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# Excitations in amorphous pyramidally bonded solids. I. Electrons

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The electronic and phonon state densities of amorphous pyramidally bonded solids are calculated. These solids are shown to exhibit a unique isomorphism between the electronic and vibrational state densities. This atypical correspondence between the state densities suggests that a study of the electronic states can be used to understand the vibrational states. Arsenic, which epitomizes pyramidally bonded solids, is chosen as a prototype. Our results reproduce the trends founds in the x-ray photoemission data (XPS) for rhombohedral and amorphous As. The effects of bond-angle variations and topological disorder upon the $s$- and $p$-like regions of the XPS spectra are investigated. A prescription is given by which the behavior of the $p$-like electrons in pyramidally bonded solids can be understood in terms of the behavior of the $s$-like electrons.

## I. INTRODUCTION

The electronic and vibrational excitations in elemental solids such as P, As, and Sb exhibit a unique isomorphism.[1] This is a consequence of several interesting properties exhibited by these solids. In both their crystalline[2] and amorphous phases,[3] atoms in these solids form a trigonal pyramidal-like configuration with their three nearest neighbors. A configuration of this type results from strong covalent bonding primarily between the three $p$-like electrons on one atom with the $p$-like electrons from each of its three neighboring atoms. Consequently, there is only a weak coupling between the $s$-like and $p$-like electrons. This weak $s-p$ mixing, strong bonding, and threefold pyramidal coordination make it possible for an isomorphism between the electrons and phonons to exist. More precisely, the isomorphism is between the $p$-like electronic states in the solid and vibrational modes. This is easily understood with the following simple argument. The vibrational energies are obtained by coupling *displacements* on different atoms through a dynamical matrix. Similarly, the $p$-like electronic states are obtained by coupling $p$-like orbitals on different sites through a Hamiltonian matrix. Since the $p$-like orbitals transform like vectors and since the symmetry of the dynamical and Hamiltonian matrices are similar, one obtains an isomorphism in the corresponding state densities.

It is the purpose of our work to study and exploit this isomorphism in order to examine the effects of disorder on both the electronic and vibrational excitations in these solids. We shall choose As as a prototype, since it exhibits some rather interesting properties. First, As is a semimetal in its crystalline (rhombohedral) phase, whereas in the amorphous phase, it is a semiconductor with a sizeable gap of about 1.0–1.4 eV. Secondly, due to its threefold coordination, As behaves more like a two-dimensional solid. Thus, it should bridge the gap between three-dimensional solids like Ge and "one-dimensional" solids like Se. In fact, As is more like Se in that it is more molecular than Ge; on the other hand, As is likely to have ring topologies which resemble Ge more than Se.

Our approach will be to use a simple yet sufficiently realistic tight-binding Hamiltonian for the electrons and a simple Born-like force constant model for the phonons. These models are adequate because of the strong localized bonding nature of the material. To simulate the structure of the amorphous phase of As, we shall use the Greaves and Davis random-network model (RNM).[4] This is a 533-atom structure whose radial distribution functions and bulk density resemble those of amorphous samples very well. In addition, this model has very interesting ring statistics which are rather different from those encountered in fourfold coordinated random-network models. The most striking of these is a clustering of rings around small orders of size 5, 6, and 7. As we shall see, this will have profound effects upon the excitation spectra.

The excitations of the RNM are studied by calculating the densities of states (DOS) using the "cluster–Bethe-lattice method" (CBLM)[5,6] and the Gaussian relaxation method (GRM).[7] These methods are discussed elsewhere and allow for a unique probe into the effects of local topologies on the DOS. Our results will be used to interpret present experimental measurements using neutron scattering,[8] infrared absorption,[9] and x-ray photoemission spectroscopy.[3,10]

In this paper (hereafter referred to as I), we concentrate on the electronic structure of As. In Sec. II, we introduce our Hamiltonian and discuss recent theoretical and experimental results. In Sec. III, we examine the effects of disorder on the DOS with particular emphasis upon the $p$-like region. Finally, in Sec. IV, we discuss the implications of our results, and we conclude with some comparisons between pyramidal and tetrahedral systems.

## II. EXPERIMENT AND HAMILTONIAN

The valence XPS crystalline (rhombohedral single crystal) and amorphous As measured by Ley *et al*, is shown in Fig. 1(a). Only the filled valence states are observed. The states between $-8$ and $-14$ eV are $s$-like in nature, while the large bump near $-4$ eV represents $p$-like bonding states. Moreover, the large dip near $-8$ eV suggests a small $s$-$p$ mixing. There are four prominent features evident upon comparing the two experimental spectra. Firstly, the dip near $-12$ eV in the crystalline phase tends to be filled in the amorphous phase. Secondly, states are introduced near $-9$ eV. Thirdly, a shoulder tends to appear near $-5$ eV. Finally, the top of the valence band shifts about 2 eV towards the Fermi energy (0 eV) in the amorphous phase.

It should be pointed out, however, that the photoemission experiment on the single crystal may not be measuring a total density of states. The layer-like nature of the crystal could produce angular-dependent effects. Shevchik[10] argues that this is indeed the case, because his recent photoemission measurements on seemingly "polycrystalline" samples show no discernible differences between the $p$-like regions of "crystalline" and amorphous As. However, the composition of Shevchik's "crystalline" sample is not certain. Further, if one believes Bullett's chemical pseudopotential band structure of As,[11] the bonding $p$-electrons are nearly degenerate at $\Gamma$. This is a strong indication that *no angular-dependent effects* could be observed since the $p$ electrons can transform into each other. Additional experimental and theoretical work is needed, however, before this matter can be fully resolved.

Nevertheless, the DOS calculation of Kelly and Bullett on rhombohedral As and the Greaves-Davis RNM[12] using a chemical pseudopotential are in remarkable agreement with Ley *et al.*'s photoemission results shown in Fig. 1(b). Whether the experiment is correct or not, the fact remains that this model gives the same trends as experiment. It is of interest, then, to understand why the Greaves-Davis model gives the results that it does.

To do this, we will want to choose a Hamiltonian that is simple enough to be tractable with nonperiodic systems, yet realistic enough to describe the main effects of disorder. There are three principal structural changes that occur in going from the crystal (rhombohedral) to the RNM. These are fluctuations in the interlayer distances, variations in bond angles, and changes in structural topology.

The effect of interlayer distances has been studied previously.[12,13] One finds that the resulting decrease of interlayer bonding in the RNM leads to an increase in the optical gap, tends to give an almost two-dimensional character to the DOS, and does not produce any discernible peaks in the spectrum. Therefore, the overall effect of such interactions on the DOS is simply to broaden it. This is supported again by a discussion in Sec. IV. Consequently, these interactions need not be considered in understanding the trends observed in the movement of peaks from the crystal's spectra to the RNM's spectra, and therefore, we restrict our Hamiltonian to intralayer interactions.

On the other hand, the effects of bond-angle vari-

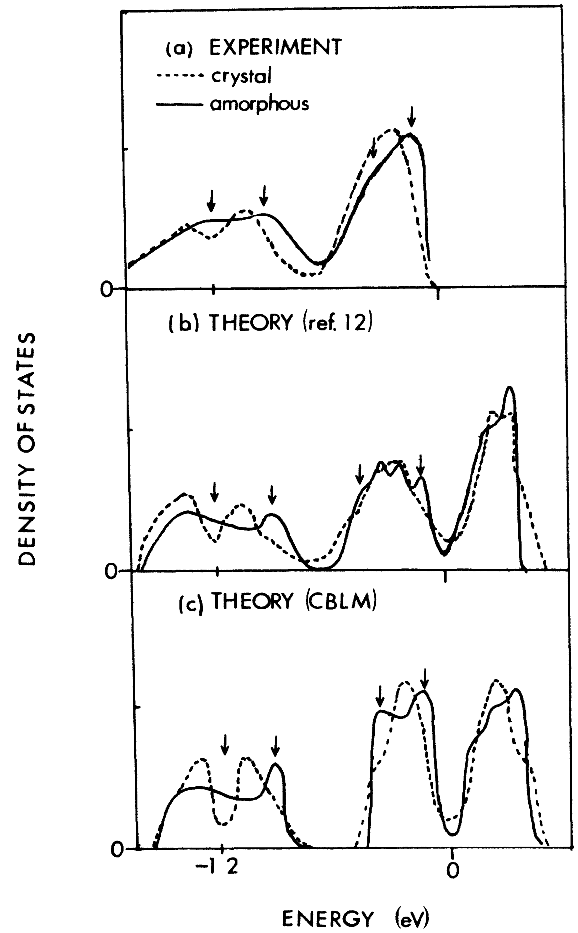

FIG. 1. (a) Experimental XPS (Ley *et al*.); (b) Kelly and Bullett theory (Ref. 12). (c) Our model (including interlayer interactions as a broadening) using CBLM. Arrows indicate the most important changes from crystal (rhombohedral) to amorphous.

ations and topological disorder in As have not been studied in any detail before. The effects of topological disorder can be probed by assuming a simple Hamiltonian that contains only the most important interactions at a fixed bond angle and neglecting weaker $s-p$ interactions. The form of the Hamiltonian is

$$\mathcal{H} = \sum_{ss'} V_{ss'} C_s^\dagger C_{s'} + \sum_{pp'} V_{pp'} C_p^\dagger C_{p'} \,, \tag{1}$$

where $V_{ss}$(=−12.0 eV) is the binding energy of an $s$ orbital, $V_{ss'}$($\equiv V=-1.0$ eV) is the interaction between neighboring $s$-orbitals, $V_{pp}$(=0.0 eV) is the binding energy of the $p$-orbitals, and $V_{pp'}$($\equiv V_\sigma = 2.5$ eV or $V_\pi = -1.2$ eV) for $p$ and $p'$ interacting with $\sigma$ or $\pi$ interactions, respectively. These parameters were fitted to the amorphous spectrum. The effects of bond-angle variations can be easily studied by removing the restriction of a fixed bond angle on the Hamiltonian.[14]

The success of (1) can be seen by comparing the DOS spectra in Fig. 1(c)[1] [which were calculated using (1) and the CBLM, and with interlayer interactions incorporated as a simple broadening of the densities of states] with those in Fig. 1(b), which include $s-p$ interactions and interlayer interactions. Both calculations show the same behavior in the $s$ and $p$ bands. The agreement between these spectra is a strong indication that the above Hamiltonian contains the essential features for an adequate description of the valence electrons. Further, this Hamiltonian allows us a simple way to investigate the causes of the trends exhibited in Fig. 1. We now proceed to study the nature of these trends.

## III. ELECTRON DENSITIES OF STATES

### A. *s* states

Previously,[1] we studied the effects of disorder upon the $s$-like states using the $s$-like portion of Eq. (1), the CBLM, and the GRM. On the basis of our analysis, we concluded that the $s$-state DOS can be interpreted primarily in terms of local ring statistics.[12,15,16] We summarize these observations in Fig. 2. It is clear from this figure that the two peaks (at ~ −11 eV and −13 eV) and dip (at ~ 12 eV) in the crystalline DOS (Fig. 1) result from the presence of the hexagonal rings which comprise each layer of the rhombohedral structure. In the amorphous spectrum, the pronounced peak at −10 eV is due to the large number of five- and sevenfold rings in the RNM, while the introduction of states in the valley at −12 eV is a result of four-, five-, seven-, and eightfold rings. Finally, it should be noted that bond-angle variations will not affect the $s$-state DOS appreciably. The second nearest-neighbor fluctuations they induce would produce a small broadening of the structure in the DOS.

### B. Effects of topology on the *p* states

Using the $p$-state portion of Hamiltonian (1), we calculate the DOS of the Bethe lattice which is shown in Fig. 3(a) (dotted curve). The spectrum is featureless and smooth, and is composed of two identical bands (bonding and antibonding) with a gap of about 1.4 eV. The DOS of crystalline As is plotted as a solid line in Fig. 3(a). The sharpness of the peaks and edges is caused by long-range order present in the crystalline structure. The conduction and valence bands have peaks at ±2.5 eV and extend from 0 to ±5 eV, respectively. In addition, the bands touch at $E=0$ eV. This is consistent with the semimetallic character of crystalline As [note Fig. 2(d) in Ref. 12, where similar behavior was found]. The structure in the crystalline spectra can be understood by examining small clusters of atoms. We separate from the rhombohedral structure a cluster of atoms with only a *single* sixfold ring passing through the central atom and attach the threefold coordinated $p$-state Bethe lattice to the surface of the cluster. The local-density-of-states (LDOS) spectrum of the central atom of the cluster is shown in Fig. 3(a) as a broken curve. Upon comparing this spectrum with the DOS spectrum of the crystal, two points can be made. First, both spectra have similar peaks at ±2.5 eV, however, as would be expected, the sharpness found in the crystalline spectrum is absent from the cluster's LDOS. Secondly, the band edges and the size of the gap are different in the two spectra. These differences are caused by changes in the long-range order of the two systems. However, the important point is that the gross features of the crystalline DOS are reproduced in the LDOS of the cluster. This implies that the bulk behavior of the $p$-like DOS is a function of the local configuration about an atom instead of the long-range topological structure. Again, it is the property of the sixfold ring that causes this structure. Recall that a similar observation was found to be true for the $s$ states.

In fact, all the above results could have been predicted by examining only the $s$-like states. If we slice the $s$-like spectrum in the middle, then the left-hand and right-hand parts of the spectrum correspond essentially to the bonding and antibonding parts of the $p$-like DOS, respectively. This is clearly shown by comparing Fig. 2(a) with Fig. 3(a). Thus, the sixfold rings that were responsible for the two peaks and dip structure in the $s$-like crystalline phase are also responsible for the cor-

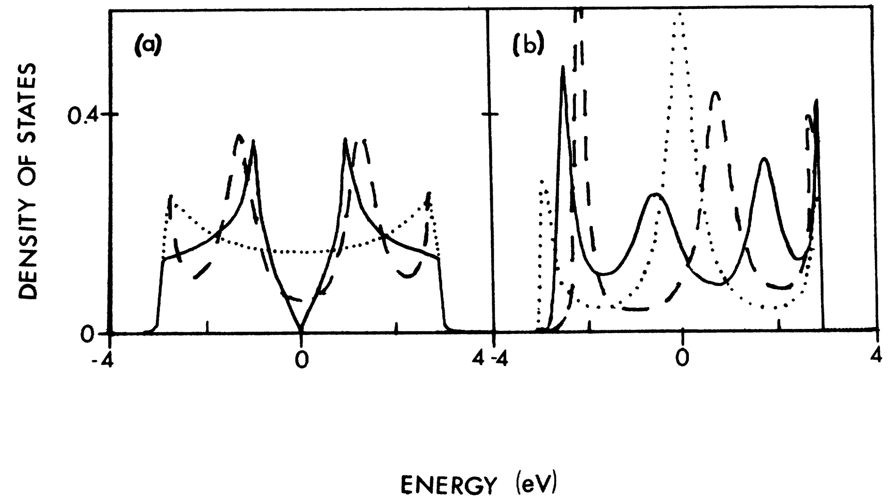

FIG. 2. DOS calculation for the $s$-like states. (a) $s$-state Bethe lattice (dotted line) and the LDOS of a cluster of atoms separated from the crystalline structure (broken line); (b) $s$-state LDOS of cluster–Bethe-lattice systems containing a single ring of type $n$ passing through the central atom. $n = 4$ (dotted line), $n = 5$ (broken line), and $n = 7$ (dashed line). (Note that the binding energy of $s$ states $V_{ss}$ has been set to zero. No broadening has been added in this figure nor in Figs. 3–6.)

responding structure in the $p$-like crystalline phase. What happens if we have different types of rings? This can be investigated by examining $p$-state cluster–Bethe-lattice systems with a *single* ring of only one type (four-, five-, or seven-fold ring) passing through the central atom. In Fig. 3(b) the resulting LDOS of the central atom of each cluster is plotted. Again the fourfold ring spectrum in Fig. 3(b) is easily understood in terms of the four-fold ring spectrum in Fig. 2(b). The oddfold ring spectra, however, are a bit more difficult to interpret. The complication arises because the relative sign of $V_\pi$ to $V_\sigma$ is now important. With oddfold rings, the limit $V_\pi = -V_\sigma = V_{ss'}$ will not give the same spectrum as $V_\pi = V_\sigma = V_{ss'}$ (which corresponds to the $s$ states). Nevertheless, grossly speaking, a simple relationship of $p$-like spectra to $s$-like spectra can be obtained from the following argument. For simplicity we take only one fivefold ring with Bethe lattices attached outside. Since $V_\sigma$ is positive, we consider first $V_\sigma = V_\pi = \frac{4}{3}$ eV. This gives the $s$-like fivefold ring spectrum shown in Fig. 4(a). This is equivalent to the spectrum shown in Fig. 2(a) with $V_{ss'} = V = +\frac{4}{3}$. Let us now take into account that $|V_\sigma| > |V_\pi|$. This will create a gap of about 1.4 eV for $|V_\sigma| \sim 2.5$ eV. We do this schematically by slicing the spectrum in Fig. 4(a) at 0 eV and separating the two parts. This is shown in Fig. 4(b). Now we must take into account that the sign of $V_\pi$ is negative for $p$-like electrons. Since $V_\pi$ is responsible for the widths in the two separated regions, a change of sign in $V_\pi$ should flip these regions about their respective centers. This is shown schematically in Fig. 4(c). The spectrum in Fig. 4(c) therefore should have the gross features of the actual $p$-like DOS. This latter spectrum is shown in Fig. 4(d). The agreement is reasonably good. Moreover, it is interesting to note

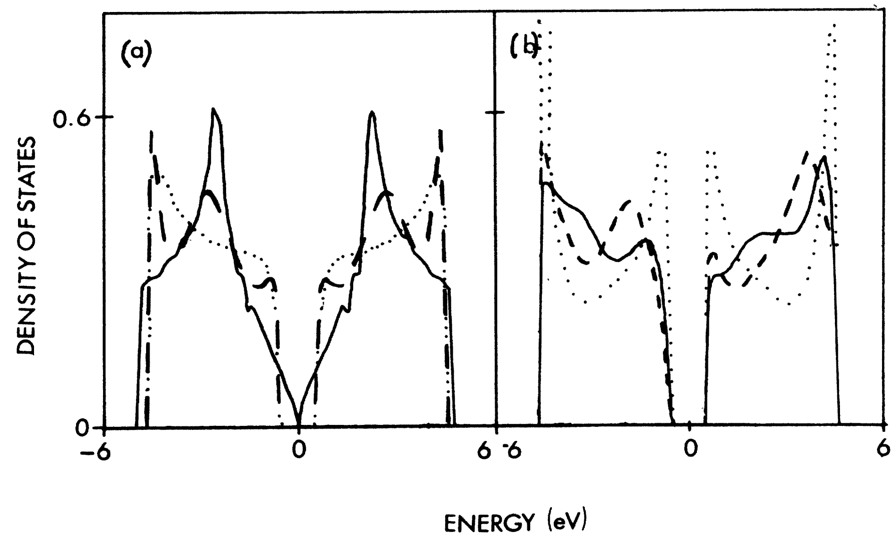

FIG. 3. DOS calculation for the $p$-like state. (a) The Bethe-lattice (dotted line), LDOS of a cluster of atoms separated from the crystal (broken line) and crystalline DOS (solid line); (b) DOS for $p$-state cluster–Bethe-lattice systems. $n = 4$ (dotted line); $n = 5$ (broken line); $n = 7$ (solid line). The valence band is at negative energies and the conduction band is at positive energies.

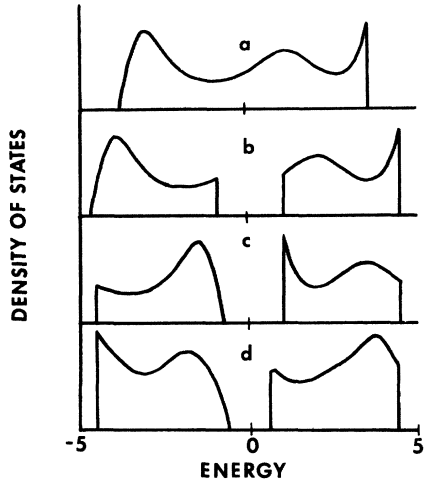

FIG. 4. Schematic representation of the relationship between the $s$-state LDOS (a) and the $p$-state LDOS (b) for a cluster–Bethe-lattice system containing only a fivefold ring of bonds (see text for details).

that in Figs. 4(c) and 4(d) all the band edges are sharp except near −1.0 eV. This can be understood by going back to Fig. 4(a) where the corresponding edge now lies near −4 eV. This edge is smooth because a fivefold ring (or any oddfold ring) of $s$-like orbitals cannot have pure antibonding states. Thus, there are fewer states at the edge of the band.

Finally, it should be noted that the effects of topological disorder on the $p$-electrons can be altered slightly if there are unusually strong non-nearest-neighbor couplings. In such cases, one can describe the extra interactions in terms of an "effective ring topology" of the system. This is precisely what occurs in orthorhombic As and will be discussed later in Sec. IV.

### C. Greaves-Davis model

To interpret the structure in the DOS of the Greaves-Davis model, it is instructive to examine the LDOS of a central atom with vacuum boundary conditions. In particular, we start with a small cluster of atoms (~50 atoms) and study the changes in the LDOS as the size of the cluster increases to form the final shape of the model (533 atoms). The results are shown in Fig. 5. Convergence is obtained only after 300-atom clusters are reached. If we now apply the CBLM to a cluster of only 15 atoms to calculate the LDOS of the same atom in the RNM, we obtain the spectrum which is superimposed as a broken curve. The agreement between the two spectra is good, and the features in the spectra can now be easily attributed to the smallest rings passing through the central atom. Using the prescription described earlier, we can interpret the peaks around −1.7 eV and 3.0 eV as a consequence of five- and sevenfold rings, while the structure at −3.7 eV is due to a lone sevenfold ring.

Consequently, the different atoms in the RNM will have different ring topologies which will manifest themselves as different structure in the LDOS. A measure of the total DOS can then be obtained by averaging over several atoms near the center of the model. This gives the result shown in Fig. 1(c) which will be discussed again in Sec. IV.

### D. Effects of bond-angle variations on $p$ states

In order to gauge the importance of bond-angle fluctuations upon the RNM's DOS, it is desirable to isolate these effects from other disorder-induced effects. We do this by considering various distorted pyramidal units taken from the RNM. Bethe lattices are then attached to the dangling bonds. The LDOS of the central atom of the unit will now contain information only about the effects of bond-angle disorder.[14] Typical spectra are shown in Fig. 6 (solid lines). For comparison, we also show the $p$-state Bethe lattice (with bond angles fixed at 90°) as a dotted curve. We notice that the spectra differ mainly from each other near the band edges. The distorted pyramids spectra show states shifted toward the Fermi energy, thereby raising the top of the valence band to slightly higher energies. This shift of states arises from the net increase in the energy of the bonding $p$ electrons because of the distortion. In fact, this effect may be partially responsible for the shift of the top of the valence band observed in the theoretical and experimental results shown in Fig. 1. However, the smallness of the shifts seen in Fig. 6 indicates that topology may also play an important role.

## IV. SUMMARY AND CONCLUSIONS

### A. Amorphous and crystalline phases

In Sec. II, it was shown that theoretical calculations give DOS spectra [Figs. 1(b) and (c)] which exhibit the same trends found in experiment [Fig. 1(a)]. It is easy to understand these trends in terms of the structural characteristics of the RNM.

The ring statistics of the RNM clearly show a clustering of small-order rings of order five, six, and seven, the largest number being fivefold rings. There are also a few fourfold and eightfold rings. Therefore, the introduction of states in the valley near −12 eV is caused by the presence of four-, five-, seven-, and eightfold rings of bonds. The pronounced peak near −10 eV is mainly caused by the large number of fivefold and sevenfold rings. These rings may also cause states to shift to −1 eV and near 4 eV. Finally, the shoulder near

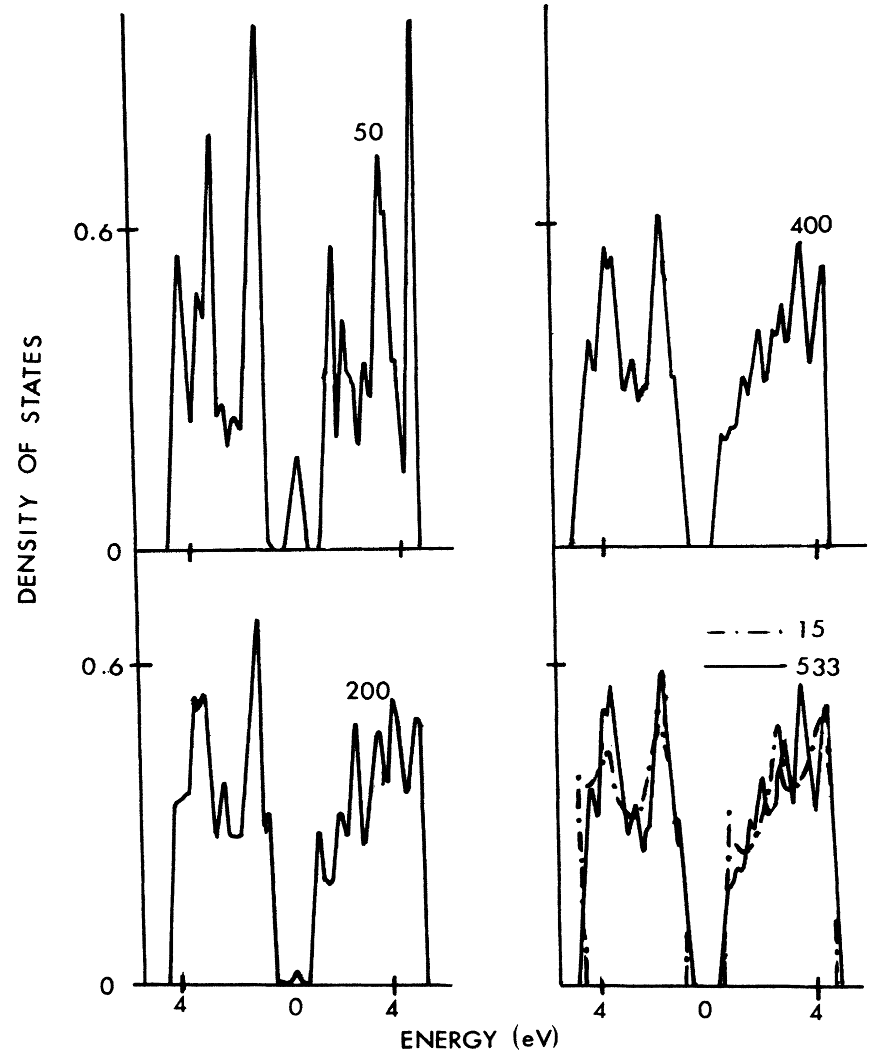

FIG. 5. Local $p$-like state densities for a central atom in various sized clusters in the RNM. CBLM results on 15-atom cluster are superimposed upon the 533-atom result.

−4 eV may be caused by sevenfold rings. We have not taken into account the effects of bond-length variations since the nearest-neighbor lengths are rather well defined experimentally.

Dihedral angle variations, however, are included explicitly in our calculation. The effect of such interactions upon the DOS is small since most of the atoms in the Greaves-Davis model tend to be bonded in a staggered configuration.[4]

There are more interesting features to be found in Fig. 1. Firstly, the band edges in the theoretical spectra indicate the two-dimensional character of the Greaves-Davis RNM. Secondly, the *bigger gap* (near 0 eV), observed in the theoretical am-

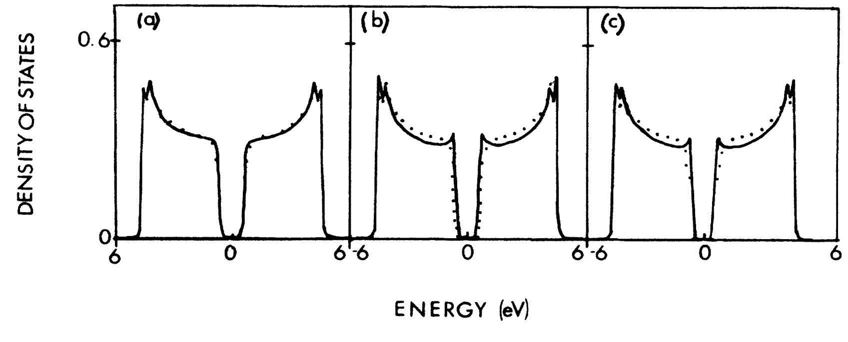

FIG. 6. LDOS of various distorted pyramidal units taken from the RNM (solid line) with 90° Bethe-lattice spectrum superimposed (broken line). (a) Atom No. 10. (b) Atom No. 6. (c) Atom No. 4.

orphous spectrum, is consistent with the semiconducting properties of *amorphous* As. This gap is not entirely caused by the Bethe lattice as is clear in Fig. 5, where there is no Bethe lattice. What tends to increase the gap then is the presence of odd-membered rings of bonds. These tend to remove states near 0.0 eV because pure "antibonding"-like states are not allowed for oddfold rings. In general, the size of the gap is also strongly influenced by the "effective" *interlayer* interactions. Krebs[13] suggested that this may be the case in the amorphous phase and, in fact, the Greaves-Davis model does have larger interlayer distances than the rhombohedral phase.

Another phase of crystalline As, the orthorhombic phase also has larger interlayer distances than the usual rhombohedral structure.[2] Consequently, the orthorhombic structure is a narrow gap semiconductor. In addition, recent pseudopotential calculations[17] show that the bonding $p$-like DOS of this structure tends to resemble the amorphous DOS. This is rather surprising since both crystalline phases of As are comprised of sixfold rings in the "chair configuration." Our studies show that if only nearest-neighbor interactions and interactions between atoms which define a bond angle are taken into account, the DOS for both structures are virtually identical. The main differences, therefore, between the electronic structure in these phases are caused by the interlayer interactions[13] in the rhombohedral phase and the interactions that arise because of the large number of nearly eclipsed bonds in the orthorhombic phase.[13] The effects of the former interactions are shown in Fig. 7(a) for the rhombohedral structure. Note that the explicit inclusion of these interactions produces a DOS spectrum similar to the broadened spectrum shown in Fig. 1(c). The latter interactions in the orthorhombic phase create weak "effective" fourfold rings which are responsible for the peaks seen in the $p$ region of the spectrum shown in Fig. 7(b). In light of these results it is intriguing to suggest that perhaps the "crystalline" samples of the Shevchik experiment[10] mentioned in Sec. II may have contained large amounts of polycrystalline orthorhombic As. This could then account for the similarities he sees between his crystalline and amorphous results in the $p$-like region, whereas the $s$-like states remain different.

### B. Pyramidally and tetrahedrally bonded solids

Finally, it would be instructive to make some comparisons between pyramidal and tetrahedral systems. For example, one observes similarities between the XPS spectra of amorphous phases of Ge and As. In going from the crystalline to the amorphous phase of Ge, the following changes are observed.[18] First, the upper region of the $p$-like states in the valence band is shifted toward the Fermi energy. Secondly, the valley between the lower region (pure $s$-like states) and the middle region (region of $s$-$p$ mixing) of the valence band in the crystalline phase is replaced by a broad peak in the amorphous phase. The observed changes are indeed somewhat analogous to those indicated above for As; however, one must be careful, for there are very important and subtle differences between them.

For instance, in amorphous As we have shown that the shift of the $p$-like peak toward the Fermi energy is primarily a consequence of the sensitivity of the $p$-like electrons to topology. In Ge, this does not seem to be the case. Recent results[14] obtained by applying a realistic tetrahedral tight-binding Hamiltonian and the CBLM to different rings and disordered tetrahedral show that the shifting of the $p$-like peak is mostly caused by bond-angle variations and the increase in energy associated with these variations.

With respect to the changes found in the lower region of the valence band, the similarities between As and Ge are somewhat stronger. The major difference between As and Ge in this region is that in As there is a strong shifting of states toward higher energies (note Fig. 1); while in Ge, there is no apparent shift of states. Earlier we attributed this shift to specific ring statistics, yet, amorphous Ge which has similar ring statistics

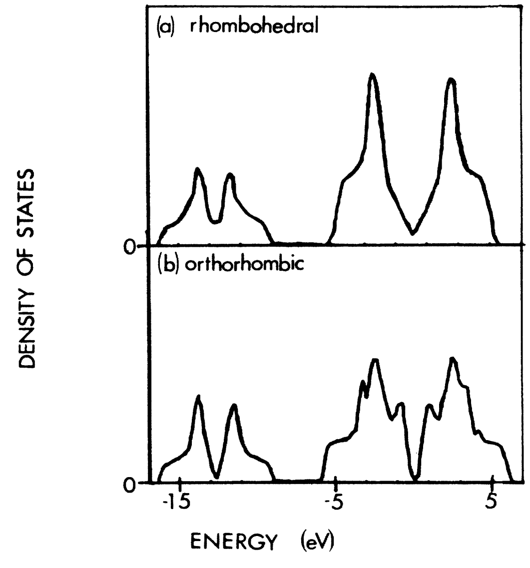

FIG. 7. DOS of the crystalline phases of As: (a) rhombohedral As with interlayer interactions included explicitly; and (b) orthorhombic As with the interactions resulting from the larger number of nearly eclipsed bands included. Further $s$-$p$ interactions have also been included here explicitly.

does not exhibit a corresponding shift. This can be attributed to two effects. First, the ring statistics in amorphous Ge are not that close to those of As. In fact, the ratio of five- to sixfold rings in Ge is typically 0.3, whereas in As it is greater than 1.0. Secondly, Ge has strong $s$-$p$ coupling between the $s$- and $p$-like bands. Whereas the lower region of the valence band in As is composed of essentially pure $s$-like states, this region in Ge consists of two bands: one which is mostly $s$-like in character and another which has mixed $s$ and $p$ character. Nevertheless, it has been shown that the energies of states in this region of Ge's valence band are related to the eigenvalues of a much simpler one-band Hamiltonian through an analytic transformation.[19] This simple one-band Hamiltonian is very similar to the $s$-like portion of Hamiltonian (1) and leads to a spectrum similar to that of As $s$ states. However, when one transforms back to the two-band case, the nature of the spectrum changes, and the similarity with the $s$-like region of As is diminished.

The ideas and results obtained from our analysis of the electrons in As are also applicable to the phonons. As we mentioned earlier, the correspondence is a consequence of an isomorphism between the electronic and vibrational state densities of pyramidally bonded solids. In the second half (II) of our investigation of these solids, we shall study in some detail the nature of this isomorphism, and will exploit it, in order to explain the vibrational properties of As.[20] Our focus will be upon recent experimental infrared and neutron scattering results for amorphous arsenic.

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[1] J. D. Joannopoulos and W. B. Pollard, Solid State Commun. 20, 947 (1976).

[2] R. W. G. Wyckoff, *Crystal Structures* (Wiley, New York, 1963), Vol. I.

[3] L. Ley, R. A. Pollack, S. P. Kowalzyk, R. McFeely, and D. A. Shirley, Phys. Rev. B 8, 641 (1973).

[4] G. N. Greaves and E. A. Davis, Philos. Mag. 29, 1201 (1974).

[5] J. D. Joannopoulos and F. Yndurain, Phys. Rev. B 10, 5164 (1974).

[6] F. Yndurain and J. D. Joannopoulos, Phys. Rev. B 11, 2957 (1975).

[7] J. D. Joannopoulos and E. Mele, Solid State Commun. 20, 729 (1976).

[8] A. J. Leadbetter, P. M. Smith, and P. Seyfert, Philos. Mag. 33, 441 (1976).

[9] G. Lucovsky and J. Knights, Phys. Rev. B 10, 4324 (1974).

[10] N. J. Shevchik, Philos. Mag. 35, 261 (1977).

[11] D. W. Bullett, Solid State Commun. 17, 965 (1975).

[12] M. J. Kelly and D. W. Bullett, Solid State Commun. 18, 593 (1976).

[13] H. Krebs, J. Non-Cryst. Solids 1, 455 (1969).

[14] J. D. Joannopoulos, Phys. Rev. 16, 2764 (1977).

[15] R. Alben, L. Von Heimendahl, P. Gallison, and M. Long, J. Phys. C 8, L468 (1975).

[16] J. Robertson, J. Phys. C 8, 3131 (1975).

[17] J. P. van Dyke, J. Non-Cryst. Solids 12, 263 (1973).

[18] T. M. Donovan and W. E. Spicer, Phys. Rev. Lett. 21, 1572 (1968); L. Ley *et al.*, Phys. Rev. Lett. 29, 1088 (1972).

[19] M. F. Thorpe and D. Weaire, B 4, 3518 (1971).

[20] W. B. Pollard and J. D. Joannopoulos, Phys. Rev. B 17, 1778 (1978) (following paper).