

# Theoretical Investigation of the Electronic Energy Band Structure of Solids

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## 1. INTRODUCTION

FOR many purposes it is possible to regard each electron in a crystalline solid as moving essentially independently in a static periodic potential field. It is assumed that this field can be so chosen as to take account of the average interaction between the electron in question and the remainder of the crystal. This viewpoint forms the basis of the band theory of solids. Because of its inherent simplicity and intuitive appeal, this theory has provided a convenient conceptual framework for qualitative and quantitative discussions of the electronic properties of crystals. Ever since its introduction nearly thirty years ago, the band theory has been used, often with striking success, as a basis for interpreting various electronic properties of crystalline solids.

Many of these properties, such as the intrinsic optical absorption spectrum of semiconductors and insulators, can be readily understood simply in terms of the fact that crystals have an energy band structure, i.e., allowed ranges of energy levels separated by forbidden ranges. However, there are other properties which cannot be thoroughly elucidated in the absence of detailed information concerning the band structure.

It is now generally recognized that the band structure of crystals can have considerable complexity, and that a detailed knowledge of this complexity is basic to the understanding of many of the electrical, magnetic, optical, thermal, and elastic properties. This explains why so much theoretical and experimental effort has been devoted recently to the study of band structure. The present paper is intended as a critical evaluation of the theoretical methods which have been developed for studying band structure. In a companion paper, Benjamin Lax discusses some of the experimental methods which have proved most fruitful for determining certain features of the band structure of crystals.

The fundamental problem of energy band theory is the determination of the one-electron states of crystals. In principle, the distribution of the one-electron energy levels, and their dependence on the reduced wave vector  $\mathbf{k}$ , which together with a band index serves to identify the various one-electron states, can be determined by direct calculation, provided the effective potential is known. This involves the construction and the subsequent solution of a set of one-electron wave equations. While considerable progress has been made in devising efficient and mathematically reliable methods for solving these equations, the proper choice

of the effective potential (upon whose existence the energy band theory is predicated) is complicated by computational difficulties, and obscured by conceptual difficulties (Mot 56).<sup>\*</sup> In order to overcome the computational difficulties, one is forced to make drastic simplifying assumptions. These tend to impair the accuracy of the results to such an extent that the band structure is usually not determined with a precision adequate for most applications. The conceptual difficulties arise when one attempts to define an effective potential which is more accurate than that given by the Hartree, the Hartree-Fock, and similar one-electron approximations.

This unfortunate situation complicates the study of certain electronic properties, such as the cohesive energy, which depend upon the behavior of all the electrons in a crystal. Here it is necessary not only to determine all the occupied one-electron states, but also to take careful account of the electron correlation effects not specifically included in the energy band theory. On the other hand, there are numerous properties, such as the electrical conductivity, which depend upon the behavior of those few electrons whose states can be changed by the application of an external force. In order to study such properties, it is usually sufficient to determine a limited portion of the band structure, i.e., that corresponding to the higher occupied states and the lower unoccupied states. While electron correlation effects also play a role here, they may be ignored in a preliminary treatment without incurring serious error.

Fortunately, the portion of the band structure just mentioned can be explored in considerable detail by combining three distinct approaches: (a) By means of group theory and perturbation theory, it is possible to obtain a complete catalog of the possible forms of the band structure, including the fine details associated with each of these forms. (b) Under special conditions, the correct form can be selected from the many possible forms with the aid of one or more carefully designed experiments. (c) Where this approach fails or proves difficult, it is helpful to carry out an energy band calculation, even if this is based on relatively crude physical assumptions. While such a calculation may yield information which of itself is too unreliable or incomplete to permit a precise determination of the band structure, it may yield a number of important clues concerning

<sup>\*</sup> Reference in parentheses will be found in the Bibliography at the end of the paper.

the probable form of the band structure. With such information, it is usually possible to reduce the number of possibilities considerably.

By combining the formal (group-theoretical and perturbation-theoretical) results, the experimental results, and those of the energy band calculation, it should always be possible to deduce the correct band structure. This contention is borne out by our recent experience with germanium and silicon, and to a lesser extent, with graphite and indium antimonide. It is our opinion that the most satisfactory approach to the study of band structure, at least in the present state of the subject, is one which involves a concerted program of experimental and theoretical endeavor.

The plan of this paper is as follows: In Sec. 2 we will present a brief review of the elements of energy band theory. The uses of group theory and perturbation theory will be examined in Sec. 3. This will be followed by a survey of numerical methods for solving the crystal wave equation. In the final section, we will illustrate complex energy band structures in terms of a few selected examples.

It is not our intention to give a complete exposition of the subject under review. Rather, we would like to bring to the attention of the reader the many theoretical techniques that are available for studying energy band structure, and to place these techniques in proper perspective. We have included a fairly representative list of references for the benefit of the reader who wishes to pursue this subject further. For additional references, the reader is referred to the review papers by Raynor (Ray 52),\* Reitz (Rei 55), Löwdin (Low 56), and Slater (Sla 56).

## 2. PHYSICAL BACKGROUND

Since it is extremely difficult to treat many-particle systems such as crystals mathematically, it is necessary to resort to simplifying assumptions in order to make any progress. Energy band theory is based on two such assumptions. In the first place, it is assumed that an actual crystal can be represented by a perfect periodic structure. In this ideal crystal, there are no structural or chemical imperfections, and all the nuclei are held fixed at their equilibrium positions. Secondly, it is assumed that each electron can be regarded as moving independently in a static potential field which somehow takes its average interaction with the rest of the crystal into account. This so-called independent-particle model shifts the emphasis from that of finding the states of the electronic system as a whole to that of finding the states of the individual electrons in the system.

The essential mathematical idea of the independent-particle model is that the wave function for the total electronic system, which depends upon the coordinates of all the electrons, can be expressed in an approximate fashion in terms of one-electron wave functions, each of which depends upon the coordinates of a single

electron. If the many-particle Hamiltonian does not contain spin-dependent terms, such as the spin-orbit interaction, it is possible to write each one-electron wave function as the product of a spatial wave function and a spin function. In the discussion to follow, we will confine ourselves to this representation.

By introducing the one-electron approximation, it is possible to reduce the many-electron wave equation to a number of one-electron wave equations. The solutions of the latter describe the one-electron states of the system. In dealing with crystals, it is convenient to impose cyclic boundary conditions on the spatial wave functions. If this is done, and if the periodic nature of the potential is taken into account, it can be shown that each one-electron state is specified by two indexes,  $\beta$  and  $\mathbf{k}$ . Hence, the set of one-electron wave equations may be written as follows

$$[-(\hbar^2/2m)\nabla^2 + V_\beta(\mathbf{k},\mathbf{r})]\psi_\beta(\mathbf{k},\mathbf{r}) = E_\beta(\mathbf{k})\psi_\beta(\mathbf{k},\mathbf{r}), \quad (2.1)$$

where  $V_\beta(\mathbf{k},\mathbf{r})$  is the potential acting on the electron represented by  $\psi_\beta(\mathbf{k},\mathbf{r})$ , and where  $E_\beta(\mathbf{k})$  is the energy level corresponding to the state  $\beta, \mathbf{k}$ . If the theory is developed in terms of the Hartree or the Hartree-Fock approximation, the potential  $V_\beta(\mathbf{k},\mathbf{r})$  will be different for different states. However, the potential for each state will have the same symmetry properties as the nuclear framework. According to the Pauli exclusion principle, each state  $\beta, \mathbf{k}$  can be occupied by no more than two electrons having opposite spins. Hence, there is a twofold spin degeneracy associated with each energy level  $E_\beta(\mathbf{k})$ .

It is possible to describe all physically distinct solutions of the above set of wave equations by confining  $\mathbf{k}$ , which represents a wave vector, to a portion of wave vector space known as the reduced zone. If one chooses a value of  $\mathbf{k}$  lying outside the reduced zone, one obtains a solution already given by a value of  $\mathbf{k}$  inside the reduced zone. If there are  $N^3$  unit cells in the cyclic crystal, there are  $N^3$  distinct values of  $\mathbf{k}$  uniformly distributed in the reduced zone.

For each of these  $N^3$  reduced wave vectors  $\mathbf{k}$ , there is a denumerably infinite manifold of solutions. These solutions are distinguished from one another by the integral index  $\beta$ . It is convenient to label the states for a given  $\mathbf{k}$  in accordance with the following prescription,

$$E_{\beta-1}(\mathbf{k}) \leq E_\beta(\mathbf{k}) \leq E_{\beta+1}(\mathbf{k}), \quad (2.2)$$

where the equality signs allow for the possibility that two or more energy levels are degenerate at a given value of  $\mathbf{k}$ .

For each value of  $\beta$ ,  $E_\beta(\mathbf{k})$  is a quasi-continuous function of  $\mathbf{k}$  throughout the entire reduced zone. Since the energy levels associated with a given  $\beta$  span a definite energy range, and thus form an energy band,  $E_\beta(\mathbf{k})$  may be called an energy band function, and  $\beta$  may be used to distinguish one energy band from another. Accordingly,  $\beta$  is known as a band index.

The energy band structure of a crystal is described

by the set of energy band functions  $E_{\beta}(\mathbf{k})$ . These in turn describe the nature of the allowed one-electron energy levels, and in particular, their functional dependence on  $\mathbf{k}$ . The arrangement and form of the various energy bands are determined by the chemical composition of the crystal, its geometrical structure, and the free atom states from which they are derived. The energy bands associated with the inner shell electrons are sharp and well separated, while those associated with the outer shell electrons are usually broad and closely spaced.

In semiconductors and insulators, a certain number of bands are fully occupied at absolute zero temperature; there is an energy gap, or forbidden band, between the top of the highest filled band (the valence band) and the bottom of the lowest unfilled band (the conduction band). This energy gap defines the minimum amount of energy required to excite an electron from the highest occupied state to the lowest unoccupied state at this temperature.

In metals and semimetals, one or more energy bands are partially filled at absolute zero temperature. The surface of constant energy separating the occupied and unoccupied states in  $\mathbf{k}$  space is known as the Fermi surface. Since there are available states immediately above the Fermi surface, it requires an infinitesimal amount of energy to excite an electron from one of the highest occupied states to one of the lowest unoccupied states.

Since many of the electronic properties of crystals depend only on that portion of the band structure which corresponds to the higher occupied states and the lower unoccupied states, there is usually greater interest in this portion than in any other. In the case of semiconductors and insulators, a knowledge of the upper reaches of the highest valence band (or bands), and of the lower reaches of the lowest conduction band (or bands) is usually sufficient in most applications of the theory. By knowing the width of the forbidden band, the location in the reduced zone of the valence and conduction band edges, and the detailed nature of these edges, it is possible to interpret many of the observed properties of such crystals. Similarly, in the case of metals and semimetals, interest focuses on that portion of the band structure which lies in the immediate neighborhood of the Fermi surface (Cha 56).

In order to determine the band structure of a crystal from first principles, it is necessary to construct and solve a set of one-electron wave equations [compare Eq. (2.1)]. The central problem here is the choice of the potential appearing in these equations. It is well to recall at this point that this potential is intended to represent the effective interaction between a given electron and the rest of the crystal. Various approximations to this effective interaction have been proposed:

(a) In the Hartree approximation, the electrons are assumed to move independently of one another, so that all correlations in the instantaneous motions of pairs of

electrons are completely ignored. This approximation fails to take account of the fact that electrons tend to avoid each other by virtue of the repulsive Coulomb force acting between them.

(b) In the Hartree-Fock approximation, the only electronic correlations which are taken into account are those which arise from the operation of the Pauli exclusion principle. This affects pairs of electrons of like spin, but not pairs having unlike spin. In this and the previous approximation, electrons in different states experience different potentials, but electrons of opposite spin in the same state have the same potential (Cor 51).

(c) In the simplified version of the Hartree-Fock method proposed by Slater (Sla 51, 53(a)) a suitable average over the potentials of all the occupied states is taken, and the resultant averaged potential is assigned to all states.

(d) In the "unrestricted" Hartree-Fock approximation [Low 55, 56; Pra 56, 57; Woo 57(a)], some correlation between electrons of unlike spin is introduced by the device of using spatially different orbitals for electrons of opposite spin. Here, each electron experiences a different potential.

(e) In the Bohm-Pines theory [Pin 55, 56(a), 56(b); Boh 57; Noz 58(a)], electronic correlation effects are taken into account by using a suitably screened Coulomb interaction between electron pairs.

(f) In the Hubbard theory (Hub 55(a), 55(b), 57), a local field correction is used to take account of correlation effects.

(g) In the Brueckner theory (Bru 54(a), 54(b), 55(a), 55(b), 55(c); Bet 56; Gol 57; Kro 57; Rod 57; Tob 57), the interaction of any two electrons is treated exactly, but the action of any further electrons on the interacting pair is replaced by an average interaction.

Although (a) through (d) are one-electron methods in the strict sense, (e) through (g) are many-electron methods, and as such are better able to take account of correlation effects. Moreover, these many-electron methods provide a great deal of physical insight into the reasons why the one-electron methods are actually as successful as they are. The same cannot be said for other many-electron methods, such as the method of configuration interaction (Nes 55), and the method of the density matrix (Low 55, McW 56(a), 56(b), 57; Chi 57). Methods (e) through (g) suggest that correlation effects can be taken into account to a very large extent if the potential acting on each electron is given the proper form. It is in this sense that they provide a theoretical justification of the usual one-electron approximation.

In order to determine rigorously the potentials acting on the various electrons in a crystal on the basis of any of the above mentioned approaches, it is necessary to carry out a self-consistent calculation. Unfortunately, such a program is ruled out by computational difficulties associated with the fact that the number of electronic states one must consider is prohibitively

large. In practice, the only feasible approach is to choose a physically plausible potential for each state, using any of the above methods as a guide, and then to solve the one-electron wave equations for these assumed potentials. It is common, though not universal practice, to use the same assumed potential for all states, since this greatly simplifies the work.

In spite of the fact that a large number of energy band calculations have already been carried out, mostly on the basis of assumed Hartree or Hartree-Fock type potentials, two crucial questions have not yet received definitive answers. These are (a) How critically does a calculated energy band structure depend upon the exact form of the assumed potentials? (b) How much error is introduced by assuming the same potential for each state?

If it turns out that the band structure does depend critically upon the assumed potential, it would be fair to conclude that an energy band calculation based on an *ad hoc* potential is not likely to provide a very reliable picture of the actual band structure. In this event, it would be necessary to calculate the band structure for a number of assumed potentials, each having a somewhat different form. The only results of the composite calculation which could be considered physically reliable would be those which are relatively insensitive to the details of the assumed potential.

Another question having theoretical interest is: (c) If a self-consistent energy band solution could actually be obtained on the basis of a particular approximation, how closely would the results agree with experiment? It would be extremely difficult to judge the adequacy of a given approximation without first having a reasonably satisfactory answer to this question. It is certainly unfair to judge the issue by comparing the results of a calculation based on an *ad hoc* potential with experiment. This type of comparison begs the question of how closely the *ad hoc* and the self-consistent potentials actually agree.

About the best that can be done at present is to carry out an energy band calculation on the basis of a crystal potential which includes the best possible estimates of the Coulomb and exchange terms, and which also contains a correlation correction, such as that suggested by the Bohm-Pines theory. Such a calculation has recently been done by Heine (Hei 57) for aluminum. Unfortunately, even when extreme pains are taken to choose the best possible potential that the present state of the theory will permit, there is still a substantial disagreement between theory and experiment. This discouraging result suggests that we have not yet found a way to account for all electronic correlation effects properly.

However, we may take some satisfaction from the fact that many energy band concepts, such as reduced wave vectors and effective masses, can be derived from a many-electron formalism (Koh 57(a)), as well as from a one-electron formalism. There is good reason to

believe that the success of the energy band theory, in accounting for a wide variety of experimental observations, is far from accidental. The essential features of the energy band theory will probably persist in future, more sophisticated theories.

### 3. FORMAL METHODS

It is possible to learn a great deal about the nature of the solutions of the crystal wave equation without solving this equation numerically. By means of group theory, the form of the various crystal wave functions can be predicted, as can the over-all form of the various energy bands in the reduced zone. By combining perturbation theory with group theory, it is also possible to predict the detailed nature of each energy band in any local region of the reduced zone. Still further information can be obtained from topological considerations.

In a classic paper, Seitz (Sei 36) showed that each crystal wave function can be classified according to its transformation properties under the operations which leave the crystal Hamiltonian invariant. For a general point in the reduced zone, the only operation which transforms a wave function into itself is the identity operation. So far as symmetry considerations are concerned, this means that each crystal eigenstate at a general point is nondegenerate (we are ignoring the spin degeneracy, and the possibility of accidental degeneracy). For a nongeneral point, operations may exist which transform a given wave function into itself, or into another wave function having the same wave vector. The set of such operations form a group, known as the group of the wave vector. The wave functions generated by the operations of this group form the bases of the irreducible representations (IR's) of this group.

From a knowledge of the structure of the group of the wave vector  $\mathbf{k}$ ,  $G(\mathbf{k})$ , it is possible to predict the types of contacts which must occur between different energy bands at  $\mathbf{k}$ . For every  $m$ -fold degenerate IR, there must exist a set of  $m$ -fold degenerate energy levels; each of these corresponds to the contact of  $m$  different bands at  $\mathbf{k}$ . Under certain conditions, a contact between bands may be wholly or partially destroyed if one moves from a point of high symmetry to a neighboring point of lower symmetry. Such behavior can be investigated by constructing compatibility or correlation tables relating the IR's at the high-symmetry point to those at the low-symmetry point.

In some cases, contacts between energy bands arise not from the crystal symmetry, but from time-reversal symmetry. Such contacts have been considered in some detail by Herring (Her 37(a)). It often happens that contacts occur which are not required by crystal or time-reversal symmetry. Such accidental contacts have also been discussed by Herring (Her 37(b)).

Group theoretical analyses have been carried out for a number of crystal structures. References to such work are given in Table I. For further information on this

TABLE I. Character tables for space groups.

Crystal structure	Single group	Double group
Simple cubic	Bou 36	Ell 54(b)
Body-centered cubic	Bou 36	Ell 54(b)
Face-centered cubic	Bou 36, Ant 52, Dre 55(c)	Ell 54(b), Dre 55(c)
Diamond	Her 42, Dor 53, Dre 55(c)	Ell 54(b), Dre 55(c)
Zincblende (sphalerite)	Par 55, Dre 55(b)	Par 55, Dre 55(b)
Hexagonal close-packed	Her 42, Ant 52	Ell 54(b)
Wurzite	Par 57, Dre 57*	Par 57, Dre 57*
Graphite (2-dimensional)	Car 53(a), Lom 55	Slo 55(a)
Graphite (3-dimensional)	Car 53(a)	Slo 55(a)
Selenium and tellurium	Ase 57(b), Fir 57	Ase 57(b), Fir 57
Miscellaneous	Ven 49, Kos 57	Kos 57

\*  $k=0$  only.

subject, the reader is referred to the following papers: Win 49; Bel 54; Kos 56, 57; Mel 56; Mar 57.

Until 1954, energy band theory was based on a crystal wave equation which did not take account of the spin-orbit interaction. In that year, Elliott (Ell 54(a), 54(b)) and others (Dre 54) recognized that this interaction could split otherwise degenerate bands, and thereby profoundly modify the band structure in regions where this splitting occurs. Elliott showed how the group-theoretical analysis of crystal wave functions and energy bands can be carried out when spin-orbit effects are included. In this case, the analysis involves a consideration of the double group (Ope 40), rather than of the single group, i.e., the space group of the crystal. The double group has already been determined for several crystal structures (compare Table I).

While it is possible to classify the crystal eigenstates at each point of the reduced zone according to their symmetry properties, the relative order of the eigenstates at a given point, or at different points in the reduced zone, cannot be determined without actually solving the crystal wave equation numerically.

However, a group-theoretical analysis might still prove fruitful in a particular application, where the overall form of the band structure is not required, and where the principal physical interest focuses on a limited portion of the band structure. For example, in the case of semiconductors and insulators, it is usually sufficient to know the detailed nature of the valence and conduction band edges, including the form of  $E(\mathbf{k})$  and the location of these edges in the reduced zone.

Under such conditions, a group-theoretical analysis can provide an exhaustive list of the possible types of energy band structure. By interpreting pertinent experimental data in terms of each of these possible types in turn, it is often possible to determine which type is actually the correct one. From this point of view, group theory provides a catalog of possible band structures, and the ultimate determination of the correct band structure is left to experiment.

The form of  $E(\mathbf{k})$  in the neighborhood of a state having a specified symmetry classification can be obtained by standard perturbation theory. The first application of perturbation theory to this type of problem is contained in a note by Shockley (Sho 50) on the band structure of germanium. Improved perturba-

tion-theoretical treatments of diamond-type crystals, particularly silicon and germanium, have since been published by a number of authors (Ell 54(a), 54(b); Ada 54; Dre 55(a), 55(c); Kan 56). Our present theoretical knowledge of the band structure of zincblende-type crystals, notably indium antimonide (Dre 55(b); Kan 57) and of graphite (Slo 55(a), 55(b); McC 57; Noz 57(b)) is based largely on perturbation-type calculations. It is also possible to determine the relationship between the band structures of geometrically similar crystals by perturbation theory (Her 55(a); Cal 57(a)).

A further source of information about energy band structure not involving numerical calculation is to be found in topology theory. Using methods developed by Morse (Mor 34, 38, 42), a number of authors, in particular Van Hove (Van 53), Phillips (Phi 56, 57), and Rosenstock (Ros 57(a)), have shown how the critical points of electronic energy level distributions can be treated. [At a critical point,  $\text{grad}_{\mathbf{k}} E_{\beta}(\mathbf{k}) = 0$ .] This work is concerned with the prediction, enumeration, and topological classification of critical points, and with the description of the analytic singularities which occur in the energy level distribution at these points. Similar problems arise in the study of lattice vibrational frequency distributions.

A group-theoretical analysis also proves useful in connection with numerical calculations. In order to map out the energy band structure of a crystal, it is necessary to solve the crystal wave equation at a representative set of points in the reduced zone. By choosing nongeneral points, and constructing trial wave functions which have the proper transformation properties under the operations of the corresponding wave vector groups, it is possible to factor the high order secular determinants arising in this work into a number of lower order determinants. Each of the latter can then be solved independently of the others. Before undertaking an energy band calculation, it is always advisable to carry out a symmetry analysis first since this greatly simplifies the calculation. The theory and practice of symmetry factorization is clearly explained in works by Koster (Kos 56) and Wilson, Decius, and Cross (Wil 55). Information on the symmetry properties of spherical harmonics, which is often helpful in this connection, may be found in a number of papers (Bet 29, Von 47, Bel 54, Mel 56, Alt 57, Ros 57(b)).

While the symmetry analysis of a crystal leads to much useful information about the band structure, such an analysis does not indicate the order in which the various electronic states are arranged on an energy scale, or their energies. In order to determine the actual arrangement of the various states, and the symmetry classification and energy of each, it is ultimately necessary to solve the crystal wave equation numerically. Methods for carrying this out are considered in the Sec. 4.

#### 4. APPROXIMATE METHODS

Since the central mathematical problem in energy band theory is the solution of the crystal wave equation, it is understandable that a great deal of effort has been devoted to the development of efficient methods for carrying out this solution. Among the many methods which have been developed for obtaining approximate solutions of the crystal wave equation, the following are worthy of mention: (a) the method of plane waves; (b) the method of orthogonalized plane waves; (c) the method of modified plane waves; (d) the method of augmented plane waves; (e) the linear combination of atomic orbitals (LCAO) method; (f) the method of Wannier functions; (g) the cellular method; (h) the scattering matrix method; (i) the variation-iteration method; and (j) the quantum defect method. Detailed descriptions of these methods may be found in a number of review articles (Ray 52, Rei 55, Low 56, Sla 56), as well as in the selected references given below. In the discussion to follow, we will confine ourselves to some general remarks about these various methods.

Although the methods listed in the foregoing differ widely in their particulars, they all have certain features in common. In the first place, each method can be formulated in terms of a suitable variational principle (Koh 52). Where several methods are based on the same variational principle, they differ among themselves through the introduction of different restrictions and simplifying assumptions. Secondly, each method makes use of the Ritz variational procedure (Mor 53). A set of suitably chosen basis functions (plane waves, atomic orbitals, etc.) is introduced, and trial wave functions are expanded in terms of these basis functions. Enough terms are included in the expansion to insure a faithful representation of the crystal wave functions. The basis functions are held fixed, and a variation of the expansion coefficients is performed. This leads to a set of linear equations of the secular type. The expansion coefficients and the corresponding energy levels are obtained by solving the secular equation.

The purpose of using the Ritz technique is to convert the difficult problem of solving a differential or integral wave equation to the simpler one of solving an equivalent secular equation. After this is done, the secular equation is easily solved by standard matrix methods. A major advantage of the Ritz technique is that it permits a considerable degree of ingenuity to be exercised in the choice of the basis functions. If these functions are properly chosen, it is possible to obtain an accurate solution with a relatively small number of such functions.

Next, each method is designed to take full advantage of the periodic nature of the crystal potential. This is accomplished by requiring each trial wave function to have the Bloch form. In methods (a) through (f), the same trial wave functions (or the same basis functions) are used everywhere in the crystal, and these are so

constructed that they automatically have the Bloch form. In the remaining methods, the crystal is decomposed into disjoint regions which fill all space, and the trial wave functions are expanded in terms of different sets of basis functions in each region. By imposing suitable boundary conditions at the surfaces of each region, it is possible to insure the continuity of the trial wave function and its first derivatives at these surfaces. In addition, it is possible to obtain wave functions which have the Bloch form everywhere in the crystal. An important advantage of the variational principle formulation is that the boundary conditions can be incorporated directly in the variational principle.

Finally, each method, with the exception of the method of plane waves, is designed to take advantage of the fact that the crystal potential is approximately spherically symmetric in the neighborhood of each nucleus, and nearly constant elsewhere in the crystal. This is particularly true for methods (g) through (j), where the decomposition of the crystal into disjoint regions is performed specifically to exploit this feature of the crystal potential. In these methods, the trial wave functions are expanded as products of radial wave functions and spherical harmonics in the neighborhood of each nucleus, since this is the natural expansion for a spherical potential. In the cellular method, the crystal is decomposed into space-filling polyhedra, one centered at each nucleus. In methods (h) through (j), the crystal is decomposed into nonoverlapping spherical regions, one surrounding each nucleus. The crystal potential is assumed to be spherically symmetric in each of these spherical regions, and constant elsewhere. While neither of these assumptions is strictly true, they do represent good first approximations. In any event, the small difference between the assumed and the actual form of the crystal potential can be taken into account by perturbation methods in a late stage of the work.

We will now make some brief remarks about each of the methods listed above.

##### (a) Method of Plane Waves

The crystal potential and the electronic wave functions are here expanded in terms of plane waves. In the case of high energy electrons (kinetic energy  $> 100$  eV), the secular equation can be solved by perturbation techniques, since the spatial fluctuation of the periodic potential is of the order of 10 eV for most crystals. Since the wave functions for such electrons can be represented quite accurately by relatively few plane wave terms, this method forms a convenient basis for the theory of electron diffraction (Bet 28, Mor 30).

It is well known that the wave functions for core, valence, and low-lying conduction band electrons fluctuate rapidly in space, and exhibit an atomic-orbital-like nodal structure in the neighborhood of each nucleus. Hence, a large number of plane waves is required to represent such wave functions. Since it is impractical

to solve the high-order secular equations which describe these electrons by perturbation theory or otherwise, the method cannot be used for quantitative work in such applications. However, in view of the inherent simplicity of the plane wave representation, the method can be used to advantage to demonstrate the qualitative features of energy band structure (Bri 30).

#### (b) Method of Orthogonalized Plane Waves

In this method, which was devised by Herring (Her 40(a)), the core wave functions are expanded in terms of linear combinations of atomic orbitals. Further, the noncore wave functions are expanded in terms of plane waves each of which has been orthogonalized to the core wave functions by the Schmidt process. The orthogonalization process serves to introduce into the wave function a nodal structure which approximates the actual one quite closely. This leaves a slowly varying portion to be represented by plane waves. One may thus expect a relatively small number of orthogonalized plane waves to be necessary to describe the wave functions for valence and low-lying conduction bands.

This expectation has in general been realized in numerous applications. These include energy band calculations of: beryllium (Her 40(b)); lithium (Par 52, Gla 57); diamond (Her 52, 54(a)); silicon (Woo 55, 57(b), Bas 57); germanium (Her 53, 54(a), 54(b)); silicon carbide (Kob 58); cesium (Cal 57(b)); iron (Cal 55(b)); potassium (Cal 56); aluminum (Hei 57, Beh 57); copper (Fuk 56); and hypothetical FCC carbon (Cas 58). As a whole, these calculations indicate that the method converges very rapidly for the lowest valence band states, but more slowly for the higher states. In all cases, however, the convergence is sufficiently rapid for the method to be considered practical.

On the credit side, this approach requires no special assumptions to be made about the form of the crystal potential, except that it have the proper symmetry. Unfortunately, the orthogonalization procedure is effective in speeding the convergence only if all the crystal states are eigenstates of the same Hamiltonian. Therefore, it is necessary to assume that the potential is the same for all states (having the same spin). In addition, there are certain noncore states which are automatically orthogonal to all core states by reasons of symmetry. For such noncore states, the orthogonalized plane waves reduce to plane waves, and the convergence rate is markedly decreased (Her 52, 54(a); Zeh 53). For further critical discussion, the reader is referred to the papers by Callaway (Cal 55(a)), Heine (Hei 57), and Woodruff (Woo 57(b)).

#### (c) Method of Modified Plane Waves

An interesting generalization of the previous method has recently been proposed by Brown and Krumhansl (Bro 58). A variational procedure is applied to a set of trial wave functions which consist mainly of plane

waves of low-wave number. In order to hasten the convergence, one or more auxiliary functions are included in the trial wave functions. These auxiliary functions are chosen so that their Fourier spectra in the high-wave number range closely approximate those of the exact eigenfunctions. In the special case where the core wave functions are used as auxiliary functions, this approach reduces to the previous one. While the present method appears to be a promising one, it is hard to judge its relative merits on the basis of the limited amount of work that has been done with it thus far.

#### (d) Method of Augmented Plane Waves

Originally proposed by Slater (Sla 37), and subsequently modified by Slater and Saffren (Sla 53(b), Saf 53), the APW method is designed to combine the best features of the plane wave and cellular methods. Here the crystal potential is assumed to be spherically symmetric inside a set of nonoverlapping spheres which surround the various nuclei, and constant elsewhere. Inside each sphere, the trial wave function is expanded as a sum of products of radial wave functions and spherical harmonics. In the constant potential region, a plane wave expansion is employed. The crystal wave equation is solved inside and outside each sphere, and the solutions are joined smoothly at their surfaces. There is a discontinuity in the slope of the wave function at each surface, but its contribution to the total energy is taken into account.

Since the APW method employs the most natural set of basis functions in each region of the crystal, it requires fewer spherical harmonic terms than the cellular method, and fewer plane wave terms than the plane wave method. Hence, the convergence rate is more favorable than that for either of these two other methods. Furthermore, the convergence rate is better than that for the OPW method, since the nodal structure is obtained in a more rigorous fashion.

There have been a number of calculations based on the APW method. These include work on copper (Cho 39, How 55), sodium (Mat 52, Saf 57), aluminum (Ant 52), and magnesium (Trl 52). These calculations, particularly those by Howarth and Saffren, suggest that the APW method is one of the most satisfactory yet devised for solving the periodic potential problem accurately and efficiently.

Leigh (Lei 56) has recently reformulated this approach in terms of a variational principle, and has introduced a number of modifications. It is still too early to decide whether Leigh's proposals will lead to any substantial improvement in the basic method.

#### (e) Method of Bloch

In the method of Bloch (also known as the tight-binding approximation), the crystal potential is represented by a superposition of atomic potentials, one



centered at each lattice site. The trial wave functions are expressed as linear combinations of atomic orbitals (LCAO's). These atomic orbitals are here taken as the eigenfunctions of the isolated atomic potentials. In order to simplify the solution of the secular equation, it is assumed that each portion of the band structure arises from a certain set of free atomic energy levels, and further, that the dominant terms in the trial wave function expansion are just those atomic orbitals which correspond to these atomic levels. On this basis, it is possible to investigate a particular portion of the band structure by limiting the expansion to the corresponding atomic orbitals. If the orbitals associated with neighboring sites do not overlap appreciably, as is the case for tightly bound states, the secular equation can be solved by standard perturbation theory (Blo 28).

This scheme is particularly appropriate for investigating the core bands of all crystals, the *d* bands of transition metals, and the lowest valence bands of ionic crystals, and other bands which arise from tightly bound atomic states. In other applications, this scheme cannot be expected to yield quantitatively reliable results, since its basic approximations are not fulfilled.

#### (f) LCAO Method of Löwdin

Löwdin (Low 50, 56) pointed out that the failure to work with an orthogonal set of functions, as is the case when Bloch's method is applied to noncore states, can lead to serious errors. In Löwdin's approach, which is a refinement of Bloch's, the crystal wave functions are expanded in terms of a mutually orthogonal set of atomic orbitals. Moreover, the LCAO secular equation is solved by exact methods, rather than by perturbation theory. The Löwdin method bears a close formal resemblance to methods employed in molecular orbital theory (Roo 51). In fact, recent developments in molecular orbital theory have influenced Löwdin's work, and vice versa (Low 56). It should perhaps be pointed out that while Löwdin has made important contributions to the LCAO method, his own work is more concerned with the cohesive energy than with the band structure.

A number of crystals have been studied by the LCAO methods of Bloch and Löwdin. These include work on nickel (Fle 51, 52; Kos 55), diamond (Mor 49(a); Hal 52, 53), bismuth (Mor 49(b)), aluminum (Mat 48), uranium (Fri 56), silicon carbide (Kob 56), selenium and tellurium (Rei 57, Ase 57(a)), boron carbide (Yam 57(b)), graphite (see Sec. 5 for references), and various ionic crystals (see Low 56 for complete references). In some studies, the matrix elements of the LCAO secular equation are estimated, or simply guessed, while in others, they are calculated from first principles. Only the work in the latter category (ionic crystals—Low 56; graphite—Cor 56) can be considered quantitatively reliable.

The principal drawback of Löwdin's method is that the generation of a mutually orthogonal set of atomic

orbitals is a cumbersome process. This is especially true if one is concerned with energy bands which arise from very loosely bound atomic states. Even though the valence and low-lying conduction bands can be determined with a fair degree of rigor, this rigor is attained only at the expense of an inordinate amount of numerical labor. For this reason, we feel that the LCAO method is not as promising as others, which attain the same rigor with far less effort.

#### (g) LCAO Interpolation Scheme

Slater and Koster (Sla 54) have recently suggested that the LCAO method be used as an interpolation scheme, rather than as a primary means for determining energy band structure. Instead of attempting to evaluate the matrix elements of the LCAO secular determinant from first principles, which is very difficult, it is proposed that these matrix elements be evaluated by making use of information derived from energy band calculations carried out by other, more efficient methods. This information usually consists of the energy levels at a limited number of points in the reduced zone, usually symmetry points. Once the matrix elements are known, the secular equation can be solved, and the band structure determined in the remainder of the reduced zone.

Slater and Koster have applied their scheme to various cubic-type crystals. Their work has been extended to hexagonal close-packed crystals by Miasek (Mia 57). While this approach to the periodic potential problem has much to recommend it, it is unlikely that the results will be particularly accurate unless a sufficient number of basis functions is employed in constructing the LCAO secular determinant. If too few basis functions are used, the interpolation scheme can introduce spurious maxima and minima in the energy bands, just as truncated Fourier series often do in other contexts.

#### (h) Method of Wannier Functions

In this approach, which owes its development to Wannier (Wan 37) and Slater (Sla 49, 52), attention is focused on the Fourier transforms of the Bloch functions, and on the Fourier coefficients of the energy band functions, rather than on the Bloch functions and the energy band functions themselves. Since the Fourier transforms of the Bloch functions, or the Wannier functions, as they are commonly called, form a mutually orthogonal set of highly localized functions (Sla 52, Car 57, Gib 57), they prove useful for discussing the formal properties of perfect and nearly perfect crystals (Sla 49, Koh 57(b)).

The problem of determining the Wannier functions has been formulated in terms of a variational principle (Kos 53, Par 53), and has been examined for a number of simple cases (Sla 52, Wai 53, Win 54). Unfortunately, the Wannier functions are not easily determined in a



direct fashion. In practice it is easier to derive the Bloch functions first, and then the Wannier functions by carrying out a Fourier transformation, rather than the other way around. For this reason, the method of Wannier functions cannot be considered a practical approach for obtaining approximate solutions of the wave equation for actual crystals.

#### (i) Cellular Method

This was originally developed by Wigner and Seitz (Wig 33, 34), and subsequently generalized and refined by Slater (Sla 34(a), 34(b)) and others. In this method, the crystal is decomposed into atomic cells or polyhedra, one centered at each lattice site. By assuming that the crystal potential is spherically symmetric in each cell, it is possible to solve the crystal wave equation in each cell by the method of separation of variables. The solutions in different cells are then joined together by imposing appropriate boundary conditions at the surfaces of these cells.

In the Wigner-Seitz version, each atomic polyhedron is approximated by a sphere of equal volume, and the boundary conditions are imposed at the surface of this sphere. In the Slater version, the boundary conditions are imposed at a certain number of points on the surface of each polyhedron. It was realized very early (Sho 37) that more and more matching points are required as one goes from the lowest noncore band to the higher bands, and that the nature of the solution is dependent upon the particular choice of matching points. A number of proposals have been made for minimizing the dependence of the solution on the choice of matching points (Von 47, How 52, Koh 52). The most satisfactory proposal is that by Kohn, who showed that the cellular method could be derived from a variational principle, and that a rigorous boundary condition criterion could be deduced thereby. Kohn's work has recently been generalized to apply to polyatomic lattices (Jen 54(a)).

Energy band calculations by the cellular method have been carried out for a large number of crystals. References to the earlier work, which is based mostly on Slater's version, may be found in other review articles (Ray 52, Low 56, Sla 56). Recent applications include work on beryllium (Don 52), sodium (How 53), lead sulfide (Bel 53), lithium (Sch 54), titanium (Sch 55, Alt 56), silicon (Hol 52; Jen 54(b), 54(c), 56; Yam 53), magnesium (Rai 50), and barium oxide (Mor 52).

At present, the principal objection to the cellular method is that the spherical harmonic expansion of the crystal wave function converges very slowly outside the inscribed sphere of the atomic polyhedron (Koh 52). Since this difficulty is removed in the method of augmented plane waves, where the wave function is expanded in terms of plane waves in this region, the method of augmented plane waves is decidedly superior.

A question which has not yet been fully resolved is how important an error is introduced by assuming the

potential to be spherically symmetric in each atomic polyhedron. It is generally believed that this error is smaller for metals than for nonmetals, since metallic structures have a higher coordination number and a more uniform charge density away from the nuclei than non-metallic structures. However, this view is not firmly established. In any event, it would be desirable to have reliable estimates of the error.

Closely related to the cellular method is the quantum defect method. Since the latter is more concerned with the determination of the cohesive energy than with the band structure, we will not discuss it here. For a detailed discussion of the quantum defect method, the reader is referred to a review paper by Ham (Ham 55).

#### (j) Scattering Matrix Method

While all the previous methods are based on a differential equation formulation of the periodic potential problem, the scattering matrix method and the next are based on an integral equation formulation. The present approach, as developed by Koringa (Kor 47), bears a close formal resemblance to the dynamical theory of x-ray diffraction. One starts by considering the problem of the scattering of an electron wave by a single spherical atom. The solution of this problem yields the relationship between the incident and the scattered wave. The electron wave incident on each spherical atom must then be given by the superposition of the electron waves scattered from all the other atoms in the crystal. This condition provides a means for determining the electron wave everywhere in the crystal.

The scattering matrix method has been applied to a variety of idealized one-dimensional crystals (Sax 49; Lut 51; All 53; Ker 54, 56), as well as to lithium (Koh 52) and niobium (Tre 54). It has been discussed briefly by Harrison (Har 53), and has been derived on the basis of a variational principle by Kohn and Rostoker (Koh 54). The latter work has been generalized to apply to polyatomic crystals by Segall (Seg 57). A similar approach to the periodic potential problem has recently been proposed by Morse (Mor 56).

By all present appearances, the scattering matrix method is the most satisfactory way yet developed for solving the crystal wave equation. It is superior to the APW method, its closest competitor, in the following respect: In the APW method, the solution inside each atomic sphere is joined to plane waves at its surface. Since this joining procedure does not include spherical waves representing the scattering of the plane waves by the atomic sphere, it cannot be exact, so that one is left with a discontinuity in slope at the surface. On the other hand, in the scattering matrix method, the solution inside each sphere is joined to incoming and outgoing spherical waves, thus eliminating the discontinuity difficulty.

Most of the labor involved in the present method is devoted to the calculation of the scattering matrix, a quantity which depends only on geometrical factors.

Once this calculation has been completed for a given crystal structure, it may be applied with relative ease to all other crystals having this structure. Thus, there is a great economy of effort in cases where one is interested in calculating the band structure of several crystals having the same crystal structure.

### (k) Variation-Iteration Method

In the variation-iteration method developed by Dank and Callen (Dan 52), one attempts to solve the integral crystal wave equation by an iterative process. In addition, one seeks to improve the convergence rate by resorting to a process of successive variation and iteration modeled after similar work in other fields (Mor 53). Not enough work has yet been done with this method, as applied to crystals, to provide a basis for judging its relative effectiveness.

Broadly speaking, an energy band calculation involves the choice of (i) an approximate crystal potential; (ii) an approximate method for solving the crystal wave equation; and (iii) a set of points in the reduced zone at which the crystal eigensolutions are to be determined.

The choice of a crystal potential has already been considered briefly in Sec. 2. The choice of a method is determined largely by the available computing facilities, though the interests and personal tastes of the investigator may also play an important role. Unless an investigator is prepared to carry out his calculations on an automatic computer, and not stop until he is satisfied that his results are "convergent," or nearly so, it is not likely that he will obtain a completely satisfactory solution, no matter what method he employs.

There is a definite correlation between the method adopted and the minimum storage capacity and speed of the computer which must be used if the calculations are to be carried out with reasonable dispatch. The scattering matrix and the APW methods require fast computers with large memories, such as the IBM 704, the Sperry-Rand Univac Scientific, or the Burroughs-Datatron 205. The cellular and the OPW methods can be carried out on smaller, slower computers, such as the Datatron 220, the IBM 650, or even the IBM CPC or the Burroughs E101. If the LCAO method is to be carried out rigorously, with all overlap integrals determined from first principles, a very large and fast computer is required. On the other hand, if a very rough solution is desired, and if the only calculational aid available is a desk calculator, the only practical approach is the LCAO method in a highly simplified form.

In principle, the results of an energy band calculation should be independent of the method employed for solving the crystal wave equation. The results should depend only upon the assumed crystal potential. In practice, so many simplifying assumptions are introduced that it is usually not possible to judge which features of the results arise from the particular choice

of crystal potential, and which from the assumptions. It is hoped that the increasing use of fast, large-memory automatic computers will minimize the need to introduce too many simplifying assumptions.

In general, the limiting factor in an energy band calculation is not the solution of the crystal wave equation, but the choice of the crystal potential. The widespread availability of high-speed automatic computers with large memories, and of powerful computational methods, has removed the computational bottleneck that has plagued energy band theory for so many years. The central problem today is the development of a theory which can provide a satisfactory potential for use in energy band calculations.

Let us now turn to the question of choosing a set of points in the reduced zone. In order to map out the band structure of a crystal, in particular the valence and low-lying conduction band structure, it is necessary to obtain solutions at enough points in the reduced zone to provide a comprehensive picture of the whole zone. Without sufficient information it is normally impossible to locate the Fermi surface (in metals and semimetals) and the valence and conduction band edges (in semiconductors and insulators). Unfortunately, the literature abounds with calculations confined to so few points in the reduced zone that the Fermi surface or the band edges cannot be located with any confidence.

Since the numerical labor is markedly reduced by choosing symmetry points or points lying on symmetry axes, most calculations encompass only such points. Once the energy eigenvalues,  $E_\beta(\mathbf{k})$ , and the crystal wave functions,  $\psi_\beta(\mathbf{k}, \mathbf{r})$  are known at a given point in the reduced zone, it is possible to determine the first and second derivatives of  $E_\beta(\mathbf{k})$  with respect to  $\mathbf{k}$  by first- and second-order perturbation theory. In practice, the gross features of the band structure in the entire zone can usually be mapped out in considerable detail once  $E_\beta(\mathbf{k})$  and its first and second derivatives are known at a selected set of symmetry points. Once the symmetry classification of the states at different points of the reduced zone is determined, the states can be arranged into bands with the aid of group-theoretical connectivity rules. It is also possible to generate the band structure everywhere in the zone from information at a few points by interpolation methods. However, the improper use of such a scheme can introduce spurious maxima and minima.

## 5. ILLUSTRATIVE EXAMPLES

In semiconductors and insulators, the valence or conduction band edges can have one of several possible forms, depending upon their location in the reduced zone, and the symmetry classification of the states which define these edges. Among the possible types of band edges are the following:

- (a) Single, nondegenerate band edge. (The band

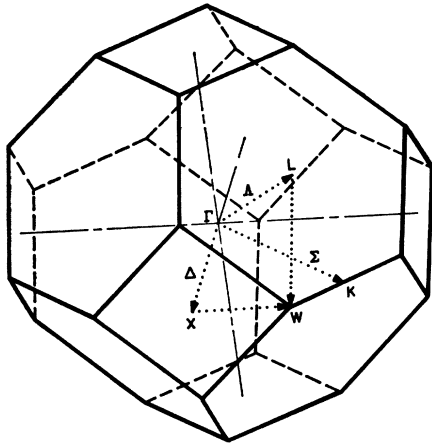


FIG. 1. Reduced zone for crystals having the translational periodicity of a face-centered cubic lattice. These include germanium and aluminum.

edge occurs at a single point in the reduced zone, and is defined by a nondegenerate state.)

(b) Single, degenerate band edge. (The band edge again occurs at a single point, but now is defined by a degenerate state.)

(c) Multiple, nondegenerate band edge. (The band edge occurs at a number of well separated, symmetrically equivalent points in the reduced zone, and is defined by a nondegenerate state at each of these points.)

(d) Multiple, degenerate band edge. (The band edge is defined by a degenerate state at each of several well spaced, symmetrically equivalent points.)

**Germanium**

Before considering still other types, we shall illustrate the above four by examining the band structure of germanium. The reduced zone for this crystal is shown in Fig. 1. Its valence and low-lying conduction band structure is shown schematically in Fig. 2. The latter figure is based on a variety of experimental results (see the companion paper by Lax), and also on theoretical work by the author (Her 54(b), 55(b)). In the interest of simplicity, the spin-orbit splitting has been ignored. In Fig. 2 (and in subsequent drawings of the same type) the symmetry classification of certain states is indicated in the standard notation (compare Table I for references).

It is known from experiment that the conduction band edge lies at the points  $L$ , and is defined by a nondegenerate state at each of these points. Although there are eight points  $L$ , one at the center of each hexagonal face, the pairs lying on opposite faces are physically equivalent, since they are separated by a reciprocal lattice vector. Hence the conduction band edge of germanium is defined by four nondegenerate minima. This is an example of band edge type (c).

As can be shown by perturbation theory, the surfaces of constant energy in the neighborhood of each of the four minima are ellipsoids of revolution. This description would apply whether the symmetry classification at the band edge were  $L_1$  (as it appears to be) or  $L_2'$ . On the other hand, if the conduction band edge were defined by the doubly-degenerate states  $L_3$  [example of type (d) band edge], the surfaces of constant energy near  $L$  would be warped or fluted surfaces.

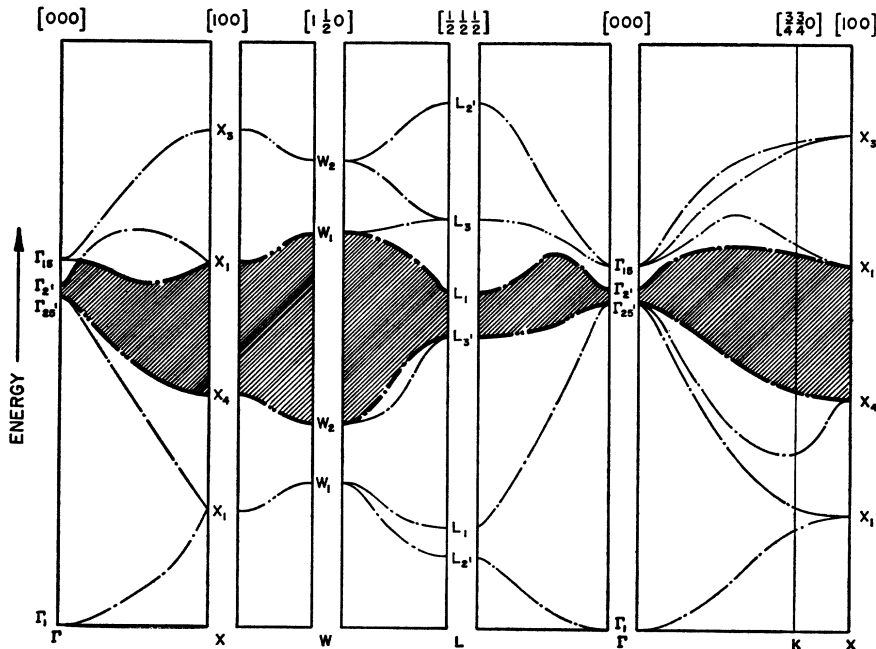


FIG. 2. Schematic diagram of the band structure of germanium. The spin-orbit splitting has been omitted.

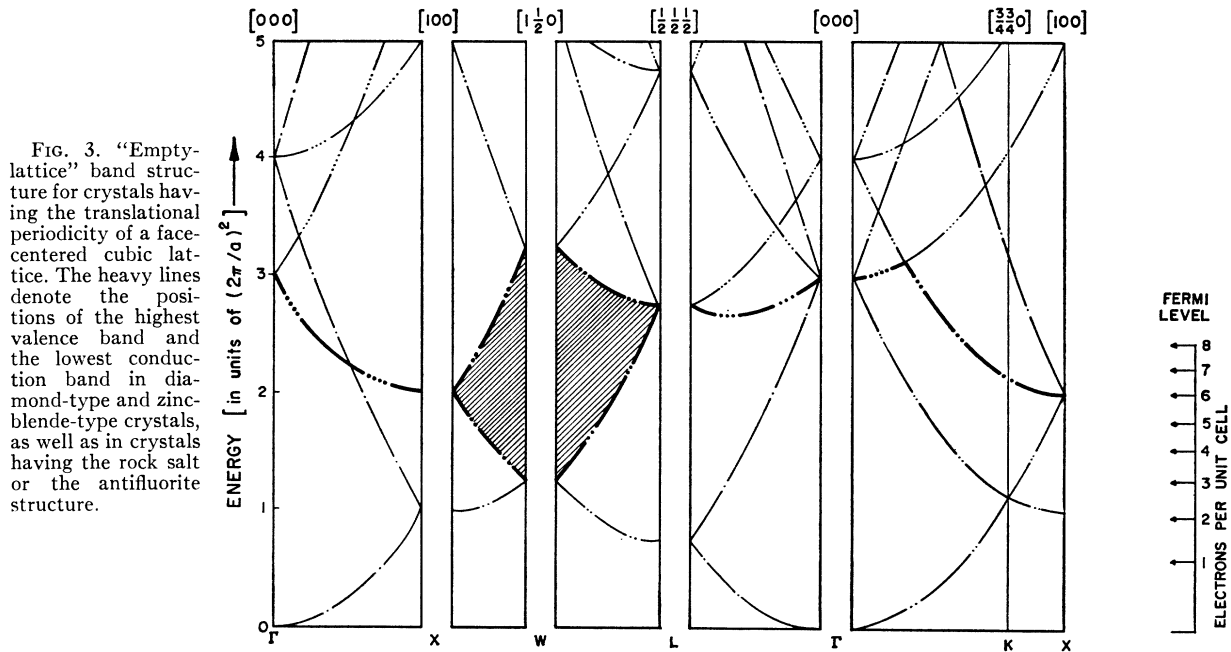


FIG. 3. "Empty-lattice" band structure for crystals having the translational periodicity of a face-centered cubic lattice. The heavy lines denote the positions of the highest valence band and the lowest conduction band in diamond-type and zincblende-type crystals, as well as in crystals having the rock salt or the antiferroite structure.

The author's calculations (Her 54(b)) predict that there are actually three sets of minima in the lowest conduction band edge of germanium. In addition to the four  $[111]$  minima which define the band edge, there are six along the  $[100]$  axes (symmetry classification  $\Delta_1$ ), and one at  $[000]$  ( $\Gamma_2'$ ). Experiment bears this out. Thus we see that the band structure of a crystal may be complicated not only by a complex band edge, but also by the presence of auxiliary extrema lying very

close to the band edge on an energy scale, but quite far apart in the reduced zone.

If the conduction band edge in a diamond-type crystal is defined by  $\Gamma_2'$ , as might prove to be the case in grey tin, we would have an example of band edge type (a). In this case, the constant energy surfaces near the band edge would be spherical.

Cyclotron resonance experiments indicate that the valence band edge in germanium lies at  $[000]$ . If the

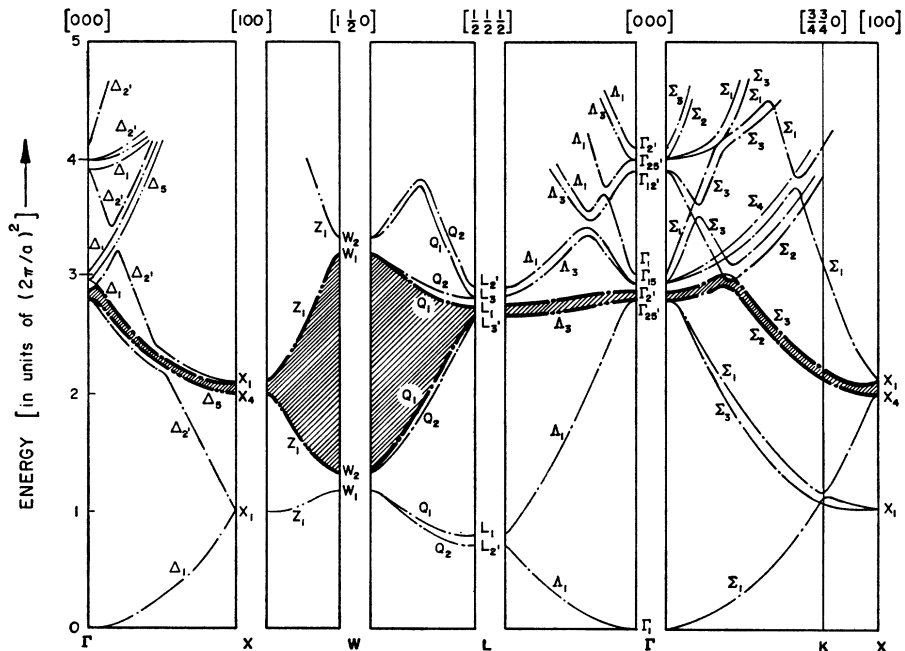


FIG. 4. "Nearly-empty lattice" band structure for germanium (and presumably for other diamond-type crystals as well).

spin-orbit interaction is ignored, the band edge is defined by the triply-degenerate state  $\Gamma_{25'}$  [an example of band edge type (b)]. Each of the three valence bands which touch at [000] have fluted, or warped

constant energy surfaces near [000]. Second order degenerate perturbation theory (Sho 50) shows that  $E(\mathbf{k})$  is given by the roots of the following secular equation,

$$\begin{vmatrix} Lk_x^2 + M(k_y^2 + k_z^2) - E(\mathbf{k}) & Nk_x k_y & Nk_x k_z \\ Nk_x k_y & Lk_y^2 + M(k_x^2 + k_z^2) - E(\mathbf{k}) & Nk_y k_z \\ Nk_x k_z & Nk_y k_z & Lk_z^2 + M(k_x^2 + k_y^2) - E(\mathbf{k}) \end{vmatrix} = 0,$$

where the zero of energy is taken at the band edge.

$E(\mathbf{k})$  is always an analytic function of  $\mathbf{k}$  at a non-degenerate band edge. Hence  $E(\mathbf{k})$  can always be expanded in a Taylor series in  $k_x$ ,  $k_y$ , and  $k_z$  in the vicinity of such an edge. On the other hand,  $E(\mathbf{k})$  is nonanalytic at a degenerate band edge. In this case,  $E(\mathbf{k})$  must be represented by a secular equation as above.

When the twofold spin degeneracy which has been ignored in the preceding discussion is taken into account, it is evident that  $\Gamma_{25'}$  actually represents a sixfold degenerate state. It can be shown that the spin-orbit interaction splits this sixfold degenerate state into an upper fourfold and a lower twofold degenerate state (Ell 54(a), 54(b); Ada 54; Dre 55(a), 55(c)). In all crystals having a center of inversion, and this includes germanium, the twofold spin degeneracy is not removed by the spin-orbit interaction. Hence the valence band edge in germanium is defined by two doubly-degenerate bands which touch at [000]. This is again an example of band edge type (b). The energy surfaces for these two bands near [000] are described by the following nonanalytic function,  $E(\mathbf{k}) = -Ak^2 \pm [Bk^4 + C(k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)]^{1/2}$ , where the zero of energy has again been taken at the band edge. The split-off band is described by  $E(\mathbf{k}) = -\Delta - Ak^2$ , where  $\Delta$  is the spin-orbit splitting [in germanium,  $\Delta = 0.29$  ev (Kan 56)].

The valence band structure in germanium near the edge illustrates another possible complication, namely, the presence of closely spaced bands in a particular region of the reduced zone. This is illustrated even more dramatically by the case of silicon, where the valence band structure is similar in form to that of germanium, and where the spin-orbit splitting is an order of magnitude smaller.

It is instructive to compare the band structure of germanium (with the spin-orbit splitting ignored) with that of a free electron gas having a density equal to the average valence electron density of germanium. If we "switch off" the periodic potential (imagine the ion cores replaced by a uniform background of positive charge), the valence and conduction band structure is described by the free electron expression  $E(\mathbf{k}) = |\mathbf{h} + \mathbf{k}|^2$ , where  $\mathbf{h}$  denotes a reciprocal lattice vector. If this is plotted in the reciprocal space for germanium, we obtain Fig. 3, which we will call an "empty-lattice" band structure. ("Empty" refers to the absence of a periodic

potential.) The spatial degeneracy of each energy band profile is indicated by the number of dots appearing between the dashes.

If the periodic potential is "switched on" again, ever so slightly, much of the degeneracy appearing in Fig. 3 is removed. This is suggested by Fig. 4, which shows the band structure of a "nearly-empty lattice." It is a simple exercise in group theory to deduce the various symmetry classifications shown in Fig. 4. In drawing this figure, we have arbitrarily removed the degeneracy in such a manner that the various energy levels appear in the same order as they do in Fig. 2. It is perhaps helpful to visualize the band structure gradually evolving from that shown in Fig. 3 to that in Fig. 4 to that in Fig. 2.

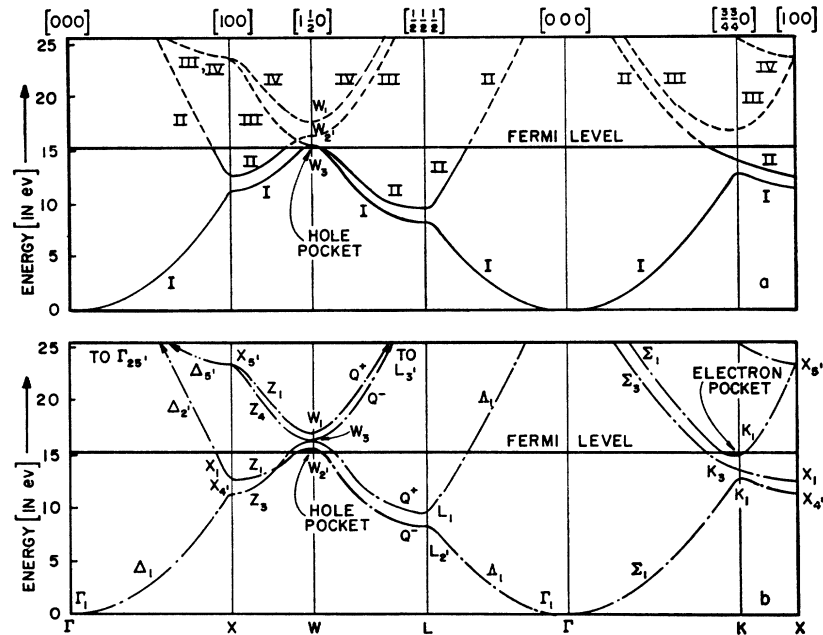
Since there are eight valence electrons per unit cell in germanium, there must be four valence bands, each of which has a two fold spin degeneracy. The forbidden band separates the highest valence band, i.e., the fourth band, counting upwards, from the lowest conduction band, i.e., the fifth band. The positions of these two bands are shown in Figs. 3 and 4 by the heavy dots and dashes. It should be observed that the fourth and fifth bands are degenerate along the [100], the [110], and the [111] axes in Fig. 3. At some places along these axes, still other bands coincide with these two. On the other hand, the fourth and fifth bands do not touch along the square and hexagonal face diagonals. The shaded regions in Figs. 3 and 4 denote the beginnings of the forbidden band.

When the band structure in Fig. 2 is compared with the related band structures shown in Figs. 3 and 4, many of its features become less "mysterious." Although there is a significant distortion in the band structure in passing from Fig. 3 to Fig. 2, some of the basic features persist. While the actual band structure can hardly be predicted from a mere knowledge of the corresponding "empty-lattice" band structure, the latter may often serve as a useful frame of reference. It is for this reason that we have included a number of other "empty-lattice" band structures below.

### Indium Antimonide

In the beginning of this section, we listed four possible types of band edges for semiconductors and insulators. This list is by no means exhaustive. Under special conditions, the gross features of the structure near a band edge may bear a superficial resemblance

FIG. 5. Schematic diagrams of the band structure of aluminum, showing alternate arrangements of certain band edges. Based on the work of Heine (Hei 57).



to one of the four types already mentioned, but closer inspection may reveal the presence of fine detail superimposed on the gross band edge. This fine detail or satellite structure may move the band edge from a given point in the reduced zone to an adjacent set of points, or it may move the band edge from a given set of widely-spaced points to sets of points clustered around each of the original points. In the former case, the band edge occurs at a single cluster of points, and in the latter, at several symmetrically equivalent clusters of points. Such single or multiple clusters can be formed when the spin-orbit interaction modifies the band structure in the neighborhood of a spatially degenerate band edge in a crystal not having a center of inversion.

For example, the valence band edge in indium antimonide appears to be described by a single cluster of points lying in the immediate neighborhood of  $[000]$  (Dre 55(b), Kan 57). At the present time, there is no known example of a semiconductor or insulator having a multiple-cluster band edge. As we will see below, the valence and conduction band edges of the semimetal graphite are believed to be of the multiple-cluster type.

### Aluminum

Aluminum is a trivalent metal having a face-centered cubic lattice structure. Its reduced zone is given by Fig. 1, and its "empty-lattice" band structure by Fig. 3. The energy band structure of aluminum has recently been explored theoretically by Heine (Hei 57), and his results are shown schematically in Fig. 5. Heine finds that the lower reaches of the band structure are quite similar to those of the "empty-lattice" band structure except near the zone faces, where significant departures

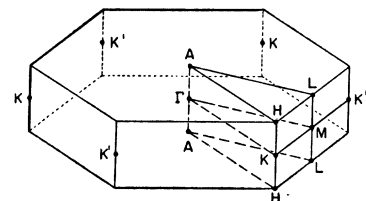
occur. The most interesting portion of the band structure is that near the zone corners (the points  $W$ ), where the four-fold spatial degeneracy in the "empty-lattice" band structure is split into two nondegenerate states ( $W_1$  and  $W_2$ ) and a doubly-degenerate state ( $W_3$ ). Heine's work suggests that  $W_1$  lies above  $W_2$ , and  $W_3$ , but there is some doubt concerning the relative order of  $W_2$  and  $W_3$ . The two possibilities are shown in Figs. 5(a) and 5(b).

Cyclotron resonance has recently been observed in aluminum by Gunnerson. Certain absorption peaks are apparently caused by holes (Cha 56). Heine is best able to account for these peaks (including their anisotropy properties) by requiring a hole pocket to exist at each of the zone corners. If  $W_3$  lies below  $W_2$ , the hole pockets are as shown in Fig. 5(a), while if  $W_2$  lies below  $W_3$ , they are as shown in Fig. 5(b). There are also absorption peaks which may be caused by electrons. These can be explained by requiring the third band (III) to dip below the Fermi level in the neighborhood of the points  $K$ , as in Fig. 5(b).

### Beryllium

Beryllium is a divalent metal which crystallizes in the hexagonal close-packed structure. Its reduced zone is the hexagonal prism shown in Fig. 6. The energy

FIG. 6. Reduced zone for hexagonal-type crystals, including hexagonal close-packed metals such as beryllium, wurtzite-type crystals, selenium, tellurium, and graphite.



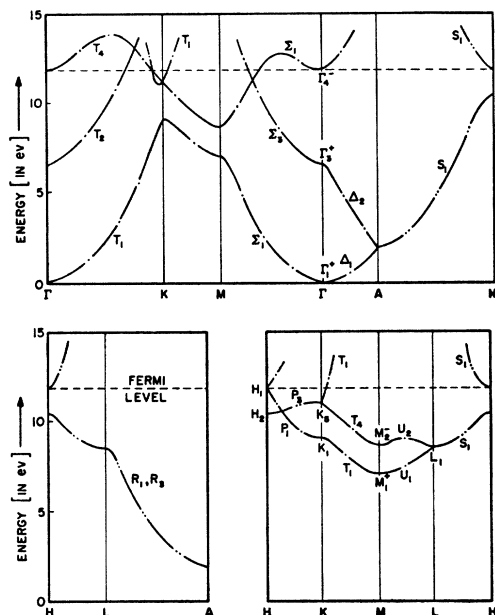


FIG. 7. Energy band structure of beryllium according to the calculations of Herring and Hill (Her 40(b)).

band structure of beryllium, as determined by Herring and Hill (Her 40(b)), is shown in Fig. 7. The electronic properties of beryllium may be expected to be quite complicated, owing to the presence of several bands in the neighborhood of the Fermi level.

For purposes of comparison, we have shown the "empty-lattice" band structure of hexagonal close-

packed and wurtzite-type crystals (ideal  $c/a$  ratio) in Fig. 8. Although this figure has been marked for wurtzite-type crystals in the same manner that Fig. 3 is marked for diamond-type crystals, this should not obscure the fact that its lowest bands are closely related to the beryllium bands shown in Fig. 7. The removal of the spatial degeneracy by the periodic potential of beryllium is clearly seen by comparing Figs. 7 and 8. It is interesting to note that the band structure of beryllium (as given by the work of Herring and Hill) is less like its "empty-lattice" band structure than is the case for aluminum. We do not pretend to know why this is so.

### Selenium

The reduced zone for selenium is again the hexagonal prism shown in Fig. 6. Its "empty-lattice" band structure is shown in Fig. 9. The "empty-lattice" and "nearly-empty lattice" band structures are compared with the theoretical results of Reitz (Rei 57) in Fig. 10. It would appear from Fig. 10(c) that the valence and conduction band edges occur at the midpoints of the hexagonal faces (the points  $A$ ). However, this cannot be considered as definitely established until the remainder of the reduced zone is systematically explored. It is not out of the question that the valence or conduction band edge lies elsewhere in the reduced zone.\*

### Graphite

Because graphite has an unusual layer structure and highly anisotropic physical properties, its band struc-

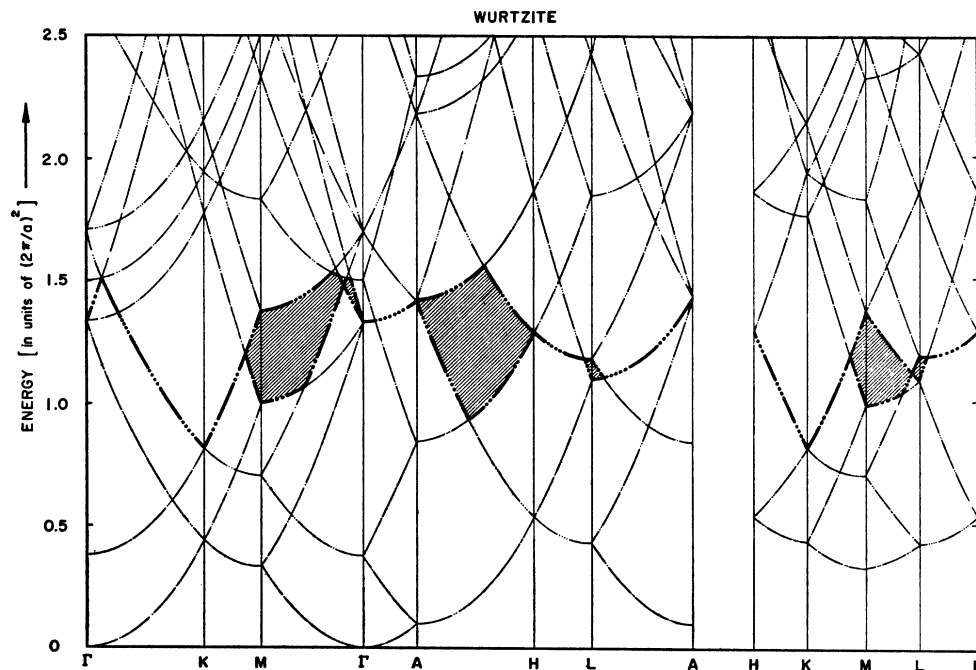


FIG. 8. "Empty-lattice" band structure for wurtzite-type crystals. If the heavy markings are ignored, this also applies to hexagonal close-packed crystals. Drawn for ideal  $c/a$  ratio.

\* Note added in proof.—Recent experimental work by Choyke and Patrick (Cho 57) suggests that the valence and conduction band edges lie at different positions in the reduced zone.



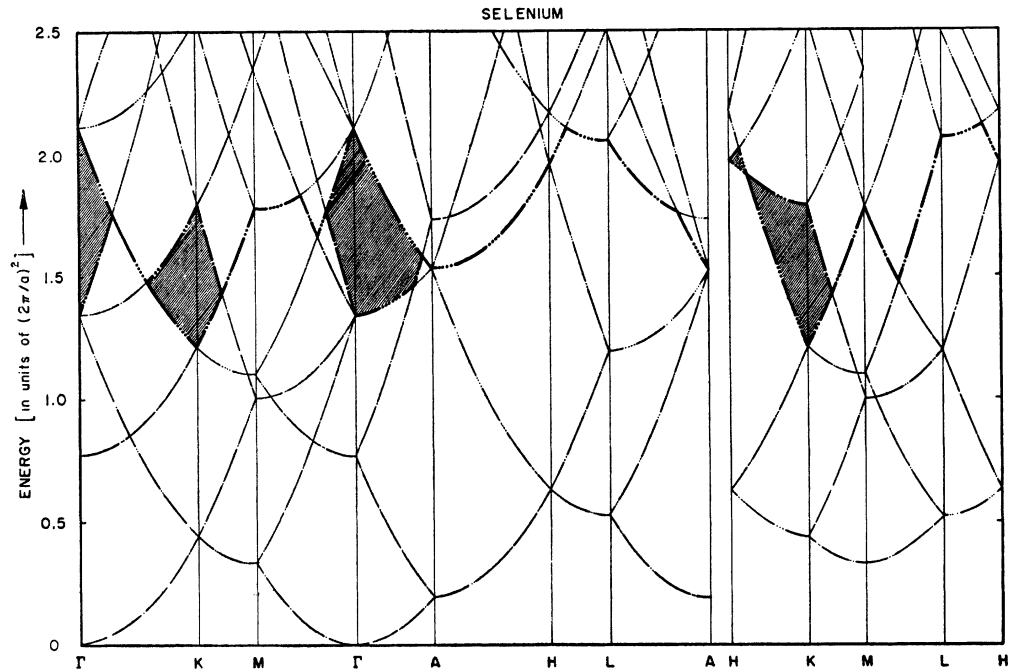


FIG. 9. "Empty-lattice" band structure for selenium. (That for tellurium is slightly different, since the  $c/a$  ratio is somewhat different.)

ture has received a great deal of attention. At present, there is no fully satisfactory theory of the over-all form of its valence and low-lying conduction band structure. However, the detailed form of its band structure near the Fermi level is fairly well understood, and this should prove sufficient for most applications.

The crystal structure of graphite is shown in Fig. 11. The atoms are arranged in hexagonal layer planes, and there are four atoms in the unit cell. Two of these atoms have neighbors directly above and below in adjacent planes, while the other two do not. The reduced zone is the hexagonal prism already shown in Fig. 6.

Since the interlayer spacing (3.37 Å) is much larger than the interatomic spacing in any one layer (1.42 Å), it is convenient to start by considering the band structure of a single layer. Of the numerous calculations which have been performed for two-dimensional graphite (Wal 47; Cou 47, 52; Car 53(b); Ari 54; Lom 55; Cor 56), the most comprehensive is that by Corbato (Cor 56). It may be seen from Corbato's results [compare Fig. 12] that the valence and conduction band edges occur at the (two-dimensional) zone corners, where they touch. Furthermore, the highest valence band and the lowest conduction band are both found to be  $\pi$  bands. (In two-dimensional graphite, the electronic states can be classified as  $\pi$  or  $\sigma$  states. The states belonging to the  $\sigma$  bands are symmetric, and those belonging to the  $\pi$  bands antisymmetric, with respect to reflection about the layer plane.) These results confirm the earlier ones of Wallace (Wal 47) and Coulson (Cou 47, 52).

We turn next to a consideration of the band structure of three-dimensional graphite. Since there are four

atoms per unit cell, rather than just two, as in the two-dimensional case, there are now eight valence bands

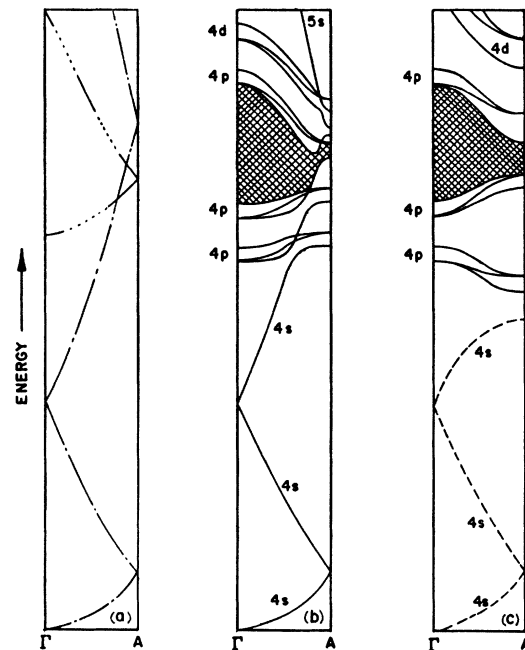


FIG. 10. Energy band structure for selenium along hexagonal axis. (a) "Empty-lattice"; (b) "Nearly-empty lattice"; (c) Results of Reitz (Rei 57). From the viewpoint of Reitz's LCAO calculation, there are three bands derived from the  $4s$  atomic states, nine from the  $4p$  atomic states, and fifteen from the  $4d$  states, etc. Since Reitz ignores the  $4s$  bands, and treats the  $4p$  and the  $4d$  bands separately, he overlooks the possible interband mixing strongly suggested by Fig. 10(b). It is conceivable, however, that in the actual band structure this interband mixing is not present.

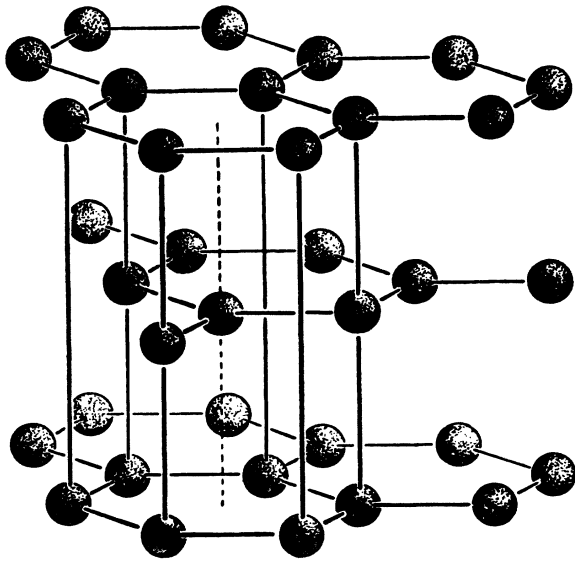


FIG. 11. Crystal structure of graphite.

rather than four. These eight bands may be expected to occur as four closely spaced pairs. Each of these pairs should occur roughly at the same energy (in the  $k_z=0$  plane) as one of the two-dimensional valence bands. There will also be a pair of conduction bands for each of the two-dimensional conduction bands. The spacing between the members of each pair should increase as one moves to higher energies. A good picture of the gross features of the three-dimensional band structure in the  $k_z=0$  plane may be had by replacing each band in Fig. 12 by a pair of more or less closely spaced bands.

(It is interesting to note that the "actual" band structure is more nearly like the "empty-lattice" band structure in two dimensions than in three dimensions. The "empty-lattice" band structure for three dimensions is shown, for what it is worth, in Fig. 13.)

Since the two-dimensional work shows that the most interesting portion of the band structure is that at the

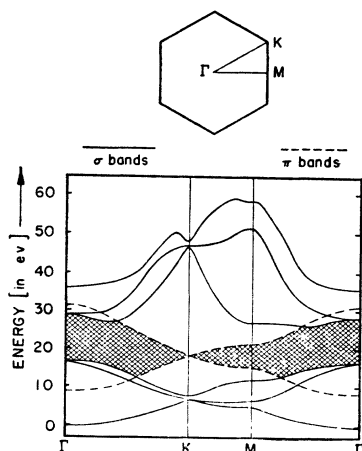


FIG. 12. (Top) Reduced zone for two-dimensional graphite. (Bottom) Energy band structure for two-dimensional graphite according to the calculations of Corbato (Cor 56).

corners of the two-dimensional zone, it follows that the most interesting portion in three dimensions is that along the triad axes, i.e., along  $HKH$  and  $H'K'H'$  in the three-dimensional zone shown in Fig. 6.

Although a number of three-dimensional band calculations have been performed (Joh 55, 56; Hea 57; Yam 57(a)) with a view to determining the " $\pi$ " band structure along (and near) the triad axes, these involve so many simplifying assumptions that the results must be treated with considerable caution.

A more fruitful approach has been that initiated by Slonczewski (Slo 55(a)), and subsequently pursued by Slonczewski and Weiss (Slo 55(b)), McClure (McC 57), and Nozières (Noz 57(b)). In this, the most general form of the band structure near the triad axes is deduced by means of group theory and perturbation theory, and the parameters which enter into this form are evaluated by comparison with pertinent experimental data.

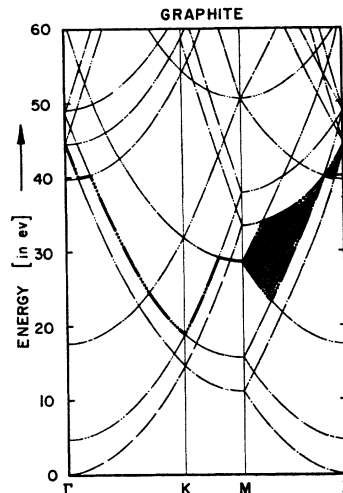


FIG. 13. "Empty-lattice" band structure for three-dimensional graphite.

The present picture of the band structure of three-dimensional graphite near the triad axes (Slo 55(a), 55(b); McC 57; Noz 57(b)) is illustrated in Figs. 14, and 15. Along the triad axes, the four " $\pi$ " bands are split into two nondegenerate bands ( $E_1$  and  $E_2$ ) and a doubly-degenerate band ( $E_3$ ). From a study of infrared emissivity, de Haas-van Alphen effect, and cyclotron resonance absorption data, Nozières concludes that the three parameters appearing in Fig. 14 have the following values:  $\gamma_1=0.14$  eV;  $\gamma_2=0.016$  eV; and  $\Delta=0.025$  eV.

If we ignore certain fine detail which will be mentioned shortly, the energy profiles in a horizontal plane ( $k_z=\text{constant}$ ) are as shown on the right-hand side of Fig. 14. The energy surfaces are circular hyperboloids. It should be noted that the degeneracy in  $E_3$  along the triad axis is removed as one moves away from the axis into the zone. The position of the Fermi level ( $E_F$ ) relative to  $E_1$ ,  $E_2$ , and  $E_3$  suggests that nearly all the electrons and holes belong to the two bands which merge at the triad axis to form  $E_3$ . Since the curvature

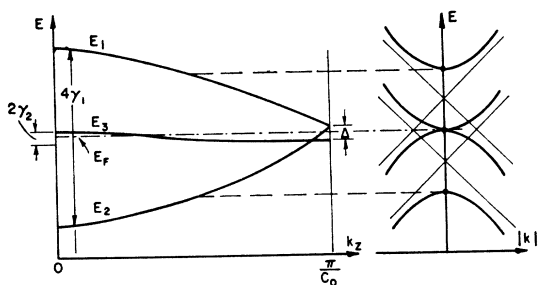


FIG. 14. Energy band structure near a triad axis ( $HK$  or  $H'K'$ ) in three-dimensional graphite ("π" bands only). (Left) Band structure along a triad axis. (Right) Band structure in a horizontal plane cutting the triad axis at an arbitrary  $k_z$ . After Nozières (Noz 57(b)).

of the two branches of  $E_3$  in a horizontal plane is a function of  $k_z$ , the electrons and holes will each have a spectrum of effective masses.

A closer inspection of the band structure reveals a satellite structure near each triad axis in any horizontal plane, as indicated in Fig. 15. The upper and lower members of  $E_3$  are no longer in contact only along the triad axis. Instead, they overlap very slightly ( $E_M \cong 0.002$  ev), giving rise to four conical energy sections.

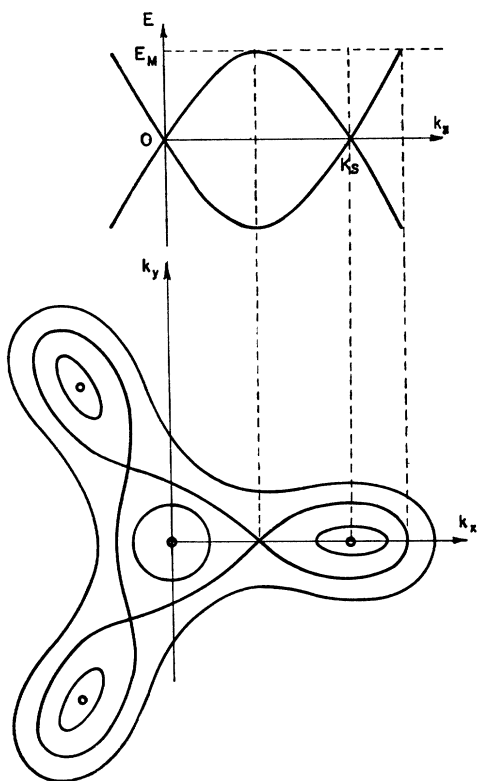


FIG. 15. Satellite structure in three-dimensional graphite. (Top) Overlapping  $E_3$  bands in an arbitrary horizontal plane in the immediate neighborhood of a triad axis.  $k_x$  may point toward or away from the hexagonal axis. (Bottom) Anisotropic constant energy profiles showing the four "feet" which merge together when  $E$  increases. After Nozières (Noz 57(b)).

One of these four lies at the triad axis, while the other three form an equilateral triangle in the immediate neighborhood of the axis. The constant energy surfaces are highly warped in the critical region. These are shown at the bottom of Fig. 15. As one moves away from the critical region, the warping fades away, and one is again left with the circular hyperboloids shown at the right of Fig. 14. From the above characterization, it may be seen that the valence and conduction band edges of graphite are of the multiple-cluster type mentioned earlier.

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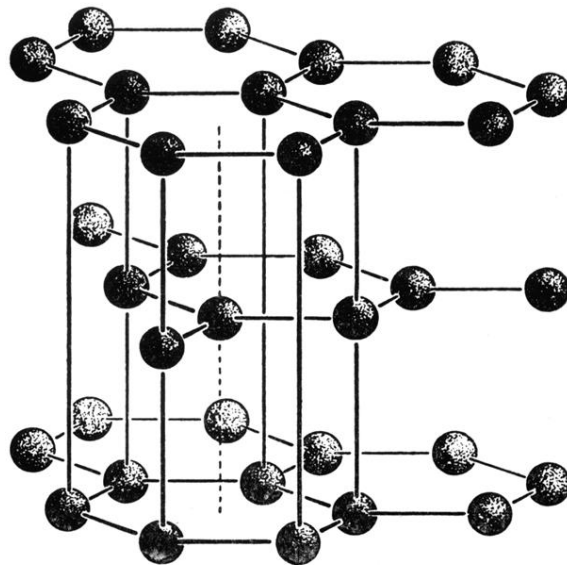


FIG. 11. Crystal structure of graphite.