather than the characters (this is about the only instance where it is necessary to know the matrices explicitly). Let

$$\begin{aligned} E\psi &= c^{2\pi iz/c} = \phi_1, & C_3\psi &= c^{2\pi i(z+c/3)/c} = \phi_2 = \omega\phi_1 & (\omega &= c^{2\pi i/3}) \\ C_3^2\psi &= \phi_3 = \omega^2\phi_1, & C_2^{(1)}\psi &= \phi_4 = c^{2\pi i(-z+c/3)} \\ C_2^{(2)}\psi &= \phi_5 = \omega\phi_4, & C_2^{(3)} &= \phi_6 = \omega^2\phi_4. \end{aligned}$$

If we write equation (9.18) in the form

$$\phi_i' = \sum_R \chi_i(R) R\phi_i \quad (12.10)$$

in order to distinguish the original and final functions, we obtain

$$\phi_1' = 1\phi_1 + 1\phi_2 + 1\phi_3 + 1\phi_4 + 1\phi_5 + 1\phi_6 = 0,$$

so that no function goes with Γ_1 . Similarly, nothing goes with Γ_2 and for Γ_3 we find the two linear combinations

$$\phi_3' = \begin{cases} \phi_1 - \phi_2/2 - \phi_3/2 + \phi_4 - \phi_5/2 - \phi_6/2 \\ (\sqrt{3}/2)(-\phi_2 + \phi_3 - \phi_5 + \phi_6). \end{cases}$$

This is what we would expect from Table XXII, and we may similarly show that functions for $z = \pm c$ belong only to the representations A_1 , A_2 , or A_3 .

13. SPACE GROUPS

The arguments which we have used to determine the compatibility relations have implications in terms of the connection between group theory and the nature of the Schrödinger equation which we would like to explore briefly. In one-dimensional form, the wave equation is

$$[(-\hbar^2/2m)(d^2/dx^2) + V(x)]\psi(x) = E\psi(x) \quad (13.1)$$

and we shall consider the problem of solving this for a linear crystal having $N + 1$ atoms which are numbered $0, 1, 2, \dots, N$ and spaced a distance a apart. Let us apply the operator T to (13.1), where T is a displacement of magnitude a . Then

$$T\left[\frac{d^2}{dx^2}\psi(x)\right] = \frac{d^2}{d(x+a)^2}\psi(x+a) = \frac{d^2}{dx^2}\psi(x+a)$$

since

$$\frac{d(x+a)}{dx} \frac{d}{d(x+a)} = \frac{d}{dx}.$$

Also

$$T[V(x)\psi(x)] = V(x+a)\psi(x+a) = V(x)\psi(x+a)$$

since $V(x)$ has a period a . Hence we may write

$$TH\psi(x) = H\psi(x+a) = HT\psi(x) \quad (13.2)$$

so that the operators T and H commute. Further, we have

$$T\psi(x) = \psi(x+a).$$

Applying T a second time gives

$$T^2\psi(x) = \psi(x + 2a),$$

and for N operations,

$$T^N\psi(x) = \psi(x + Na). \quad (13.3)$$

Now, if the Born-von Karman cyclic conditions are used by bending the chain into a circle with the atoms labeled 0 and N coinciding, then (13.3) reduces to

$$T^N = 1$$

or

$$T = \exp(2\pi il/N) \quad [l = 0, 1, \dots, N - 1] \quad (13.4)$$

which has the same form as (12.7).

Equation (13.3) is thus equivalent to

$$T^N\psi(x) = \exp(i2\pi l/N)\psi(x) \quad (13.5)$$

which we may regard as an eigenvalue equation; i.e., the eigenvalues of the operator T are the characters of the irreducible representations of the Abelian translation group T , T^2 , T^{N-1} , E . We also note that this group is one which leaves the Hamiltonian invariant. From (12.9), we see that (13.5) may also be written as

$$T^N\psi(x) = \exp(ika)\psi(x), \quad (13.6)$$

thus demonstrating the logic behind the Bloch form of the wave functions. We note that this relation is analogous to the vector form of Taylor's theorem, namely

$$f(\mathbf{r} + \mathbf{a}) = \exp(i\mathbf{a} \cdot \nabla) f(\mathbf{r})$$

where the term $\exp(i\mathbf{a} \cdot \nabla)$ is known as the displacement operator. Koster¹⁴ has shown how to extend these results to three dimensions. For a lattice determined by (9.3) written in the form

$$\mathbf{R}_n = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3 \quad (13.7)$$

and with N atoms along each of the three principal directions, there will be three one-dimensional groups with representations of the form

$$\exp[i(2\pi l_1/N)] = \exp[i(2\pi l_1/N_{1a_1})a_1] = \exp(ik_1a_1) \quad (13.8)$$

where

$$k_1 = 2\pi l_1/N_{1a_1} \quad (13.9)$$

in accordance with (12.9). Multiplying three such relations together the

representations are then $\exp(i\mathbf{k} \cdot \mathbf{R}_n)$ where

$$\mathbf{k} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3 \quad (13.10)$$

since

$$\mathbf{a}_i \cdot \mathbf{b}_j = \delta_{ij}. \quad (9.4)$$

Then the three-dimensional equation corresponding to (13.3) is

$$[E, \mathbf{R}_n] \psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{R}_n) \psi_{\mathbf{k}}(\mathbf{r}) \quad (13.11)$$

where the symbol $[\Theta, \mathbf{R}_n]$ is used to denote a space group formed by combining a point group Θ and a translational group \mathbf{R}_n . Hence, (13.11) is an eigenvalue equation for the translational group of the crystal. Koster also points out the vector \mathbf{k} of (13.10) defines a set of points in the first Brillouin zone, each one of which corresponds to an irreducible representation of the translation group, and since \mathbf{k} is specified by k_1 , k_2 , and k_3 , which by (13.9) may have N values each, there are N^3 such points. This idea may be expressed in another form if we assume that \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 define a unit cell in the crystal. Then there will be N^3 of these cells so that the number of \mathbf{k} values—or the number of states—in the Brillouin zone is numerically equal to the number of unit cells in the direct lattice.

The discussion of compatibility relations we have given above leads also to the introduction of some additional group theoretical concepts. Let us return to the group C_{3v} of Table I and define the concept of a *coset* of a subgroup. Let H be a subgroup of C_{3v} and let X be an element of C_{3v} not in H . Then the set HX is called the *right coset* of H and the set XH is the *left coset*. For example, if

$$H = (E, D, F) \quad \text{and} \quad X = A$$

then

$$HX = (E, D, F)A = (A, C, B).$$

We note that any group can be completely broken down into a given subgroup and all its nonequivalent cosets. If

$$H = (E, A)$$

then

$$\begin{aligned} C_{3v} &= (E, A) + (E, A)(B \text{ or } D) + (E, A)(C \text{ or } F) \\ &= (E, A) + (B, D \text{ or } D, B) + (C, F \text{ or } F, C). \end{aligned}$$

Next, we define an *invariant subgroup* as one composed of complete classes; e.g., (E, D, F) is an invariant subgroup, but (E, A) is not.

Now consider an invariant subgroup I and form all its nonequivalent cosets IX, IY, \dots . The set I, IX, IY, \dots forms a hypergroup called the *factor group* (or *quotient group*) in which I plays the role of the unit ele-

ment. To be more explicit, let

$$I = (E, D, F).$$

The only nonequivalent coset is

$$(E, D, F)A = (A, C, B)$$

so that

$$\begin{aligned} C_{3v} &= (I, IA) \\ &= [(E, D, F), (A, C, B)]. \end{aligned}$$

Now let us treat I and IA as two single elements of a hypergroup of order 2. To multiply the elements of this factor group, we use the rule, for I^2 as an example, that

$$\begin{aligned} II &= (E, D, F)(E, D, F) = (E^2, ED, EF, DE, D^2, DF, FE, FD, F^2) \\ &= (E, D, F, D, F, E, F, E, D) = I. \end{aligned} \quad (13.12)$$

This procedure defines the *direct product* of two sets, which is the product of each element in one set by every element in the other set. In a similar fashion we can obtain the Cayley table

$$\begin{array}{c|cc} & I & IA \\ \hline I & I & IA \\ IA & IA & I \end{array}$$

showing that (a) the two elements I and IA can be treated as a group and (b) the invariant subgroup I acts like a unit element for the factor group. A notation commonly used for a factor group is

$$(I, IA) = (C_{3v}/I).$$

Then we have

$$(C_{3v}/I)I = (I, IA)I = C_{3v}$$

and this expression shows why the factor group is also called a quotient group.

The physical significance of the factor group comes from the statement (which we shall justify) that the space group of any crystal is a factor group, with the translational group corresponding to I and all the other symmetry elements to the remainder of the cosets. To verify this, we first recall the notation $[\Theta, T]$ introduced above for a symmetry operation with a rotational part Θ and a translational part T . The product of two

such operations is

$$[\Theta_2, T_2][\Theta_1, T_1] = [\Theta, T] \quad (13.13)$$

where

$$\Theta = \Theta_2\Theta_1.$$

But

$$T = \Theta_2 T_1 + T_2$$

since the operation Θ_2 will act on the translation T_1 . Further, if S is a symmetry operation $[\Theta, T]$, then its inverse is

$$S^{-1} = [\Theta^{-1}, -T\Theta^{-1}], \quad (13.14)$$

for by (13.13)

$$\begin{aligned} SS^{-1} &= [\Theta\Theta^{-1}, \Theta(-T\Theta^{-1}) + T] \\ &= [E, E] = S^{-1}S. \end{aligned}$$

Now consider a symmetry operation of the form $S^{-1}TS$, which can be expanded as

$$\begin{aligned} S^{-1}TS &= [\Theta^{-1}, -T\Theta^{-1}][E, T][\Theta, T] \\ &= [\Theta^{-1}, -T\Theta^{-1}][\Theta, T + T] \\ &= [E, \Theta^{-1}(2T) - T\Theta^{-1}] \\ &= [E, \Theta^{-1}T]. \end{aligned} \quad (13.15)$$

But the last term in this relation is a pure translation and must be a member of the group of translations. Hence (13.15) is equivalent to

$$S^{-1}TS = T \quad (13.16)$$

so that the subgroup of translations is composed of complete classes and is hence an invariant subgroup.

The space group of any crystal is then a factor group, with T corresponding to I . In some cases, it is possible to obtain the space group from the translation group by taking the direct product. This is the situation for the seventy-three simple or *symmorphic* space groups—those involving the simple symmetry operations of pure translation and pure rotation. But the remaining space groups ($230 - 73 = 157$) involve compound elements; a translation plus a rotation yielding a screw axis or a translation and a reflection giving a *glide plane*. In this chapter we can consider the symmetry properties of only a few selected examples, but the classic series of papers by Seitz¹⁸ presents the symmetry properties of all the space groups.

Simple examples which illustrate some of these points are given by

¹⁸ F. Seitz, *Z. Krist.* **88**, 413 (1934); **90**, 289 (1935); **91**, 336 (1935); **94**, 100 (1936).

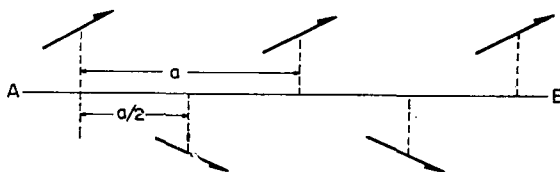


FIG. 28. A glide line.

Buerger.¹⁹ Figure 28 shows a glide operation with the line AB acting as a mirror (thus obtaining a glide line rather than a glide plane). Note that the glide operation must be repeated twice to obtain the original configuration, so that the lattice spacing is a , as shown. Now a group of such operations then has the form

$$E, \quad mt, \quad (mt)^2, \quad (mt)^3, \quad (mt)^4, \quad (mt)^5, \dots$$

where m is the mirror operation and t is a translation of $a/2$. Since $m^2 = E$, this can be written as

$$E, \quad mt, \quad t^2, \quad mt^3, \quad t^4, \quad mt^5, \dots$$

and if we let $T = t^2$, where T is a lattice translation, then the sequence becomes

$$E, \quad mt, \quad T, \quad mtT, \quad T^2, \quad mtT^2, \dots$$

or

$$(E, T, T^2, \dots)(mt, mtT, mtT^2, \dots)$$

showing that the original group contains the translation group as an invariant subgroup and that the remaining coset is the direct product of this group with the glide operation.

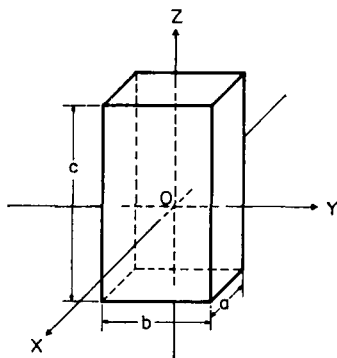


FIG. 29. A rectangular prism.

¹⁹ M. J. Buerger, "Elementary Crystallography." Wiley, New York, 1956.

Next, let us consider the group D_{2v} illustrated by the rectangular prism of Fig. 29. Each coordinate axis is a two-fold axis and each coordinate plane is a mirror plane. However, the group is completely specified by the operations

$$\begin{array}{ll} E & \text{the identity,} \\ C_2 & 180^\circ \text{ rotation about } OZ, \end{array} \quad \begin{array}{ll} m_x & \text{reflection in } YOZ \\ m_y & \text{reflection in } XOZ. \end{array}$$

Then the multiplication table is

	E	C_2	m_x	m_y
E	E	C_2	m_x	m_y
C_2	C_2	E	m_y	m_x
m_x	m_x	m_y	E	C_2
m_y	m_y	m_x	C_2	E

Now, if we have mirror operations, as in this example, or a screw axis, as found in tellurium, then we know that the unit cell must contain more than one atom—even in an elemental crystal—and its structure must reflect the basic symmetries of the crystal. We also note in the case of tellurium that each revolution of 120° has associated with it a translation of $c/3$ and in the same way, for the glide line of Fig. 28, there are two mirror operations per unit cell, each with an associated translation of magnitude $a/2$. Further, since the glide and screw operations have these associated translations the translations must satisfy a multiplication table of the same form as the pure rotation or mirror operations, since the direct product of the two gives the space group table. Further, what is true for the group operations is true for the characters as well, and this is the justification for Table XXIII, which represents the direct product of the translational and rotational characters.

We can substantiate the statement we have just made about the direct product of characters by considering the group composed solely of the identity E and the inversion J . By the method of Section 4, the character system for this group, designated as \mathcal{G} , is

	E	J
\mathcal{G}_1	1	1
\mathcal{G}_2	1	-1

since we must satisfy the relations

$$\chi_1^2 = \chi_1, \quad \chi_2^2 = \chi_1.$$

Then the character table for the group O_h , Table XI, is immediately seen to be the direct product of its upper left-hand corner, which is the character system for the octahedral group O , and of \mathcal{G} . We symbolize this by

$$O_h = O \times \mathcal{G} \quad (13.17)$$

and this equation also states that O_h is the direct product of the two subgroups O and \mathcal{G} .

Returning now to the group C_{2v} above, there may be associated a translation t_i ($i = 1, 2, 3, 4$) with each of the four elements of the point group C_2, m_x, m_y, E (where t_4 corresponds to E), and there will then be a Cayley table of the same form as above, namely

	E	t_1	t_2	t_3
E	E	t_1	t_2	t_3
t_1	t_1	E	t_3	t_2
t_2	t_2	t_3	E	t_1
t_3	t_3	t_2	t_1	E

where we are arbitrarily making the associations

$$t_1 \leftrightarrow C_2, \quad t_2 \leftrightarrow m_x, \quad t_3 \leftrightarrow m_y.$$

Note that the two subgroups are *isomorphic*—there is a one-to-one correspondence in multiplication tables. Now t_1 may be only O or $c/2$, but t_2 and t_3 may assume the values

$$O, \quad (a/2), \quad (b/2), \quad (c/2), \quad (a/2 + b/2), \quad (a/2 + c/2), \\ (b/2 + c/2), \quad (a/2 + b/2 + c/2)$$

and we must systematically investigate all combinations satisfying the above table. These combinations are enumerated in Table XXV.

To discuss this table, we note that, of the first eight entries, two are repetitions, since they are symmetrical in a and b , which represent physically equivalent displacements. The remaining entries—those for $t_1 = c/2$ —correspond to space groups with twofold screw axes, designated by 2_1 in the Hermann-Mauguin notation. A complete discussion of Bravais lattices and space group notation will be found in Nussbaum²⁰; for our purposes

²⁰ A. Nussbaum, "Semiconductor Device Physics." Prentice-Hall, Englewood Cliffs, New Jersey, 1962.

here we note that the various space groups are denoted in the Schoenflies system by adding an arbitrary superscript to the symbol C_{2v} , and that the items of Table XXV list the possible orthorhombic lattices, which can be simple, body-centered, face-centered, or base-centered.

To verify that C_{2v}^2 , for example, contains a screw axis, we consider an asymmetrical atom grouping at the origin, as represented by the arrow of Fig. 30 (note that the arrow itself is asymmetrical). The dotted arrow is an intermediate step and we see the existence of a twofold screw axis AB . Thus, we see how some of the simple concepts of group theory can lead to an enumeration of crystalline space groups. A tabulation of all 230 groups is given by Zachariasen,²¹ where a discussion of their properties will also be found.

14. THE NEARLY FREE AND TIGHT-BINDING APPROXIMATIONS FOR TELLURIUM

Prior to the application of group theory to tellurium, an LCAO calculation of the band structure was made by Reitz.²² We shall briefly consider his results because they are related to those obtained by the use of group-theoretical methods.

Denoting the p functions as $\phi_1 = p_x$, $\phi_2 = p_y$, $\phi_3 = p_z$, the solution to the Schrödinger equation again has the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{j,n,s} B_{ns} \exp \{i\mathbf{k} \cdot \mathbf{R}_{js}\} \phi_n(\mathbf{r} - \mathbf{R}_{js}) \quad (14.1)$$

where the subscript s refers to a summation over the three nonequivalent lattice sites in the unit cell. Again writing V as $V_a + V'$, introducing $\psi_{\mathbf{k}}$ above into the Schrödinger equation, and multiplying it in turn by ϕ_1^* , ϕ_2^* , and ϕ_3^* , followed by an integration, we obtain a 9×9 secular equation. As a first approximation towards solving this 9×9 determinant, Reitz made the simplifying assumption that the interbond angles between adjacent atoms in a chain were 90° instead of the true value 102.6° . Referring to Fig. 31, we label the three atoms in a unit cell as A , B , and C and let \mathbf{R}_λ , \mathbf{R}_μ , and \mathbf{R}_ν denote the three nearest-neighbor directions, so that the lattice constant along the trigonal axis can be expressed

$$c = -\mathbf{R}_\lambda + \mathbf{R}_\mu + \mathbf{R}_\nu.$$

Considering only nearest-neighbor integrals and denoting the location of a function by a subscript A , B , or C , the following are the integrals in-

²¹ W. H. Zachariasen, "Theory of X-Ray Diffraction in Crystals." Wiley, New York, 1945.

²² J. R. Reitz, *Phys. Rev.* **105**, 1233 (1957).

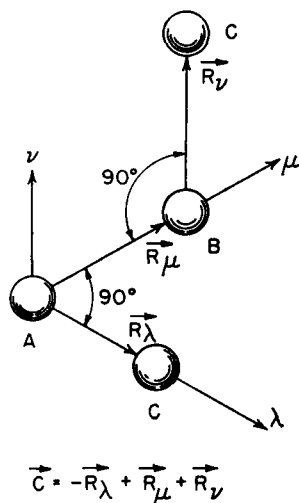


FIG. 31. An approximation to the true tellurium chain.

volving p_λ functions:

$$(p_{\lambda A} | V' | p_{\lambda A}) = (p_{\lambda C} | V' | p_{\lambda C}) \quad (14.2a)$$

$$(p_{\lambda B} | V' | p_{\lambda B}) \quad (14.2b)$$

$$(p_{\lambda A} | V' | p_{\lambda B}) = (p_{\lambda B} | V' | p_{\lambda A}) \quad (14.2c)$$

$$(p_{\lambda B} | V' | p_{\lambda C}) = (p_{\lambda C} | V' | p_{\lambda B}) \quad (14.2d)$$

$$(p_{\lambda C} | V' | p_{\lambda A}) = (p_{\lambda A} | V' | p_{\lambda C}) \quad (14.2e)$$

The relations among these integrals come from the fact that their values depend upon the relative orientation of the two p functions in each integrand. Since two different p functions are orthogonal, all terms of the form $(p_{\lambda A} | V' | p_{\mu A})$ vanish in this approximation, and the 9×9 determinant reduces to the form

$$\begin{vmatrix} \lambda & 0 & 0 \\ 0 & \mu & 0 \\ 0 & 0 & \nu \end{vmatrix} = 0$$

where λ denotes a 3×3 block involving p_λ functions only and 0 denotes a 3×3 block composed entirely of zeros.

Equating the λ block separately to zero gives a cubic equation E , which

can be solved by making some further approximations. It is estimated that integrals of the form $(p_{\lambda A} | V' | p_{\lambda B})$ are about one third the magnitude of those like $(p_{\lambda A} | V' | p_{\lambda C})$ and we assume that the integrals in (14.2a) and (14.2b) are the same. Introducing a relative energy E_R by

$$E_R = E = E_a - (p_{\lambda A} | V' | p_{\lambda A})$$

and the abbreviation

$$\sigma = (p_{\lambda A} | V' | p_{\lambda C})$$

and the secular equation becomes

$$-E_R^3 + (11/9)E_R\sigma^2 + (2/9)\sigma^3 \cos k_z c = 0. \quad (14.3)$$

The dotted curves of Fig. 32 show the three roots of this equation as

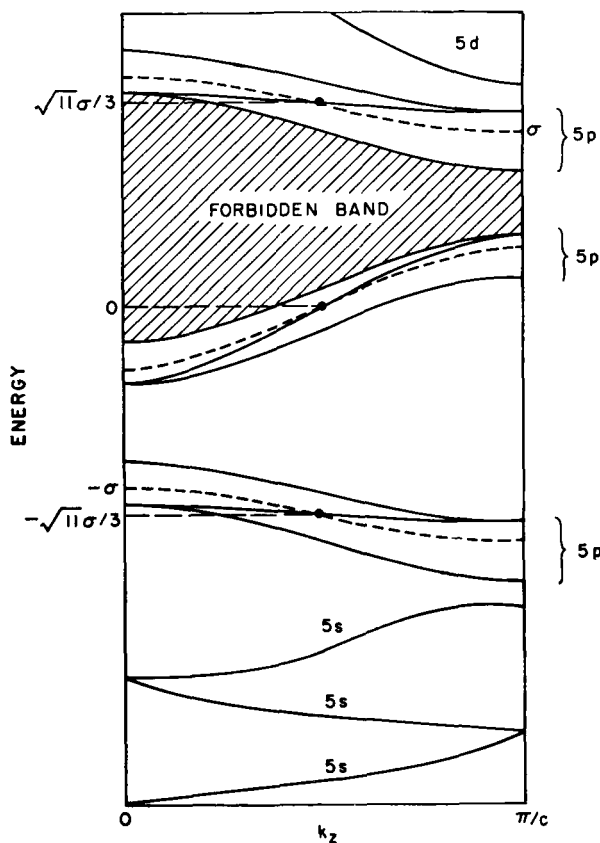


FIG. 32. Tight banding energy bands for tellurium.

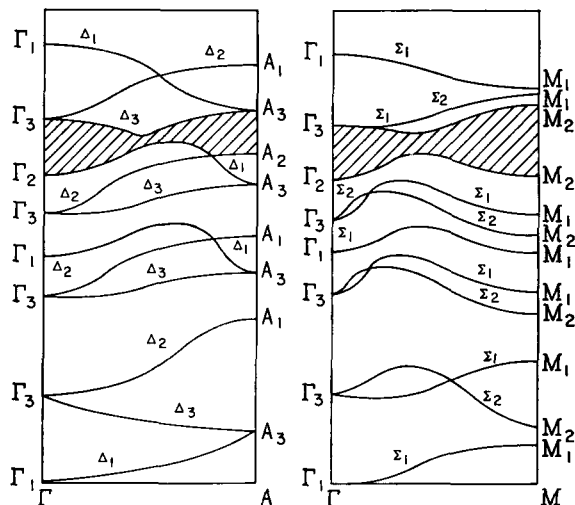


FIG. 33. The nearly free approximation applied to tellurium.

a function of k_z . The same set of curves will also come from the μ and ν equations and the bands are triply degenerate. This degeneracy can be removed by stretching the bond angles to their true value of 102.6° , which results in the introduction of additional integrals of the form $(p_{\lambda A} | V' | p_{\mu B})$ into the secular equation. Reitz has solved this 9×9 equation by making further approximations and obtained the solid curves of Fig. 32. In this diagram, we have added the s bands based on the free-electron approximation of Section 12, and the forbidden gap is located as previously described.

A different approach to this problem was taken by Nussbaum and Hager,²³ who made a qualitative determination of the tellurium band structure starting with the free-electron scheme shown in Figs. 26 and 27. The presence of the crystalline field in tellurium will remove all the degeneracies at the center and edges of the Brillouin zone except those inherent in the irreducible representations and obeying the compatibility relations. By following these principles, and using Figs. 26 and 27 as a rough guide, we can sketch the bands as shown in Fig. 33. We see, for example, that the crystal field removes the degeneracy at the intersection of the (001) and (002) curve for the point A. Also, Table XXIV shows that $\Gamma_3 \rightarrow \Delta_2 + \Delta_3$ and $A_3 \rightarrow \Delta_1 + \Delta_3$, so that the curve joining Γ_3 and A_3 can only belong to Δ_3 .

The energy bands for tellurium given in this figure are seen to differ

²³ A. Nussbaum and R. J. Hager, *Phys. Rev.* **123**, 1958 (1961).

considerably from those of Reitz. For example, we show the maxima in both the valence and conduction bands as lying about halfway along the Δ -axis, rather than at the top. This means that the energy surfaces are ellipsoidal and the symmetry of the crystal requires the presence of six ellipsoids per band. Although this approximation is qualitative, it has helped to interpret some of the anomalous electrical properties of tellurium.

A group-theoretical treatment of tellurium has been given by Asendorf,²⁴ from whose work the character tables and compatibility relations (Tables XXII, XXIII, and XXIV) are taken. However, his procedure involved some simplifications which were somewhat analogous to those of Reitz, and the results obtained were the same.

VI. The Band Structure of Silicon and Germanium

15. THE OPW METHOD

The most intensive band structure calculations have been carried out on the column IV semiconductors silicon and germanium using the method of *orthogonalized plane waves* (OPW), which we shall outline here. The unperturbed wave functions in an approximate calculation are taken as the free-electron solutions. These were shown to be

$$\psi_{\mathbf{k}} = \exp [i(\mathbf{k} - 2\pi\mathbf{lB}) \cdot \mathbf{r}]. \quad (9.10)$$

This may be written as

$$\psi_{\mathbf{k},\mathbf{h}} = \exp [i(\mathbf{k} + \mathbf{h}) \cdot \mathbf{r}] \quad (15.1)$$

where

$$\mathbf{h} = -i2\pi\mathbf{lB} \quad (15.2)$$

and this quantity has the dimensions of a wave vector.

We now solve the Schrödinger equation

$$H\phi = E\phi \quad (15.3)$$

using the variational method with the trial function taken as a linear combination of plane waves like (15.1). That is, let

$$\phi = \sum_{i=1}^n a_i \psi_i. \quad (15.4)$$

This method is often used when the ψ_i are n -fold degenerate and the per-

²⁴ R. H. Asendorf, "A Group Theoretical Approach to the Band Structure of Tellurium," Ph.D. dissertation, University of Pennsylvania, Philadelphia, Pennsylvania, 1956; also *J. Chem. Phys.* **27**, 11 (1957).

turbation removes the degeneracy. Multiplying (15.3) by ϕ^* and integrating gives

$$E = \int \phi^* H \phi \, d\mathbf{r} / \int \phi^* \phi \, d\mathbf{r} \quad (15.5)$$

where we are assuming that ϕ is not normalized. Substituting (15.4) into (15.5) shows that

$$E = \sum a_i^* a_j \mathcal{H}_{ij} / \sum a_i^* a_j A_{ij} \quad (15.6)$$

where \mathcal{H}_{ij} and A_{ij} are matrix elements defined by

$$\mathcal{H}_{ij} = \int \psi_i^* H \psi_j \, d\mathbf{r}, \quad (15.7)$$

$$A_{ij} = \int \psi_i^* \psi_j \, d\mathbf{r}.$$

Differentiating (15.6) with respect to a_k^* , we obtain

$$(\partial E / \partial a_k^*) \sum a_i^* a_j A_{ij} + E \sum a_j A_{kj} = \sum a_j \mathcal{H}_{ij}. \quad (15.8)$$

For the energy to be a minimum, we use the condition

$$\partial E / \partial a_k^* = 0 \quad [k = 1, 2, \dots, n]$$

and the n simultaneous equations (15.8) then have a solution if their determinant vanishes, or

$$\begin{vmatrix} \mathcal{H}_{11} - A_{11}E & \mathcal{H}_{12} - A_{12}E & \cdots & \mathcal{H}_{1n} - A_{1n}E \\ \vdots & & & \\ \mathcal{H}_{n1} - A_{n1}E & \cdots & \cdots & \mathcal{H}_{nn} - A_{nn}E \end{vmatrix} = 0 \quad (15.9)$$

This secular determinant can be simplified by utilizing the free-electron functions (15.1). For the off-diagonal elements, let

$$\psi_i = \exp [i(\mathbf{k}_i + \mathbf{h}_i) \cdot \mathbf{r}], \quad \psi_j = \exp [i(\mathbf{k}_j + \mathbf{h}_j) \cdot \mathbf{r}]. \quad (15.10)$$

Since we are evaluating the matrix elements at given points in the Brillouin zone, $\mathbf{k}_i = \mathbf{k}_j$ and we have

$$\begin{aligned} \mathcal{H}_{ij} = \int \exp [-i(\mathbf{k}_i + \mathbf{h}_i) \cdot \mathbf{r}] \{ (-\hbar^2/2m) \nabla^2 + V(\mathbf{r}) \} \\ \times \exp [i(\mathbf{k}_i + \mathbf{h}_j) \cdot \mathbf{r}] \, d\mathbf{r} \end{aligned} \quad (15.11)$$

where $V(r)$ is the crystal potential energy. Using

$$\nabla^2 \exp [i(\mathbf{k} + \mathbf{h}) \cdot \mathbf{r}] = -(\mathbf{k} + \mathbf{h})^2 \exp [i(\mathbf{k} + \mathbf{h}) \cdot \mathbf{r}]$$

makes the first integral in (15.11) vanish by orthogonality. The second integral may be written as

$$V_{\mathbf{h},i} = \int V(\mathbf{r}) \exp [-i(\mathbf{h}_i - \mathbf{h}_j) \cdot \mathbf{r}] d\mathbf{r} \quad (15.12)$$

where

$$\mathbf{h}_{ij} = \mathbf{h}_i - \mathbf{h}_j \quad (15.13)$$

is 2π times a vector of the reciprocal lattice. Thus

$$\mathcal{H}_{ij} = V_{\mathbf{h}_{ij}}. \quad (15.14)$$

The diagonal elements of (15.9) have the form

$$H_{ii} - A_{ii}E = \int \psi_i^* [(-\hbar^2/2m)\nabla^2 + V]\psi_i d\mathbf{r} = E \int \psi_i^* \psi_i d\mathbf{r} \quad (15.15)$$

Assuming the ψ_i are normalized, the second term on the right-hand side reduces to $-E$. The first term becomes

$$\int \psi_i^* [(-\hbar^2/2m)\nabla^2 + V]\psi_i d\mathbf{r} = \int (\psi_i^* E_0 \psi_i + V\psi_i^2) d\mathbf{r}. \quad (15.16)$$

The quantity E_0 is the free-electron energy and appears because $-\hbar^2\nabla^2/2m$ is the free-electron Hamiltonian. The second term on the right of (15.16) reduces to

$$V_{000} = \int V\psi_i^2 d\mathbf{r} \quad (15.17)$$

which is the average of $V(\mathbf{r})$ over a unit cell. Hence, the diagonal element becomes

$$H_{ii} - A_{ii}E = E_0 + V_{000} - E. \quad (15.18)$$

The secular determinant of order $n \times n$ may be further simplified by using orthogonalized linear combinations of the free-electron functions, as determined from group theory. We shall illustrate the procedure with a simple example, again taken from Amsterdam.⁹ Consider the ΓM axis of beta-brass, for which $\xi = \eta$ and $\zeta = 0$. At the point M we have four degenerate functions, specified by $\mathbf{l} = (000)$, (100) , (010) , and (110) . We note from (15.1) that these four sets of integers will also specify \mathbf{h} , since

$$\mathbf{h} = (2\pi/a)\mathbf{l} \quad (15.19)$$

for the cubic lattice. It is customary to denote the associated functions in the following way:

$$\psi_{000} = [000], \quad \psi_{100} = [100], \quad \psi_{010} = [010], \quad \psi_{110} = [110]. \quad (15.20)$$

These functions correspond to a reducible representation with characters given by:

$$\begin{array}{cccc} E & C_2 & JC_4^2 & JC_2 \\ \chi & \left| \begin{array}{cccc} 4 & 2 & 4 & 2 \end{array} \right. \end{array}$$

This result was obtained from Table XVI by considering the effect of the symmetry operations on the function

$$\psi_k = \exp \{i[(\xi - 2\pi l_1)x + (\eta - 2\pi l_2)y + (-2\pi l_3)z]/a\}. \quad (15.21)$$

Since $[000]$ and $[110]$ are invariant under all operations and $[100]$ and $[010]$ are invariant only under E and JC_4^2 , we see that the values of χ are correct. By (4.1), we have

$$n_1 = 3, \quad n_2 = 0, \quad n_3 = 0, \quad n_4 = 1.$$

Then from (101) and Table XVI

$$\varphi_1 = \begin{cases} 4[000] \\ 2[100] + 2[010], \\ 4[110] \end{cases} \quad \varphi_4 = 2[100] - 2[010] \quad (15.22)$$

where the three functions ϕ_1 belong to Σ_1 and ϕ_4 belongs to Σ_4 . These combinations are mutually orthogonal and we will designate them as

$$\begin{aligned} \psi_1 &= [000], & \psi_2 &= \{[100] + [010]\}/\sqrt{2} \\ \psi_3 &= [110], & \psi_4 &= \{[100] - [010]\}/\sqrt{2}. \end{aligned} \quad (15.23)$$

We can now enumerate the elements H_{ij} of the 4×4 secular determinant. Those involving only ψ_1 and ψ_3 are

$$H_{11} = \mathcal{H}_{11} - A_{11}E = E_0 + V_{000} - E = H_{33}, \quad H_{13} = V_{110} = H_{31}.$$

For the others, we must make use of some symmetry properties of the quantities in (15.14). For a cubic crystal

$$V(\mathbf{r}) = V(-\mathbf{r}).$$

From this, it follows that

$$V_{110} = -V_{1\bar{1}0},$$

for example, for if we replace x by $-x$, then $d\mathbf{r}$ in (15.12) reverses sign, $V(\mathbf{r})$ is unchanged, and the coefficient of x in the exponent reverses sign. Similarly, it follows that all relations of the form

$$V_{010} = V_{100}$$

are valid; that is, $V_{h_1 h_2 h_3}$ is independent of the order of the integers in the subscript.

Returning to the H_{ij} , we now have

$$\begin{aligned} H_{22} &= \mathcal{H}_{22} - A_{22}E = \int \{[100] + [010]\}^* H \{[100] + [010]\} d\mathbf{r} \\ &\quad - E \int \{[100] + [010]\}^* \{[100] + [010]\} d\mathbf{r} \\ &= E_0 + \int \{[100] + [010]\}^* V(\mathbf{r}) \\ &\quad \times \{[100] + [010]\} d\mathbf{r} - E \\ &= E_0 + V_{000} - E + \int V(\mathbf{r}) \\ &\quad \times \{[100]^* [010] + [010]^* [100]\} d\mathbf{r} \\ &= E_0 + V_{000} - E + V_{110} = E_0 + V_{000} - E - V_{110} \\ H_{12} &= \int [000]^* V(\mathbf{r}) \{[100] + [010]\} d\mathbf{r} / \sqrt{2} \\ &= \{V_{100} + V_{010}\} / \sqrt{2} = \sqrt{2} V_{100}. \end{aligned}$$

The secular determinant then becomes

$$\begin{array}{cccc|c} & \psi_1 & \psi_2 & \psi_3 & \psi_4 & \\ \hline \psi_1 & E_0 + V_{000} - E & \sqrt{2} V_{100} & V_{110} & 0 & \\ \psi_2 & \sqrt{2} V_{100} & E_0 + V_{000} - E - V_{110} & \sqrt{2} V_{100} & 0 & \\ \psi_3 & V_{110} & \sqrt{2} V_{100} & E_0 + V_{000} - E & 0 & \\ \psi_4 & 0 & 0 & 0 & E_0 + V_{000} - E + V_{110} & \\ \hline & \underbrace{\hspace{10em}}_{\Sigma_1} & & & \underbrace{\hspace{10em}}_{\Sigma_4} & \\ & & & & & = 0 \end{array} \quad (15.24)$$

The cubic corresponding to Σ_1 can be solved analytically. Let

$$V_{110} = g, \quad V_{100} = k, \quad E_0 + V_{000} = b.$$

Then

$$(b - E)^2(b - E - g) + 4gk^2 - 4k^2(b - E) - g^2(b - E - g) = 0$$

or

$$(b - E - g)[(b - E)^2 - g^2 - 4k^2] = 0$$

from which

$$b - E - g = 0, \quad b - E = \pm(g^2 + 4k^2)^{1/2}$$

and

$$\left. \begin{aligned} E_1 &= b - g \\ E_2 &= b + (g^2 + 4k^2)^{1/2} \\ E_3 &= b - (g^2 + 4k^2)^{1/2} \end{aligned} \right\} \Sigma_1 \quad E = b + g \quad \Sigma_4.$$

Since

$$(V_{110}^2 + 4V_{100}^2)^{1/2} > |V_{110}|$$

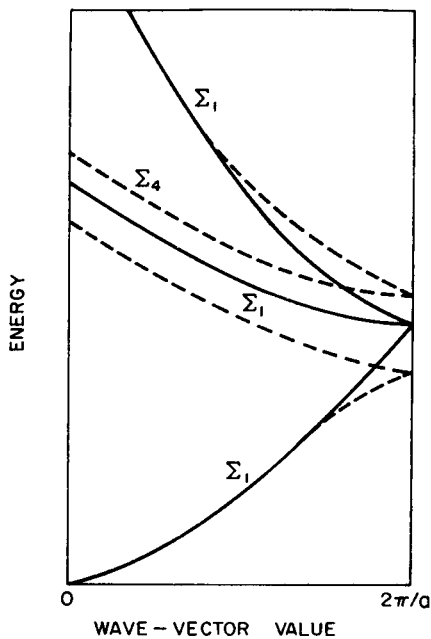


FIG. 34. The OPW method applied to beta-brass.

we see that the root E_2 is the largest of the four and E_3 is the smallest. The intermediate Σ_1 root E_1 is then separated from the Σ_4 root E by an amount $2V_{110}$, and the perturbing potential $V(\mathbf{r})$ has removed the degeneracy. The resultant shape of the bands might appear as shown in Fig. 34.

16. THE SYMMETRY OF THE DIAMOND LATTICE

The diamond structure consists of two identical, interlocking face-centered-cubic lattices, as may be seen by examining Fig. 35. One of the lattices is displaced from the other by a distance $(a/4, a/4, a/4)$ where a is the lattice constant, and this feature is illustrated in Fig. 36. A face-centered-cubic direct lattice has a body-centered-cubic reciprocal lattice, and the first Brillouin zone is shown in Fig. 37.

The space group O_h ⁷ for diamond can be described with reference to Fig. 36. We shall choose the atom in the lower left-hand corner of the diagram as the origin 0, and place a set of axes along the cube edges. The

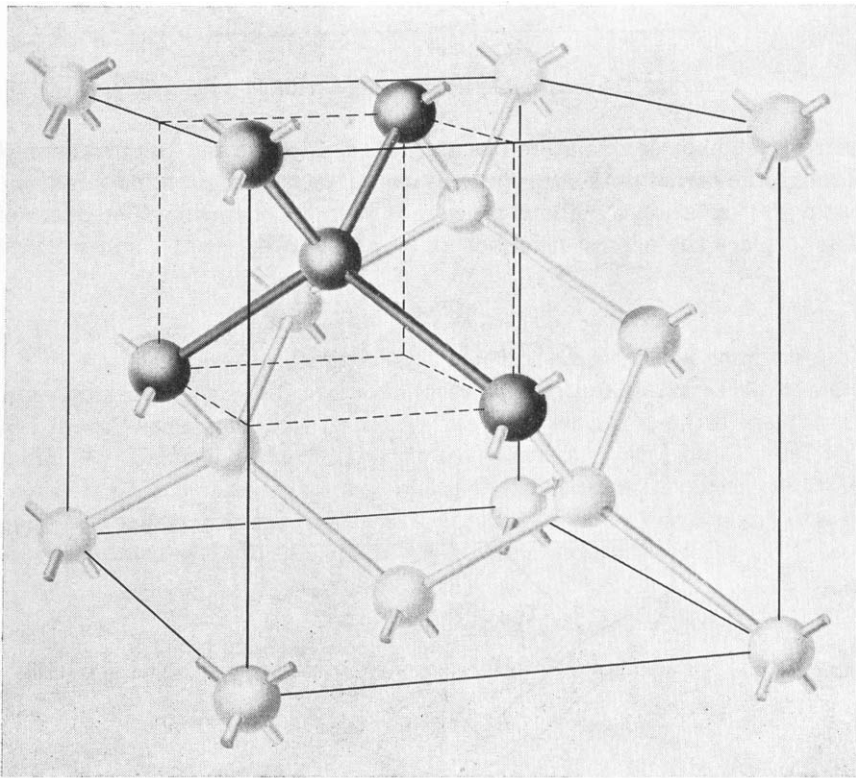


FIG. 35 The diamond lattice.

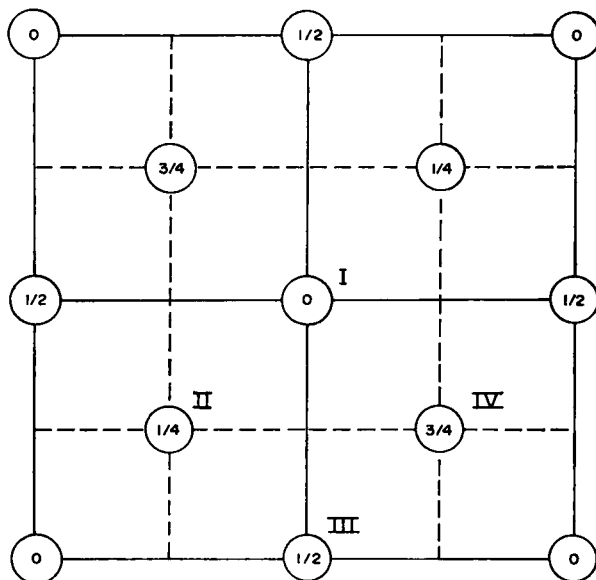


FIG. 36. The diamond lattice showing a fourfold screw axis.

nearest neighbor of this atom lies at $(a/4, a/4, a/4)$, and the inversion J through the corner does not represent a symmetry operation for this atom, but a 180° rotation J_4^2 about an edge is such an operation. The effect of J is to place the nearest-neighbor at $(-a/4, -a/4, -a/4)$, and we then

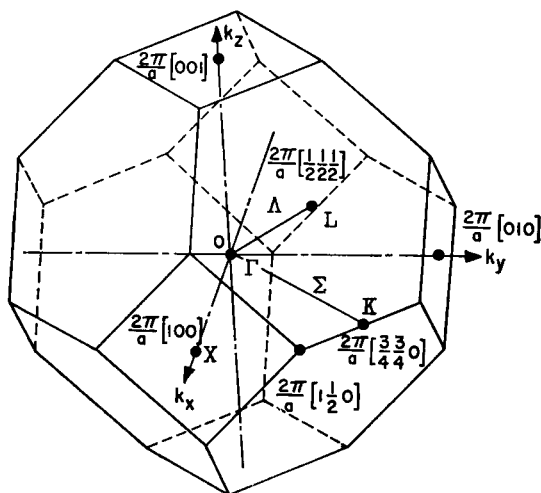


FIG. 37. The Brillouin zone for diamond-type crystals.

return it to a lattice position by a translation \mathbf{T} , where

$$\mathbf{T} = (a/4, a/4, a/4). \quad (16.1)$$

It can be seen that twenty-four of the elements of O_h leave the lattice invariant, and these are given in the top half of Table XXVI. The other twenty-four must be combined with the translation \mathbf{T} , and the table shows the effect on a general point x, y, z expressed with respect to axes along the cube edges. If we shift the origin O from $(0, 0, 0)$ to the point $(a/8, a/8, a/8)$, we obtain what has been called the *standard origin* S by Mariot,²⁵ whose discussion is based on Herman's thesis.²⁶

As an example, consider (J, \mathbf{T}) . For the origin O , this gives

$$x \rightarrow \bar{x}, \quad y \rightarrow \bar{y}, \quad z \rightarrow \bar{z}$$

followed by

$$\mathbf{T} = a/4, \quad a/4, \quad a/4$$

so that

$$(J, \mathbf{T})(xyz) = (\bar{x} + a/4, \bar{y} + a/4, \bar{z} + a/4)$$

as shown.

If (xyz) is now specified with respect to S , but J is referred to O , then J has the effect

$$x \rightarrow \bar{x} - a/4, \quad y \rightarrow \bar{y} - a/4, \quad z \rightarrow \bar{z} - a/4$$

and \mathbf{T} again produces the entry in the table.

The ten operations of Table XXVI can be regarded as a combination of the point group elements and a compound operation known as a *diagonal glide*. Jones¹² has shown how to define this glide with respect to the origin S (Fig. 38). Using the coordinate systems shown, a typical glide operation G consists of a displacement $a/4$ along the y' -axis, a displacement $a/4$ along the z' -axis, and a reflection in the plane $x' = 0$. For a point (xyz) in the unprimed system, this operation can be expressed as

$$G(x, y, z) \rightarrow (-x + a/4, y + a/4, z + a/4).$$

This operation is equivalent to Tm , where T is defined by (16.1) and

²⁵ L. Mariot, "Group Theory and Solid State Physics." Prentice-Hall, Englewood Cliffs, New Jersey, 1960.

²⁶ F. Herman, "Electronic Structure of Diamond-Type Crystals," Ph.D. thesis, Columbia University, New York, 1953.

TABLE XXVI. SYMMETRY OPERATIONS OF THE DIAMOND LATTICE

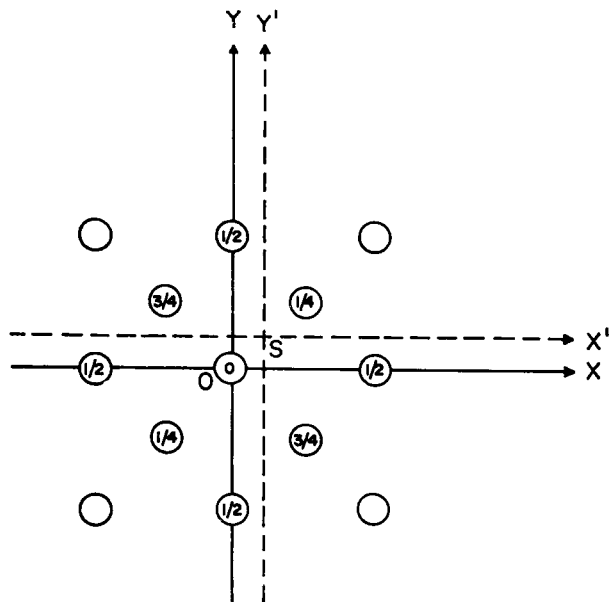
Operation	O			S		
(E_20)	xyz			x	y	z
$(C_4^2, 0)$	$\bar{x}\bar{y}z$			$\bar{x} - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$	z
	$x\bar{y}\bar{z}$			x	$\bar{y} - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$
	$\bar{x}y\bar{z}$			$\bar{x} - \frac{1}{4}a$	y	$\bar{z} - \frac{1}{4}a$
$(JC_4, 0)$	$y\bar{x}\bar{z}$			y	$\bar{x} - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$
	$\bar{y}x\bar{z}$			$\bar{y} - \frac{1}{4}a$	x	$\bar{z} - \frac{1}{4}a$
	$\bar{x}z\bar{y}$			$\bar{x} - \frac{1}{4}a$	z	$\bar{y} - \frac{1}{4}a$
	$\bar{x}\bar{z}y$			$\bar{x} - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$	y
	$\bar{z}\bar{y}x$			$\bar{z} - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$	x
	$z\bar{y}\bar{x}$			z	$\bar{y} - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$
	$\bar{y}\bar{x}z$			$\bar{y} - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$	z
$(JC_2, 0)$	$\bar{z}y\bar{x}$			$\bar{z} - \frac{1}{4}a$	y	$\bar{x} - \frac{1}{4}a$
	$x\bar{z}\bar{y}$			x	$\bar{z} - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$
	yxz			y	x	z
	zyx			z	y	x
	xzy			x	z	y
	zxy			z	x	y
	yzx			y	z	x
$(C_2, 0)$	$\bar{x}\bar{z}\bar{y}$			z	$\bar{x} - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$
	$\bar{y}\bar{z}x$			$\bar{y} - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$	x
	$\bar{z}\bar{x}y$			$\bar{z} - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$	y
	$\bar{y}z\bar{x}$			$\bar{y} - \frac{1}{4}a$	z	$\bar{x} - \frac{1}{4}a$
	$\bar{z}x\bar{y}$			$\bar{z} - \frac{1}{4}a$	x	$\bar{y} - \frac{1}{4}a$
	$y\bar{z}\bar{x}$			y	$\bar{z} - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$
	$\bar{x} + \frac{1}{4}a$	$\bar{y} + \frac{1}{4}a$	$\bar{z} + \frac{1}{4}a$	\bar{x}	\bar{y}	\bar{z}
(J, T)	$\bar{x} + \frac{1}{4}a$	$\bar{y} + \frac{1}{4}a$	$\bar{z} + \frac{1}{4}a$	\bar{x}	\bar{y}	\bar{z}
(JC_4^2, T)	$x + \frac{1}{4}a$	$y + \frac{1}{4}a$	$\bar{z} + \frac{1}{4}a$	$x + \frac{1}{4}a$	$y + \frac{1}{4}a$	\bar{z}
	$\bar{x} + \frac{1}{4}a$	$y + \frac{1}{4}a$	$z + \frac{1}{4}a$	\bar{x}	$y + \frac{1}{4}a$	$z + \frac{1}{4}a$
	$x + \frac{1}{4}a$	$\bar{y} + \frac{1}{4}a$	$z + \frac{1}{4}a$	$x + \frac{1}{4}a$	\bar{y}	$z + \frac{1}{4}a$
(C_4, T)	$\bar{y} + \frac{1}{4}a$	$x + \frac{1}{4}a$	$z + \frac{1}{4}a$	\bar{y}	$x + \frac{1}{4}a$	$z + \frac{1}{4}a$
	$y + \frac{1}{4}a$	$\bar{x} + \frac{1}{4}a$	$z + \frac{1}{4}a$	$y + \frac{1}{4}a$	\bar{x}	$z + \frac{1}{4}a$
	$x + \frac{1}{4}a$	$\bar{z} + \frac{1}{4}a$	$y + \frac{1}{4}a$	$x + \frac{1}{4}a$	\bar{z}	$y + \frac{1}{4}a$
	$x + \frac{1}{4}a$	$z + \frac{1}{4}a$	$\bar{y} + \frac{1}{4}a$	$x + \frac{1}{4}a$	$z + \frac{1}{4}a$	\bar{y}
	$z + \frac{1}{4}a$	$y + \frac{1}{4}a$	$\bar{x} + \frac{1}{4}a$	$z + \frac{1}{4}a$	$y + \frac{1}{4}a$	\bar{x}
	$\bar{z} + \frac{1}{4}a$	$y + \frac{1}{4}a$	$x + \frac{1}{4}a$	\bar{z}	$y + \frac{1}{4}a$	$x + \frac{1}{4}a$
	$y + \frac{1}{4}a$	$x + \frac{1}{4}a$	$\bar{z} + \frac{1}{4}a$	$y + \frac{1}{4}a$	$x + \frac{1}{4}a$	\bar{z}
(C_2, T)	$z + \frac{1}{4}a$	$\bar{y} + \frac{1}{4}a$	$x + \frac{1}{4}a$	$z + \frac{1}{4}a$	\bar{y}	$x + \frac{1}{4}a$
	$\bar{x} + \frac{1}{4}a$	$z + \frac{1}{4}a$	$y + \frac{1}{4}a$	\bar{x}	$z + \frac{1}{4}a$	$y + \frac{1}{4}a$
	$\bar{y} + \frac{1}{4}a$	$\bar{x} + \frac{1}{4}a$	$\bar{z} + \frac{1}{4}a$	\bar{y}	\bar{x}	\bar{z}
	$\bar{z} + \frac{1}{4}a$	$\bar{y} + \frac{1}{4}a$	$\bar{x} + \frac{1}{4}a$	\bar{z}	\bar{y}	\bar{x}
	$\bar{x} + \frac{1}{4}a$	$\bar{z} + \frac{1}{4}a$	$\bar{y} + \frac{1}{4}a$	\bar{x}	\bar{z}	\bar{y}
	$\bar{y} + \frac{1}{4}a$	$\bar{x} + \frac{1}{4}a$	$\bar{z} + \frac{1}{4}a$	\bar{y}	\bar{x}	\bar{z}
	$\bar{z} + \frac{1}{4}a$	$\bar{y} + \frac{1}{4}a$	$\bar{x} + \frac{1}{4}a$	\bar{z}	\bar{y}	\bar{x}

TABLE XXVI—Continued

Operation	<i>O</i>			<i>S</i>		
(JC_3, T)	$\bar{z} + \frac{1}{4}a$	$\bar{x} + \frac{1}{4}a$	$\bar{y} + \frac{1}{4}a$	\bar{z}	\bar{x}	\bar{y}
	$\bar{y} + \frac{1}{4}a$	$\bar{z} + \frac{1}{4}a$	$\bar{x} + \frac{1}{4}a$	\bar{y}	\bar{z}	\bar{x}
	$\bar{x} + \frac{1}{4}a$	$x + \frac{1}{4}a$	$y + \frac{1}{4}a$	\bar{z}	$x + \frac{1}{4}a$	$y + \frac{1}{4}a$
	$y + \frac{1}{4}a$	$z + \frac{1}{4}a$	$\bar{x} + \frac{1}{4}a$	$y + \frac{1}{4}a$	$z + \frac{1}{4}a$	\bar{x}
	$z + \frac{1}{4}a$	$x + \frac{1}{4}a$	$\bar{y} + \frac{1}{4}a$	$z + \frac{1}{4}a$	$x + \frac{1}{4}a$	\bar{y}
	$y + \frac{1}{4}a$	$\bar{z} + \frac{1}{4}a$	$x + \frac{1}{4}a$	$y + \frac{1}{4}a$	\bar{z}	$x + \frac{1}{4}a$
	$z + \frac{1}{4}a$	$\bar{x} + \frac{1}{4}a$	$y + \frac{1}{4}a$	$z + \frac{1}{4}a$	\bar{x}	$y + \frac{1}{4}a$
	$\bar{y} + \frac{1}{4}a$	$z + \frac{1}{4}a$	$x + \frac{1}{4}a$	\bar{y}	$z + \frac{1}{4}a$	$x + \frac{1}{4}a$

m is a reflection in the plane $x = 0$ (rather than $x' = 0$). We note that cubic symmetry implies that m could just as well be a reflection in the planes $y = 0$ or $z = 0$, and this symbol will denote any of the three possibilities.

The forty-eight operations of Table XXVI can be expressed as com-

FIG. 38. The normal (*O*) and standard (*S*) origins for the diamond lattice.

binations of the forty-eight-point group operations with Tm by the rules

$$\begin{aligned}(\Theta, 0) &\rightarrow \Theta, & (\Theta, T) &\rightarrow TmJ\Theta \\(J\Theta, 0) &\rightarrow J\Theta, & (J\Theta, T) &\rightarrow Tm\Theta.\end{aligned}$$

Thus, we have the correspondences

$$\begin{aligned}(E, 0) &\rightarrow E, & (J, T) &\rightarrow Tm \\(C_4^2, 0) &\rightarrow C_4, & (JC_4^2, T) &\rightarrow TmC_4^2 \\(JC_4, 0) &\rightarrow JC_4, & (C_4, T) &\rightarrow TmJC_4 \\(JC_2, 0) &\rightarrow JC_2, & (C_2, T) &\rightarrow TmJC_2 \\(C_3, 0) &\rightarrow C_3, & (JC_3, T) &\rightarrow TmC_3.\end{aligned}$$

We may remark here that the diagonal glide is not a unique compound operation, since it is equivalent to a fourfold screw axis. Such an axis is indicated in Fig. 36 by the Roman numerals I–IV. It should also be noted that the operations listed above do not form a group, the situation being analogous to that of tellurium. For example,

$$TmTm(x, y, z) \rightarrow (x, y + a/2, z + a/2).$$

However, we see that $(Tm)^2$ corresponds to a displacement $(0, 1/2, 1/2)$,

TABLE XXVII. CHARACTER TABLE FOR THE GROUP O_h^7 ALONG THE Δ -AXIS^a

	E	C_4^2	JC_2	JC_4^2	C_4
Δ_1	1	1	1	α	α
Δ_2	1	1	-1	α	$-\alpha$
Δ_2'	1	1	-1	$-\alpha$	$-\alpha$
Δ_1'	1	1	-1	$-\alpha$	α
Δ_5	2	-2	0	0	0

^a $\alpha = 3^{ik}$.

so that any atom in the lattice is moved to the site of its nearest neighbor. Then we can make the identification

$$(\mathbf{T}m)^2 = E$$

which is similar to Eq. (11.2), or to $T^2 = E$, for tellurium. A Cayley table may then be constructed and the forty-eight operations are isomorphic to those of the point group, so that the character table applicable to Γ is Table XI. It has been shown by Herman²⁶ that the first half of the table corresponds to free-electron functions which are symmetrical with respect to $\mathbf{T}m$ and the second half to functions which are antisymmetrical.

A complete analysis of twenty space groups, including D_3^4 for tellurium and O_h^7 for diamond, has recently been published by Slater.²⁷ As our discussion of tellurium would lead us to expect, the presence of compound operations leads to the introduction of exponential factors into the character tables at point other than the center or ends of the Brillouin zone. Table XXVII shows Slater's results for the Δ -axis, for example. Character tables, symmetry operator matrices, and compatibility relations for all the special points and axes in the Brillouin zone will be found in Appendix 3 of this reference.

17. ENERGY BANDS FOR SILICON AND GERMANIUM

The free-electron energy curves for germanium as given by Herman²⁸ or Slater,²⁷ are shown in Fig. 39a. The calculations are analogous to those for tellurium, and the position of the gap is determined by the location of the first four levels, so that the division is a curve rather than the shaded regions of Fig. 26. In Fig. 39b, the energy bands for germanium, obtained partly by use of the OPW method and partly by symmetry arguments, is shown. This diagram is the result of a computer calculation by Herman, and another version,²⁹ showing the way the band edges vary as a function of distance in the Brillouin zone, is given in Fig. 40b. A similar diagram for silicon is given in Fig. 40a. We shall consider the two lower diagrams, showing the effect of spin-orbit splitting, in a later section.

As we have seen in connection with beta-brass, the OPW method involves two separate procedures. One is the use of group theory to simplify the secular determinants and the other (which we have not considered so far) is the evaluation of integrals involving the crystal potential $V(\mathbf{r})$.

²⁷ J. C. Slater, "Quantum Theory of Molecules and Solids," Vol. 2. McGraw-Hill, New York, 1965.

²⁸ F. Herman, *Rev. Mod. Phys.* **30**, 102 (1958).

²⁹ F. Herman, *Proc. IRE* **43**, 1703 (1955).

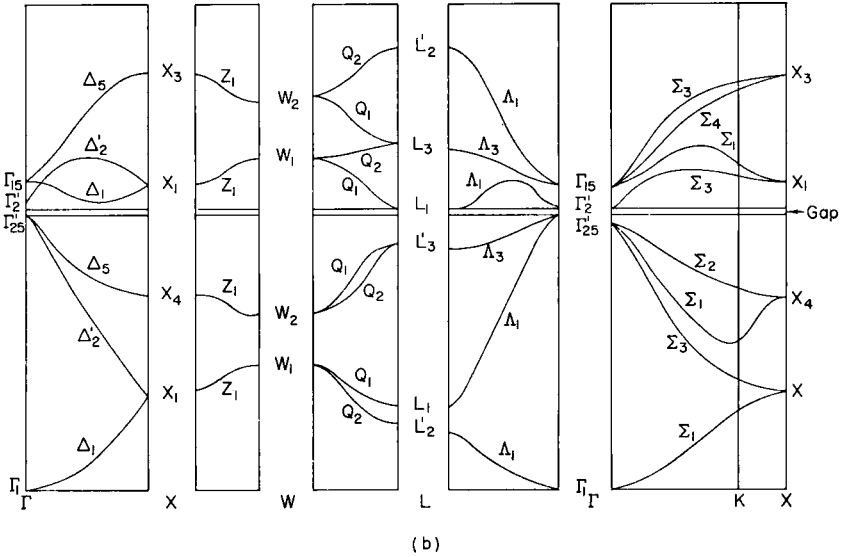
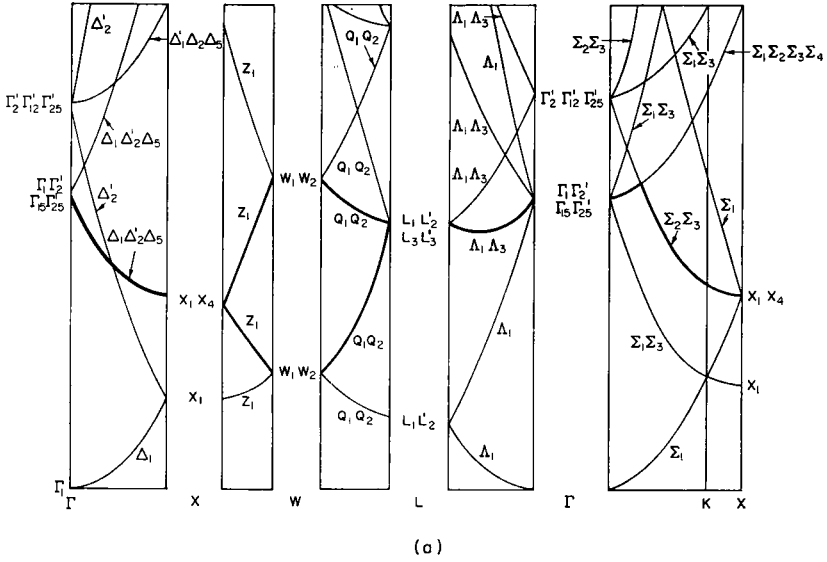


FIG. 39. (a) Free-electron energy bands for the diamond lattice; (b) energy bands in germanium as determined by Herman. (From J. C. Slater, "Quantum Theory of Molecules and Solids" Vol. 2. McGraw-Hill, New York, 1965, with permission.)

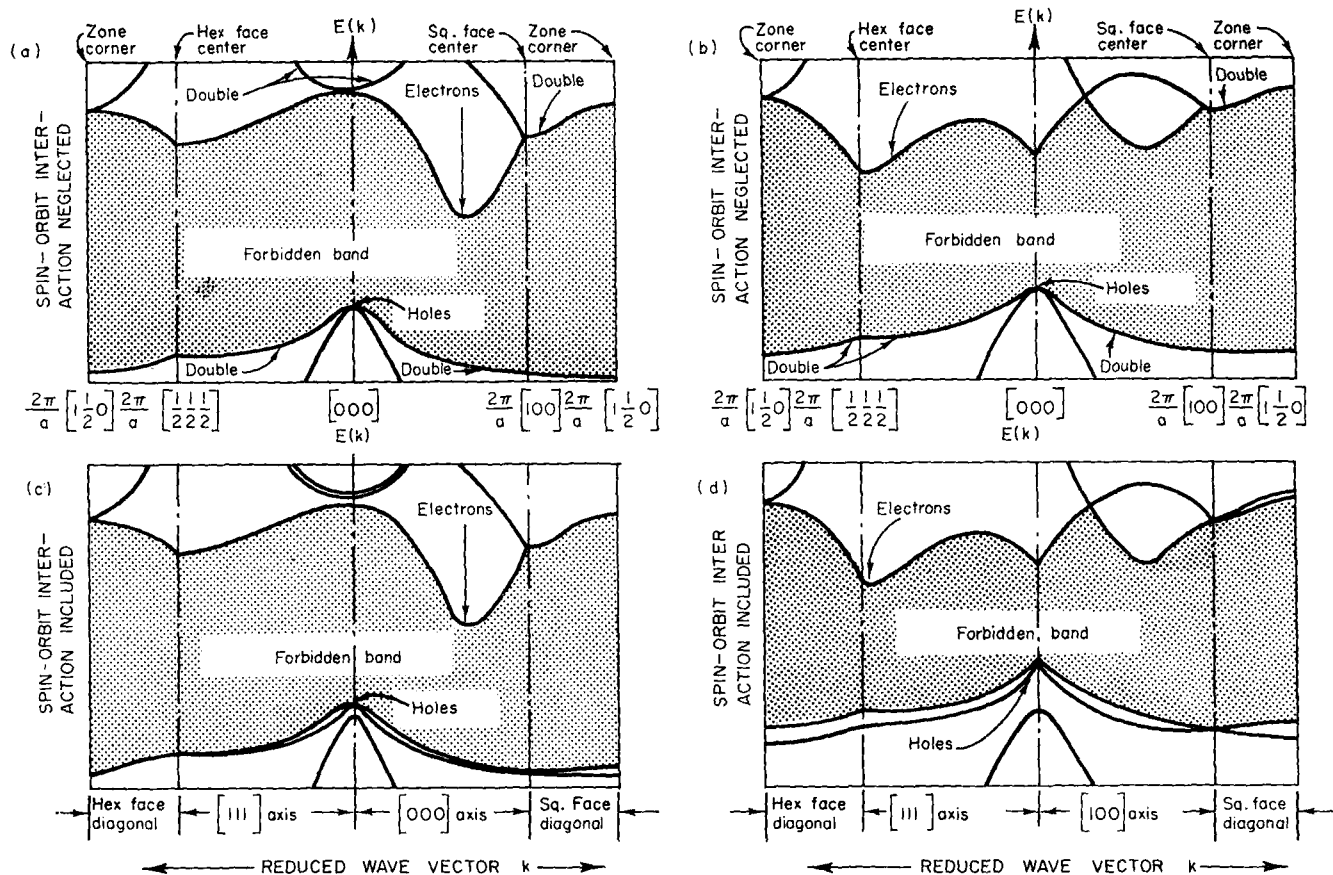


FIG. 40. Energy bands for silicon and germanium (from F. Herman, *Proc. IRE* **43**, 170s (1955) with permission).

Let us consider as an example the plane waves associated with $\mathbf{l} = (111)$ at the center Γ of the zone. Since $\xi = \eta = \zeta = 0$, Eq. (9.12) shows that this point corresponds to an eightfold degeneracy. That is, \mathbf{l} may take on the values $(\pm 1, \pm 1, \pm 1)$. The secular determinant involving these eight plane waves is

	(111)	(1 $\bar{1}\bar{1}$)	($\bar{1}\bar{1}\bar{1}$)	($\bar{1}\bar{1}1$)	($\bar{1}\bar{1}\bar{1}$)	($\bar{1}11$)	(1 $\bar{1}1$)	(11 $\bar{1}$)
(111)*	V_{000} $+E_0 - E$	$V_{02\bar{2}}$	$V_{\bar{2}0\bar{2}}$	$V_{\bar{2}\bar{2}0}$	$V_{\bar{2}\bar{2}\bar{2}}$	$V_{\bar{2}00}$	$V_{0\bar{2}0}$	$V_{00\bar{2}}$
(1 $\bar{1}\bar{1}$)*	V_{022}	V_{000} $+E_0 - E$	$V_{\bar{2}20}$	$V_{\bar{2}02}$	$V_{\bar{2}00}$	V_{222}	V_{002}	V_{020}
($\bar{1}\bar{1}\bar{1}$)*	V_{202}	$V_{2\bar{2}0}$	V_{000} $+E_0 - E$	$V_{0\bar{2}2}$	$V_{0\bar{2}0}$	V_{002}	$V_{2\bar{2}\bar{2}}$	V_{200}
($\bar{1}\bar{1}1$)*	V_{220}	$V_{20\bar{2}}$	$V_{02\bar{2}}$	V_{000} $+E_0 - E$	$V_{00\bar{2}}$	V_{020}	V_{200}	$V_{22\bar{2}}$
($\bar{1}\bar{1}\bar{1}$)*	V_{222}	V_{200}	V_{020}	V_{002}	V_{000} $+E_0 - E$	V_{022}	V_{202}	V_{220}
($\bar{1}11$)*	V_{200}	$V_{2\bar{2}\bar{2}}$	$V_{00\bar{2}}$	$V_{0\bar{2}0}$	$V_{0\bar{2}\bar{2}}$	V_{000} $+E_0 - E$	$V_{2\bar{2}0}$	$V_{20\bar{2}}$
(1 $\bar{1}1$)*	V_{020}	$V_{00\bar{2}}$	$V_{\bar{2}2\bar{2}}$	$V_{\bar{2}00}$	$V_{\bar{2}0\bar{2}}$	$V_{\bar{2}20}$	V_{000} $+E_0 - E$	$V_{02\bar{2}}$
(11 $\bar{1}$)*	V_{002}	$V_{0\bar{2}0}$	$V_{\bar{2}00}$	$V_{\bar{2}\bar{2}\bar{2}}$	$V_{\bar{2}\bar{2}0}$	$V_{\bar{2}02}$	$V_{0\bar{2}\bar{2}}$	V_{000} $+E_0 - E$

where the subscripts on the V_{ijk} are the differences between the column and row subscripts.

In order to work with the projection operators, as we did for beta-brass, it is convenient to number the operations in Table XXVI from 1 to 48, in the order given, and to label the eight plane waves as

$$\begin{aligned}
 \psi_1 &= [111], & \psi_2 &= [1\bar{1}\bar{1}] \\
 \psi_3 &= [\bar{1}\bar{1}\bar{1}], & \psi_4 &= [\bar{1}\bar{1}1] \\
 \psi_5 &= [\bar{1}\bar{1}\bar{1}], & \psi_6 &= [\bar{1}11] \\
 \psi_7 &= [1\bar{1}1], & \psi_8 &= [11\bar{1}].
 \end{aligned}$$

TABLE XXVIII. EFFECT OF DIAMOND LATTICE OPERATIONS ON [111] PLANE WAVES

		Function index							
		1	2	3	4	5	6	7	8
Operation index	1	1	2	3	4	5	6	7	8
	2	-4	3	2	-1	-8	7	6	-5
	3	-2	-1	4	3	-6	-5	8	7
	4	-3	4	-1	2	-7	8	-5	6
	5	-3	-1	4	2	-7	-5	8	6
	6	-2	4	-1	3	-6	8	-5	7
	7	-4	3	-1	2	-8	7	-5	6
	8	-3	4	2	-1	-7	8	6	-5
	9	-2	3	4	-1	-6	7	8	-5
	10	-4	-1	2	3	-8	-5	6	7
	11	-4	2	3	-1	-8	6	7	-5
	12	-3	2	-1	4	-7	6	-5	8
	13	-2	-1	3	4	-6	-5	7	8
	14	1	3	2	4	5	7	6	8
	15	1	4	3	2	5	8	7	6
	16	1	2	4	3	5	6	8	7
	17	1	4	2	3	5	8	6	7
	18	1	3	4	2	5	7	8	6
	19	-4	-1	3	2	-8	-5	7	6
	20	-2	4	3	-1	-6	8	7	-5
	21	-3	2	4	-1	-7	6	8	-5
	22	-4	2	-1	3	-8	6	-5	7
	23	-2	3	-1	4	-6	7	-5	8
	24	-3	-1	2	4	-7	-5	6	8
	25	5	6	7	8	1	2	3	4
	26	-8	7	6	-5	-4	3	2	-1
	27	-6	-5	8	7	-2	-1	4	3
	28	-7	8	-5	6	-3	4	-1	2
	29	-7	-5	8	6	-3	-1	4	2
	30	-6	8	-5	7	-2	4	-1	3
	31	-8	7	-5	6	-4	3	-1	2
	32	-7	8	7	-5	-3	4	2	-1
	33	-6	7	8	-5	-2	3	4	-1
	34	-8	-5	6	7	-4	-1	2	3
	35	-8	6	7	-5	-4	2	3	-1
	36	-7	6	-5	8	-3	2	-1	4
	37	-6	-5	7	8	-2	-1	3	4
	38	5	7	6	8	1	3	2	4
	39	5	8	6	7	1	4	3	2
	40	5	6	8	7	1	2	4	3
	41	5	8	6	7	1	4	2	3
	42	5	7	8	6	1	3	4	2
	43	-8	-5	7	6	-4	-1	3	2
	44	-6	8	7	-5	-2	4	3	-1
	45	-7	6	8	-5	-3	2	4	-1
	46	-8	6	-5	7	-4	2	-1	3
	47	-6	7	-5	8	-2	3	-1	4
	48	-7	-5	6	8	-3	-1	2	4

Using the origin S , the effect of each operation can be determined by starting with the plane wave solution in the form

$$\psi_1 = [111] = \exp \{-2\pi i[l_1x + l_2y + l_3z]/a\} \quad (17.1)$$

as obtained from (9.13). Then

$$\begin{aligned} (JC_4^2, \mathbf{T})[111] &= \exp \{-2\pi i[l_1(x + a/4) + l_2(y + a/4) - l_3z]/a\} \\ &= [11\bar{1}] \exp(-\pi i/2) \exp(-\pi i/2) = -[11\bar{1}]. \end{aligned} \quad (17.2)$$

All operations of this type are given in Table XXVIII, taken from Mariot.²⁵

Combining the information in this table with Table XI, the reducible characters are

	E	C_4^2	JC_4	JC_2	C_3	J	JC_4^2	C_4	C_2	JC_3
χ	8	0	0	4	2	0	0	0	0	0

By (4.1), we have

$$n_{\Gamma_1} = 1, \quad n_{\Gamma_2'} = 1, \quad n_{\Gamma_{26}'} = 1, \quad n_{\Gamma_{15}} = 1$$

with all other n_i vanishing. Thus, this representation can be decomposed into two nondegenerate irreducible representations and two triply degenerate ones.

Herman²⁶ has extended this process to plane waves of the form $[200]$, $[220]$, $[311]$, $[222]$, etc., since the accuracy of the approximation is improved as the number of plane waves increases. However, Slater points out that the convergence of the OPW method is very slow, and one soon reaches the maximum number of functions which are feasible even for a large computer.

It is possible to simplify the process of finding the roots of the reduced determinant because of relations among the elements. These are based on the realization that Eq. (15.12) has the form of the customary expression for the coefficients in a Fourier expansion. That is, we express the periodic potential $V(\mathbf{r})$ as the Fourier series

$$V(\mathbf{r}) = \sum V_{\mathbf{h}_i} \exp [i(\mathbf{h}_i - \mathbf{h}_j) \cdot \mathbf{r}]. \quad (17.3)$$

Multiplying by $\exp [=i(\mathbf{h}_i - \mathbf{h}_j) \cdot \mathbf{r}]$ and integrating over the unit cell then gives (15.12).

Now (15.12) shows that if we change \mathbf{r} to \mathbf{r}' by a symmetry operation of the space group, the Fourier coefficients will be transformed in accordance with

$$V_{\mathbf{h}_i'} = \exp [i\Delta(\mathbf{h} \cdot \mathbf{r})] V_{\mathbf{h}_i} \quad (17.4)$$

where $\Delta(\mathbf{h} \cdot \mathbf{r})$ is the change in the exponents. This relation follows from the invariance of $V(\mathbf{r})$ under the operation. Since \mathbf{h} is 2π times a reciprocal lattice vector, and since the change in \mathbf{r} is a lattice vector or some simple fraction of one in direct space, Eq. (17.2) will have the form

$$V_{\mathbf{h}_{ii}'} = \exp [2\pi i(l_1 u_1 + l_2 u_2 + l_3 u_3)] V_{\mathbf{h}_{ii}} \quad (17.5)$$

where \mathbf{u} is the direct-lattice displacement. It follows that when the u_i are interchanged among themselves by a symmetry operation, the Fourier coefficients for a given set l_1, l_2, l_3 are likewise interchanged.

Applying this to the diamond lattice, we see that the operation which transforms (xyz) into (yxz) , for example, transforms V_{202} into V_{022} , or vice versa, so that these quantities are equal. Further, it follows by an argument similar to that of (17.2) that there will be additional relations of the form $V_{200} = -V_{\bar{2}00}$. The complete set of such relations, when applied to the secular determinant above, gives the following simpler one:

	(111)	(1 $\bar{1}\bar{1}$)	($\bar{1}$ 1 $\bar{1}$)	($\bar{1}\bar{1}$ 1)	($\bar{1}\bar{1}\bar{1}$)	($\bar{1}$ 11)	(1 $\bar{1}$ 1)	(11 $\bar{1}$)
(111)*	$V_{000} + E_0 - E$	V_{220}	V_{220}	V_{220}	V_{222}	$-V_{200}$	$-V_{200}$	$-V_{200}$
(1 $\bar{1}\bar{1}$)*	V_{220}	$V_{000} + E_0 - E$	$-V_{220}$	$-V_{220}$	$-V_{200}$	V_{222}	V_{200}	V_{200}
($\bar{1}$ 1 $\bar{1}$)*	V_{220}	$-V_{220}$	$V_{000} + E_0 - E$	$-V_{220}$	$-V_{200}$	V_{200}	V_{222}	V_{200}
($\bar{1}\bar{1}$ 1)*	V_{220}	$-V_{220}$	$-V_{220}$	$V_{000} + E_0 - E$	$-V_{200}$	V_{200}	V_{200}	V_{222}
($\bar{1}\bar{1}\bar{1}$)*	V_{222}	V_{200}	V_{200}	V_{200}	$V_{000} + E_0 - E$	V_{220}	V_{220}	V_{220}
($\bar{1}$ 11)*	V_{200}	V_{222}	$-V_{200}$	$-V_{200}$	V_{220}	$V_{000} + E_0 - E$	$-V_{220}$	$-V_{220}$
(1 $\bar{1}$ 1)*	V_{200}	$-V_{200}$	V_{222}	$-V_{200}$	V_{220}	$-V_{220}$	$V_{000} + E_0 - E$	$-V_{220}$
(11 $\bar{1}$)*	V_{200}	$-V_{200}$	$-V_{200}$	V_{222}	V_{220}	$-V_{220}$	$-V_{220}$	$V_{000} + E_0 - E$

It is quite evident that computing eight projection operators each involving forty-eight terms is a long and tedious process, so that we shall merely state the results. It is found that

$$E - E_0 = V_{000} - 3V_{220} + V_{222}:\Gamma_1$$

$$E - E_0 = V_{000} - 3V_{220} - V_{222}:\Gamma_2'$$

$$E - E_0 = V_{000} + V_{220} + V_{222}:\Gamma_{25}'$$

$$E - E_0 = V_{000} + V_{220} - V_{222}:\Gamma_{15}$$

Herman²⁶ has given an explicit example of a factorized secular determinant involving [000], [111], [200], and [220] type plane waves; this is given as Table VII in his thesis.

The remaining part of the procedure for calculating the energy bands shown in Figs. 39 and 40 is essentially numerical. Since the purpose of the present article is to indicate the relation between symmetry, group theory, and the nature of the band structure, we shall refer the reader to the article by Woodruff³⁰ in Volume IV of this series.

18. SPIN AND DOUBLE GROUPS

One of the refinements in energy band theory which has been found to be significant in the case of silicon and germanium is the effect of spin. Spin introduces a new symmetry operation into any space group, because the arrangement of the spins must be consistent with the other symmetries.

To consider quantitatively the effect of spin, we realize that the solutions to the Schrödinger equation for a spherically symmetric potential $V(r)$ are of the form

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

where

$$\Phi(\phi) = \exp(\pm im_l \phi).$$

A rotation of coordinate axes about the z -axis through an angle α can be expressed as

$$(\alpha, E)\psi = R\Theta \exp[\pm im_l(\phi - \alpha)] = \exp[\mp im_l \alpha].$$

For a given value of l , there are $(2l + 1)$ values of m_l , and the effect of this rotation on the associated atomic orbitals can be expressed in terms

³⁰ T. O. Woodruff, *Solid State Phys.* **4**, 367 (1957).

of the matrix

$$\Gamma^{(l)}(\alpha) = \begin{bmatrix} \exp(-il\alpha) & 0 & & 0 & \cdots & 0 \\ 0 & \exp[-i(l-1)\alpha] & 0 & & \cdots & 0 \\ 0 & 0 & \exp[-i(l-2)\alpha] & \cdots & 0 & \\ \cdot & \cdot & \cdot & \cdot & \cdot & \\ \cdot & \cdot & \cdot & \cdot & \cdot & \\ \cdot & \cdot & \cdot & \cdot & \cdot & \\ 0 & 0 & 0 & \cdots & \exp(il\alpha) \end{bmatrix}$$

The character is then

$$\begin{aligned} \chi^{(l)}(\alpha) &= \exp(-il\alpha) + \cdots + \exp(il\alpha) = \exp(-il\alpha) \sum_{k=0}^{2l} [\exp(i\alpha)]^k \\ &= \exp(-il\alpha) (\{\exp[i(2l+1)\alpha] - 1\} / [\exp(i\alpha) - 1]) \\ &= \frac{\exp[i(l + \frac{1}{2})\alpha] - \exp[i(l - \frac{1}{2})\alpha]}{\exp(i\alpha/2) - \exp(-i\alpha/2)} = \frac{\sin(l + \frac{1}{2})\alpha}{\sin(\alpha/2)}. \end{aligned} \quad (18.1)$$

For a rotation $(\alpha + 2\pi)$

$$\chi^{(l)}(\alpha + 2\pi) = \frac{\sin[(l + \frac{1}{2})(\alpha + 2\pi)]}{\sin(\alpha/2 + \pi)} = \frac{\sin(l + \frac{1}{2})\alpha}{-\sin\alpha/2} = -\chi^{(l)}(\alpha).$$

For $\alpha + 4\pi$, we find that

$$\chi^{(l)}(\alpha + 4\pi) = \chi^{(l)}(\alpha).$$

Hence, the characters change sign after a rotation of 2π , but come back to their original value for a second such rotation. We make the artificial stipulation that a rotation of 2π does not map the lattice into itself, but that a rotation of 4π does. The 2π rotation can be considered as a new symmetry element \bar{E} , called the *anti-identity*, which reverses the signs of the characters. We then have the relation

$$\bar{E}^2 = E \quad (18.2)$$

so that \bar{E} is analogous to the operator T introduced in connection with Table XXI. The effect of T on the character table is to double the number of operations at the top or bottom of the Brillouin zone. A similar result will hold for \bar{E} , leading to what are known as *double groups*. Double groups have twice as many operations as ordinary groups and more classes (although not necessarily twice the number).

Our discussion above has been in terms of orbital angular momentum,

TABLE XXIX. CHARACTER TABLE FOR POINT GROUP T_d

	E	$3C_4^2$	$8C_3$	$6JC_4$	$6JC_2$
Γ_1	1	1	1	1	1
Γ_2	1	1	1	-1	-1
Γ_3	2	2	-1	0	0
Γ_4	3	-1	0	-1	1
Γ_5	3	-1	0	1	-1

but it could equally well apply to total (orbital plus spin) angular momentum, or to spin alone. If we associate the possibilities of spin up or spin down with each lattice point, then we are led to double groups, because an additional symmetry element is introduced. Such groups are also known as Shubnikov³¹ or *black-and-white* groups and are of importance in the theory of magnetism. Suppose that the operation \bar{E} , instead of being a rotation, has the effect of changing a lattice point from black to white, or vice versa. This operation could not be combined with a threefold rotation, C_3 , for example, for we cannot construct an equilateral triangle with alternating black and white corners. However, a hexagon can be made in this fashion, so that in the group D_{6h} (the symmetry group of the hexagonal prism), \bar{E} would combine with some operations but not with others.

Let us consider the tetrahedral group T_d as an example. The characters of the single group are given in Table XXIX. The double group will then have forty-eight operations, but only eight classes, because C_4^2 belong to one class, and so do JC_2 and RJC_2 . Jones¹² proves this analytically by considering the properties of the transformation matrix for an arbitrary displacement which leaves one point invariant (i.e., one involving the Euler angles). However, we can intuitively anticipate this, since C_4^2 and JC_2 are both equivalent to a rotation of π . Now Eq. (18.1) shows that for such an operation, $\chi = 0$, since this corresponds to $\sin(l + \frac{1}{2})\pi$, where l is an integer. It may be surprising to find a color reversal associated with a threefold operation C_3 , but it will be realized that when a cube is viewed along a body diagonal—or a (111)-axis—the resultant figure is a hexagon, so that the corners can be alternately black and white.

³¹ A. V. Shubnikov, N. V. Belov, and others, "Colored Symmetry." Macmillan, New York, 1964.

TABLE XXX. CHARACTER TABLE FOR DOUBLE GROUP $\bar{E} \times T_d$

	E	\bar{E}	$6C_4^2$	$8C_3$	$8\bar{E}C_3$	$6JC_4$	$6\bar{E}C_4$	$12JC_2$
Γ_1	1	1	1	1	1	1	1	1
Γ_2	1	1	1	1	1	-1	-1	-1
Γ_3	2	2	2	-1	-1	0	0	0
Γ_4	3	3	-1	0	0	-1	-1	1
Γ_5	3	3	-1	0	0	1	1	-1
Γ_6	2	-2	0	1	-1	$\sqrt{2}$	$-\sqrt{2}$	0
Γ_7	2	-2	0	1	-1	$-\sqrt{2}$	$\sqrt{2}$	0
Γ_8	4	-4	0	-1	1	0	0	0

Since we have forty-eight operations and eight classes, the dimensionalities of the irreducible representations are given by the relation

$$1^2 + 1^2 + 2^2 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2 = 48 \quad (18.3)$$

so that the three additional representations are of degree 2, 2, and 4. Again using Bethe's method, we obtain Table XXX for the double group.

Proceeding as before, character tables corresponding to the Δ , Λ , and Σ axes may also be calculated and compatibility relations determined from them. Dresselhaus³² has pointed out that this table predicts the nature of the *spin-orbit splitting* in crystals. That is, the Schrödinger equation goes over into the Dirac equation and the Hamiltonian contains a term

TABLE XXXI. COMPATIBILITY RELATIONS FOR DOUBLE CUBIC GROUP

Γ_6	Γ_7	Γ_8
Δ_5	Δ_5	$\Delta_5\Delta_6$
Λ_6	Λ_6	$\Lambda_4\Lambda_5\Delta_6$
$\Sigma_3\Sigma_4$	$\Sigma_3\Sigma_4$	$\Sigma_3\Sigma_3\Sigma_4\Sigma_4$

³² G. Dresselhaus, *Phys. Rev.* **100**, 580 (1955).

$(e^2/4m^2c^2) \text{grad } V \times \mathbf{p} \cdot \boldsymbol{\sigma}$, where the components of $\boldsymbol{\sigma}$ are the Pauli spin matrices. Table XXXI indicates that the spin-orbit energy splits the levels which are highly degenerate at Γ into single or doubly degenerate levels along the axes. This is similar to the situation shown in Herman's calculations for the valence bands of silicon and germanium (Figs. 40b and d). Hence, spin-orbital splitting is responsible for the existence of several kinds of holes in these materials.

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