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*Now at Department of Physics, Lakehead University, Thunder Bay, Ontario, Canada.

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Electronic Properties of an Amorphous Solid. I. A Simple Tight-Binding Theory

D. Weaire and M. F. Thorpe
Becton Center, Yale University, New Haven, Connecticut 06520

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Using a simple Hamiltonian of the tight-binding type, rigorous bounds are derived for the density of states of a tetrahedrally bonded solid. These include inner bounds which define a band gap between occupied and unoccupied states. The derivation uses only the assumed perfect coordination of nearest neighbors, and so it holds for all tetrahedrally bonded crystal structures and random networks of the kind proposed for amorphous Si and Ge. Various other results are obtained for the fractional s- and p-like character of wave functions, the attainment of bounds, and other features of the density of states. A band-structure calculation for the diamond cubic structure serves as a test case.

I. INTRODUCTION

Two broad classes of disordered systems are encountered in solid-state theory (see Fig. 1). In the case of what we shall call *quantitative* disorder, one defines a periodic array of potentials which are not identical. They may, for instance, be of two types, randomly distributed, in which case the theoretical model would be appropriate to a disordered binary alloy. On the other hand, one may define an array of potentials which are identical but not periodically positioned. One might call this positional disorder. Such a model would be appropriate for, say, a liquid metal.

If a positionally disordered system has the same coordination of nearest neighbors everywhere and we describe it with a Hamiltonian which involves only nearest-neighbor coordination, we have the special case of *topological* disorder. The distinction between this case and that of quantitative disorder is somewhat clearer. The matrix elements which specify the Hamiltonian are the same everywhere throughout the structure. It is the connectivity of the structure which is disordered. Such a topologically disordered Hamiltonian would seem to be an appropriate starting point for a theory of the electronic properties of amorphous elemental semiconductors, and in the subsequent sections the model will be analyzed in detail.

The motivation for this study lies in recent experimental work[1-6] on amorphous Si and Ge. From the outset it was evident that these substances were highly disordered, and yet in many respects their electronic properties are closely similar to those of the corresponding crystals. In particular, a band gap between valence and conduction bands persists in the amorphous state. The extent to which such a gap contains a small density of states tailing off from the two bands is still a subject of debate. Be that as it may, this remains a remarkable experimental result.

A model for the structure of these elemental amorphous semiconductors which has gained wide acceptance is the *random network* model, in which every atom is almost perfectly tetrahedrally coordinated with its nearest neighbors. Distortions of bond lengths and angles from the values in the crystalline state are of the order of 10%, and yet the distribution of second and further neighbors is highly disordered.[7] It is by no means obvious that such a geometrical arrangement can be constructed in practice. However, this appears to

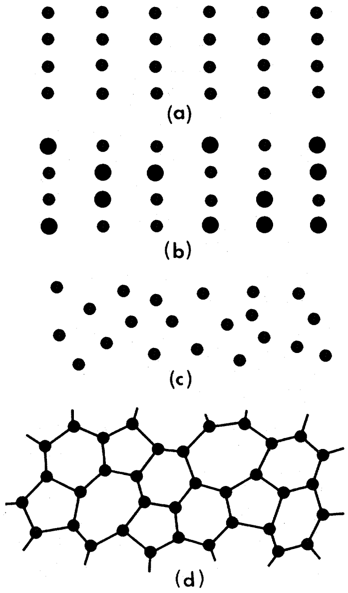

FIG. 1. Various types of disorder, encountered in the study of the electronic properties of solids, are schematically illustrated; (a) perfect order, (b) quantitative disorder, (c) positional disorder, (d) topological disorder.

have been convincingly demonstrated in an empirical fashion by Polk.[8] Some aspects of this structure are illustrated in Fig. 2. Amorphous semiconductors, as prepared in the laboratory, will of course contain voids or other defects[7] distributed throughout such an ideal structure. There is an urgent need for more experimental investigation of such defects and their dependence on the methods of preparation used.

Clearly, it is a reasonable first approximation to neglect the slight distortions of the nearest-neighbor relationships from their ideal values at each site. If we then use a simple tight-binding model, the overlap integrals of basis functions associated with an atom and its nearest neighbors are the same for all atoms and we have precisely the case of topological disorder mentioned above.

It should perhaps be emphasized that these assumptions do *not*, in general, simply reduce the Hamiltonian to a periodic one. One cannot, in the topologically disordered case, define a "unit cell" such that knowledge concerning the matrix elements of the Hamiltonian associated with those atoms belonging to it is sufficient to construct the entire Hamiltonian. Equally, one cannot apply Bloch's Theorem to the system.

Our approach will be to concentrate on the *local* relationships between the coefficients in a tight-binding wave function. We use these to generate results for the bounds on the electronic density of states and various related properties. We essentially use only the assumed tetrahedral coordination of every atomic site. The results obtained, therefore, apply to the entire class of networks which have this property, including those which correspond to periodic crystal structures (diamond cubic, wurtzite, etc.) and the random tetrahedral network assumed for amorphous Si and Ge. It is rather surprising that much can be said about the electronic states associated with the Hamiltonian on the basis of so few assumptions. It is, however, merely the mathematical realization of a well-known empirical generalization, namely, that the type and degree of the *long*-range order is responsible for only the finer structure of the density of states. This may offend the instincts of a solid-state theorist, but accords well with that of a chemist or indeed anyone who has scrutinized the experimental results referred to above. The electronic properties of solids are dominated by short-range order.[9] It is only theory that is dominated by long-range order because of the convenience of Bloch's Theorem.

The Hamiltonian which we use provides a reasonable idealized model for amorphous Si and Ge, but it is too crude to yield a precise description of these systems. We will postpone comparisons with more realistic Hamiltonians, together with various generalizations and extensions of the model to sub-

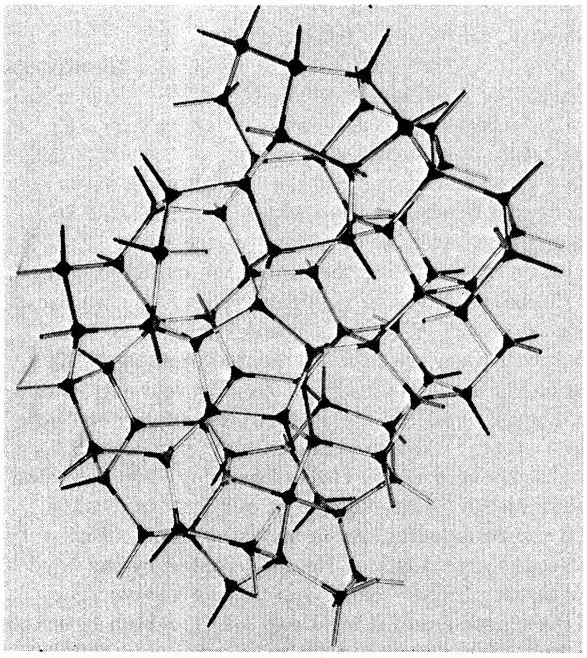

FIG. 2. Some features of a random network structure similar to that constructed by Polk (Ref. 8). Fivefold, sixfold, and sevenfold closed rings of bonds are evident. For a photograph of a more extended structure of this type see Ref. 8 or M. H. Cohen, Phys. Today 24, 26 (1971).

sequent papers.[10] Here we will simply explore the basic properties of the Hamiltonian in its simplest form. Section II defines this Hamiltonian. Sections III and IV present, respectively, the principal result for bounds on the density of states (with a somewhat expanded version of the already published proof[11]) and various details of the allowed bands. An instructive test case, that of the diamond cubic structure, is discussed in Sec. V, and the main conclusions are summarized in Sec. VI.

Various mathematical proofs and manipulations are relegated to appendices so as not to divert attention from the main line of argument.

II. TIGHT-BINDING FORMULATION OF THE PROBLEM

In this section the problem of the determination of the band structure of a topologically disordered system is put into a precise mathematical form by the definition of a Hamiltonian.

Let us label the atoms of a tetrahedrally coordinated structure by a site index i and the bonds by a site index j. Localized functions ϕ_{ij} are associated with each atom and bond such that they form an orthonormal set and the Hamiltonian has matrix elements only between basis functions ϕ_{ij} associated with the same atom or the same bond. We have

$$H=\sum_{i,j\neq j'} V_1 |\phi_{ij}\rangle\langle\phi_{ij'}| + \sum_{i\neq i',j} V_2 |\phi_{ij}\rangle\langle\phi_{i'j}| \ , \tag{1}$$

where V_1 and V_2 are defined to be real.

Note that if we switch off V_2 we have a Hamiltonian describing completely decoupled atoms, each with a singly degenerate eigenstate at energy $E=3V_1$ and triply degenerate eigenstates at $E=-V_1$. On the other hand, for $V_1=0$ the Hamiltonian describes decoupled bonds, each of which is associated with eigenstates at $E=\pm V_2$. Clearly, the ratio $|V_1/V_2|$ must be critical in determining the qualitative form of the band structure resulting from (1). In practice, for real systems of interest, this ratio is such that the V_2 matrix elements dominate. Thus, the bands are essentially of bonding and antibonding character, split by the V_2 term and broadened by the V_1 term. The two matrix elements V_1 and V_2 might, therefore, be called "banding" and "bonding" parameters. The essence of our task is to show that the broadening of the bands by the banding term does not destroy the gap created by the bonding term. Heine[12] has given an alternative proof of the existence of a band gap for (1) which is based on just such a picture and is consequently rather more transparent than ours.

The functions ϕ_{ij} may be visualized as the familiar sp^3 hybridized orbitals of tight-binding theory. We shall indeed call this a tight-binding Hamiltonian although it might be more properly called an equivalent molecular orbital Hamiltonian in view of the assumed orthogonality of the basis functions ϕ_{ij}.

The Hamiltonian is certainly a very simple one, but note that for a topologically disordered system it nevertheless cannot be decoupled in any obvious way. In attempting to discuss the eigenvalues of such a Hamiltonian for a structure with N atoms we are faced with the determinant of a $(4N\times 4N)$ secular matrix which cannot, in general, be reduced to a matrix whose dimension is of order unity, as in the periodic case.

We have not, up to now, said anything about the structure except that it is tetrahedrally coordinated. However, in order that the main results of Secs. III and IV shall hold, we need to make one further stipulation, namely, that the structure shall have a bounded variation of density. To be more precise, the Hamiltonian (1) is assumed to correspond to a structure in which each atom i has four nearest-neighbor bonds j and a volume Ω can be defined such that the number of atoms in any volume Ω is bounded above and below, the lower bound being nonzero. This condition of bounded variation of density which was implicit in the earlier discussion of this model[11] avoids mathematically pathological cases and entails a negligible loss of generality, as far as systems of physical interest are concerned.

Something remains to be said about boundary conditions. In a previous paper[11] the structure was assumed to be infinite and wave functions were required to be normalizable. While we believe this procedure to be correct, a treatment of the problem using a finite number of atoms and explicitly taking the limit as this number tends to infinity in order to isolate *bulk* properties seems, perhaps, more satisfactory. Such a treatment is given here. We assume, therefore, a structure composed of N atoms, and it is assumed, purely for convenience, to occupy a spherical volume V. It is assumed that homogeneous boundary conditions are applied at the surface of this spherical volume. For convenience we give a proof for "free" boundary conditions. By this we mean that if a given bond j is cut by the surface and the atom associated with it within the surface is labeled i, then the basis function ϕ_{ij} is not coupled to any other by the second term of (1). It is readily seen that the given proof can be generalized to apply to any other homogeneous boundary conditions. The special choice of *quasiperiodic* boundary conditions leads to an even simpler analysis, but this is, indeed, a special case and is in, at least, one respect misleading in that the condition of bounded variation of density is no longer necessary. By *quasiperiodic* boundary conditions we mean that each bond cut by the surface is considered to be connected to another such bond. (It is easily shown that the number of such surface bonds is *even*, which makes this possible.)

III. BOUNDS ON THE DENSITY OF STATES

In this section we show that the bulk density of states of a system, described by the Hamiltonian defined in Sec. II, must be zero in certain regions of energy. This has already been shown in a previous paper,[11] but we shall give a less abbreviated treatment and, as explained in Sec. II, we will examine a finite system of N atoms rather than an infinite one.

We begin by projecting out that part of the Schrödinger equation $(H-E)\,\psi=0$ which lies in the subspace spanned by ϕ_{ij} for some given i and $j=1-4$. We define the coefficients a_{ij} by

$$\psi=\sum_{ij} a_{ij}\,\phi_{ij} \tag{2}$$

and a_{ij} for $j=1-4$ are considered as the components of a vector $\vec{u}(i)$. Note that i does *not* label the components of $\vec{u}$. Each component of $\vec{u}(i)$ is associated with a certain bond j. Now the coefficients $a_{i'j}$ of the other orbitals associated with these bonds may be considered as a second vector $\vec{v}_i$. This procedure is illustrated by Fig. 3. Now the Schrödinger equation gives

$$M\vec{u}(i)=-V_2\vec{v}(i)\ , \tag{3}$$

where

$$M=\begin{bmatrix} -E & V_1 & V_1 & V_1\\ V_1 & -E & V_1 & V_1\\ V_1 & V_1 & -E & V_1\\ V_1 & V_1 & V_1 & -E \end{bmatrix}\ .$$

This relation holds at every site and we will, for the present, drop the site index i. It is the fact that the relation (3) holds at every site that forms the essential basis for our analysis. For a periodic system there are only n independent relations of this type, where n is the number of atoms in the unit cell, but, in general, the problem cannot be so reduced. The matrix M has eigenvalues

$$\lambda_1=-E+3V_1 \tag{4}$$

and

$$\lambda_2=-E-V_1 \text{ (triply degenerate)}\ . \tag{5}$$

Note that they are functions of energy E. Taking the scalar product of both sides of (2) with their respective conjugate vectors, we obtain

$$\vec{u}^*\cdot M^2\vec{u}=V_2^2|\vec{v}|^2. \tag{6}$$

By expanding $\vec{u}$ in eigenvectors of M, the following inequalities are readily obtained from (6):

$$\max(\lambda_n^2)\,|\vec{u}|^2\geq V_2^2|\vec{v}|^2\geq\min(\lambda_n^2)\,|\vec{u}|^2\ , \tag{7}$$

where $\max(\lambda_n^2)$ and $\min(\lambda_n^2)$ are the maximum and minimum squared eigenvalues.

We shall show that if the energy E is such that

$$\max(\lambda_n^2)<V_2^2 \tag{8}$$

or

$$\min(\lambda_n^2)>V_2^2\ , \tag{9}$$

then (7) implies a zero bulk density of states at that energy. We first note that *either* of the inequalities (8) and (9), together with (7) implies that

$$\big|\,|\vec{u}|^2-|\vec{v}|^2\big|>\theta|\vec{u}|^2\ , \tag{10}$$

where $\theta>0$ and furthermore, $|\vec{v}|^2-|\vec{u}|^2$ has a sign which is the same for all atoms, i.e., independent of the implicit site index i. Consider then a range of energy $E_0\leq E\leq E_1$ for which such relations hold and let θ henceforth denote its minimum value in that range (which cannot be zero).

We define an integrated density of states I by

$$I=\int_{E_0}^{E_1}dE\,n(E)\ , \tag{11}$$

where $n(E)$ is the normalized density of states, that is, we have

$$4=\int_{-\infty}^{\infty}dE\,n(E)\ . \tag{12}$$

For a finite system, I is just the number of states ψ between E_0 and E_1 which satisfy the boundary conditions, divided by the number of atoms N.

Consider a particular state with wave function ψ_n which corresponds to an energy between E_0 and E_1. For such a wave function we sum the quantity $|\vec{u}|^2-|\vec{v}|^2$ over all atoms, noting first that because of the cancellation associated with each bond in the interior of the structure and the assumed "free" boundary condition this reduces to

$$\sum_i\left(|\vec{u}(i)|^2-|\vec{v}(i)|^2\right)=\sum_{\substack{\text{surface}\\ \text{atoms } i,\\ \text{component } m}}|\vec{u}_m(i)|^2\ . \tag{13}$$

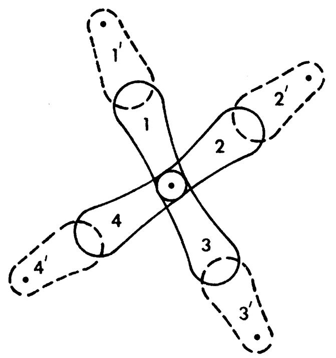

FIG. 3. Coefficients of the basis functions 1–4 associated with a given atom, in the expansion of a given wave function, are the elements of the vector $\vec{u}$ defined in the text. The coefficients of 1'–4' form the vector $\vec{v}$.

A surface atom is an atom with at least one surface bond, i.e., one not connected to another atom in the structure. The subscript m labels the components of $\vec{u}$ corresponding to such surface bonds.

We now define a surface *layer* of atoms such that all surface atoms are included. The conditions of bounded variation of density imply that this can be done in such a way that for large N the number N_s of atoms in the surface layer satisfies

$$N_s < \nu N^{2/3} , \tag{14}$$

where ν is a constant independent of N. Then (10) and (13) give the following chain of inequalities and equations for the components of any wave function:

$$\theta \sum_{i=1}^{N} |\vec{u}(i)|^2 < \sum_{i=1}^{N} \Big| |\vec{u}(i)|^2 - |\vec{v}(i)|^2 \Big| , \tag{15}$$

$$\sum_{i=1}^{N} \Big| |\vec{u}(i)|^2 - |\vec{v}(i)|^2 \Big| = \Big| \sum_{i=1}^{N} \left(|\vec{u}(i)|^2 - |\vec{v}(i)|^2 \right) \Big| , \tag{16}$$

$$\Big| \sum_{i=1}^{N} \left(|\vec{u}(i)|^2 - |\vec{v}(i)|^2 \right) \Big| < \sum_{\substack{i,\ \text{surface} \\ \text{layer only}}} |\vec{u}(i)|^2 . \tag{17}$$

Note that we have used the constancy of the sign of $|\vec{u}|^2 - |\vec{v}|^2$.

Combining (15)–(17) together with the normalization condition for the wave function

$$\sum_{i=1}^{N} |\vec{u}(i)|^2 = 1 , \tag{18}$$

we obtain

$$\sum_{\substack{i,\text{surface} \\ \text{layer}}} |\vec{u}(i)|^2 > \theta . \tag{19}$$

Now it may easily be shown that the quantity on the left-hand side of (19), if summed over *all* $4N$ wave functions, as well as over all N_s atoms in the surface layer, equals $4N_s$. Hence, if we perform a summation only over those wave functions between E_0 and E_1, such a sum must be *less* than $4N_s$ and so we have

$$NI\theta < 4N_s , \tag{20}$$

recalling that NI is the number of such wave functions. Therefore, it follows that

$$I < 4\theta^{-1}(N_s/N) . \tag{21}$$

Now θ is greater than zero and independent of N. The ratio (N_s/N) must tend to zero as N tends to infinity (14), hence we have

$$\lim_{N\to\infty} I = 0 , \tag{22}$$

which is the result which we set out to prove, namely, that the normalized integrated density of states between E_0 and E_1 is zero in the infinite limit. This means that the "bulk" density of states in the usual sense is zero between E_0 and E_1 and hence for all ranges of energy in which either of the inequalities (8) and (9) applies.

For the special case of quasiperiodic boundary conditions, the right-hand side of Eq. (13) vanishes identically. The same analysis then leads to the conclusion that there is a zero density of states for regions of energy in which either (8) or (9) holds, *even for finite N.* The limiting argument given above and the condition of bounded density variation used in it is not necessary for this special case.

Before examining the bounds on the density of states which this result entails, we will proceed to analyze the character of the allowed bands in the bulk density of states, which we do in Sec. IV.

IV. DENSITY OF STATES IN THE ALLOWED BANDS

The same method which was used above to prove the existence of regions of energy in which the bulk density of states is zero may also be used to derive certain properties of the allowed bands. In particular, we shall show that the average fractional s- and p-like character and the average bonding and antibonding character of a wave function are functions only of the energy E.

To show this, we consider a particular wave function normalized to unity over the whole system and expand the vector $\vec{u}$ associated with a given site in terms of eigenvectors of M. The eigenvector $\vec{u}^{(s)}$ with eigenvalue (4) we call s like, and *any* eigenvector $\vec{u}^{(p)}$ with eigenvalue (5) is called p like. Both are normalized to unity. We have

$$\vec{u} = c^{(s)}\vec{u}^{(s)} + c^{(p)}\vec{u}^{(p)} . \tag{23}$$

Now Eq. (6) may be rewritten as

$$\lambda_1^2 |c^{(s)}|^2 + \lambda_2^2 |c^{(p)}|^2 = V_2^2 |\vec{v}|^2 \tag{24}$$

or

$$|\vec{v}|^2 - |\vec{u}|^2 = (\lambda_1^2 V_2^{-2} - 1)|c^{(s)}|^2 + (\lambda_2^2 V_2^{-2} - 1)|c^{(p)}|^2 . \tag{25}$$

Now consider the quantity

$$b = \sum_{i=1}^{N} \left(|\vec{v}(i)|^2 - |\vec{u}(i)|^2 \right) . \tag{26}$$

For a system with quasiperiodic boundary conditions this again vanishes identically, and we immediately have

$$\frac{F_s}{F_p} = -\frac{\lambda_2^2 - V_2^2}{\lambda_1^2 - V_2^2} , \tag{27}$$

where

$$F_s = \sum_{i=1}^{N} |c^{(s)}|^2 , \tag{28}$$

$$F_p = \sum_{i=1}^{N} |c^{(p)}|^2 . \tag{29}$$

These may be called the fractional s- and p-like characters of the wave function. Without *quasi-periodic* boundary conditions these results become true in the $N\rightarrow\infty$ limit.

Using $F_s+F_p=1$, we obtain

$$F_s=\frac{\lambda_2^2-\lambda_1^2}{\lambda_2^2-V_2^2}\ . \qquad (30)$$

Thus F_s is determined for any wave function only by the energy E which defines λ_1, λ_2, and hence, (30). This breaks down only for $|V_1/V_2|=\frac{1}{2}$ when the relation (27) is indeterminate for $E=V_1$.

We may further obtain the fractional bonding character by taking the scalar product of (2) with $\vec{u}^*$. We have

$$\vec{u}^*\cdot M\vec{u}=-V_2\vec{u}^*\cdot\vec{v}\ . \qquad (31)$$

This may be written

$$\lambda_1|c^{(s)}|^2+\lambda_2|c^{(p)}|^2=-V_2\vec{u}^*\cdot\vec{v}\ . \qquad (32)$$

Now it is natural to define the fractional bonding character by

$$F_b=\frac{1}{2}+\frac{1}{2}\sum_{i=1}^{N}\vec{u}^*\cdot\vec{v}\ , \qquad (33)$$

in which case (32) and (33) yield

$$F_b=\tfrac{1}{2}-\tfrac{1}{2}V_2^{-1}(\lambda_1F_s+\lambda_2F_p)\ . \qquad (34)$$

It is clear that the results (28) and (34) entail *sum rules* on the density of states $n(E)$. This follows easily from the theorem that the trace of an operator is invariant under a unitary transformation; the appropriate operator in the case of (28) is

$$S=\sum_{i=1}^{N}|s\rangle\langle s|\ , \qquad (35)$$

where s is the s-like combination of basis functions ϕ_{ij} associated with atom i. The resultant sum rule is

$$\int_{-\infty}^{\infty}dE\,n(E)\,F_s(E)=1\ , \qquad (36)$$

while (34) gives

$$\int_{-\infty}^{\infty}dE\,n(E)\,F_b(E)=2\ . \qquad (37)$$

Note that $n(E)$ by itself satisfies the sum rule (12). Figures 4–7 illustrate the results obtained so far. In Fig. 4 the forbidden regions of energy are indicated for each value of the ratio of the two overlap parameters V_1 and V_2. Here, these are assumed to be both negative. This choice corresponds most closely to the state of affairs in real physical systems. (Bonding states lie below antibonding in energy, and s states below p states.) Figure 4 thus corresponds to the left-hand side of the previously published diagram.[11] Note that there is always a band gap between two allowed bands, except for the one value $|V_1/V_1|=\frac{1}{2}$ at which they touch. Figure 4 also contains indications of the *type* of the allowed bands which are based on the results of this section. F_p and F_b are plotted in Figs. 5–7 for the values $V_1/V_2=\frac{1}{4}$, $\frac{1}{2}$, and 1. In Fig. 5 we see that the two bands are, respectively, bonding and antibonding, and in each band the states range from pure s to pure p. This is true for all $|V_1/V_2|<\frac{1}{2}$. Figure 7 presents the case $|V_1/V_2|>\frac{1}{2}$ and we see that the bands are now s and p like with states ranging in character from pure bonding to pure antibonding. Figure 6 shows the critical case where the two allowed bands touch. Note that in all cases the functions defining F_p and F_b take values outside the range 0–1 in the forbidden ranges of energy. Each of the band limits in Fig. 4 can be seen to correspond to states which are either pure s or pure p, and either pure bonding or antibonding. These four possibilities are sketched in Fig. 8.

There are several more things to be said about the allowed bands, but since their justification involves various digressions we have relegated it to Appendix A, and will merely state the results here.

First, we note that of the four bounds three are

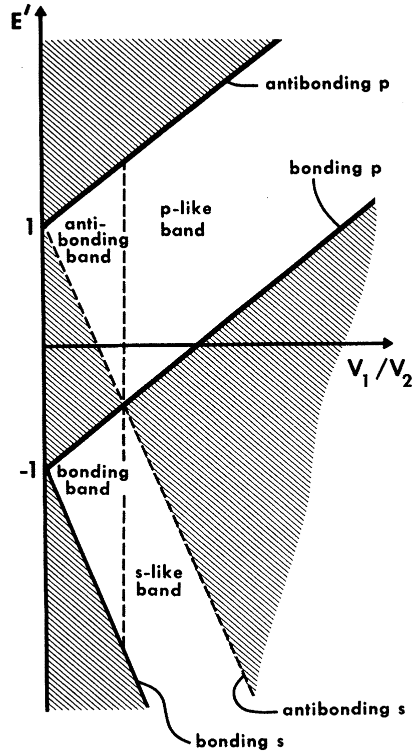

FIG. 4. Bounds on the density of states, and various features of the allowed bands. $E'=E/|V_2|$. Shaded regions are forbidden, unshaded are allowed. The only bound not attained, in general, is indicated by a dashed line. The bounds marked with heavy lines are associated with δ functions in the density of states.

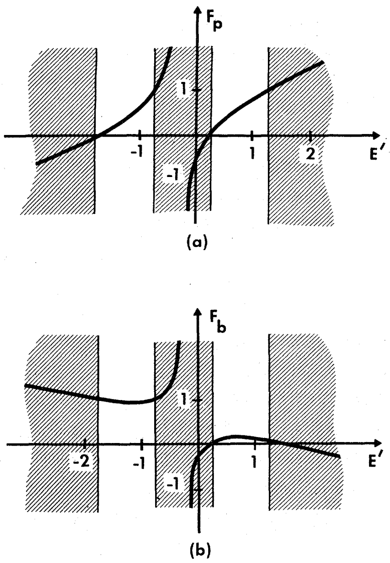

FIG. 5. Fractional p-like character F_p and bonding character F_b of wave functions, as a function of energy for the case $V_2 = -1$, $V_1 = -\frac{1}{4}$.

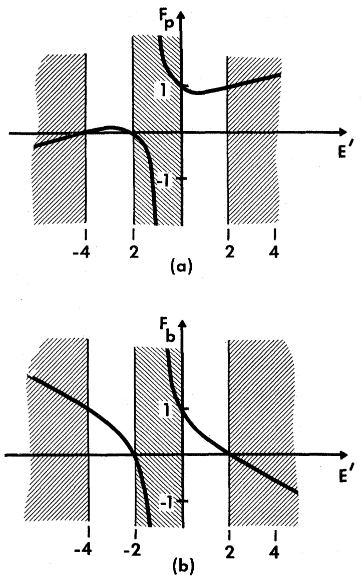

FIG. 7. Fractional p-like character F_p and bonding character F_b of wave functions, as a function of energy for the case $V_2 = -1$, $V_1 = -1$.

actually attained, in general. The one which is not attained, in general, is the antibonding s state and we have indicated this by a dashed line in Fig. 4.

For $|V_1/V_2| < \frac{1}{2}$ there are two states per atom in each band, as might be expected. For $|V_1/V_2| > \frac{1}{2}$ there are three in the p band, one in the s band. This would seem to pose a dilemma since there appears to be a contradiction at $|V_1/V_2| = \frac{1}{2}$. However, it turns out that for any *connected* structure we can show that both of the pure p states are associated with δ functions of unit strength in the density of states. Hence, the bonding p state carries with it, on crossing from one band to the other, one state per atom. Thus does the camel pass through the eye of the needle!

The reader is referred to Appendix A for a further discussion of these points. We pass on to an il-

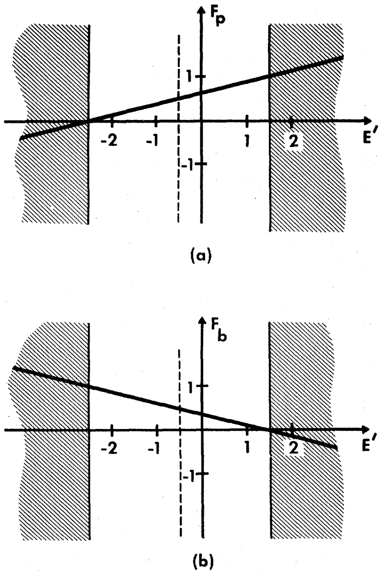

FIG. 6. Fractional p-like character F_p and bonding character F_b of wave functions, as a function of energy for the case $V_2 = -1$, $V_1 = -\frac{1}{2}$. The dashed line indicates where the two bands touch.

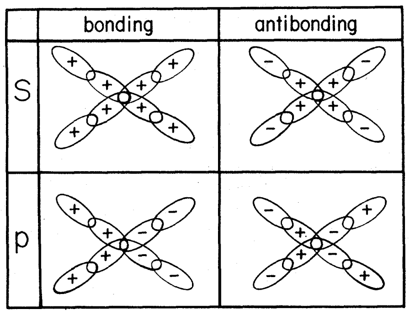

FIG. 8. Bonding and antibonding s and p states have coefficients of equal magnitude associated with each basis function and the signs indicated in this figure. Because of the degeneracy of the p states there are, of course, other possibilities for these beyond those which are shown.

lustration based on the simplest test case—the diamond cubic structure.

V. A TEST CASE–THE DIAMOND CUBIC STRUCTURE

The results obtained in Secs. III and IV and Appendix A apply to all tetrahedrally coordinated structures (subject to the minor reservations noted). These include the familiar crystal structures of the group-IV elements and related compounds—the diamond cubic structure, the wurtzite structure, and SiC polytype structures. The easiest test case is, therefore, provided by the simplest of all these crystal structures, namely, the diamond cubic structure. We should perhaps emphasize at this point that by "diamond" we do not imply "carbon."

Figures 9–11 present the results of a band-structure calculation for the diamond cubic structure using the Hamiltonian (1). The density of states is shown in Fig. 12. (The calculational details are contained in Appendix B.) Once again the three cases $|V_1/V_2| < \frac{1}{2}$, $|V_1/V_2| = \frac{1}{2}$, and $|V_1/V_2| > \frac{1}{2}$ are examined. We see that in the case of the diamond cubic structure, all the bounds on the density of states are always attained and the pure *p* states are associated with δ functions of unit strength in the density of states, which is in accordance with Sec. IV and Appendix A.

The density of states shown in Fig. 12 has an intriguing symmetry. If the δ functions are disregarded, what remains is symmetric about the center of the gap. This is, in fact, a general property of the Hamiltonian, i.e., it holds for *any* structure. This is by no means obvious and its proof requires a more sophisticated mathematical treatment which is postponed to a subsequent paper.[10]

VI. CONCLUSIONS

We have found that the electronic structure of a system with a Hamiltonian, as given by Eq. (1), is in many important respects quite independent of the structure in which the atoms are distributed, provided only that the local coordination of four neighbors is maintained throughout the structure.

The rigorous demonstration of the existence of a gap in the density of states, regardless of the structure involved, has important consequences for the interpretation of the experimental results for amorphous semiconductors alluded to in Sec. I. There has been, in the past, some reluctance to acknowledge the possibility of a zero density of states in the gap as being a reasonable postulate even for an ideally prepared amorphous structure. In the model considered here, not only is the gap preserved in the amorphous state but it is presumably larger than in the diamond cubic structure, since in the latter case all bounds are attained and the gap has its minimal value.

In reality, amorphous semiconductors have a certain amount of quantitative disorder as well as topological disorder. Throughout the structure bonds are stretched and bent somewhat and consequently the quantities V_1 and V_2 cannot be precisely the same everywhere. Furthermore, it is only the nearest neighbors that are coordinated in very nearly the same way throughout the structure. This means that if matrix elements between more

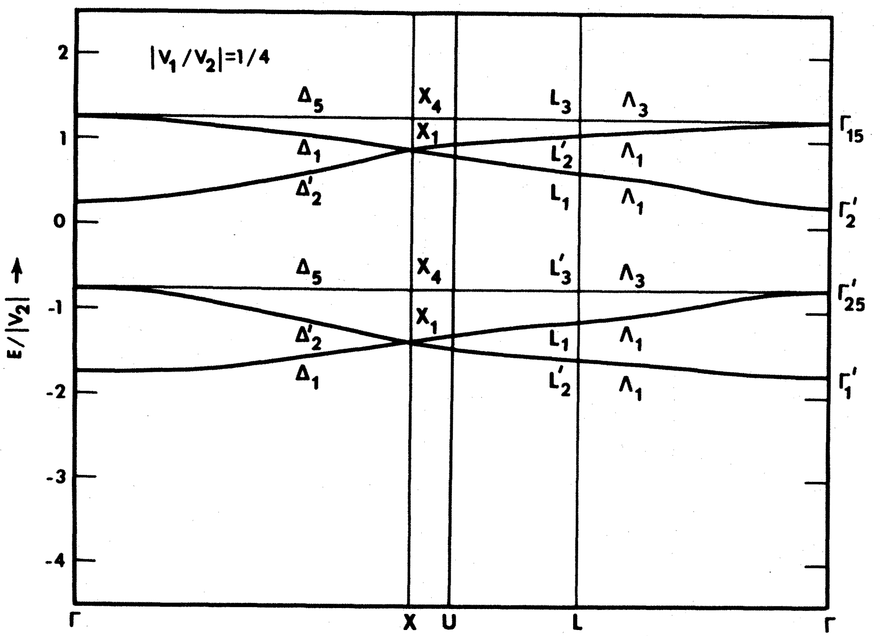

FIG. 9. Band structure for the special case of the diamond cubic structure, with $V_2 = -1$, $V_1 = -\frac{1}{4}$.

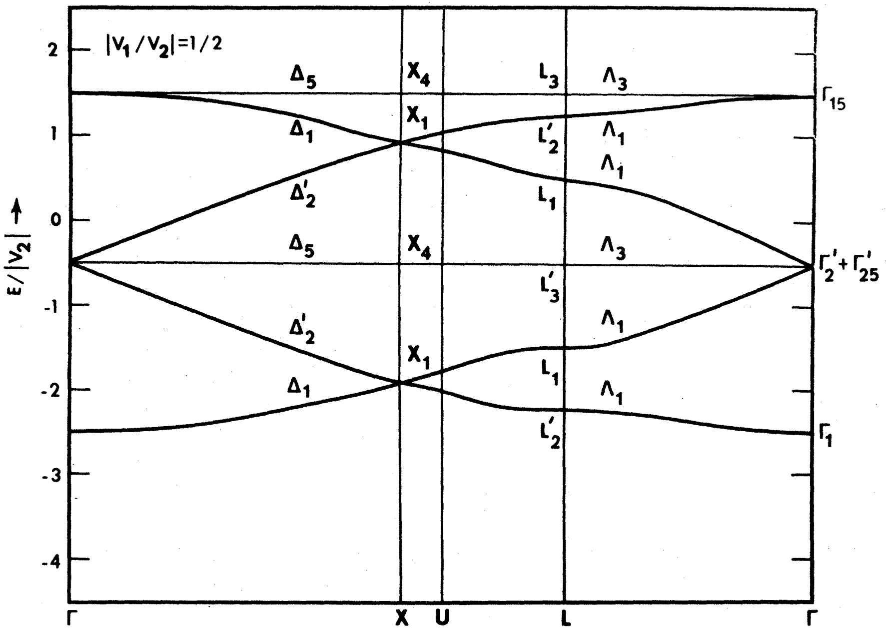

FIG. 10. Band structure for the special case of the diamond cubic structure, with $V_2=1$, $V_1=-\frac{1}{2}$.

widely separated orbitals were to be incorporated in an attempt to refine the theory, it would not even be a reasonable first approximation to consider these to have constant values throughout the structure. Thus, there is some quantitative disorder imposed on the topological disorder which is the main characteristic of these solids.

The present work has shown that topological disorder by itself produces no narrowing of the gap. However, it remains to be seen what the effect of the superimposed quantitative disorder may be. Economou and Cohen[13] have studied Hamiltonians of a simple type with (purely) quantitative disorder, discussing, especially, the formation of band tails of localized states. Since the study of topologically *and* quantitatively disordered systems looks forbiddingly difficult, interpretation of experiment must, for the present, be based on the independent study of each type of disorder and the synthesis of ideas from both. Our results should, therefore,

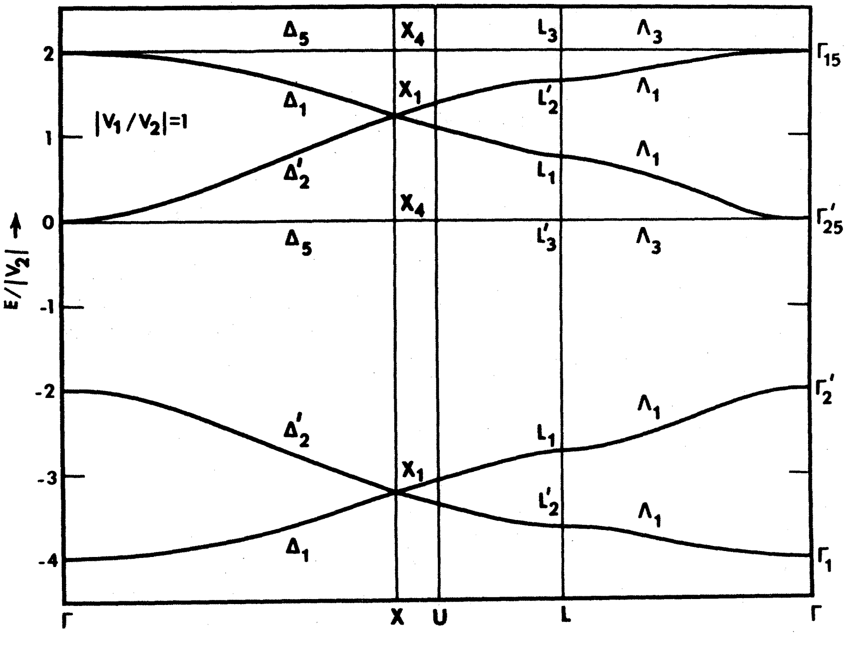

FIG. 11. Band structure for the special case of the diamond cubic structure, with $V_2=-1$, $V_1=-1$.

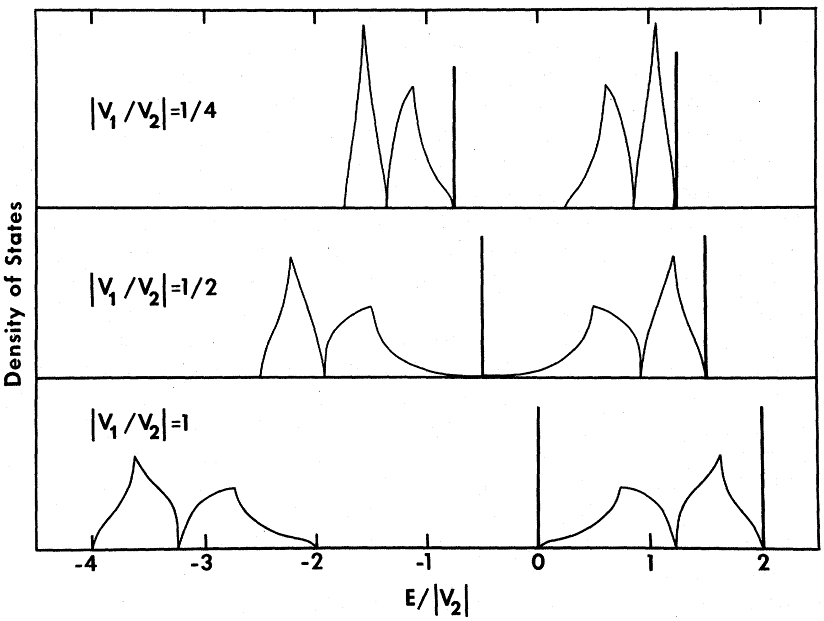

FIG. 12. Density of states for the diamond cubic structure with the same overlap parameters as in Figs. 9–11. Note the δ functions, which correspond to flat bands in Figs. 9–11.

not be set in opposition to those of Economou and Cohen,[13] but rather should be considered as complementary. On the other hand, they should help to correct a prevalent notion that topological and quantitative disorder amount to much the same thing and that the insights gained by a study of quantitative disorder alone are sufficient for interpretation of the properties of amorphous solids. The implications of the present study for such interpretation will receive more attention in subsequent papers,[10] together with various extensions, generalizations, and applications of the basic theory.

ACKNOWLEDGMENTS

We wish to thank Dr. V. Heine and Professor A. Herzenberg for helpful conversations.

APPENDIX A: SOME PROPERTIES OF THE ALLOWED BANDS

This Appendix contains the justification for some of the remarks of Sec. IV concerning the distribution of the density of states in the allowed bands, and in particular, at the band edges. The analysis of Sec. IV demonstrates that states at the band edges are of four types. They are bonding *s* state, antibonding *s* state, bonding *p* state, antibonding *p* state (Fig. 8). These correspond, respectively, to $\Gamma_1 \Gamma'_2$, Γ'_{25}, and Γ_{15} for the diamond cubic structure.[14] The existence and degeneracy of these states depends critically on the *topology* of the structure. For instance, an antibonding *s* state must have a wave function of opposite sign on nearest neighbors. This is impossible if the structure has fivefold rings, as does the random network model, and hence, this state cannot, in general, be constructed and the corresponding bound on the density of states is not, in general, attained. It may be that states infinitesimally close to it are attained, but such questions must depend sensitively on the details of the structure.

The topological arguments necessary for a discussion of these states have been set forth elsewhere.[14] Whereas the antibonding *s* state is not, *in general*, realizable, the other three are and hence the corresponding bounds are expected to be attained in general. In the case of the bonding *s* state, the latter statement rests on the assumption that the existence of this singly degenerate eigenstate, which by itself is of negligible weight in an infinite system, is indicative of the presence of a band edge at that energy. We suspect that this is always the case for systems which obey the condition of bounded density variation, but this has not been proved. The other two attained bounds are associated with δ functions in the density of states (i.e., states whose degeneracy is of order N) so the problem does not arise for them.

The δ functions in the density of states were explicitly demonstrated for the diamond cubic structure in Sec. V. In that case they arose from flat bands in the calculated band structure $E(\vec{k})$. We shall now show that such δ functions are a general feature of the Hamiltonian and prove, subject to the condition that the network be connected, that these δ functions always have strength unity. Each contains one state per atom. (Here and elsewhere we do *not* include a factor of 2 for spin degeneracy in counting states.)

It is again most convenient to use periodic boundary conditions. Then we require to find how many orthogonal bonding or antibonding wave functions of pure p type can be assembled. If we do not require any matching condition between atoms there are $3N$ orthogonal p functions in all. These may be regarded as defining a $3N$-dimensional vector space. The question is, if we require perfect antibonding everywhere, how many orthogonal vectors can be constructed from these $3N$ vectors to satisfy this condition. It is easily seen that the antibonding (or bonding) conditions may be represented by $2N$ linear relations among the elements of the vector defining any p function, since there is one matching condition per bond and two bonds per atom. This means that there are *at least* $3N-2N=N$ functions satisfying these constraints. It is not, however, obvious that these constraints are independent. However, we can show that at least $2N-1$ of them are independent, provided that the system is connected, i.e., we can connect any two atoms by an unbroken chain of bonds. If this is so, then we can construct a wave function which obeys all of the matching conditions except those associated with any given *pair* of bonds A and B. To do so, we first construct a p function obeying *all* the matching conditions and such that the coefficients of orbitals ϕ_{ij} along a path connecting A and B are $++--++--\ldots$ in the bonding case or $+-+-+-\ldots$ in the antibonding case. This can always be done by the kind of construction used in Ref. 14. Now a reversal of sign of all coefficients along this line preserves the p-like character of the wave function and results in an infringement of the matching conditions at A and B *only*. Hence, the remaining conditions are independent of those at A and B and so at least $2N-1$ matching conditions (and the corresponding linear constraints) are independent. It follows that the dimensionality of the space spanned by the bonding (or antibonding) p functions is N or $N+1$. In the limit as N tends toward infinity there is *one* p function of each type *per atom* and such states, therefore, produce δ functions of unit strength in the density of states.

Finally, we ask how many states are contained in each band. In either of the limits $V_1=0$ or $V_2=0$ the answer is trivial since the Hamiltonian decouples. In the case $V_1=0$ we have two bonding states and two antibonding states per atom. For finite N and quasiperiodic boundary conditions we can infer that there are two states in each band for $0<|V_1/V_2|<\frac{1}{2}$. This follows because the eigenvalues of a finite real symmetric matrix are continuous functions of its matrix elements.[15] Thus the $2N$ eigenstates in each band cannot leave the region of energy defined by the bounds on the density of states as we change $|V_1/V_2|$ between 0 and $\frac{1}{2}$. Similarly, we can show that for all $\frac{1}{2}<|V_1/V_2|<\infty$ there are three states per atom in the p band and one in the s band. Again, these statements apply only in the infinite limit if we do not have quasiperiodic boundary conditions.

APPENDIX B: BAND STRUCTURE FOR THE DIAMOND CUBIC STRUCTURE

In this Appendix, the band structure of a diamond cubic crystal is worked out using the Hamiltonian (1). This calculation parallels that of Hall,[16] although we have pursued it further to obtain an analytic expression for the density of states. The diamond cubic structure is conveniently viewed as fcc with two atoms at each lattice point. A single cube of the diamond cubic structure is shown in Fig. 13 with the unit cell indicated with dotted lines. Each atom has four states associated with it and so there are eight states in the unit cell. These are indicated by numbers which go from 1 to 8, where each number refers to an sp^3 orbital $|n\rangle$ directed along that particular band. Because of the translational symmetry we can use Bloch's Theorem and have only to diagonalize an 8×8 matrix $H_{\vec{k}}$ at each point in $\vec{k}$ space, where $H_{\vec{k}}$ is given by

$$H_{\vec{k}}=\begin{bmatrix} 0 & V_1 & V_1 & V_1 & V_2 & 0 & 0 & 0 \\ V_1 & 0 & V_1 & V_1 & 0 & V_2 & 0 & 0 \\ V_1 & V_1 & 0 & V_1 & 0 & 0 & V_2 & 0 \\ V_1 & V_1 & V_1 & 0 & 0 & 0 & 0 & V_2 \\ V_2 & 0 & 0 & 0 & 0 & V_1\gamma_y\gamma_z & V_1\gamma_z\gamma_x & V_1\gamma_x\gamma_y \\ 0 & V_2 & 0 & 0 & V_1\gamma_y^*\gamma_z^* & 0 & V_1\gamma_x\gamma_y^* & V_1\gamma_z^*\gamma_x \\ 0 & 0 & V_2 & 0 & V_1\gamma_z^*\gamma_x^* & V_1\gamma_x^*\gamma_y & 0 & V_1\gamma_y\gamma_z^* \\ 0 & 0 & 0 & V_2 & V_1\gamma_x^*\gamma_y^* & V_1\gamma_z\gamma_x^* & V_1\gamma_y^*\gamma_z & 0 \end{bmatrix}$$

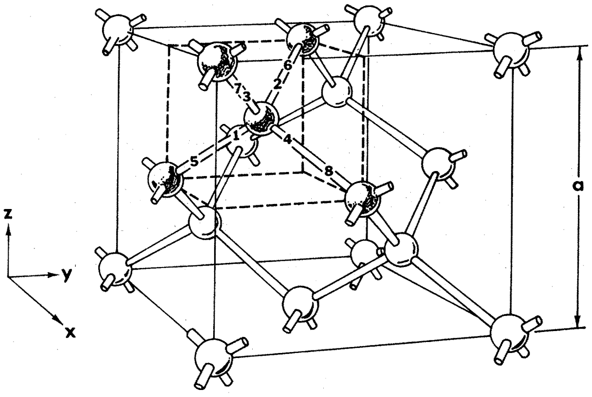

FIG. 13. A unit cell of the diamond cubic structure, illustrating the notation used to set up the secular determinant.

and the basis states are

$$|n\rangle_{\vec{k}}=\left(\frac{2}{N}\right)^{1/2}\sum_{\vec{r}_i} e^{i\vec{k}\cdot\vec{r}_i}|n\rangle\ , \qquad \text{(B1)}$$

with n going in sequence from 1 to 8. The summation over $\vec{r}_i$ is over unit cells, where $N/2$ is the number of unit cells in the structure and the unit cell in Fig. 13 is taken as the origin of coordinates. We also have

$$\gamma_x=\exp(ik_x a/2),\quad \gamma_y=\exp(ik_y a/2),\quad \gamma_z=\exp(ik_z a/2)\ ,$$

where a is the side of the unit cube as shown in Fig. 13.

The energy levels $E_{\vec{k}}$ at $\vec{k}$ are determined by putting

$$\mathrm{Det}|H_{\vec{k}}-E_{\vec{k}}|=0\ ,$$

i.e.,

$$[(E_{\vec{k}}+V_1)^2-V_2^2]\{[(E_{\vec{k}}+V_1)(E_{\vec{k}}-3V_1)-V_2^2]^2 - 4V_1^2V_2^2(1+\alpha_{xyz})\}=0\ , \qquad \text{(B2)}$$

where α_{xyz} is given by

$$\alpha_{xyz}=\cos\tfrac{1}{2}k_x a\cos\tfrac{1}{2}k_y a+\cos\tfrac{1}{2}k_y a\cos\tfrac{1}{2}k_z a + \cos\tfrac{1}{2}k_z a\cos\tfrac{1}{2}k_x a\ .$$

The eight roots of the eigenvalue equation (B2) are given by

$$\begin{aligned} E_{\vec{k}}&=-V_1+V_2\,\text{(twice)}\ ,\\ E_{\vec{k}}&=-V_1-V_2\,\text{(twice)}\ ,\\ E_{\vec{k}}&=V_1\pm[4V_1^2+V_2^2\pm 2V_1V_2(1+\alpha_{xyz})^{1/2}]^{1/2}\ . \end{aligned} \qquad \text{(B3)}$$

The band structure from these roots is shown in Figs. 9–11 for three different values of the ratio $|V_1/V_2|$. V_1 and V_2 are both chosen to be negative so that the s states and bonding states have the lowest energy. The band structure is shown along the path $\Gamma XUL\Gamma$ in Figs. 9–11 for the Brillouin zone of an fcc lattice.[17] The notation for the symmetry types of the eigenfunctions follows that of Herring.[18] It can be seen from (B3) that the bonding and antibonding p states give flat bands and lead to δ functions in the density of states at energies of $-V_1\pm V_2$, both with weight N. The density of states per atom due to the other four branches may be written

$$\begin{aligned} n(E)&=\frac{1}{N}\sum_{\vec{k}}\delta(E-E_{\vec{k}})=-\frac{1}{\pi N}\mathrm{Im}\sum_{\vec{k}}\frac{1}{E-E_{\vec{k}}}\\ &=-\frac{1}{\pi N}\mathrm{Im}\sum_{\vec{k}}\left(\frac{1}{E-V_1+[4V_1^2+V_2^2+2V_1V_2(1+\alpha_{xyz})^{1/2}]^{1/2}}+\frac{1}{E-V_1-[4V_1^2+V_2^2+2V_1V_2(1+\alpha_{xyz})^{1/2}]^{1/2}}\right.\\ &\qquad\left.+\frac{1}{E-V_1+[4V_1^2+V_2^2-2V_1V_2(1+\alpha_{xyz})^{1/2}]^{1/2}}+\frac{1}{E-V_1-[4V_1^2+V_2^2-2V_1V_2(1+\alpha_{xyz})^{1/2}]^{1/2}}\right)\\ &=-\frac{4}{\pi N}[(E-V_1)^2-4V_1^2-V_2^2](E-V_1)\,\mathrm{Im}\sum_{\vec{k}}\frac{1}{[(E-V_1)^2-4V_1^2-V_2^2]^2-4V_1^2V_2^2(1+\alpha_{xyz})}\ , \end{aligned} \qquad \text{B4)}$$

where the only $\vec{k}$ dependence in the summation in (B4) enters through α_{xyz}. Im denotes the imaginary part when a small imaginary part is added to E. This density of states can be expressed in terms of the Green's functions for an fcc lattice $I_{\mathrm{fcc}}(\epsilon)$ which have been calculated numerically by Frikee[19]:

$$I_{\mathrm{fcc}}(\epsilon)=\left(\frac{1}{2\pi}\right)^3\int_{-\pi}^{\pi}\!\!\int\!\!\int\frac{dx\,dy\,dz}{\epsilon-(\cos x\cos y+\cos y\cos z+\cos z\cos x)}\ . \qquad \text{(B5)}$$

Therefore,

$$n(E) = -\frac{1}{\pi}\left(\frac{[(E-V_1)^2-4V_1^2-V_2^2\ ][E-V_1]}{2V_1^2V_2^2}\right)\operatorname{Im} I_{\mathrm{fcc}}\left(\frac{[(E-V_1)^2-4V_1^2-V_2^2]^2}{4V_1^2V_2^2-1}\right) . \tag{B6}$$

Notice that adding a small imaginary part to ϵ is equivalent to adding a small imaginary part to E, apart from a possible sign change. However, this sign change is exactly compensated for by the factor in curly brackets in (B6) with the result that the density of states is always positive. In a recent paper, Joyce[20] has expressed the integrals $I_{\mathrm{fcc}}(\epsilon)$ in terms of complete elliptic integrals of the first kind. We refer the reader to Joyce's paper for this further reduction. The density of states (B6) is shown in Fig. 12 together with the δ functions at $-V_1 \pm V_2$.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 8 15 OCTOBER 1971

Charge-Transfer Model of the Nonlinear Susceptibilities of Polar Semiconductors*

C. L. Tang† and Chr. Flytzanis‡
Division of Engineering and Applied Physics, Harvard University,
Cambridge, Massachusetts 02138

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The second-order optical susceptibilities of III-V and II-VI compounds are calculated on the basis of a charge-transfer model and shown to be in close agreement with the experimental values. The importance of the d-electron contributions to the determination of the sign of the nonlinear susceptibilities of polar semiconductors and other compounds is also discussed.

In the optical transparency region, the behavior of the second-order susceptibilities $\chi^{(2)}$ in dielectrics is closely related to the characteristics of the valence electronic distribution. For simple structures this quantity can be calculated now by molecular-orbital methods.[1,2] For polar diatomic semiconductors simpler methods,[3-6] based upon the prescriptions of Phillips and van Vechten, have also been used to describe[7] the macroscopic dielectric susceptibility for sp^3-bonded III-V and II-VI compounds. The bond-charge model[4,5] yields results apparently in good agreement with experiments. However, the adjustable parameters and assumptions used are not easily justified.

Here we want to show that exactly the same results can be obtained simply, without any of the troublesome assumptions about the bond charge, by a completely different model that sheds more

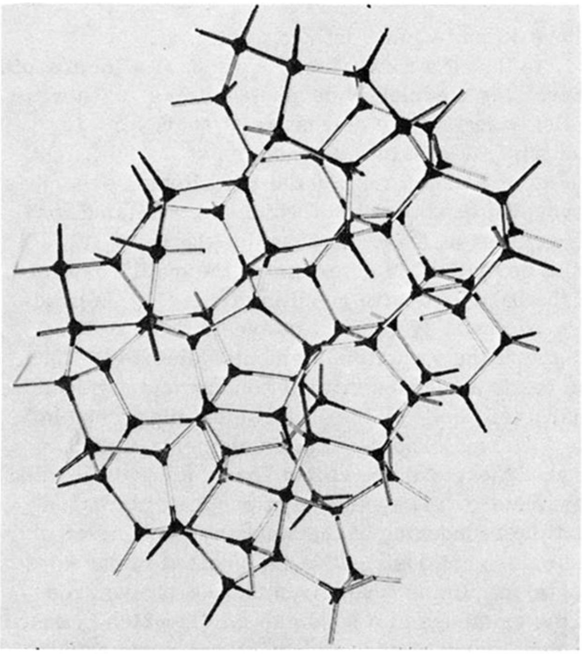

FIG. 2. Some features of a random network structure similar to that constructed by Polk (Ref. 8). Fivefold, sixfold, and sevenfold closed rings of bonds are evident. For a photograph of a more extended structure of this type see Ref. 8 or M. H. Cohen, Phys. Today 24, 26 (1971).