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"Cluster–Bethe-lattice" method: The electronic density of states of heteropolar systems*

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The "cluster–Bethe-lattice" method is extended to the study of heteropolar systems. The Bethe lattice is solved for binary compounds of arbitrary coordination using simple tight-binding models. In particular systems with tetrahedral coordination, such as the zinc-blende, BC-8, and random-network structures are examined in detail. The results are compared with recent experimental photoemission data on the amorphous phases of binary compounds and interpreted in terms of topology.

I. INTRODUCTION

The "cluster–Bethe-lattice"[1] method is a particularly useful tool for studying infinite connected systems, which may be periodic or not, in terms of the local configurations of the atoms in these systems. The method involves treating part of the system exactly (as a cluster) and replacing the effects of the rest of the infinite environment by a Cayley tree[2] (or Bethe lattice). Results on homopolar systems indicate the importance of local atomic configurations and ring topologies in determining structure in the electronic density of states (DOS). A natural extension of this method is to heteropolar systems. In this way one can in principle study the alloy problem, as well as amorphous binary systems.

In this paper the method will be set up for the study of infinite connected binary systems of arbitrary coordination. To do this, a heteropolar Bethe lattice of arbitrary coordination will be solved in detail. This, in general, permits a study of a large class of problems including alloys and amorphous binary systems. The focus here, however, will be to use the cluster–Bethe-lattice method to study the effects of topology on the DOS of amorphous tetrahedrally coordinated binary compounds. In particular, only structures which can be made with no like-atom bonds will be studied. Specifically, the DOS's of binary systems constructed using the atomic positions of the diamond, BC-8,[3] and Connell random-network[4] structures will be calculated and examined in detail. These systems form a series of structures whose local atomic configurations become increasingly more disordered.

The format of the paper is as follows. In Sec. II the cluster–Bethe-lattice method is discussed, simple one-orbital and four-orbital tight-binding Hamiltonians[5] are defined, a transformation between the states of a one-orbital and four-orbital Hamiltonian is introduced for heteropolar systems, and an example of the cluster–Bethe-lattice method using these Hamiltonians is given. In Sec. III the Bethe lattice is solved analytically for heteropolar systems using the one-orbital Hamiltonian. Local densities of states for the cation and anion are obtained separately and effects of heteropolarity are studied explicitly. In Sec. IV the amorphous phases of III-V compounds are discussed and the results for the binary structures made from the diamond, BC-8, and Connell random-network structures are presented and examined in detail. Finally, Sec. V is concerned with a summary and concluding remarks.

II. CLUSTER-BETHE-LATTICE METHOD

The purpose of the cluster-Bethe-lattice method is to provide a simple and physical way of obtaining the total DOS of an infinite system of atoms, which may or may not have periodicity. The procedure is as follows. Consider an infinite connected network of atoms of coordination m. Any arbitrary atom is picked as a reference point. A cluster of atoms surrounding and including this atom is then removed from the system. The cluster is chosen such that every atom in the cluster is part of a ring passing through the central or reference atom. A Bethe lattice[2] (or Cayley tree) is then attached to the dangling bonds so as to simulate the effects of the original infinite environment. The Bethe lattice is an infinite connected system of atoms of coordination m such that every atom is equivalent and there are no rings of bonds in the system. Once the solution of the Bethe lattice is known the local Green's function $\langle 0|g|0\rangle$ of the central or reference atom can be obtained exactly. The Bethe lattice therefore serves two useful purposes. First, it provides the mathematical convenience of solving exactly an infinite system without periodicity. Second, it provides the physically attractive characteristic of preserving the connectivity and the coordination of the system.

The Hamiltonians that will be used consist of simple one-orbital (h) and four-orbital (H) Hamiltonians[5] for systems with no like-atom bonds. These are given in the orbital representation by

$$h=\pm\Lambda\sum_{i}|i\rangle\langle i|+V\sum_{\substack{i,i'\\ i\pm i'}}|i\rangle\langle i'| \tag{1}$$

and

$$H=\pm\Delta\sum_{i,j}|ij\rangle\langle ij|+V_1\sum_{\substack{i,j,j'\\ j\neq j'}}|ij\rangle\langle ij'|+V_2\sum_{\substack{i,i',j\\ i\neq i'}}|ij\rangle\langle i'j|\,. \tag{2}$$

h represents a system where an s-like localized orbital $|i\rangle$ is placed on each atom i and only nearest-neighbor interactions V are taken into account. The diagonal terms are positive or negative depending on whether atom i is a cation or anion, respectively. Similarly H represents a system where four sp^3-like orbitals $|ij\rangle$ are placed on each atom i with $j=1,4$. V_1 represents the interaction between different orbitals on the same atom and V_2 represents the interaction between orbitals on different atoms, but along the same bond. Finally, a positive or negative Δ characterizes a cation- or anion-directed orbital. H is very useful, because it supplies a simple yet relatively good description of the DOS region everywhere except at the top of the valence band. Here the upper p-like bonding states form a flat band or equivalently a δ-function peak in the DOS. (For the purposes of this investigation, however, this is not very important since it will be shown in Sec. IV that the primary concern here is to examine the middle peak region of the DOS.) If one takes $\Delta=\Lambda=0$, then the eigenvalues of H (except those that lie in the δ-function peak) are related by an analytic transformation[5] to the eigenvalues of the much simpler Hamiltonian h. This, however, is also true for $\Delta\neq 0\neq\Lambda$. For this case a similar analysis gives the transformations

$$E=2V_1\pm(4V_1^2+V_2^2+\Delta^2+V_1V_2\,\epsilon/V)^{1/2} \tag{3}$$

and

$$\Delta=\Lambda V_2/4V, \tag{4}$$

where ϵ and E are the eigenvalues of (1) and (2) respectively. Thus one can now use the much simpler Hamiltonian h for heteropolar systems in order to calculate eigenvalues and *local* DOS's and use the transformations (3) and (4) to give the corresponding eigenvalues and *local* DOS's for the Hamiltonian H.

To obtain the DOS of any system in a Green's-function formalism using the Hamiltonian h one must first define

$$g=1/(\epsilon-h)=1/\epsilon+(1/\epsilon)hg. \tag{5}$$

The total DOS $n(\epsilon)$ is then given by

$$n(\epsilon)=(-1/\pi)\,\mathrm{Im}[\mathrm{Tr}\,g(\epsilon)] \tag{6}$$

and one is interested in the diagonal matrix elements of $g(\epsilon)$. So that taking matrix elements of (5) between a basis set $\{|i\rangle\}$, one obtains

$$\epsilon\langle i|g|j\rangle=\delta_{ij}+\sum_{l}\langle i|h|l\rangle\langle l|g|j\rangle. \tag{7}$$

The local DOS $n_i(\epsilon)$ of the ith atom is then given by

$$n_i(\epsilon)=-(1/\pi)\,\mathrm{Im}\langle i|g|i\rangle \tag{8}$$

and

$$n(\epsilon)=\sum_i n_i(\epsilon). \tag{9}$$

As a simple example of how the cluster–Bethe-lattice method works, consider the cluster of atoms in the diamond structure shown in Fig. 1. The reference atom is labeled 0 and from symmetry many atoms are equivalent and therefore labeled with the same number. Thus, there are only four inequivalent atoms in a cluster of 29 atoms. Furthermore, there are 12 sixfold rings of bonds passing through the central atom. A zinc-blende–Bethe-lattice system can now be constructed by placing cations or anions on all the odd or even numbered atomic positions and attaching a corresponding heteropolar Bethe lattice to the dangling bonds of atoms 2 and 3. The local DOS for atom 0 of this infinite system can now be solved analytically using Eq. (7). One obtains

$$\begin{aligned}(\epsilon\pm\Lambda)\langle 0|g^{\mp}|0\rangle&=1+4V\langle 1|g^{\mp}|0\rangle,\\ (\epsilon\mp\Lambda)\langle 1|g^{\mp}|0\rangle&=V\langle 0|g^{\mp}|0\rangle+3V\langle 2|g^{\mp}|0\rangle,\\ (\epsilon\pm\Lambda)\langle 2|g^{\mp}|0\rangle&=V\langle 1|g^{\mp}|0\rangle+2V\langle 3|g^{\mp}|0\rangle\\ &\quad+\phi^{\mp}\langle 2|g^{\mp}|0\rangle,\\ (\epsilon\mp\Lambda)\langle 3|g^{\mp}|0\rangle&=2V\langle 2|g^{\mp}|0\rangle+2\phi^{\pm}\langle 3|g^{\mp}|0\rangle,\end{aligned} \tag{10}$$

where g^- and g^+ represent the Green's functions for the case of an anion and cation central atom, respectively, and ϕ^- and ϕ^+ are the fields of a heteropolar Bethe-lattice acting, along *one* bond, on an anion and cation, respectively. The fields $\phi^{\pm}$ are, in general, complex functions of energy and depend only on the properties of the Bethe lattice. Section III will be devoted to their solution. Assuming, however, that the $\phi^{\pm}$ are known the local Green's functions, $\langle 0|g^{\mp}|0\rangle$ can be obtained trivially from the linear equations (10). The result is

$$\langle 0|g^{\mp}|0\rangle=(\epsilon\pm\Lambda-4V^2\{\epsilon\mp\Lambda-3V^2[\epsilon\pm\Lambda-\phi^{\mp}-4V^2(\epsilon\mp\Lambda-2\phi^{\pm})^{-1}]^{-1}\}^{-1})^{-1} \tag{11}$$

and

$$n_0^{\mp}(\epsilon)=-(1/\pi)\,\mathrm{Im}\langle 0|g^{\mp}|0\rangle, \tag{12}$$

where $n_0^-(\epsilon)$ and $n_0^+(\epsilon)$ are the local DOS's of an anion or cation central atom, respectively. These results will be examined again in Sec. III once the solutions for $\phi^{\pm}$ are obtained.

III. HETEROPOLAR BETHE LATTICE

This section will be concerned with solving the total and local Green's functions of a heteropolar

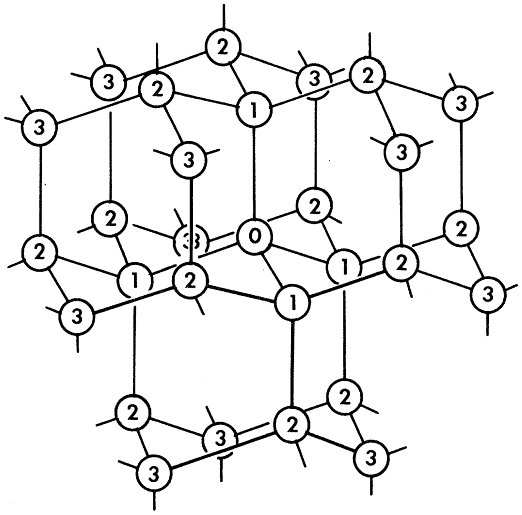

FIG. 1. Cluster of atoms in the diamond structure. The central or reference atom is labeled 0. All equivalent atoms are labeled with the same number. The Bethe lattice is connected to the one and two dangling bonds of atoms 2 and 3, respectively.

Bethe lattice (with no like-atom bonds) using the Hamiltonian h defined in Sec. II. This will be accomplished by using a mean-field formalism so that fields $\phi^{\pm}$ will be obtained which can then be used to attach the heteropolar Bethe lattice to any cluster of atoms.

Consider a heteropolar Bethe lattice made up of atoms with coordination m. Choose any atom in the Bethe lattice and remove it and $m-1$ of its nearest neighbors from the system. Assume now for simplicity that the atom chosen is an anion and is labeled 0. Its nearest neighbors are labeled 1. Atom 0 has only one dangling bond, whereas atoms 1 have $m-1$ dangling bonds. If the Bethe lattice is now attached to the dangling bonds of atoms 0 and 1 through the fields $\phi^{\pm}$ one again obtains a complete Bethe lattice and the following equations from (7):

$$\begin{aligned}(\epsilon+\Lambda)\langle 0|g^{-}|0\rangle &= 1+(m-1)V\langle 1|g^{-}|0\rangle \\ &\quad +\phi^{-}\langle 0|g^{-}|0\rangle, \\ (\epsilon-\Lambda)\langle 1|g^{-}|0\rangle &= V\langle 0|g^{-}|0\rangle \\ &\quad +(m-1)\phi^{+}\langle 1|g^{-}|0\rangle.\end{aligned} \tag{13}$$

Now consider again atom 0 but now remove it and all of its m nearest neighbors from the Bethe-lattice system. The Bethe lattice is then attached to the $m-1$ dangling bonds of atoms 1 and one obtains the following equations from (7):

$$\begin{aligned}&(\epsilon+\Lambda)\langle 0|g^{-}|0\rangle = 1+mV\langle 1|g^{-}|0\rangle, \\ &(\epsilon-\Lambda)\langle 1|g^{-}|0\rangle = V\langle 0|g^{-}|0\rangle+(m-1)\phi^{+}\langle 1|g^{-}|0\rangle.\end{aligned} \tag{14}$$

Comparing Eqs. (13) and (14) and using the plus and minus symmetry of the system gives

$$\phi^{\pm}=V^2/(\epsilon\pm\Lambda-(m-1)\phi^{\mp}) \;. \tag{15}$$

Solving (20) for $\phi^{\pm}$ gives

$$\phi^{\pm}=\phi_R^{\pm}+i\,\phi_I^{\pm}, \tag{16}$$

with

$$\phi_R^{\pm}=(\epsilon\mp\Lambda)/2(m-1) \tag{17}$$

and

$$\phi_I^{\pm}=[\pm]\frac{[4(m-1)V^2(\epsilon^2-\Lambda^2)-(\epsilon^2-\Lambda^2)^2]^{1/2}}{2(m-1)(\epsilon\pm\Lambda)}. \tag{18}$$

The choice of sign in the brackets $[\pm]$ in (18) depends only on the values of ϵ and not on whether the connecting atom is an anion or cation. The minus sign must be taken when $\epsilon>\Lambda$ and the plus sign when $\epsilon<-\Lambda$.

The local Green's function for the heteropolar Bethe lattice is now given by

$$\langle 0|g^{\mp}|0\rangle=(\epsilon\pm\Lambda-m\phi^{\mp})^{-1} \tag{19}$$

and the local DOS of the Bethe lattice $n_B^{\mp}(\epsilon)$ from

$$n_B^{\mp}(\epsilon)=-(1/\pi)\,\mathrm{Im}\,\langle 0|g^{\mp}|0\rangle; \tag{20}$$

therefore

$$n_B^{\mp}(\epsilon)=-\frac{1}{\pi}\frac{m\phi_I^{\mp}}{(\epsilon\pm\Lambda-m\phi_R^{\mp})^2+m^2(\phi_I^{\mp})^2}\,. \tag{21}$$

The band edges can be obtained from (18) and occur at

$$\epsilon=\pm[\Lambda^2+4(m-1)V^2]^{1/2} \tag{22}$$

and

$$\epsilon=\pm\Lambda. \tag{23}$$

An examination of (21) shows that $n_B^{-}(\epsilon)$ and $n_B^{+}(\epsilon)$ have square-root singularities at $\epsilon=-\Lambda$ and $\epsilon=+\Lambda$, respectively. These singularities are actually a general feature of the h and H Hamiltonians and will occur for all structural systems with no like-atom bonds. Furthermore, although $n_B^{\mp}(\epsilon)$ is singular at $\epsilon=\mp\Lambda$, it is zero at $\epsilon=\pm\Lambda$. This indicates that the states occurring at the singularities $\epsilon=+\Lambda$ and $\epsilon=-\Lambda$ represent *pure* cation and *pure* anion states, respectively. $n_B^{-}(\epsilon)$ and $n_B^{+}(\epsilon)$ are plotted in Fig. 2(a) as a dotted and dashed line, respectively, with $V=1$ and $\Lambda=2V$. The sum of these two curves (which is not shown) is of course the total DOS of the heteropolar Bethe lattice.[5] This is very similar to that of a homopolar Bethe lattice except that there is now a gap between (and singularities at) $\epsilon=\pm\Lambda$. The local DOS $n_B^{-}(\epsilon)$ for an anion is clearly concentrated at low energies with a small amount of states at high energies. The cation local DOS is of course just the mirror image of $n_B^{-}(\epsilon)$ about $\epsilon=0$.

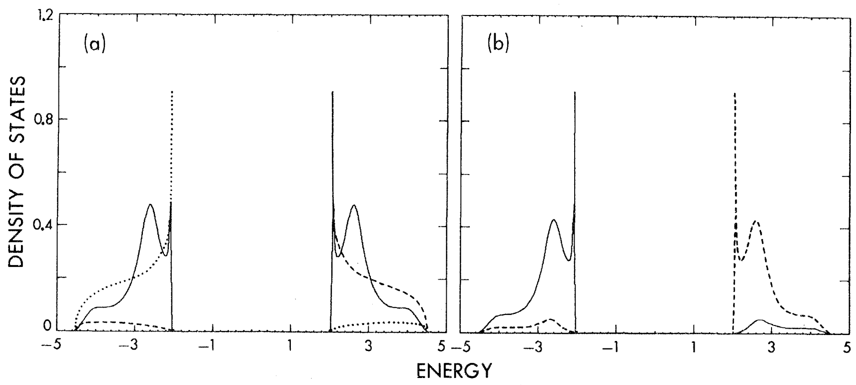

FIG. 2. Densities of states using the one-orbital Hamiltonian. (a) Local anion (dotted line) and cation (dashed line) densities of states for a binary Bethe lattice and the density of states (solid line) of a zinc-blende-Bethe-lattice system with the cluster of atoms shown in Fig. 1. (b) The local densities of states for the anion (solid line) and cation (dashed line) for the same zinc-blende–Bethe-lattice system. The energy is in units of the one-orbital interaction parameter V.

In Fig. 2(a) is also shown (as a solid line) the DOS of the zinc-blende–Bethe-lattice system obtained by adding $n_0^-(\epsilon)$ and $n_0^+(\epsilon)$ from Eq. (12). The cluster in this system was described in Sec. II and drawn in Fig. 1. It contains 29 atoms in a zinc-blende configuration. The peaks around ±2.5 V arise from the 12 sixfold rings of bonds passing through the central atom of this cluster. In Fig. 2(b), the separate contributions of $n_0^-(\epsilon)$ (solid line) and $n_0^+(\epsilon)$ (dashed line) for the anion and cation, respectively, are shown. Again the spectra are mirror images of each other about $\epsilon = 0$ with the anion and cation having considerably more states at low and high energies, respectively. Furthermore, the singularities of the local DOS's $n_0^{\pm}(\epsilon)$ at $\epsilon = \pm 2$ V occur along with $n_0^{\mp}(\epsilon) = 0$ at $\epsilon = \mp 2$ V. This implies that the electron states at $\epsilon = -2$ V and $\epsilon = +2$ V have wave functions which have zero coefficients for the orbitals $|i\rangle$ localized on all the cation and anion atoms, respectively. These states therefore represent pure cation or anion states occurring at the energies for isolated atoms.

As an example of a transformation from the states of h to H, consider a comparison of Figs. 2(b) and 3(a). In Fig. 3(a), the filled valence bands of the local DOS's of the zinc-blende–Bethe-lattice system mentioned above using the Hamiltonian H is plotted. These curves were obtained by using the transformation equations (3) and (4) introduced in Sec. II with $V_1 = -2.2$ eV and $V_2 = -6.2$ eV. To complete the filled valence band in Fig. 3 a δ function of pure p-like bonding states must be introduced near -2.7 eV. This δ function (containing 2 states/atom) is only a property of H and independent of

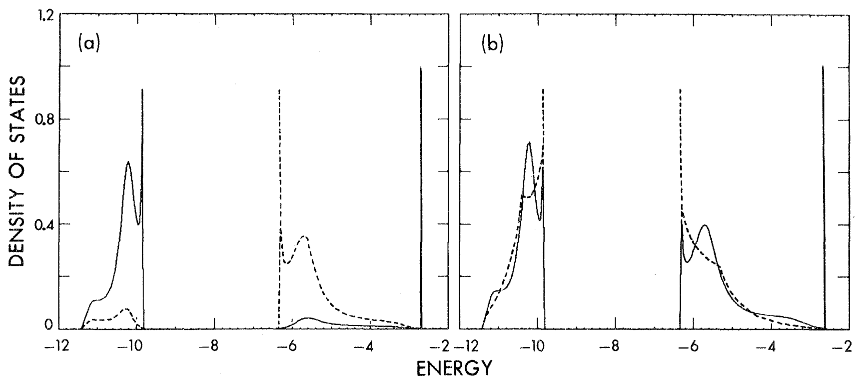

FIG. 3. Densities of states using the four-orbital Hamiltonian. (a) Local anion (solid line) and cation (dashed line) densities of states for a zinc-blende–Bethe-lattice system with the cluster of atoms shown in Fig. 1. (b) The density of states (solid line) for this zinc-blende–Bethe-lattice system as obtained by adding the local anion and cation densities of states and the density of states (dashed line) for a normal crystalline zinc-blende structure. The energy is in units of eV and the p-like δ-function peak near -2.7 eV is shown as a solid line.

the structure of a system as long as no like-atom bonds are present. It will always occur near − 2.7 eV and represents the p-like region of the density of states. The effects on the valence band by transforming from h to H are rather small. The most important differences, as seen by comparing Figs. 2(b) and 3(a), are a narrowing of the low-energy anion band and a widening of the high-energy or cation band.

Figure 3(b) shows (as a solid line) the sum of the two local DOS's shown in Fig. 3(a). This is compared with the total DOS of the zinc-blende structure (dashed line) as obtained from a band-structure calculation using the Hamiltonian H. The agreement between the two curves in Fig. 3(b) is very good considering that the zinc-blende-Bethe-lattice system has only 29 atoms in a zinc-blende configuration. This again emphasizes the importance of local atomic configurations in determining the structure in the DOS.

IV. DISCUSSION OF AMORPHOUS PHASES

Experimentally, information about the DOS can be obtained from x-ray (XPS) and ultraviolet (UPS) photoemission spectroscopy. XPS[6] and UPS[7] spectra on crystalline and amorphous III-V compounds reveal DOS's that are rather similar. The most easily resolved differences between the crystalline and amorphous spectra occur in the dip region between the middle peak and the upper p-like bonding peak at the top of the valence band. (The upper p-like bonding peak is analogous to the δ-function peak obtained using H.) In the amorphous phase states seem to shift from the middle peak into this dip, thereby filling it in partially and making it less prominent than in the crystalline phase.

Theoretically, effects of disorder on the DOS of amorphous binary systems have been studied by Joannopoulos and Cohen[8] and by Kramer and Treusch.[9] In the former study specific types of disorder (e.g., bond length, bond and dihedral angle distortions, differences in topology, effects of like-atom bonds, etc.) are examined by calculating the DOS, using pseudopotentials, of various complex binary crystals made specifically by using the atomic positions of polytypes and polymorphs[3] of Ge and Si. Since the systems studied are stoichiometric crystals with large unit cells this method leads to an explicit examination of short-range disorder. The results of Joannopoulos and Cohen[8] can be used to draw two main conclusions. First that the presence of like-atom bonds will tend to decrease the gap, fill up the dip region, and also form a shoulder or peak at the lower energy and of the s-like region of the DOS spectrum. This last effect does not seem to be observed experimentally. Second, that systems without like-atom bonds but with bond-angle distortions of about ±10% and some variations in dihedral angle and topology will produce relatively small differences from the zinc-blende DOS.

This is in contrast to the work of Kramer and Treusch[9] who attempt to deal with homopolar systems and heteropolar systems with no like-atom bonds, and to understand the effects of variations in dihedral angles. Their method is most easily and conveniently described using only a homopolar system. The extension to heteropolar systems is straightforward. Their method involves taking a finite cluster of atoms (in a diamond-structure configuration) consisting of four tetrahedral units connected to a common central atom. The tetrahedral units can then be rotated by arbitrary amounts to yield changes in dihedral angle. An "effective" potential $\bar{\nu}(\vec{g})$ is then defined as a weighted average over the potentials $\bar{\nu}(\vec{q})$ of the atoms in the cluster with

$$\bar{\nu}(\vec{g}) = \frac{1}{N}\sum_{i=1}^{N} e^{i\vec{q}\cdot\vec{\Delta}_i}\,\nu(\vec{q}), \tag{24}$$

where N is the total number of atoms in the cluster and $\vec{\Delta}_i$ represents the difference in position between an atom in the cluster and in a diamond structure. As a first approximation this effective potential is then introduced at the atomic positions of a diamond structure creating an effective total potential given by

$$V(\vec{q}) = \bar{\nu}(\vec{q})\,e^{i\vec{q}\cdot\vec{\tau}} + \bar{\nu}(\vec{q})^*\,e^{-i\vec{q}\cdot\vec{\tau}}, \tag{25}$$

where $\pm\vec{\tau}$ represent the positions of the basis atoms in the diamond structure. For the case where the tetrahedral units are not rotated all the $\vec{\Delta}_i = 0$ and one returns to $\bar{\nu}(\vec{q}) = \nu(\vec{q})$. In general, therefore, the effective diamond structure (25) can be solved using conventional band-structure methods. The results of Kramer and Treusch using an effective diamond and zinc-blende structure indicate that dihedral angle variations will cause a broadening of the DOS spectrum and a decrease in the fundamental gap. This would agree well with what is observed experimentally. Care, however, should be taken in interpreting these results, because they are not caused explicitly by dihedral angle rotations. This is clear since substituting (24) into (25) gives

$$V(\vec{q}) = \frac{1}{N}\sum_{i=1}^{N} \nu(\vec{q})\,e^{i\vec{q}\cdot(\vec{\tau}+\vec{\Delta}_i)} + \nu(\vec{q})\,e^{-i\vec{q}\cdot(\vec{\tau}+\vec{\Delta}_i)}, \tag{26}$$

which reveals that $V(\vec{q})$ is just the average potential of a system of N fcc structures with basis atoms at positions $\pm(\vec{\tau}+\vec{\Delta}_i)$. This change in basis positions will, in general, create *diamond* and *zinc-blende* structures with both bond-angle and bond-length distortions. Thus $V(\vec{q})$ should not be a good representation of the amorphous phase.

To examine the properties of heteropolar systems with only unlike atom bonds further the cluster-Bethe

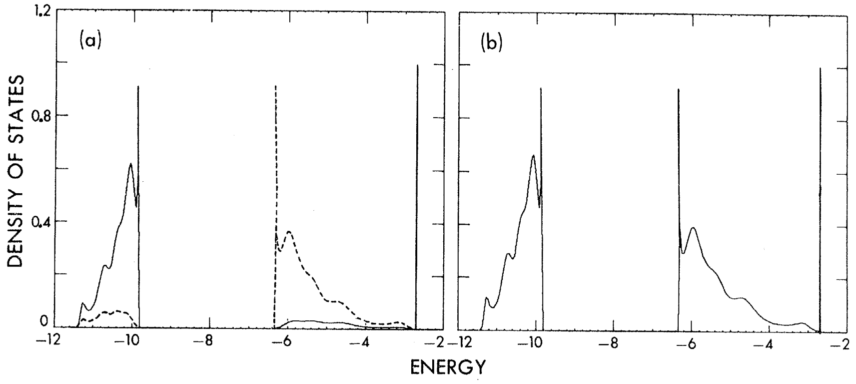

FIG. 4. Densities of states using the four-orbital Hamiltonian. (a) Local anion (solid line) and cation (dashed line) densities of states for a zinc-blende–Bethe-lattice system with a cluster containing all tenfold rings of bonds passing through the central atom. (b) The density of states for this system as obtained by adding the anion and cation local densities of states. The energy is in units of eV and the p-like δ-function peak near -2.7 eV is shown as a solid line.

lattice method will be used to study the effects of topology and short-range disorder on the DOS of a series of structures whose total atomic arrangements become increasingly more disordered. These structures will not be periodic, will contain no like-atom bonds and will include the local atomic configurations found in the diamond BC-8,[3] and Connell random-network[4] structures. The Connell model is of particular interest since it is a random network model with a radial distribution function that agrees very well with experiments.[10] In addition, it contains only even-numbered rings of bonds and therefore offers the possibility of having a random network structure with only like-atom bonds.

The clusters that will be taken from the diamond BC-8 and Connell random network structures to be used as cluster–Bethe-lattice systems will be chosen so that they include all tenfold rings of bonds passing through the central atom. This is the condition[1] on the size of a cluster that guarantees very good convergence. This is particularly true for amorphous systems. For the diamond and BC-8 structures all the atoms are equivalent so that the total DOS's are equal to the local DOS's. For the Connell model all the atoms are inequivalent so that in principle one would need to average over the local DOS of every atom to obtain the total DOS. In this model, however, the local DOS of various atoms studied were very similar. Therefore, in these calculations as in those for homopolar systems[1] only an average over five central atoms is taken.

The results of the DOS's for the aforementioned three cluster-Bethe lattice structures are shown in Figs. 4–6 using the Hamiltonian H. In Fig. 4(a), the local DOS's of the anion (solid line) and cation (dashed line) are shown for the zinc-blende–Bethe lattice system. Figure 4(b) shows the DOS of the zinc-blende–Bethe lattice system obtained by adding the two curves in Fig. 4(a). The cluster in this zinc-blende–Bethe-lattice system (as we have mentioned) contains all tenfold rings of bonds passing through the central atom. Therefore, it

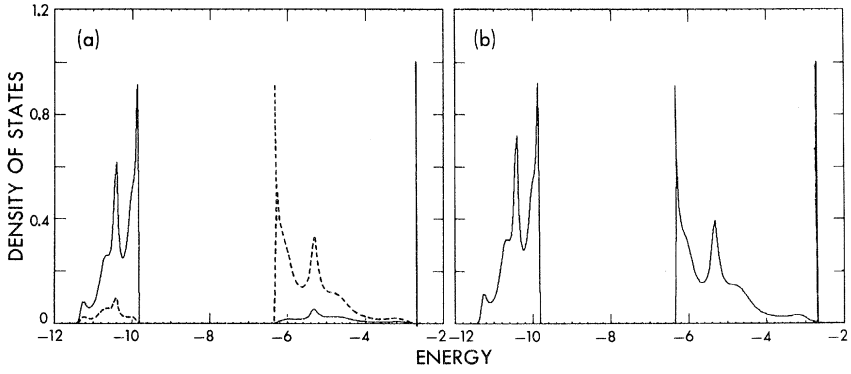

FIG. 5. Densities of states using the four-orbital Hamiltonian. (a) Local anion (solid line) and cation (dashed line) densities of states for a binary BC-8 Bethe-lattice system with a cluster containing all tenfold rings of bonds passing through the central atom. (b) The density of states for this system as obtained by adding the anion and cation local densities of states. The energy is in (units of eV) and the p-like δ function near -2.7 eV is shown as a solid line.

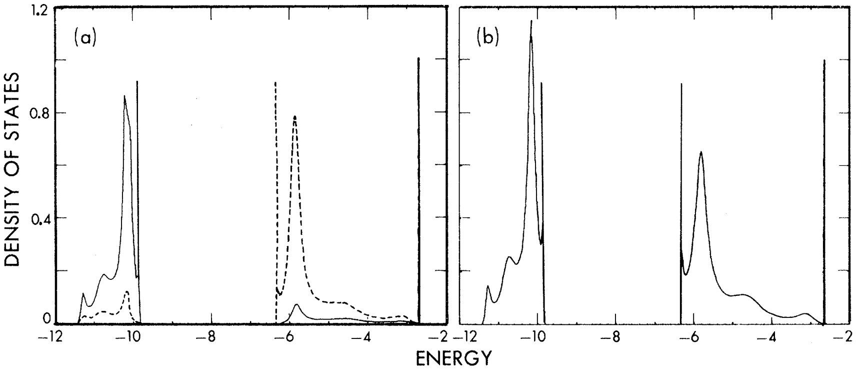

FIG. 6. Densities of states using the four-orbital Hamiltonian. (a) Local anion (solid line) and cation (dashed line) densities of states for one atom in the Connell-cluster–Bethe-lattice system with a cluster containing all tenfold rings of bonds passing through the central atom. (b) The density of states for the Connell-cluster–Bethe-lattice system as obtained by averaging over the local anion and cation densities of states of five atoms near the center of the Connell random network model.

is interesting to compare Fig. 4 with Fig. 3, which contains the crystalline zinc-blende DOS and a zinc-blende–Bethe lattice system with a zinc-blende cluster containing only all sixfold rings of bonds passing through the central atom. Figure 4 shows the correct trend of shifting states closer to the singularities. Furthermore, the shoulder near − 5.2 eV appears to be developing although the sharpness of this shoulder in the crystalline DOS is a consequence of periodicity. In Fig. 5(a), the local DOS's of the anion (solid line) and cation (dashed line) are shown for a binary system constructed from the atomic positions of a BC-8–Bethe-lattice system. Figure 5(b) shows the DOS of this binary BC-8–Bethe-lattice system as obtained by adding the two curves in Fig. 5(a). The BC-8 structure (with eight atoms in a primitive cell) is more complicated topologically than the diamond or zinc-blende structure. Furthermore, the ring statistics of the atoms in these two structures are quite different. For instance, diamond has 12 sixfold and 24 eightfold rings of bonds passing through a given atom while the BC-8 structure has nine sixfold and 36 eightfold rings of bonds. This smaller number of sixfold rings of bonds and larger number of eightfold rings of bonds is responsible[1] for the noticeable shift of states closer to the singularities in Fig. 5 as compared with Fig. 4. Moreover the binary BC-8–Bethe-lattice system also seems to have slightly more states in the dip region between the middle p-like peak (near − 6 eV) and the upper p-like bonding states (δ function near − 2.7 eV). This rather small effect was also observed[8] using pseudopotentials on a crystalline binary BC-8 structure.

Finally in Fig. 6(a), the local DOS's of the anion (solid line) and cation (dashed line) are shown for a binary system constructed from the atomic positions of a Connell-cluster–Bethe-lattice system. These local DOS's, however, are only for one atom in the Connell random network structure located near the center of the network. The anion peak near − 10 eV actually goes slightly off the scale. The DOS of an averaged (over five atoms) binary Connell-cluster–Bethe-lattice system is shown in Fig. 6(b). As it was mentioned earlier the average DOS is very similar to individual local atomic DOS's. There is, however, a very interesting difference between Fig. 6(b) and Figs. 5(b) and 4(b). The peak near − 6 eV is now very sharp and strong and a comparison of this spectrum with the crystalline results in Fig. 3(b) does not reveal any filling up of the dip region as it is observed experimentally for the amorphous phase. Topologically this strong peak observed in the Connell model is a direct result of the rather large number of sixfold rings of bonds present in this network. Specifically there are on an average about 16 sixfold rings of bonds passing through a given atom. The differences in bond angles and dihedral angles have of course been omitted in this study; however, judging from the pseudopotential results[8] on the BC-8 structure where they were included, one would expect their effects to be rather small.

V. SUMMARY AND CONCLUSIONS

The cluster–Bethe-lattice method has been extended to the study of heteropolar systems. This is accomplished by solving a binary Bethe lattice of arbitrary coordination using simple tight-binding models. From these solutions effective binary Bethe-lattice fields $\phi^{\pm}(\epsilon)$ are obtained which attach the Bethe lattice to any cluster system of atoms of arbitrary coordination. The tight-binding models used include a one-orbital and four-orbital Hamiltonian. A transformation between the eigenvalues of the simple one orbital Hamiltonian to those of the more realistic four-orbital Hamiltonian was also obtained.

The cluster–Bethe-lattice method was then used to study amorphous tetrahedrally coordinated binary compounds. To do this the atomic positions of a series of structures were chosen to build binary cluster–Bethe-lattice systems. These structures included the diamond BC-8 and Connell random network[4] structures and represent materials whose local atomic configurations are, respectively, increasingly more disordered. The Connell random network structure is particularly interesting since it has a radial distribution function which agrees very well with that of the amorphous phase.[10] In addition, it only has even numbered rings of bonds and consequently can be constructed as a binary system with no like-atom bonds. However, using only topological considerations the results here show that this random network model does not seem to reproduce features in the DOS as observed experimentally[6,7] for the amorphous binary compounds. These results are explained in terms of the very large number of sixfold rings of bonds passing through the atoms in this network.

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