Brillouin zones and crystal symmetry We have seen that the energy eigenvalues of the periodic potential problem are periodic in the reciprocal lattice: ek+G — els> thus to label the eigenvalues uniquely it is necessary to restrict k to a primitive cell of the reciprocal lattice. The primitive cell may be chosen in various ways, but the standard convention is to bound the cell by the planes which bisect the lines joining k	Vùng Brillouin và đối xứng tinh thể 4 h 45 Chúng ta thấy rằng trị riêng năng lượng của bài toán thế tuần hoàn cũng tuần hoàn trong mạng đảo: Do đó, để đặt tên các trị riêng một cách hợp lý, chúng ta cần giới hạn k trong một ô nguyên thủy của mạng đảo. Ô nguyên thủy được chọn theo nhiều cách khác nhau, nhưng cách thông thường là giới hạn ô bằng các mặt phẳng chia đôi các đường thẳng nối k=0 với điểm gần nhất của

= 0 to the nearest points of the reciprocal lattice. This cell is called the Brillouin zone, or first Brillouin zone. Unless otherwise specified, our k's are under¬stood to be reduced to this zone. The Brillouin zone of the linear lattice is shown in Fig. 1, of the square lattice in Fig. 2, the sc lattice in Fig. 3, the bcc lattice in Fig. 5, and the fee lattice in Fig. 7. The construction of the zones is described in ISSP, Chapter 12.

mạng đảo. Ô này được gọi là vùng Brillouin, hoặc vùng Brillouin thứ nhất. Nếu không có phát biểu ngược lại, chúng ta hiểu k của chúng ta quy về vùng này. Vùng Brillouin của mạng tuyến tính được biểu diễn trong H.1, của mạng vuông trong hình 2, mạng sc trong H.3, mạng bcc trong H.5, và mạng fcc trong H.7. Việc xây dựng các vùng được mô tả trong ISSP, chương 12.

There are certain useful symmetry properties of the hamiltonian for the periodic crystal potential which are most easily discussed with the help of elementary group theory. The reader without benefit of group theory may acquire the needed elements from Chapter 12 in Landau and Lifshitz. The modest object of this chapter is to make it possible for a reader equipped with a knowledge of point symmetry groups and their representations to extend his knowledge to the important symmetry properties of the Brillouin zone. We also sum¬marize in tabular form results which are frequently used. The symmetry properties are first discussed without spin, and later the spin is added.

Có những tính chất đối xứng hữu ích của Hamilton đối với thế tinh thể tuần hoàn có thể phân tích dễ dàng bằng lý thuyết nhóm cơ bản. Những độc giả chưa có kiến thức về lý thuyết nhóm có thể tham khảo một số kiến thức cơ bản cần thiết trong Chương 12 sách của Landau và Lifshitz. Mục đích chương này chỉ dừng lại ở việc trang bị cho người đọc một số kiến thức về nhóm đối xứng điểm và biểu diễn của chúng để áp dụng vào các tính chất đối xứng quan trọng của vùng Brillouin. Chúng tôi cũng tóm tắt các kết quả thường được dùng nhất dưới dạng bảng. Trước hết chúng ta sẽ thảo luận những tính chất đối xứng này khi không có spin, sau đó thảo luận trong trường hợp có spin.

In a crystal the group G of the hamiltonian is the space group of the crystal structure plus the operation of time reversal. We recall that the lattice and thus the hamiltonian is invariant under all translations of the form

(1) Tx = x + t, where t is a vector in the direct lattice:

(2) t = la. + mb + wc; I, m, n — integers;

and a, b, c are the primitive basis vectors. Thus for a Bloch function

(3) T<pk = etkt<pk;

the <pk belong to one-dimensional representations of the translation group T

and have the eigenvalue etk'\ We restrict our discussion at the beginning to crystal structures which are themselves bravais lattices. That is, we defer discussion of space groups which contain screw axes or glide planes.1 Crystallographic nomenclature is sum¬marized in ISSP, Chapter 1.

We now study the effect of the operations of the point group R. Let PR be an operator of the point group. The result of operating on a function/(x) with R is defined to be

W PjtK*) « /(ir'x),

where R is a real orthogonal transformation.

The rotation R transforms a Bloch function <pk(x) = elk'*uk(x) into a new function <pk>(x), where k' is derived from k by a rotation R applied in k space. This result is intuitively obvious on observing that k ■ /£_1x = x • i?k.

THEOREM. If <pk(R~lx) is a solution of the wave equation, then <pr [k] (x) is a solution with the same energy, where R is an element of the group of the Schrodinger equation.

Proof: We have

(5) <pk {R~lx) = e^R~lxuk(R~lx) = eiR^'xuk{R~lx).

Now uk(x) is a solution of

(6) ji(p2 + 2k-p + fc2) + F(x)

1 For full details of these space groups, see H. Jones, Theory of Brillouin zones and electronic states in crystals, North-Holland, Amsterdam, 1960; V. Heine, Group theory in quantum mechanics, Pergamon, London, 1960; G. F. Koster, Solid state physics 5, 174-256.

(7) j — (p2 + 2k • R V + k2) + 7(x)J uk{R lx) =» \kuk(R *x)

where we have used the relations

ViR-'x) = 7(x),

R *p • R *p = p2.

/2[k]. p = k • irx[P],
JR[k] • R[k] = k2,

so that <p.R[k](x) is a solution of the same equation as tpk{R *x) and has the same energy. Note that <pfl[k] (x) is an eigenfunction of the lattice translation operator T, with the eigenvalue
We can therefore generate a representation of R by letting R operate on k in k space or by letting R~l operate on x in real space. If there is only a single <pk for each k, we may replace (4) by
-FWk(x) = <Pfi[k](x)-

If the point group h^s n elements, the degenerate <pk form (for a non¬special k) an n-dimei^sional representation of the group of the Schro- dinger equation.

If a certain k0 is invariant with k0 = #'k0 under certain operations R' forming a subgroup of R, these operations form the group of k0. That is, if there are symmetry elements which leave special wave-vectors invariant, these symmetry elements form a group which is called the group of the wavevector. Because of the periodicity of the reciprocal lattice we treat k and k + G as identical (not merely equiv¬alent) wavevectors, where G is a vector in the reciprocal lattice. This statement is consistent with the correct enumeration of states (Chap¬ter 1). Suppose that the states <pkft of given k are degenerate in energy: the operations of the group of k transform <pkll into a <^x with the same k, and the <p's are said to form a representation of the group of k. The representation is known as the small representation.

We consider first the trivial example of a linear lattice, of lattice constant a; the Brillouin zone is shown in Fig. 1. The first zone is

FIG. 1. Brillouin zone of linear lattice.

bounded by —w/a and w/a. If the potential V(x) is even with V(—x) = V{x), then the group of the hamiltonian includes the reflection operation in a plane through the origin, and k\ and — k\ are degenerate in energy. We denote the reflection operation normal to the x axis by mx.

The special points in k space in this example are —w/a and w/a; they differ by the reciprocal lattice vector 2w/a and are therefore identical points in every respect. It follows that

thus the point w/a is invariant under mx. The operations E and mX) where E is the identity, are the group of the wavevector w/a. The representations of this group are one dimensional and are trivial; they are either even or odd under mx, so that ^,/0 = ± <p-w/a, and either

(14) <p9fa = sin (wx/a)uv/a(x),

or

<P*la = COS (wx/a)urla(x).

We see that the Bloch functions at the boundaries of this zone are standing waves. The u's in (14) and (15) need not be identical, because the ^'s belong to different representations and thus to differ¬ent energies.

We notice another feature of the zone boundary. The point (2w/a) is identical with k\ because the points differ only by a vector in the reciprocal lattice. Recall that ±kx are degenerate in energy. Thus the energies satisfy

e(ki) = e(k2) = B(-k i);

if we let k\ approach w/a, we see that k2 approaches —w/a, so that

(17) lim £
5—► +0
This implies that the energy is even about ±v/a, whence
(18)
at the points ±v/a.

SQUARE LATTICE

The Brillouin zone of the square lattice is shown in Fig. 2. The point group symmetry of the lattice is denoted by the symbol 4mm; there is a fourfold axis containing two sets of mirror planes, one set made up of m* and mVi and the other made up of two diagonal planes designated mds md>. For a discussion of crystal symmetry elements, see ISSP, Chapter 1.

There are six special types of points or lines in the Brillouin zone of the square lattice—the points T, M, X, and the lines A, Z, 2. The point T which lies at k = 0 transforms into itself under all the opera¬tions of the point group. Under the same operations M transforms directly into itself or into the other corners of the square. The corners are connected to each other by vectors in the reciprocal lattice, and therefore the four corners represent only a single point. Trans¬forming one corner into another is equivalent to taking a corner M into itself. The point X is invariant under the operations 2Z, mx, mv> where the reflection mx and the twofold rotation 2* carries r/a into the identical point —w/a.

The special lines 2, A, and Z are invariant respectively under the mirror operations m^, mv, and mx; the invariance of Z under mx follows

FIG. 2. Brillouin zone of the square lattice; the point group symmetry is 4mm.

because the operation takes Z into a point connected to Z by a recip-rocal lattice vector. Thus the points labeled G and F

are related by mx and differ by the reciprocal lattice vector (2ir/a,0,0). For the square lattice we see that the argument of (17) applies to every point on the zone boundary, so that gradk £ = 0 on the zone boundary. This property of the energy is inseparable from the presence of the mirror plane; the property does not hold, for example, at the (111) faces in the fee problem (Fig. 7) because there is no mirror plane normal to the [111] direction.

TABLE 1

CHARACTER TABLES OF THE SMALL REPRESENTATIONS OF THE SPECIAL POINTS AND LINES OF THE SQUARE LATTICE

The character tables for the special points and lines of the square lattice are given in Table 1. We can usefully label a band by the set of labels of its irreducible representations at special points; thus a band might be labeled as Y$&\X±ZtM§ 2i.

COMPATIBILITY RELATIONS

Within a single energy band the representations at the special points and lines are not entirely independent. The representations must be compatible. Suppose that the band has the representation Zt at Z, so that the state is odd under the mirror operation mx. This representation is not compatible at the point X on the line Z with the representations X\ and X3, which are even under mx; further, Z2 is not compatible with M \ and Mh because these representations are even under mx. The question of Mb requires attention, but ilf5 is reducible under the group E, mx into Z\ and Z2, so that Af5 is compatible with either Z\ or Z%. The complete compatibility relations for the square lattice are simple to work out and are

given in Table 2.

TABLE 2

COMPATIBILITY RELATIONS FOR THE SQUARE LATTICE

Representation Compatible with

SIMPLE CUBIC LATTICE

The full cubic point group is 4/m 3 2/m. There are four special points R, M, X, T and five special lines A, S, T, 2, Z, as shown in Fig. 3.

FIG, 3. Brillouin zone of the simple cubic lattice, with special poijits labeled, T, R.

The point T at the center of the zone obviously transforms into itself under all the operations of the cubic group. The point R at the corner is connected to the other corners by reciprocal lattice vectors, so that all eight corners are a single point. The eight corners transform into each other under the cubic group; thus R and T have the same representations, as given in Table 3, which is given in every textbook on group theory. The point H is included for use with the bcc lattice.

TABLE 3

CHARACTER TABLE OF THE SMALL REPRESENTATIONS OF T, R, H

In Table 4 we compare three of the common notations used for the representations of the cubic group, and give the lowest-order basis functions which transform according to these representations. For x, y, z we could equally well write kX} kv, kz. Basis functions of higher orders are given in Table II of the paper by Von der Lage and Bethe.

X, M. The point equivalent to X lies at the intersection of the kz axis with the lower face of the cube. There are three points equivalent to M, at the intersections of the kxky plane with the vertical edges; the points X and M have the same symmetry

elements, 4/mmm. The representations and symmetry types are given in Table 5. Character tables may be found in Jones, pp. 99 and 104; Bouckaert, Smoluchowski and Wigner, p. 64.

A, T. The point T is equivalent to three points on the other vertical edges. The point group is 4mm; the point A has the same point group. The basis functions below are referred to the z axis:

TABLE 4

SYMMETRY TYPES AT POINTS T, R, H OF CUBIC LATTICES

Note: BSW = Bouckaert, Smoluchowski, and Wigner, Phys. Rev. 60, 58(1936).

LB = Von der Lage and Bethe, Phys. Rev. 71, 612(1947).

Chem = used by most chemists; also in the text by Heine, reference 1.

TABLE 5

SYMMETRY TYPES OF POINTS X, M OF CUBIC LATTICES (REFERRED TO THE Z AXIS)

Representation Basis Functions

A. The point group is 3m. The basis functions are referred to the [111] axis:

The representations of F are identical with that of A.

2, S. The groups are holomorphie to 2mm. For operations referred to kx = ky and kz = 0, the basis functions are:

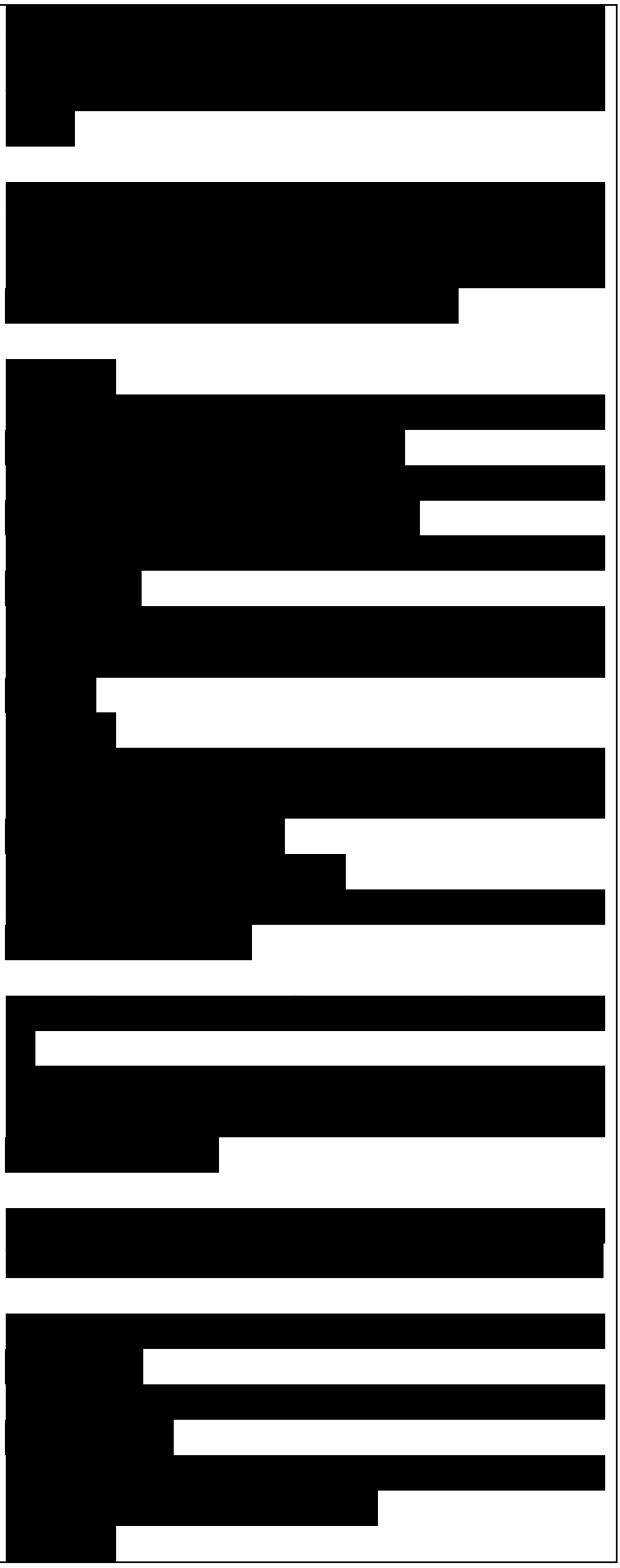
Z. The point Z has two mirror planes and a twofold axis; with basis functions referred to the z axis:

The representations of G, K, U, D are identical with those of Z.

The compatibility relations for the sc lattice are given in Table 6.

COMPATIBILITY RELATIONS FOR THE SIMPLE CUBIC LATTICE

TABLE 6



CLASSIFICATION OF PLANE WAVE STATES IN THE EMPTY LATTICE

In Chapter 13 on the calculation of energy bands we shall discover reasons why the sequence of bands in a crystal often has a strong resemblance to the sequence of plane wave states, with the crystal field considered as a potential which lifts certain accidental degeneracies which occur for plane waves. One gains a very powerful insight into band structure by considering the perturbed plane waves. ,

We wish to rewrite a plane wave of general wavevector k':

(19) ^ =

so that it appears in the reduced zone scheme. We can always find a reciprocal lattice vector G such that

(20) k = k' - G

lies in the first Brillouin zone. Then we define

(21) ** = ** = elk‘*«k(x), with

(22) nk(x) = ek - ^ (k + G)2 = ek-.

Here etG'x has the periodicity of the direct lattice, as required.

Energy versus k in Reduced Zone, SC Lattice. We consider now the behavior and degeneracies of the energy bands in the reduced zone, for an empty sc lattice of unit lattice constant (a = 1) and F(x) = 0. The lowest energy occurs for G = 0 and gives us the band A sketched in Fig. 4:

(23) Sjk = 2m kK Define band B for G = 2t(100); according to (22)

(24) Sfik = ^ {(&* — 27r)2 + ky2 + kz2\.

At k = 0, eBo = (1/2w)(2t)2, and Bsk. drops as we go out in the [100] direction to make contact with band A at the point X (k = t00). The band C is defined for G = 27r(100). The bands D, E, F, G are defined for G/2t = (010), (OlO), (001), (OOl). The

next set contains 12 bands, for G = 2ir(110) and equivalent G's.

We consider the effect of a weak cubic crystal potential in lifting the accidental parts of the degeneracies evident in the band scheme of Fig. 4. There is in the empty lattice a sixfold degeneracy at r for G = 2T(100) and equivalent G's. The unperturbed wavefunctions at r may be written as

k in [100] direction

FIG. 4. Reduced zone scheme for free electrons in empty simple cubic lattice for a = 1. Degeneracies are indicated in parentheses. Representative values of the extended waveveetors are given for several boundary points.

At r the group of the wavevector is that of the full cubic point group. We can construct irreducible representations of this group from the <pi by determining the characters of the <pi and then reducing the represen¬tation or, perhaps more easily, by expanding the <pi in series for small arguments and then using ingenuity, guided by Table 4. Thus, to quadratic terms in the coordinates,

(26)

We emphasize that the elements R' of the group of the wavevector are elements which operate on the coordinates. We may form several representations from (26):

Thus for G = 2x(100) we reduce the sixfold degenerate r to

(30) r = Tt + r15 + Ti2 + p + dy,

by analogy with atomic orbitals. The sixfold degeneracy splits into one, two, and threefold states.

At the lowest point X the states are

(31) <pi = erix; <p% = e~*ix.

From these we may form the combinations

(32) X\ ~ cos TX] X^ ~ sin TX.

If the ion-core potential is attractive, it is likely that X1 will lie lower in energy than X4, because the cosine piles up more charge on an ion core centered at x = 0 than does the sine.

BODY-CENTERED CUBIC LATTICE

The Brillouin zone of the bcc lattice is the rhombic dodecahedron shown in Fig. 5; the form of the zone is derived in ISSP, Chapter 12. The symmetry operations for r, A, A, 2 are identical with those of the

FIG. 5. The Brillouin zone of the body-centered cubic lattice showing the sym¬metry points and axes.

same points in the sc lattice. The point H has the full cubic sym-metry, as for r. The characters and symmetry types of N and P are given by Jones. The classification of the representations of the energy bands in the empty lattice is given in Fig. 6.

FACE-CENTERED CUBIC LATTICE

The form of the Brillouin zone is given in Fig. 7; the zone is a truncated octahedron. Special points of unusual interest are L at the center of each hexagonal face; X at the center of each square face; and W at each corner formed by two hexagons and one square. Their coordinates in terms of the side a of the unit cube of the direct lattice are

(33)

The classification of the represen¬tations of the energy bands is given in Fig. 8. We note that there is no mirror plane normal to the [111] direction in the fee lattice; thus there is no need for gradk £ to be zero across the hexagonal faces. For details of the behavior on the hexagonal faces, see Jones, p. 47.

HEXAGONAL CLOSE-PACKED AND DIAMOND STRUCTURES

The space groups of these structures

contain glide planes or screw axes which are not inherent in the primitive translational lattice. The irreducible representations of wavevectors lying within the zone are not radically changed by the new operations, but there is a serious change at the surface points of the zone. Because of the new opera¬tions it can happen that at a special point, along a whole line, or on a

FIG. 7. The Brillouin zone of the face-

FIG. 8. Free particle energy bands centered cubic lattice showing the sym-for-a face-centered cubic lattiee. metry points and axes.

whole zone face the irreducible representations are only two dimen-sional. One says that the glide planes and screw axes cause the bands to stick together on the special surface lines and planes. We emphasize that our discussion of zone symmetry is still worded as if electron spin did not exist.

We illustrate the effect by a simple example in two dimensions. Consider the rectangular Brillouin zone shown in Fig. 9; let the space group of the direct crystal have mirror planes m normal to the a axis at x = ia and fa, and a glide plane g parallel to the a axis. The space group is p2mg. Suppose that X(x,y) is a solution of the wave equation at k = r/a(10), which we denote by X. The glide operation implies

(34) gX(x,y) - X(x + ^a; — y).

This space group necessarily contains the inversion J, so that

JX{x,y) = X(-x)-y).

The mirror plane at x = implies

(36) mX(x,y) = X(—x + ia;y).

Then we see that

(37) gX(x,y) = mJX(x,y).

Suppose that the representation were one-

dimensional: then because J2X(x,y) = X(x,y), we would have JX(x,y) = ±X(x,y). Because m2X(x,y) = X(x,y), it would follow that mX(x,y) = ±X(x,y), From (37)

(37) g2X(x,y) = mJmJX(x,y) = (±1)2(±1) %X(x,y) = X(z,y). However,

(38) g2X(x,y) = gX(x + ia,-y) = X(x + a,y)

= eik*aX(x,y) = eirX(x,y) = -X(x,y),

which contradicts (38). Therefore the representation in this space group at X cannot be one-dimensional. The bands must stick at X.

By using time reversal invariance we show that the bands stick on the boundary line through XZ. Let K be the time reversal oper¬ator; we know from the preceding chapter that in the absence of spin

(39) K<pk(x,y) = <p-k(x,y).

But on the boundary k = (w/a,ky) we have

(40) -k=(-1 -*,,) - (*. -kty

Thus, from (37) and assuming the state k to be nondegenerate,

(41) gK<pk(x,y) = mJ<p_k(x,y) = m<pk(x,y) = <pk(x,y)»

where in the last step we have used the relation m~ (^> k^j

(a* instead of letting mx act on the coordinates. However,

gKgK<pk(x,y) = g <pk(x,y); and by the argument of (39)

(42) g2<f>k(x,y) = <pk(x + *,y) = -<pk(x,y),

which is inconsistent with (42). Thus the <pk and gK<pk must be independent functions; their energy must be the same because the hamiltonian is invariant under the operations g and K. The bands stick on the boundary line through XZ; there can be no energy gap between these two

bands.

A similar argument applied to the hexagonal close-packed structure [C. Herring, Phys. Rev. 52, 361 (1937); J. Franklin Institute 233, 525 (1942)] shows that only doubly-degenerate states exist on the hexagonal faces of the Brillouin zone, Fig. 10. This result is important because it implies that no energy gap exists across the hexagonal face. It has been shown, however, [M. H. Cohen and L. M. Falicov, Phys. Rev. Letters 5, 544 (I960)] that the degeneracy is lifted by the spin- orbit interaction. For the diamond structure, see the paper by Elliott cited in footnote 2; for the zinc blende structure, the paper by Dresselhaus.

SPIN-ORBIT COUPLING2

We now add the electron spin to the Brillouin zone problem. Adding the spin without turning on the spin-orbit coupling simply doubles the degeneracy of every state. But the spin-orbit interaction will lift some of the degeneracy—not, however, at k values for which the states are only doubly-degenerate in the presence of spin, because the Kramer theorem on time reversal symmetry requires at least two¬fold degeneracy. A p-like state (such as r15 in a cubic crystal, according to Table 4) is threefold degenerate without spin; sixfold degenerate with spin; and with spin-orbit interaction the state behaves as a Px, PH se^ in atomic spectroscopy: the sixfold level splits into one fourfold level like p# and one twofold level like py,.

The small representations are changed by spin-orbit coupling. For the group r of Table 4, the representations with spin are given in terms of the representations without spin.

Ti Ti r2 r12 IV iv IV iY • • •

r< x DVi re r7 rs re + r g r7 + r8 r§ ry • • •

The representations r6, r7, r8 are two-, two-, and four-dimensional, respectively. Character tables for special points are given in the paper by Elliott; results for the point T are given in Table 7.

TABLE 7

CHARACTER TABLE OF THE EXTRA REPRESENTATIONS IN THE DOUBLE GROUP OF T

(The operations with bars overhead are isomorphous to those without them)

[redacted]