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THE "CLUSTER-BETHE LATTICE" METHOD: THE ELECTRONIC DENSITY OF STATES OF HETEROPOLAR SYSTEMS *

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ABSTRACT

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 zincblende, 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 electromic 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 section 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 section 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 section 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, section V is concerned with a summary and concluding remarks.

II. The "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 function $\langle o|g|o\rangle$ of the central or reference atom can be obtained exactly. The Bethe Lattice therefore serves two useful purposes. Firstly it provides the mathematical convenience of solving exactly an infinite system without periodicity. Secondly 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

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

and

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

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 delta function peak in the DOS. (For the purposes of this investigation, however, this is not very important since it will be shown in section IV that the primary concern here is to examine the middle peak region of the DOS). If one takes $\Delta=\Lambda=o$, then the eigenvalves of H (except those that lie in the delta function peak) are related by an analytic transformation [5] to the eigenvalves of the much simpler Hamiltonian h. This, however, is also true for $\Delta \neq o \neq \Lambda$ as will now be shown. Consider any infinite tetrahedrally connected network of atoms with a basis set $\{|ij\rangle\}$.

For any atom i in the system the following equations can be obtained as part of the secular equation with H.

$$E\, C_j^i = \Delta\, C_j^i + V_1 \sum_{j'} C_{j'}^i + V_2\, C_j^{i'} \qquad (3)$$

$$E\, C_j^{i'} = \Delta\, C_j^{i'} + V_1 \sum_{j'} C_{j'}^{i'} + V_2 C_j^i \qquad (4)$$

where C_j^i represents the coefficient of $|ij)$ in the expansion of the one electron wanefunction of the total system. In these equations atom i is taken, arbitrarily, to be a cation for simplicity the sums over j include j'=j. Solving for $C_j^{i'}$ from (4) and substituting into (3) one obtains

$$(E^2 - \Delta^2 - V_2^2)\; C_j^i = (E+\Delta)\, V_1 \sum_{j'} C_{j'}^i + V_1 V_2 \sum_{j'} C_{j'}^{i'} \qquad (5)$$

Summing now over all j and defining $\alpha_i = \sum_j C_j^i$,equation (5) reduces to

$$(E^2 - \Delta^2 - 4V_1 E - V_2^2)\; \alpha_i = 4V_1 \Delta\, \alpha_i + V_1 V_2 \sum_{i'} \alpha_{i'} \qquad (6)$$

This last equation holds for every atom i and is very similar to the secular equation one would obtain for the same system using h, i.e.

$$E\alpha_i = \Lambda\alpha_i + V \sum_{i'} \alpha_{i'} \qquad (7)$$

Comparing (6) and (7) gives the required transformations

$$E = 2V_1 \pm (4V_1^2 + V_2^2 + \Delta^2 + V_1V_2\ \varepsilon/V)^{1/2} \tag{8}$$

and

$$\Delta = \Lambda V_2/4V \tag{9}$$

Thus one can now use the much simpler Hamiltonian h for heteropolar systems in order to calculate eigenvalues and <u>local</u> DOS's and use the transformations (8) and (9) to give the corresponding eigenvalues and <u>local</u> DOS's for the Hamiltonian H.

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

$$g = \frac{1}{\varepsilon - h} = \frac{1}{\varepsilon} + \frac{1}{\varepsilon}\, hg. \tag{10}$$

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

$$n(\varepsilon) = \frac{1}{\pi}\ \mathrm{Im}\ [\mathrm{Tr}g(\varepsilon)] \tag{11}$$

and one is interested in the diagonal matrix elements of $g(\varepsilon)$. So that taking matrix elements of (10) between a basis set $\{|i\rangle\}$ one obtains

$$\varepsilon\ \langle i|g|j\rangle = \delta_{ij} + \sum_l \langle i|h|l\rangle\langle l|g|j\rangle. \tag{12}$$

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

$$n_i(\varepsilon) = -\frac{1}{\pi} \operatorname{Im} \langle i|g|i\rangle \tag{13}$$

and

$$n(\varepsilon) = \sum_i n_i(\varepsilon) \tag{14}$$

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 o 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 twelve six-fold rings of bonds passing through the central atom. A "zincblende-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 o of this infinite system can now be solved analytically using equation (12). One obtains

$$(\varepsilon\pm\Lambda)\ \langle o|g^{\mp}|o\rangle = 1 + 4V\ \langle 1|g^{\mp}|o\rangle$$

$$(\varepsilon\pm\Lambda)\ \langle 1|g^{\mp}|o\rangle = V\langle o|g^{\mp}|o\rangle + 3V\langle 2|g^{\mp}|o\rangle$$

$$(\varepsilon\pm\Lambda\ \ \langle 2|g^{\mp}|o\rangle = V\langle 1|g^{\mp}|o\rangle + 2V\langle 3|g^{\mp}|o\rangle + \phi^{\mp}\langle 2|g^{\mp}|o\rangle$$

$$(\varepsilon\pm\Lambda)\ \langle 3|g^{\mp}\ o\rangle = 2V\langle 2|g^{\mp}|o\rangle + 2\phi^{\pm}\langle 3|g^{\mp}|o\rangle$$

where g^- and g^+ represent the Green 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 functions $\langle o|g^\mp|o\rangle$ can be obtained trivially from the linear equations (15). The result is

$$\langle o|g^\mp|o\rangle = \left\{ \varepsilon\pm\Lambda-4V^2[\varepsilon\mp\Lambda-3V^2[\varepsilon\pm\Lambda-\phi^\mp -4V^2[\varepsilon\mp\Lambda-2\phi^\pm]^{-1}]^{-1}]^{-1} \right\}^{-1} \quad (16)$$

$$\text{and} \quad n_o^\mp(\varepsilon) = -\frac{1}{\pi}\,\mathrm{Im}\,\langle o|g^\mp|o\rangle \quad (17)$$

where $n_o^-(\varepsilon)$ and $n_o^+(\varepsilon)$ are the local DOS's of an anion or cation central atom respectively. These results will be examined again in the next section once the solutions for $\phi^\pm$ are obtained.

III The Heteropolar Bethe Lattice

This section will be concerned with solving the total and local Green functions of a heteropolar Bethe Lattice (with no like-atom bonds) using the Hamiltonian h defined in section 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 o. It's nearest neighbors are labeled 1. Atom o 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 o and 1 through the fields $\phi^{\pm}$ one again obtains a complete Bethe Lattice and the following equations from (12)

$$(\varepsilon+\Lambda)\ \langle o|g^-|o\rangle = 1 + (m-1)V\langle 1|g^-|o\rangle + \phi^-\ \langle o|g^-|o\rangle$$

$$(\varepsilon-\Lambda)\ \langle 1|g^-|o\rangle = V\langle o|g^-|o\rangle + (m-1)\ \phi^+\langle 1|g^-|o\rangle \qquad (18)$$

Now consider again atom o 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 quations from (12)

$$(\varepsilon+\Lambda)\ \langle o|g^-|o\rangle = 1 + mV\ \langle 1|g^-|o\rangle$$

$$(\varepsilon-\Lambda)\ \langle 1|g^-|o\rangle = V\langle o|g^-|o\rangle + (m-1)\ \phi^+\ \langle 1|g^-|o\rangle \qquad (19)$$

Comparing equations (18) and (19) and using the plus and minus symmetry of the system gives

$$\phi^{\pm} = \frac{V^2}{\varepsilon \pm \Lambda - (m-1)\phi^{\mp}} \tag{20}$$

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

$$\phi^{\pm} = \phi_R^{\pm} + i\,\phi_I^{\pm} \tag{21}$$

with

$$\phi_R^{\pm} = \frac{\varepsilon \mp \Lambda}{2(m-1)} \tag{22}$$

and

$$\phi_R^{\pm} = [\pm]\ \frac{\left[4(m-1)V^2(\varepsilon^2-\Lambda^2) - (\varepsilon^2\Lambda^2)^2\right]^{1/2}}{2(m-1)(\varepsilon \pm \Lambda)} \tag{23}$$

The choice of sign in the brackets [±] in (23) depends only on the value of ε and not on whether the connecting atom is an anion or cation. The minus sign must be taken when $\varepsilon > \Lambda$ and the plus sign when $\varepsilon < -\Lambda$

The local Green function for the heteropolar Bethe Lattice is now given by

$$\langle o|g^{\mp}|o\rangle = \{\varepsilon \pm \Lambda - m\phi^{\mp}\}^{-1} \tag{24}$$

and the local DOS of the Bethe Lattice $m_B^{\pm}(\varepsilon)$ from

$$n_B^{\mp}(\varepsilon) = -\frac{1}{\pi} \mathrm{Im}\langle o|g^{\mp}|o\rangle \tag{25}$$

therefore

$$n_B^{\mp}(\varepsilon) = -\frac{1}{\pi} \frac{m\phi_I^{\mp}}{(\varepsilon \pm \Lambda - m\phi_R^{\mp})^2 + m^2 (\phi_I^{\mp})^2} \tag{26}$$

The bond edges can be obtained from (23) and occur at

$$\varepsilon = \pm (\Lambda^2 + 4(m-1)V^2)^{1/2} \tag{27}$$

and

$$\varepsilon = \pm\Lambda \tag{28}$$

An examination of (26) shows that $n_B^-(\varepsilon)$ and $n_B^+(\varepsilon)$ have square root singularities at $\varepsilon = -\Lambda$ and $\varepsilon = +\Lambda$ 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 $n_B^{\mp}(\varepsilon)$ is singular at $\varepsilon = \mp\Lambda$, it is zero at $\varepsilon = \pm\Lambda$. This indicates that the states occuring at the singularities $\varepsilon = +\Lambda$ and $\varepsilon = -\Lambda$ represent <u>pure</u> cation and <u>pure</u> anion states respectively. $n_B^-(\varepsilon)$ and $n_B^+(\varepsilon)$ 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) $\varepsilon = \pm\Lambda$. The local DOS $n_B^-(\varepsilon)$ 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 $n_B^-(\varepsilon)$ about $\varepsilon = o$.

In Fig. 2(a) is also shown (as a solid line) the DOS of the "zincblende Bethe Lattice" system obtained by adding $n_o^-(\varepsilon)$ and $n_o^+(\varepsilon)$ from equation (17). The cluster in this system was described in section II and drawn in Fig. 1. It contains 29 atoms in a zincblende configuration. The peaks around ± 2.5 V arise from the twelve six-fold rings of bonds passing through the central atom of this cluster. In Fig 2 (b), the separate contributions of $n_o^-(\varepsilon)$ (solid line) and $n_o^+(\varepsilon)$ (dashed line) for the anion and cation respectively are shown. Again the spectra are mirror images of each other about $\varepsilon = o$ with the anion and cation having considerably more states at low and high energies respectively. Furthermore, the singularities of the local DOS's $n_o^\pm(\varepsilon)$ at $\varepsilon = \pm 2V$ occur along with $n_o^\pm(\varepsilon) = o$ at $\varepsilon = \mp 2V$. This implies that the electron states at $\varepsilon = -2V$ and $\varepsilon = +2V$ have wavefunctions 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 occuring 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 "zincblende-Bethe Lattice" system mentioned above using the Hamiltonian H is plotted. These curves were obtained by using the transformation equations (8) and (9) derived in section II with V_1 =-2.2eV and V_2 = -6.2eV. To complete the filled valence bond in Fig. 3 a delta function of pure p-like bonding states must be introduced near -2.7eV. This delta function, (containing 2 states/atom) is only a property of H and independent of the structure of a system as long as no like-atom bonds are present. It will always occur near -2.7 eV and will therefore not be shown explicitly in any of the figures. 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 2(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 zincblende 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 "zincblende-Bethe Lattice" system has only 29 atoms in a zincblende 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 spectrascopy. 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 delta 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 effort does not seem to be observed experimentally. Secondly 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 zincblende DOS.

In the work of Kramer and Treusch [9] an attempt is made 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 straight forward. 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

$$\bar{\nu}(\vec{g}) = \frac{1}{N} \sum_{i=1}^{N} e^{i\vec{q}\cdot\vec{\Delta}_i} \nu(\vec{q}) \tag{29}$$

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

$$V(\vec{q}) = \bar{\nu}(\vec{q})\, e^{i\vec{q}\cdot\vec{\tau}} + \bar{\nu}(\vec{q})^* e^{-i\vec{q}\cdot\vec{\tau}} \tag{30}$$

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 $\vec{\Delta}_i = o$ and one returns to $\bar{\nu}(\vec{q}) = \nu(\vec{q})$. In general, therefore, the "effective" diamond structure (30) can be solved using conventional band structure methods. The

results of Kramer and Treusch using an "effective" diamond and zincblende structure indicate that dihedral angle variations will cause a broadening of the DOS spectrum and a decrease in the fundamental gap. Care, however, should be taken in interpreting these results, because they are not caused explicitly by dihedral angle rotations. This is clear since substituting (29) into (30) gives

$$V(\vec{q}) = \frac{1}{N}\sum_{i=1}^{N} \nu(\vec{q})\, e^{i\vec{q}\cdot(\vec{\tau}+\vec{\Delta}_i)} + \nu(\vec{q})\, e^{-i\vec{q}\,(\vec{\tau}+\vec{\Delta}_i)} \tag{31}$$

which reveals that $V(\vec{q})$ is just the average potential of a system of N f.c.c. structures with basis atoms at positions $\pm\,(\vec{\tau}+\vec{\Delta}_i)$. This change in basis positions will in general create diamond and zincblende structures with both bond angle and bond length distortions. Such distortions may be quite large and unphysical.

In this section the "Cluster-Bethe 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 ten fold 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 5 central atoms is taken.

The results of the DOS's for the aforementioned three "Cluster-Bethe Lattice" structures are shown in Figs. 4 to 6 using the Hamiltonian H. (As it has already been mentioned the pure p-like delta function near -2.7eV is not shown). In Fig. 4(a),

the local DOS's of the anion (solid line) and cation (dashed line) are shown for the "zincblende-Bethe Lattice" system. Fig. 4(b) shows the DOS of the "zincblende-Bethe Lattice" system obtained by adding the two curves in Fig. 4(a). The cluster in this "zincblende Bethe Lattice" system (as we have mentioned) contains all ten-fold rings of bonds passing through the central atom. Therefore, it is interesting to compare Fig. 4 with Fig. 3, which contains the crystalline zincblende DOS and a "zincblende Bethe Lattice" system with a zincblende cluster containing only all six-fold rings of bonds passing through the central atom. Fig. 4 shows the correct trend of shifting states closer to the singularities. Furthermore the shoulder near -5.2eV 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. Fig. 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 8 atoms in a primitive cell) is more complicated topologically than the diamond or zincblende structure. Furthermore, the ring statistics of the atoms in these two structures are quite different. For instance, diamond has 12 six-fold and 24 eight-fold rings of bonds passing

through a given atom while the BC-8 structure has 9 six-fold and 36 eight-fold rings of bond. This smaller number of six-fold rings of bonds and larger number of eight-fold rings of bonds is responsible [1] for the noticeable shift of states chosen 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 -6eV) and the upper p-like bonding states (delta function near -2.7eV). 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 -10eV actually goes slightly off the scale. The DOS of an averaged (over 5 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 six-fold rings of bonds present in this network. Specifically there are on an average about 16 six-fold 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 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 $\phi^{\pm}(\varepsilon)$ 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 six-fold rings of bonds passing through the atoms in this network.

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REFERENCES

1. F. Yndurain, J. D. Joannopoulos, M. L. Cohen and L. M. Falicov, Solid State Comm. (in press); J. D. Joannopoulos, F. Yndurain, L. M. Falicov and M. L. Cohen IBM International Topical Conference on Tetrahedrally Bonded Amorphous Semiconductors (in press); and J. D. Joannopoulos and F. Yndurain, Phys. Rev. B (in press).

2. C. Domb, Adv. Phys. 9, 145 (1960).

3. J. D. Joannopoulos and M. L. Cohen, Phys. Rev. B7, 2644 (1973).

4. N. Connell, IBM International Topical Conference on Tetrahedrally Bonded Amorphous Semiconductors (in press).

5. M. F. Thorpe and D. Weaire, Phys. Rev. B4, 3518 (1971).

6. L. Ley, private communication.

7. N. Shevchik, J. Tejeda and M. Cardona, Phys. Rev. B9, 2627 (1974).

8. J. D. Joannopoulos and M. L. Cohen, Phys. Rev. B (in press).

9. B. Kramer and J. Treusch, Proceeding of the 12th International Conference on the Physics of Semiconductors (in press).

10. N. Shevchik and W. Paul, J. non-cryst solids 13, 1 (1973).

FIGURE CAPTIONS

Figure 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.

Figure 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 "zincblende Bethe Lattice" system with the cluster of atoms shown in Figure 1. (b) The local densities of states for the anion (solid line) and cation (dashed line) for the same "zincblende Bethe Lattice" system. The energy is in units of the one orbital interaction parameter V.

Figure 3 Densities of states using the four orbital Hamiltoniam. (a) local anion (solid line) and cation (dashed line) densities of states for a "zincblende Bethe Lattice" system with the cluster of atoms shown in Figure 1. (b) The density of states (solid line) for this "zincblende Bethe Lattice"

system as obtained by adding the local anion and cation densitites of states and the density of states (dashed line) for a normal crystalline zincblende structure. The energy is in units of eV and the p-like delta function peak near -2.7eV is not shown.

Figure 4 Densities of states using the four orbital Hamiltonian. (a) local anion (solid line) and cation (dashed line) densities of states for a "zincblende Bethe Lattice" system with a cluster containing all ten fold 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 delta function peak near -2.7 eV is not shown.

Figure 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 ten fold 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 delta function near -2.7 eV is not shown.

Figure 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 ten-fold 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 5 atoms near the center of the Connell random network model.

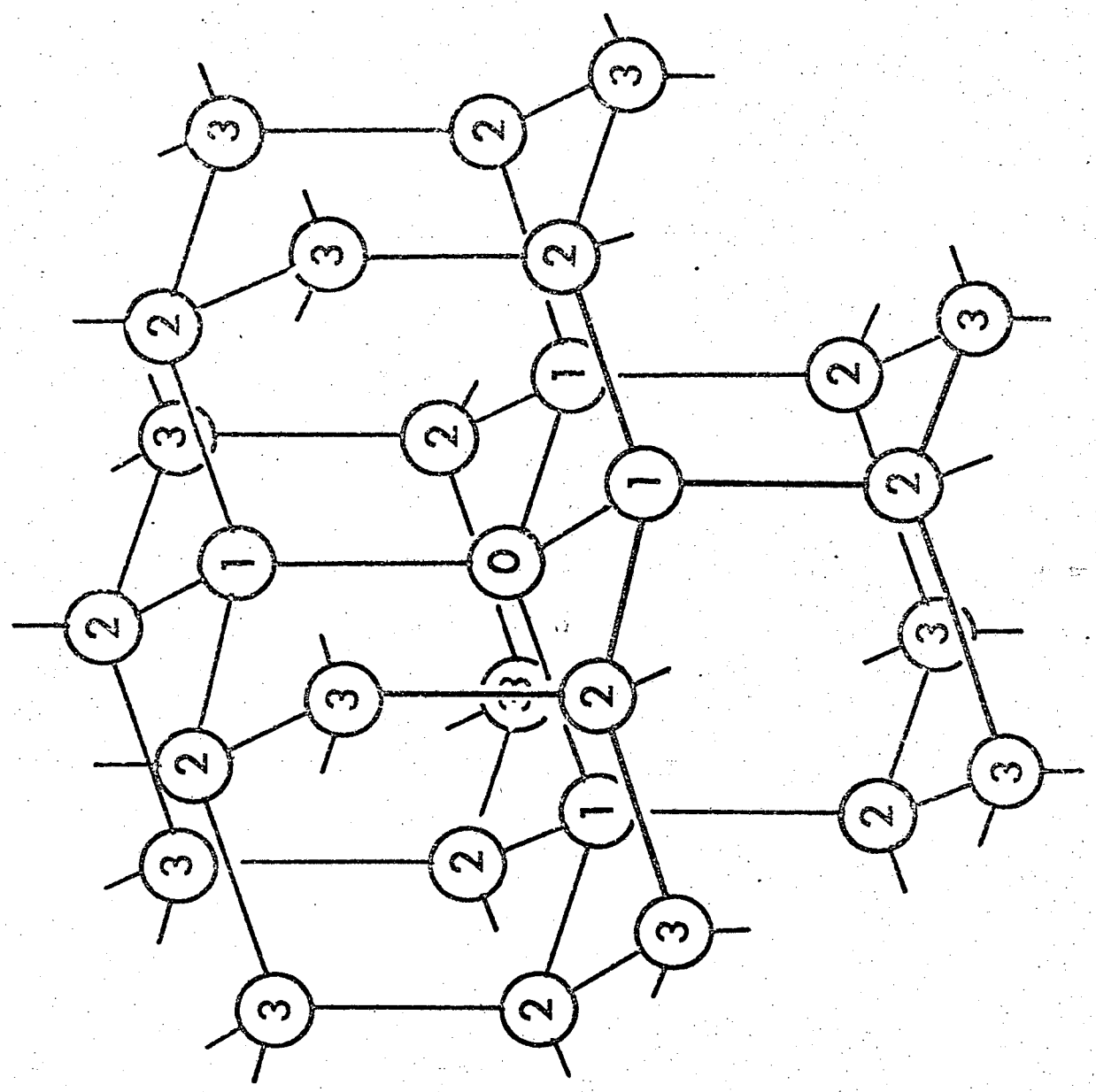

Fig. 1

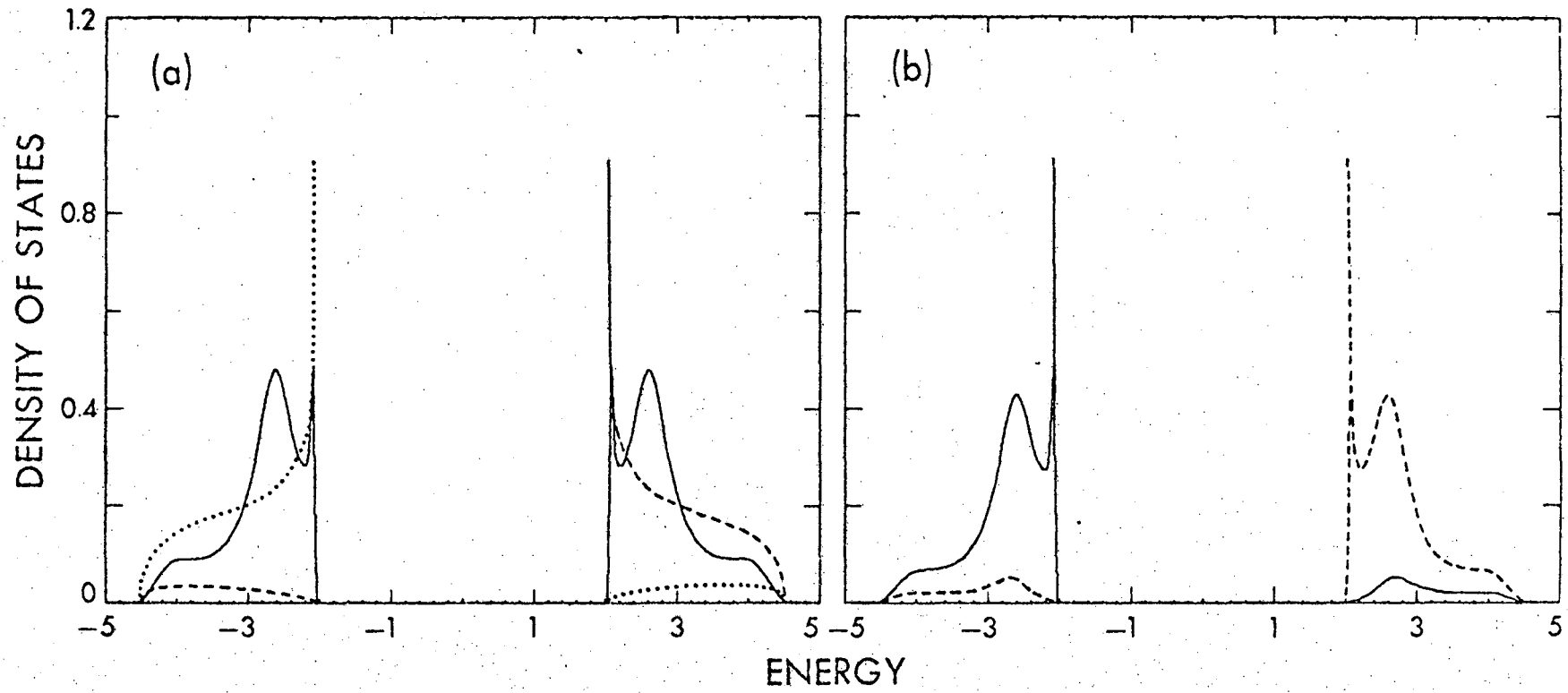

Fig. 2

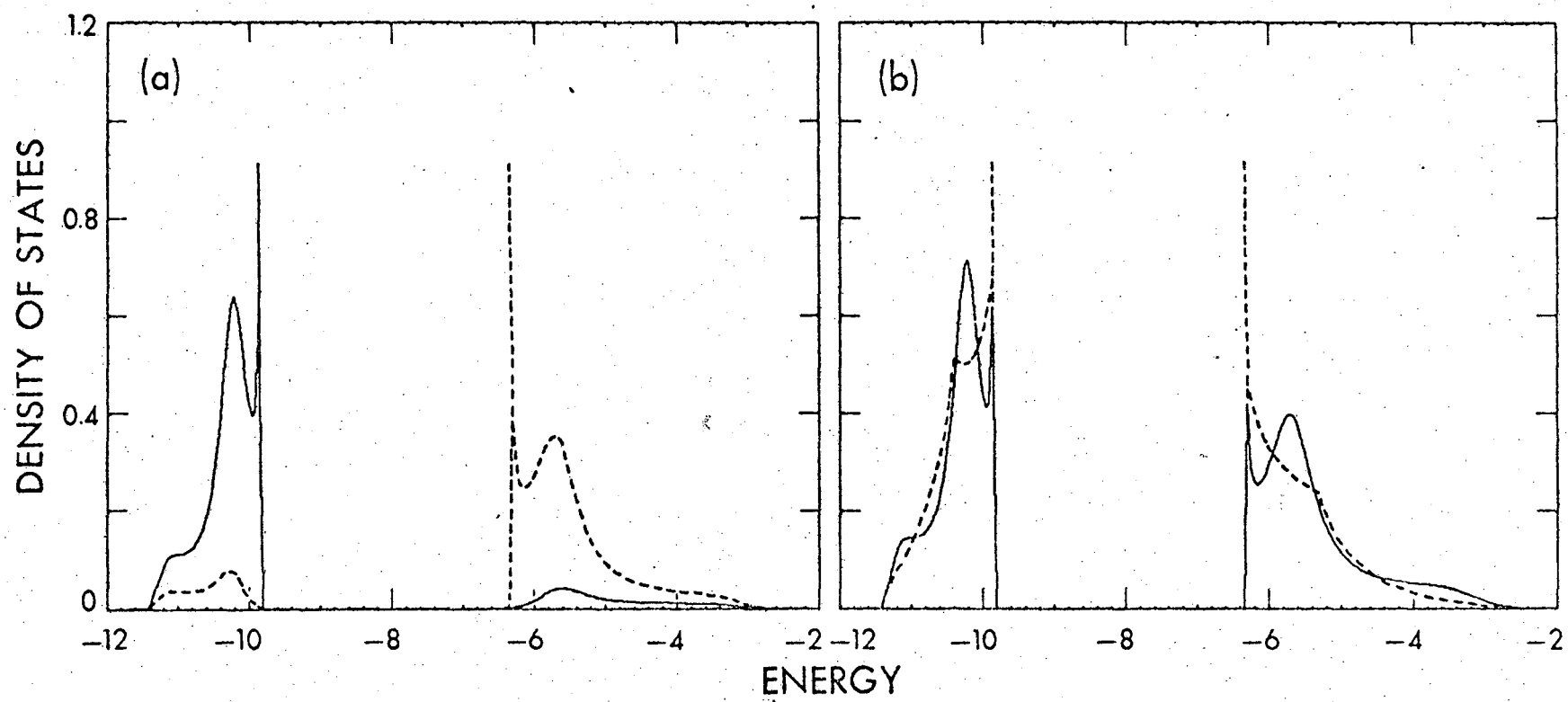

Fig. 3

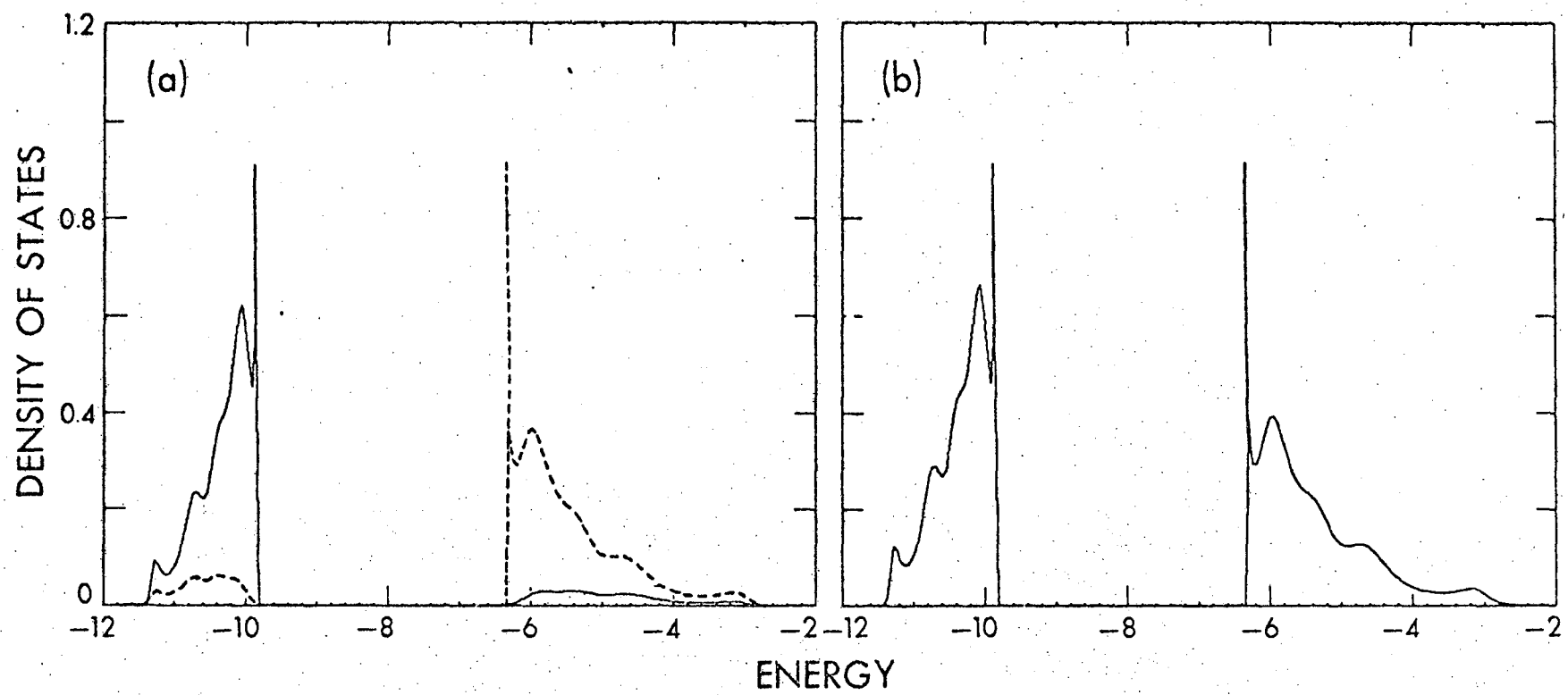

Fig. 4

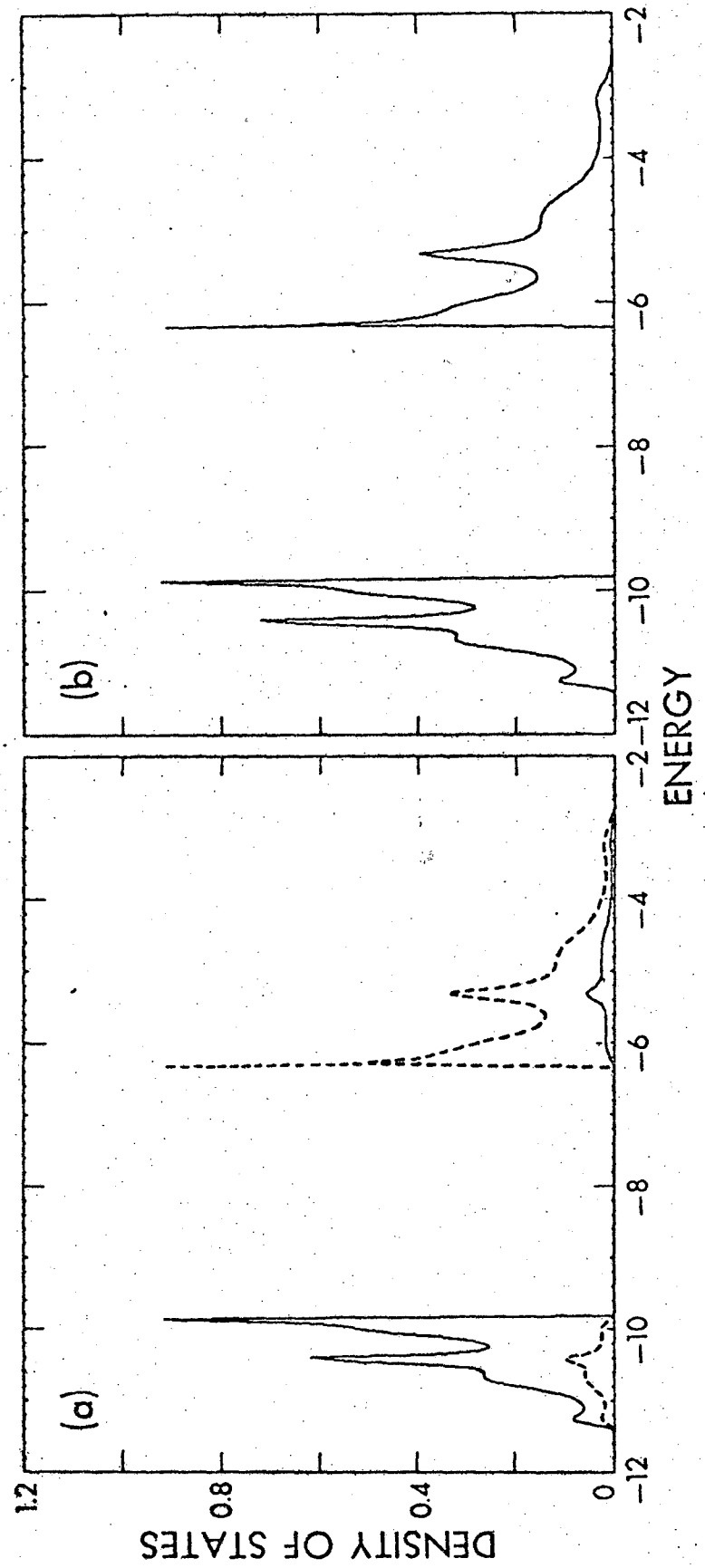

Fig. 5

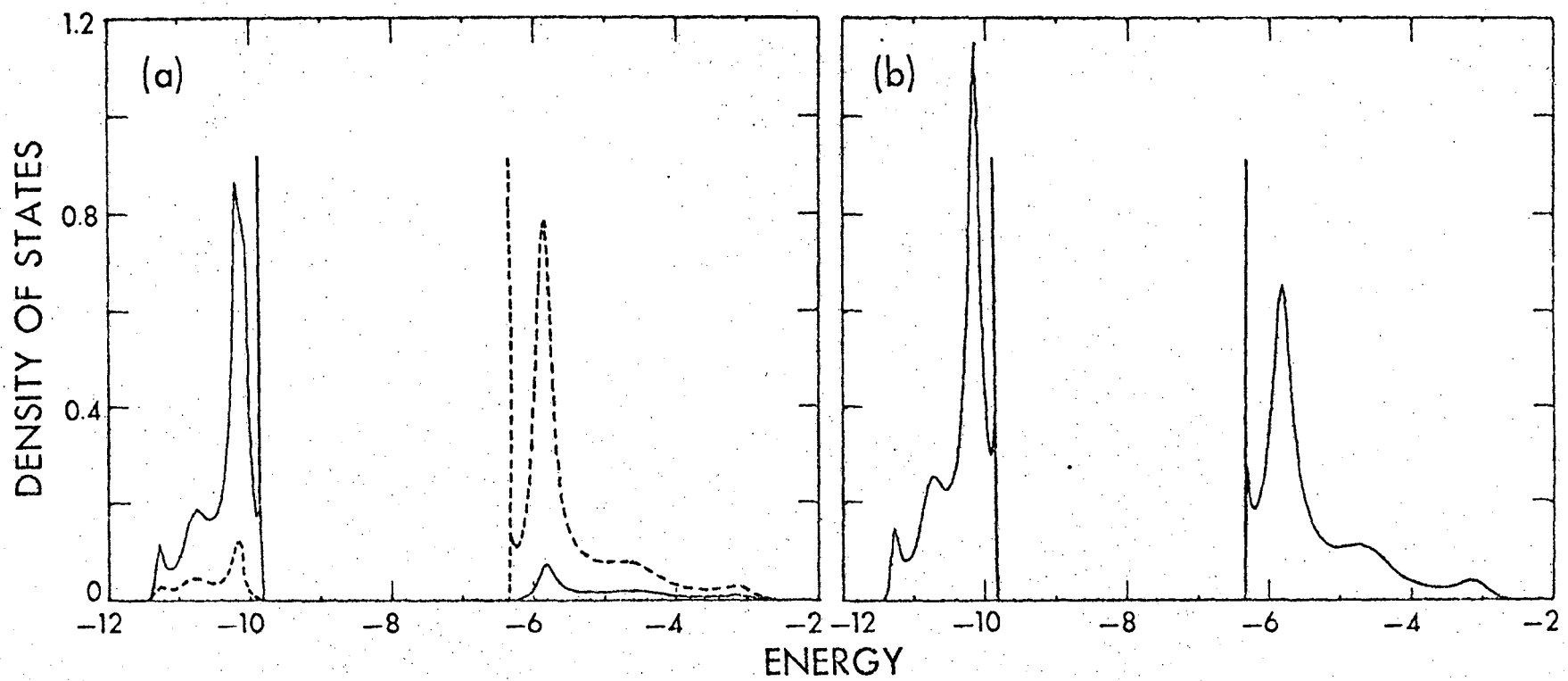

Fig 6

0 0 0 0 4 2 0 0 0 5 4

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