

## Effects of disorder on the electronic density of states of III-V compounds\*

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We investigate the effects of two types of disorder on the electronic density of states of III-V semiconductors using simple tight-binding models and the empirical pseudopotential method. For the first type of disorder we consider a stoichiometric system with fourfold coordination, all bonds satisfied, variations in the bond lengths and angles, and only *unlike-atom bonds*. The second type of disorder includes the properties of the first with the addition of *like-atom bonds*. These two types of disorder are studied explicitly by taking GaAs as a *prototype* and making various GaAs structures using the atomic positions of certain crystal structures with short-range disorder. These structures are crystals; however, they have atoms in the primitive cells arranged in varying fashions. A comparison of the trends observed in the densities of states with the inclusion of different types of disorder reveals valuable information concerning the relationship of the structural nature of an amorphous system to its density of states. We present a model of the density of states of our amorphous prototype GaAs, for each type of disorder, which we believe would be consistent with some of the present experimental radial-distribution-function data. The effects of these types of disorder are discussed in general, and hopefully they will be useful in identifying specific types of disorder in amorphous samples.

### I. INTRODUCTION

For many years there has been considerable experimental and theoretical interest in the transport, optical, and electronic properties of amorphous group-IV elements like Ge and Si.<sup>1</sup> In addition, particular interest has been given to the structural nature of the amorphous phase. Many techniques have been developed to prepare amorphous samples and usually special care is taken to minimize the number of microvoids present so as to obtain a sample approaching a connected network of atoms with a minimum number of dangling bonds.

However, only recently have experimental measurements yielded any information related to the electronic density of states of the complete valence band. This has been accomplished mostly through ultraviolet (UPS) and x-ray (XPS) photoemission spectroscopy.<sup>2-4</sup> The differences observed between the crystalline and amorphous density of states spectra have proven to be valuable in probing the structural nature of amorphous Ge and Si.<sup>5,6</sup> In particular, these calculations suggest that these differences are associated with the presence of fivefold and sevenfold rings of bonds and deviations in the bond angles in the amorphous phase.

In this paper we would like to investigate in some detail the effects of disorder on the electronic density of states of amorphous III-V semiconductors. We shall restrict our disorder to topologically disordered stoichiometric structures with atoms in fourfold coordination and no dangling bonds. We will divide this disorder into two main types which we shall call disorder (U) and disorder

(L). Disorder (U) describes a disordered connected network of atoms with deviations from the ideal tetrahedral bond lengths and angles but with the restriction of having only *unlike-atom bonds* (i. e., only III-V atom bonds). On the other hand disorder (L) can also have *like-atom bonds* (i. e., III-III and V-V bonds). As we shall see this division of disorder into these two types is useful since the effects of like-atom bonds on the density of states are very strong and for the most part overshadow effects from disorder (U). Structures with disorder (L) will always have equal numbers of III-III and V-V bonds since we are assuming stoichiometric systems.

We wish to examine the effects and differences of disorder (U) and disorder (L) on the electronic density of states. The purpose of this would be to examine an experimental amorphous density-of-states spectrum and to determine the type of disorder present.

To understand the influences of disorder (U) and disorder (L) on the density of states we shall be interested primarily in effects due to (i) topological arrangement of atoms, (ii) bond-angle and bond-length distortions, (iii) percentage of like-atom bonds, (iv) different clustering configurations of like atoms, and (v) topological variations of clusters of like atoms.

These effects can be studied in the context of short-range disorder as we have done previously in our work on amorphous Ge and Si.<sup>5,6</sup> We can take a series of crystals whose primitive cells are becoming gradually larger. This permits, and in fact we have, an increase in the positional disorder of the atoms. Thus a study of the trends observed

in the density of states for these crystals can give us specific information about the effects of particular types of disorder.

As we have shown in our work on complex structures of Ge and Si, the effects of long-range disorder (i. e., the fact that we do not have crystals) are of secondary importance.

In this paper we shall take the *2H-4* (wurtzite), *4H-8* (hexagonal *4H*), *BC-8* (Si III), *ST-12* (Ge III), and *SC-16* (*BC-8* taken as a simple-cubic lattice) structures as a basis for our studies. In the case of disorder (U) we shall use the *2H-4*, *4H-8*, and *SC-16* structures while in the case of disorder (L) we shall examine the *2H-4*, *4H-8*, *BC-8*, and *ST-12* structures. The reasons for these choices will be given later.

To study these crystal structures we shall use simple three-parameter tight-binding models<sup>7</sup> and the empirical pseudopotential method (EPM).<sup>8</sup> The tight-binding scheme will be used to discern prominent structural features in the density of states and the EPM will provide a more realistic examination of the density of states. We also present charge-density calculations in order to examine the nature of like-atom bonds.

In all our calculations we shall take GaAs as a prototype of the III-V compounds and we assume that our results on the effects of disorder will be applicable to all III-V compounds. However we are not able at the present to predict with any certainty what III-V compounds could exist with disorder (U) or disorder (L).

In Sec. II we shall give a description of the crystal structures studied and the notation that we shall use describing their topological properties. In Secs. III and IV we shall present and discuss the results of our calculations for disorder (U) and disorder (L), respectively. Finally in Sec. V we present a summary and some concluding remarks.

## II. STRUCTURES AND STATISTICS

In this section we shall examine the structural and topological properties of the *2H-4*, *4H-8*, *BC-8*, *ST-12*, and *SC-16* structures. If we place equal numbers of Ga and As atoms at the atomic positions defining the basis for each of these five basic crystal structures we find that we can make  $N! / [(N/2)!]^2$  different substructures respectively assuming each atomic position to be distinct, where  $N$  is the total number of atoms in the primitive cell. Some of these substructures are of course identical and many of them are quite similar. In what follows we shall break up each group of substructures into smaller groups defined by the percentage of like-atom bonds present. We shall then break up each of the smaller groups into subgroups depending upon the number of like-atom bonds for each atom. This is of interest since it charac-

terizes each substructure by the immediate environment of each of its atoms. Now the substructures in the subgroups can be divided further into classes depending upon the particular clustering configurations of like atoms. However, from stability considerations we restrict ourselves to substructures that have atoms with only two or less like-atoms nearest neighbors. The total energy per atom of these structures was obtained from a small extension of the work of Keating<sup>9</sup> and Martin.<sup>10</sup>

With this restriction we are effectively left with substructures that have like atoms which can cluster into chainlike configurations which may be open or closed. A chain is defined by a series of nearest-neighbor like atoms. These substructures can be very conveniently characterized or identified by using the following notation:

$$(N_{\text{Ga}}^1, N_{\text{Ga}}^2, \dots, N_{\text{Ga}}^M / N_{\text{As}}^1, N_{\text{As}}^2, \dots, N_{\text{As}}^L), \quad (1)$$

where  $M$  ( $L$ ) is the total number of chains of Ga (As) atoms in the primitive cell and  $N_{\text{Ga}}^i$  ( $N_{\text{As}}^i$ ) is the number of Ga (As) atoms in the  $i$ th chain. The fraction of like-atom bonds in a particular structure is given by

$$\frac{\sum_{i=1}^M (N_{\text{Ga}}^i - 1)}{2 \sum_{i=1}^M N_{\text{Ga}}^i} = \frac{N_T - 2M}{2N_T}, \quad (2)$$

where  $N_T$  is the total number of atoms in the primitive cell. Since we are dealing with stoichiometric structures an equivalent expression to Eq. (2) could be obtained by replacing  $N_{\text{Ga}}^i$  by  $N_{\text{As}}^i$ .

We may now proceed to analyze the *2H-4*, *4H-8*, *BC-8*, *ST-12*, and *SC-16* structures using the aforementioned notation as an aid to our characterization and discussion. We shall not study all the possible distinct substructures that can be made but rather we shall select and describe those which are most useful for our purposes. Furthermore, in many cases the notation  $(N_{\text{Ga}}^1, \dots, N_{\text{Ga}}^M / N_{\text{As}}^1, \dots, N_{\text{As}}^L)$  does not uniquely define a particular substructure. For instance, we may have many substructures forming a set in which they are all of type  $(I, J/K, L)$ . In this case we shall, arbitrarily, use stability requirements as a discerning factor in choosing one substructure to study out of this set. It should be noted however that the densities of states of all the substructures of a given type are very similar, so that the method used in choosing one substructure is relatively unimportant.

### A. *2H-4*

The *2H-4* structure is a wurtzitelike *2H* structure with four atoms in a primitive cell and is described by lattice constants  $a$  and  $c$  and a parameter  $u$ . The  $a$  and  $c$  lattice constants were chosen so as to make the bulk density of the *2H-4* structure the same as that of GaAs in the zinc-blende

structure and such that  $c/a=1.633$ . If we also take  $u=0.375$  then we have an ideal wurtzite structure and an ideal tetrahedral arrangement of atoms with a nearest-neighbor distance equal to that of GaAs (zinc-blende). Out of the possible substructures that can be made with the  $2H-4$  structure we shall be interested only in two. These can be designated by  $(1, 1/1, 1)$  and  $(2/2)$ . In the first case we have the wurtzite structure with zero like-atom bonds and in the second case we have a fraction of  $1/4$  like-atom bonds, with the Ga-Ga and As-As bonds occupying the two vertical bond positions in the unit cell. The first structure can be used as a starting point for the study of disorder (U) while the second can be used to study the effects of like-atom bonds on structures without short-range disorder. The  $(2/2)$  structure contains the smallest fraction, other than zero, of like-atom bonds that can be made in the  $2H-4$  structure.

#### B. $4H-8$

The  $4H-8$  structure is a  $4H$  structure with eight atoms in a primitive cell. The lattice constants and internal parameter that describe it are the same as those of  $2H-4$  except that we now take the lattice constant  $c_{4H-8}=2c_{2H-4}$ . Again we have an ideal tetrahedral arrangement of atoms except that we now have a bit more topological disorder in the  $z$  direction. The  $4H-8$  structure presents two useful options. First the  $(1, 1, 1, 1/1, 1, 1, 1)$  substructure can be an aid in the study of disorder (U) since it contains some topological variations. Secondly the  $(2, 1, 1/2, 1, 1)$  substructure contains only a fraction of  $1/8$  of like-atom bonds and thus contains the smallest fraction of like-atom bonds other than zero that can be obtained from any of the substructures of all the basic five structures we are studying. The  $(2, 1, 1/2, 1, 1)$  structure has Ga-Ga and As-As bonds occupying two of the four vertical bond positions in the unit cell.

#### C. BC-8

The BC-8 or Si III<sup>11</sup> structure is body-centered cubic with eight atoms in the primitive cell and it is completely specified by a lattice constant  $a$  and an internal parameter  $x$ . We take  $a=6.896 \text{ \AA}$  and  $x=0.1$ . The BC-8 structure is a high-density metastable structure of Ge and Si formed under high pressure but persists at normal pressures and temperatures. One quarter of the bonds are about 2% smaller and the rest of the bonds are about 2% larger than the ideal bond length found in the zinc-blende structure. There are also two types of bond angles approximately equal to  $118^\circ$  and  $100^\circ$ , respectively. An interesting feature of the BC-8 structure is that although it only has even numbered rings of bonds we *cannot* create any substructures with a total of zero like-atom bonds without

going to a unit cell with 16 atoms, as we shall see in Sec. II D. In the first group, containing the smallest fraction  $1/4$  of like-atom bonds, there are six substructures and they are all of the type  $(2, 2/2, 2)$ . The second group, containing the next largest fraction  $3/8$  of like-atom bonds, contains 32 substructures. This group can be divided further into two subgroups containing 24 and eight substructures, respectively. The former contains four atoms with one like-atom nearest neighbor and four atoms with two like-atom nearest neighbors, while the latter contains six atoms with two like-atom nearest neighbors and two atoms with zero like-atom nearest neighbors. We used stability considerations to choose one structure out of the first group of six and one structure out of the second group of 32 which is of the type  $(4/4)$ . These two structures will be studied using the tight-binding model and we shall single out the  $(2, 2/2, 2)$  structure for an EPM calculation using stability again as a discerning factor.

#### D. SC-16

This structure can be obtained by just considering the BC-8 structure as a simple-cubic lattice with a basis of 16 atoms. All the BC-8 substructures can therefore be obtained from the SC-16 structure. The purpose and usefulness of the SC-16 structure is that it provides us with a substructure that has zero like-atom bonds along with short-range disorder. It is therefore very useful in studying disorder (U). The substructure that we chose was necessarily of the type  $(1, 1, 1, 1, 1, 1, 1, 1/1, 1, 1, 1, 1, 1, 1, 1)$ .

The atoms were then allowed to relax slightly to a state of lower energy by a random process similar to that used by Henderson and Ortenburger.<sup>12</sup> This resulted in a small increase in randomness in the bond lengths and angles. In particular we obtained bond lengths that were up to 3% smaller and 5% larger than the ideal bond lengths, and bond angles that varied from  $97^\circ$  to  $119^\circ$ .

Unfortunately there is no SC-16 substructure that can be found with a fraction of like-atom bonds which is smaller than  $1/4$  other than zero.

#### E. ST-12

The ST-12 or Ge III<sup>11</sup> structure is a simple tetragonal unit cell with 12 atoms as a basis. It is completely specified by two lattice constants  $a$  and  $c$  and four internal parameters  $x_1, x_2, x_3,$  and  $x_4$ . We took  $a=5.91 \text{ \AA}$  and  $c=6.955 \text{ \AA}$ , with  $x_1=0.09$ ,  $x_2=0.173$ ,  $x_3=0.378$ , and  $x_4=0.25$ . The ST-12 structure is a high-density metastable state of Ge formed in a similar manner as that of Si III. In the ST-12 structure the bond lengths are all about the same length and about 1% larger than the nearest-neighbor distance of GaAs in the zinc-blende

structure. The bond angles however range from 20% to about 25% greater than the ideal tetrahedral bond angle. Since this structure contains odd-numbered rings of bonds there are necessarily no substructures with a total of zero like-atom bonds. The smallest fraction of like-atom bonds that can be found in these substructures is  $1/3$ . The size of the group of substructures with a fraction of  $1/3$  like-atom bonds is 216. This can be broken into three subgroups containing the following statistics: (i) 24 substructures with four atoms having two like-atom nearest neighbors and eight atoms with one like-atom nearest neighbor; (ii) 48 substructures with six atoms having two like-atom nearest neighbors, four atoms with one like-atom nearest neighbor and two atoms with zero like-atom nearest neighbors; (iii) 144 substructures with five atoms having two like-atom nearest neighbors, six atoms with one like-atom nearest neighbor, and one atom with zero like-atom nearest neighbors.

Out of the first subgroup we pick a substructure of the type (3, 3/3, 3) and out of the second subgroup we pick a substructure of the type (5, 1/5, 1). From the third subgroup we choose a substructure of type (4, 2/5, 1). These will be studied using our tight-binding model and we shall again single out one substructure (4, 2/5, 1), using stability considerations, whose atomic positions we shall relax. This structure will then be studied by the EPM.

Although the fraction  $1/3$  of like-atom bonds in these structures is rather large from a realistic point of view, nevertheless the ST-12 structure provides us with a series of substructures which have atoms in a variety of topological configurations and this is useful for studying the effects of these configurations in a simple and realistic way.

### III. RESULTS FOR DISORDER (U)

In the study of disorder (U) we are interested in investigating effects on the density of states caused by the following features: (i) topology and (ii) bond-angle and bond-length variations. As we have already mentioned these features can be studied with the concept of short-range disorder. In this case we take GaAs in the 2H-4, 4H-8, and SC-16 structures. The first two structures have ideal tetrahedral arrangements of atoms and provide a comparison of purely topological properties. In the 2H-4 structure each atom sees a hexagonal neighborhood which is different from the cubic neighborhood of the zinc-blende structure. This difference starts at the third nearest neighbor. On the other hand in the 4H-8 structure each atom sees alternate layers of cubic and hexagonal neighborhoods. The SC-16 structure provides us with distorted tetrahedral units and therefore has variations in bond lengths and angles. It also provides for a new topology although it is very similar to the 2H-4

structure in that it has the same type of third-nearest-neighbor environment.

#### A. EPM calculations

The tight-binding model is not very useful in studying these structures with disorder (U) since one would find no difference between the 2H-4 and 4H-8 structures and only small differences with the SC-16 structure. In addition the simplicity of the model would be destroyed by the introduction of many parameters to take into account bond-length and bond-angle deviations. On the other hand the EPM is very useful and the results of our calculations using the EPM are shown in Figs. 1(a)-1(c), where we have plotted the density of states of GaAs in the 2H-4 (1, 1/1, 1), 4H-8 (1, 1, 1, 1/1, 1, 1, 1), and SC-16 structures. The filled valence band is shown at negative energies and part of the conduction band is shown at positive energies. These are unsmoothed computer plots and no interest should be paid to the small wiggles along the curves. Before we compare these spectra, however, it would be useful to have some information about the average distribution of electrons in each band. From the charge-density calculations of Walter and Cohen<sup>13</sup> we know that the region of the density of states (Fig. 1) from about -10 to -12 eV contains electrons which are primarily concentrated on the As atoms. They are essentially the As *s*-like states and we shall be calling this the "*s*-like region" of the density of states. The middle peak around -6 eV is actually part of a band that tails all the way to 0 eV. Charge-density calculations for this band show that the electrons are now more concentrated in the bond with some charge on the Ga atoms. Part of the bonding nature of this band is probably coming from the tail. Actually if we just took a simple two-potential-well model in the tight-binding sense, the lower-energy state would be *s*-like bonding primarily around the As atom, and the higher-energy state would be *s*-like antibonding primarily around the Ga atom. Although this model is certainly too simple it does give us some feeling for the region around -6 eV, which we shall be referring to as the "middle-peak" region. Finally the region in the density of states from -4 to 0 eV contains electrons which are almost entirely concentrated in the bonds, as in Ge and Si. We shall be referring to this region in the density of states as the "*p*-like region."

Let us now compare and examine the trends in the density-of-states spectra shown in Fig. 1. As we go from the 2H-4 structure to the 4H-8 structure the spectra seem to be almost identical. All the widths are the same for the two cases and the only difference is in the structure in the *p*-like region between -1.5 and -3.5 eV. What we are

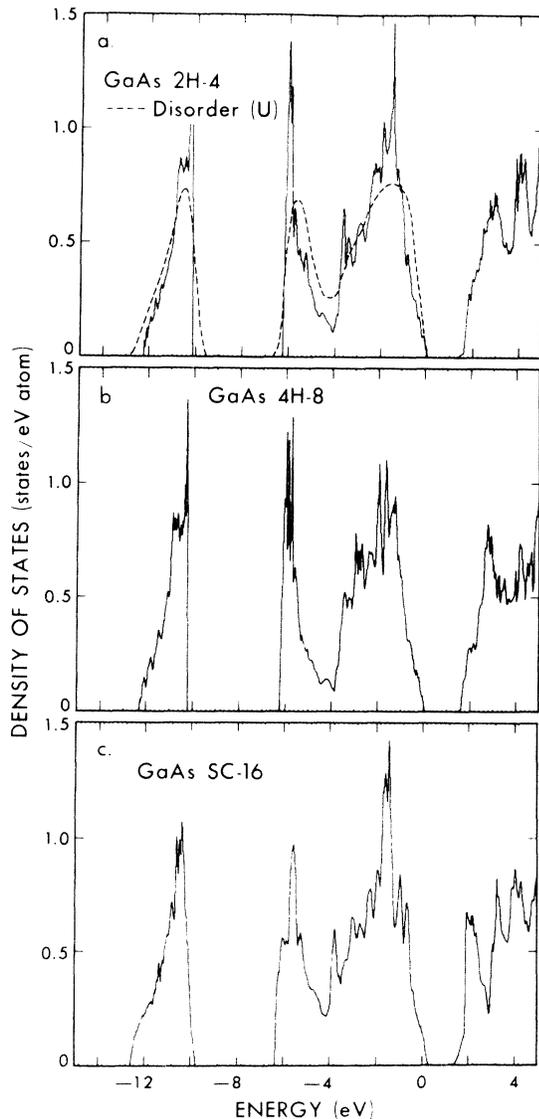


FIG. 1. Density of states of GaAs in the (a) 2H-4, (b) 4H-8, and (c) SC-16 structures using the EPM. The dashed line in (a) represents the consequences of disorder (U) for a III-V compound taking GaAs as a prototype as described in the text.

seeing here are the effects caused by purely topological differences. In particular, in the 4H-8 structure we have the effects of averaging over cubic and hexagonal environments. In fact the only way to have an amorphous structure with purely topological disorder is to randomly stack two-dimensional hexagonal layers of atoms such that the bonds form either eclipsed or staggered configurations. From our results we would expect that the effects of such an amorphous structure would be to smooth out the peaks in the  $p$ -like region and leave everything else essential intact.

If we now compare the 2H-4 and 4H-8 density of states with that of SC-16 we notice some small but interesting differences. First we notice a slight broadening of the  $s$ -like states. This is caused by variations in the second-nearest-neighbor distances due to bond-angle and bond-length distortions. These variations cause variations in the overlap integrals of the As  $s$ -like states and consequently a broadening of this band. This broadening corresponds to about a 0.2-eV increase in the width. For the  $p$ -like states we first notice a steepening of the band edge by the introduction of states at the top of the valence band around 0.5 eV. This is caused most likely by the deviations of the bond angles from the ideal tetrahedral angle which produce the same effects as in Ge. Second, we notice that the  $p$ -like region also gets broadened. This could be caused by the rather large distribution of first-nearest-neighbor distances in the SC-16 structure as we discussed in Sec. II D. The presence of smaller bond lengths than the ideal bond length would tend to broaden the  $p$ -like region as is the case with the SC-16 structure, while structures with only larger bond lengths would get a narrowing of the  $p$ -like region as is the case with Ge ST-12. These effects however are clearly very small. In the middle-peak region the most prominent difference is a slight shift of the main peak to higher energies by about 0.5 eV. Perhaps this is also due to the bonding character of the states in this region although it is not really clear what is happening here.

#### B. Model for disorder (U)

We can get some idea of the distribution of bond lengths and angles in the amorphous case from the radial distribution functions (RDF) of Shevchik and Paul.<sup>14</sup> The RDF's of their amorphous III-V samples were very similar to that of amorphous Ge. In fact the RDF of amorphous GaAs is almost identical to that of amorphous Ge. Unfortunately an RDF is not a sufficient condition for a particular structure nor can one prove the existence of five-fold rings of bonds with an RDF. Therefore if we were to hypothesize a random-network structure which gives the same RDF as amorphous GaAs but with disorder (U), we would expect to get the density of states shown by a dashed line in Fig. 1(a). First we would expect the  $p$ -like behavior to be very similar to that of amorphous Ge since the distribution of bond angles and bond lengths of amorphous Ge and GaAs are very nearly the same. Second we would probably get a slight shift of the main peak in the middle-peak region to higher energies as in the case of SC-16. Finally, we would expect to get a smaller broadening of the  $s$ -like region in the amorphous GaAs case than in the SC-16 structure since the distribution of second-

nearest-neighbor distances is centered at slightly larger distances in the amorphous phase<sup>14</sup> than in the SC-16 case.

As we shall see in Sec. IV, however, the effects of disorder (U) are rather small and mostly insignificant when compared with the effects of disorder (L).

#### IV. RESULTS FOR DISORDER (L)

In a recent communication<sup>15</sup> we described in general terms the effects of disorder (L) on the density of states based on a very simple charge-density model. We suggested that the entire spectrum would be broadened because of an increase in the overlap integral between like atoms and the different types of bonding states that are now permissible. We estimated at least a 1.0-eV broadening of the *s*-like region and we suggested that one may be able to distinguish As-As (Ga-Ga) bonding states at the low- (high-) energy side of the *p*-like region.

In this section we shall examine these ideas more carefully and analyze them on a more firm theoretical basis. In particular we would like to

study explicitly the effects on the density of states produced by the following features: (i) topological arrangement of atoms, (ii) bond-angle and bond-length variations, (iii) percentage of like-atom bonds, (iv) different clustering configurations of like atoms, and (v) topological variations in clustering configurations.

The first two features were discussed in Sec. III and are overshadowed for the most part by features (iii)–(v). In what follows, we shall concentrate primarily on the effects of (iii)–(v), which can also be studied in the context of short-range disorder. Thus we will use the tight-binding model and EPM to examine the various substructures of the 2*H*-4, 4*H*-8, BC-8, and ST-12 structures mentioned in Sec. II. We shall also calculate charge densities for a 2*H*-4 substructure using EPM wave functions.

##### A. Tight-binding calculations

In Figs. 2(a)–2(f) we show the densities of states for the 2*H*-4 (1, 1/1, 1), 2*H*-4 (2/2), BC-8 (2, 2/2, 2), BC-8 (4/4), ST-12 (3, 3/3, 3), and ST-12 (5, 1/5, 1) structures using the tight-binding model.

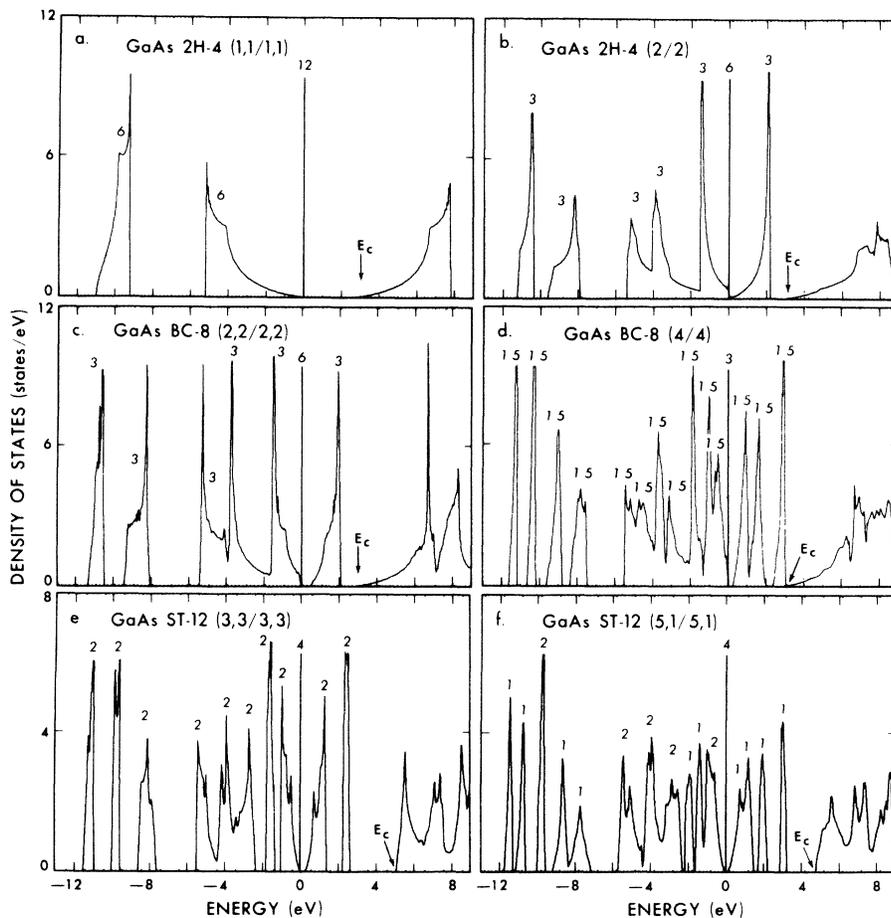


FIG. 2. Density of states of GaAs in the (a) 2*H*-4 (1, 1/1, 1), (b) 2*H*-4 (2/2), (c) BC-8 (2, 2/2, 2), (d) BC-8 (4/4), (e) ST-12 (3, 3/3, 3), and (f) ST-12 (5, 1/5, 1) structures calculated from the simple tight-binding model discussed in the text. The solid line at 0.0 eV represents a  $\delta$ -function peak in the density of states. The bottom of the conduction band is designated by  $E_c$  and the numbers on top of the peaks represent the approximate strength of these peaks.

The valence band is mostly at negative energies and with the  $\delta$  function set at 0 eV and  $E_c$  designates the bottom of the conduction band. Each spectrum is normalized to 24 for ease in comparisons and the small numbers on top of the peaks give the relative weight of each peak. The solid line at 0 eV represents a  $\delta$  function of pure GaAs  $p$ -like bonding states whose degeneracy can be obtained easily by subtracting the total number of GaAs bonds from the total number of GaAs  $p$ -like functions that can be made. The fraction of like-atom bonds for each structure is given by Eq. (2), so that for  $2H-4$  (1, 1/1, 1),  $2H-4$  (2/2), BC-8 (2, 2/2, 2), BC-8 (4/4), ST-12 (3, 3/3, 3), and ST-12 (5, 1/5, 1) we have 0, 25, 25,  $37\frac{1}{2}$ ,  $33\frac{1}{3}$ , and  $33\frac{1}{3}\%$  of like-atom bonds, respectively.

When we examine the trends in the density of states as we go from  $2H-4$  (1, 1/1, 1) to  $2H-4$  (2/2) we notice that the peaks in both the  $s$ -like region and the middle-peak region have now split into two. In addition, in the  $p$ -like region there is one peak at higher and lower energies with respect to the position in energy of the  $\delta$  function. We get the same qualitative results when we examine the density of states for BC-8 (2, 2/2, 2). The  $2H-4$  (2/2) and BC-8 (2, 2/2, 2) substructures have different topological properties; however they do have the same type of like-atom clustering configurations. This suggests therefore that the splitting of the peak in the  $s$ -like region is due to the clustering of As atoms into chains of order two which produces essentially a bonding-antibonding splitting. In a similar way the splitting in the middle-peak region is essentially due to the clustering of Ga atoms into chains of order two, although we must again be careful here, as with disorder (U), since the states in this region are not purely Ga  $s$ -like states. As for the  $p$ -like region the single peaks at high and low energies, respectively, are probably due to the different binding energies of the like-atom bonds which cluster into chains of order one. Since the As atomic valence states lie lower in energy than the Ga atomic valence states we would expect that the lower-energy peak contains mostly As-As bonding states while the higher-energy peak contains Ga-Ga bonding states. We shall return to discuss this point with some evidence later. These ideas are further corroborated by an examination of the density of states of BC-8 (4/4), ST-12 (3, 3/3, 3), and ST-12 (5, 1/5, 1). In the first case we have the effects of like atoms in chains of order four and like-atom bonds in chains of order three. We notice that the  $s$ -like region has now split into four peaks, which is exactly what would happen in a system consisting of localized states in a chain of order four with only nearest-neighbor interactions. In fact the eigenvalues of any such chain of order  $N$  are just the roots of an

$N$ th-order Chebyshev polynomial of the second kind. We can also distinguish four peaks in the middle-peak region presumably caused by the Ga-atom chains. In the  $p$ -like region we now have three lower-energy peaks and three higher-energy peaks. This lends support to the idea that these peaks represent like-atom bonding states and are caused by the like-atom bonds clustering in chains of order three.

The density of states for ST-12 (3, 3/3, 3) and ST-12 (5, 1/5, 1) show the same behavior of the  $s$ -like and  $p$ -like regions when analyzed in terms of chains of atoms and bonds, respectively, even though they have quite different topological properties from the BC-8 and  $2H-4$  substructures. For ST-12 (5, 1/5, 1) we notice the superposition of states in the  $s$ -like region due to chains of atoms of order five and order one. For the  $p$ -like states we can almost distinguish four lower and higher energy peaks caused by the like-atom bonds that are only forming chains of order four. The middle-peak regions for these two ST-12 substructures however do not follow very closely the characteristics of chainlike behavior. Nevertheless they are sensitive to the Ga-atom clustering configurations as can be seen by an examination of the wave functions in this region.

By using the tight-binding model we have observed some very large effects in the density of states caused by disorder (L) which could be understood quite easily. In particular we found that the  $s$ -like and  $p$ -like regions in this model follow some very simple tight-binding rules which are intimately related to the clustering configurations of the like atoms and like-atom bonds. We must ask, however, how realistic in fact are these large effects. Use of the EPM provides the answer and as we shall show below many of these large effects actually carry through in a more complicated calculation. Thus the tight-binding model serves the valuable purpose of providing a simplicity that aids in the understanding of the effects of disorder (L) using a more realistic model.

#### B. EPM calculations

In Figs. 3(a)–3(d) we have plotted the density of states using the EPM for the ST-12 (4, 2/5, 1), BC-8 (2, 2/2, 2),  $2H-4$  (2/2), and  $4H-8$  (2, 1, 1/2, 1, 1) substructures which have  $33\frac{1}{3}$ , 25, 25, and  $12\frac{1}{2}\%$  like-atom bonds, respectively. Like the tight-binding case, these densities of states are normalized to 24 for each substructure and the numbers on top of the peaks represent the approximate strength of those peaks. In addition there is an overlap between conduction- and valence-band states near 1 eV. We notice immediately that the effects of disorder (L) using the EPM are just as spectacular as with the simple tight-binding model.

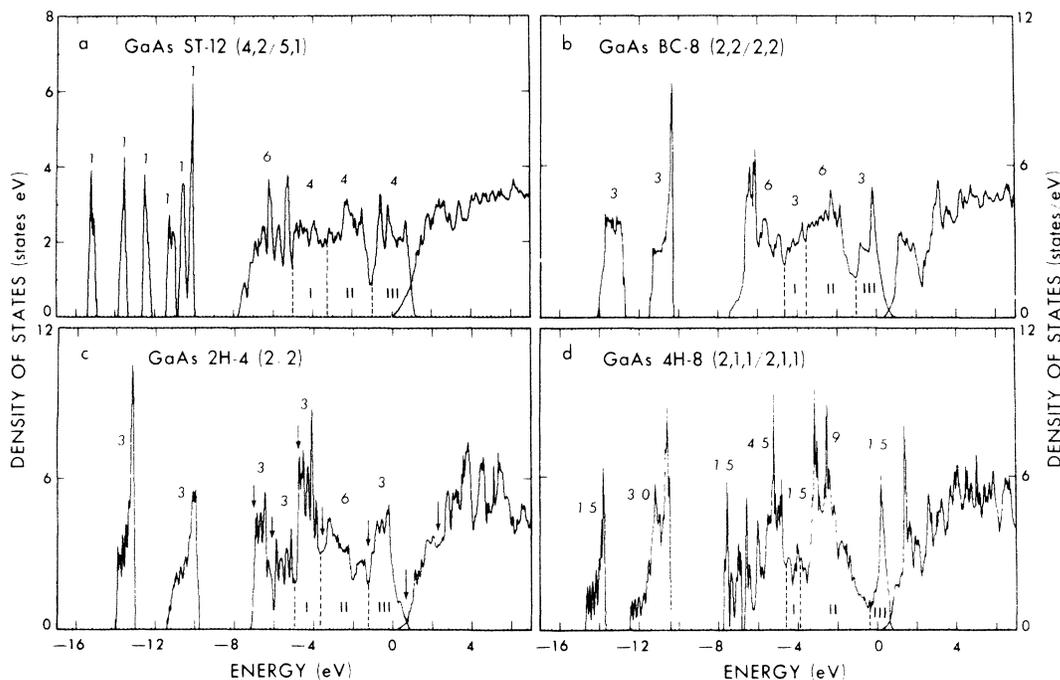


FIG. 3. Density of states of GaAs in the (a) ST-12 (4, 2/5, 1), (b) BC-8 (2, 2/2, 2), (c) 2H-4 (2/2), and (d) 4H-8 (2, 1, 1/2, 1, 1) structures using the EPM. There is an overlap of the valence and conduction bands near 1 eV. Regions I, II, and III represent the  $p$ -like region of the density of states where region II is analogous to the  $\delta$ -function peak using the tight-binding model. The small numbers on top of the densities of states represent the approximate strength of various regions and peaks in these densities of states.

Let us first examine the  $s$ -like region of the density of states. For the ST-12 (4, 2/5, 1) substructure we find six peaks which correspond to the superposition of peaks from As chains of order four and order two. However these peaks are not symmetrically situated around the  $s$ -like peak of As atoms in chains of order one as we would expect from our tight-binding results. This is caused to a major extent by the increase in the potential between the atoms in chains of order greater than one which causes a shift of these states to lower energies. This is similar to shift of the one-electron  $s$ -like energies in the hydrogen molecule-ion. In the latter case this shift is always greater or nearly equal to half the splitting or width of the bonding-antibonding states. Similarly in the case of all the substructures we have studied with the EPM, this shift is approximately equal to half the broadening of the  $s$ -like states. So as a general rule the highest-energy peaks of an  $s$ -like chain will overlap with the  $s$ -like peak of chains of order one. Therefore one of the two highest-energy peaks in the  $s$ -like region of ST-12 (4, 2/5, 1) is a band representing the As atoms in chains of order one. In the  $s$ -like region for the 2H-4 (2/2) and BC-8 (2, 2/2, 2) substructures we only get two peaks. This is due to the As atoms clustering into chains of order two as we saw in the tight-binding

case. The similarities between shape and energy splitting of these two peaks for the 2H-4 (2/2) and BC-8 (2, 2/2, 2) substructures show that the  $s$ -like region is relatively insensitive to the topological variations of the atomic chainlike configurations. We also notice that the higher-energy  $s$ -like peak for both substructures lies very close in energy to the  $s$ -like peak for the As atoms in chains of order one (Fig. 1). Finally in the 4H-8 (2, 1, 1/2, 1, 1) substructure which contains both As-atom chains of order one and order two we can again see, directly, the overlap between the antibonding like state (weight one) of the As-atom chain of order two and the band (weight two) of As atoms in chains of order one. Furthermore the splitting between bonding like and antibonding like states for the As-atoms in chains of order two is very nearly the same as that for the 2H-4 (2/2) and BC-8 (2, 2/2, 2) substructures. Therefore the size of this splitting, which also happens to be the smallest possible broadening of the  $s$ -like region under disorder ( $L$ ), is also unaffected by the percentage of like-atom bonds present in the substructure. Using the charge-density model<sup>15</sup> we estimated a minimum width of about 3 eV in the amorphous case. This is not too far from the results of the present calculations.

If we were not to assume that the amorphous

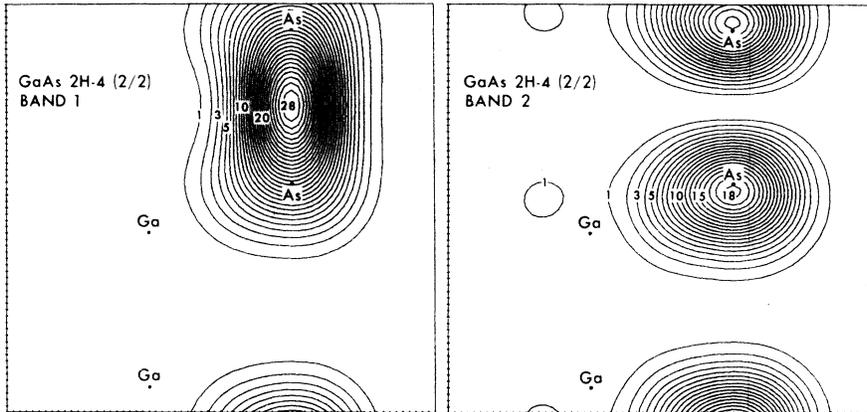


FIG. 4. GaAs 2H-4 (2/2) charge density in the (110) plane for bands 1 and 2.

phase with disorder (L) would tend to favor like atoms clustering in chains of order no larger than two, then we could estimate the percentage of like-atom bonds in principle by measuring the strength of the two  $s$ -like peaks. The fraction of like-atom bonds would then be given by  $1/2(1+H/L)$ , where  $H/L$  is the fraction of strength of the higher- and lower-energy peaks in the  $s$ -like region. Generally speaking however the effects of disorder (U) are a broadening of the  $s$ -like region and a shift of the center of mass of this region to lower energies. In addition the width of this region depends primarily on the types of chain present and not on the percentage of like-atom bonds or the particular topological configuration of these chains.

Let us now examine the  $p$ -like regions for these substructures. The  $p$ -like regions are bounded from below approximately by the dashed lines at about  $-5$  eV. These regions are further approximately subdivided into sections (I, II, and III) representing particular types of bonding characteristics. A comparison of the  $p$ -like region for ST-12 (4, 2/5, 1) using the EPM and the tight-binding model suggests that the lower-energy region of the

$p$ -like states (region I) should presumably represent As-As bonding states while the high-energy region (III) should characterize Ga-Ga bonding states. The middle  $p$ -like region (II) represents the  $\delta$ -function peak whose nature remains unaffected to first order by effects of disorder (L). This middle  $p$ -like region then retains the character of the  $p$ -like region without disorder and represents the Ga-As bonding states. Similar classifications can be made with the  $p$ -like regions of the other three substructures in this figure. A comparison of the middle  $p$ -like regions for the BC-8 (2, 2/2, 2) and 2H-4 (2/2) substructures reveals that the shape of this region is rather sensitive to the topological properties of the structure. The difference in strength of the two peaks in the middle  $p$ -like region for the 2H-4 (2/2) case is most likely caused by the fact that the lower-energy  $p$ -like region for 2H-4 (1, 1/1, 1) contains states that mostly describe diagonal unlike-atom bonds, while the higher-energy region represents mostly vertical (along  $\hat{z}$  direction) unlike-atom bonds. Therefore, since the 2H-4 (2/2) structure has only diagonal unlike-atom bonds, this anisotropy in the strength of

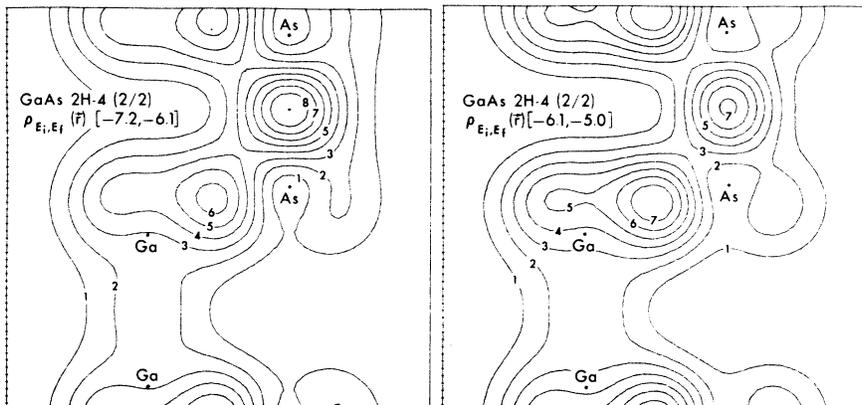


FIG. 5. GaAs 2H-4 (2/2) charge density in the (110) plane for the regions of the density of states in the energy intervals  $[-7.2$  eV,  $-6.1$  eV] and  $[-6.1$  eV,  $-5.0$  eV] designated by arrows in Fig. 4(c).

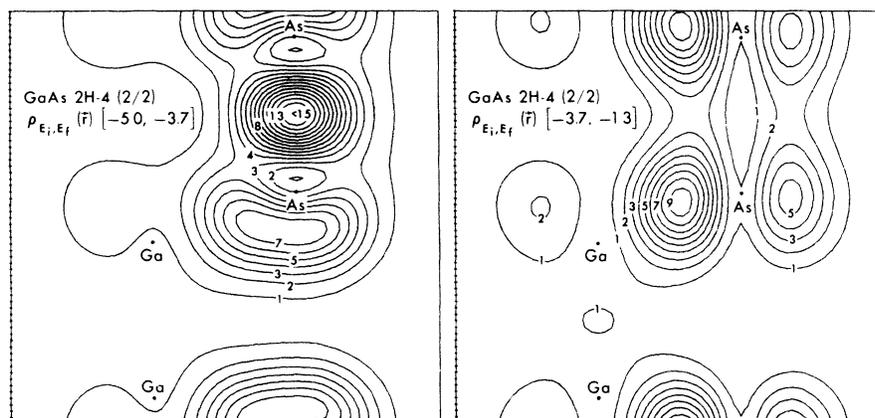


FIG. 6. GaAs 2H-4 (2/2) charge density in the (110) plane for the regions of the density of states in the energy (eV) intervals  $[-5.0, -3.7]$  and  $[-3.7, -1.3]$  designated by arrows in Fig. 4(c).

these two peaks is understandable. In an amorphous structure however we would not expect this type of anisotropy, so that the middle  $p$ -like region should look more like the one in the BC-8 (2, 2/2, 2) substructure. The effects on the  $p$ -like region obtained by reducing the percentage of like-atom bonds while retaining similar types of like-atom clustering configurations can be seen from Fig. 3(d). The  $p$ -like region for the 4H-8 (2, 1, 1/2, 1, 1) substructure is just slightly broader than the BC-8 (2, 2/2, 2) and 2H-4 (2/2) substructures. In addition the most important change seems to be just a reduction in strength of the As-As and Ga-Ga bonding-state regions.

Finally, all that we can say about the middle-peak regions for these four substructures is that we obtain an over-all broadening in each case as compared with the middle-peak region for 2H-4 (1, 1/1, 1). As for the conduction bands we notice that we get a shift to lower energies when compared to the bottom of the conduction bands for the corresponding substructures without like-atom bonds. In fact the states at the bottom of the conduction

band under disorder (L) are most probably As-As antibondinglike states in addition to being plane-wave-like. This is due to the fact that the low-lying conduction states should be orthogonal to the top of the valence band and  $s$  like. At the same time the deeper As-As potential would have a stronger influence on these states and would try to bring them down to a lower energy. However the effects of shifting of the conduction band and broadening of the  $p$ -like region due to like-atom bonds have some very serious consequences.

We have found that all our EPM calculations related to disorder (L) yield semimetals. Experimentally<sup>16</sup> a large decrease in the gap has been found for amorphous III-V compounds and our results are consistent with Connell's<sup>16</sup> suggestion that this decrease might be caused by like-atom bonds. Before we go into this in any more detail, however, let us first look at some charge-density calculations which will verify the suggestions we have been making regarding the character of various regions of the density of states and will give us some idea of the nature of the like-atom bond.

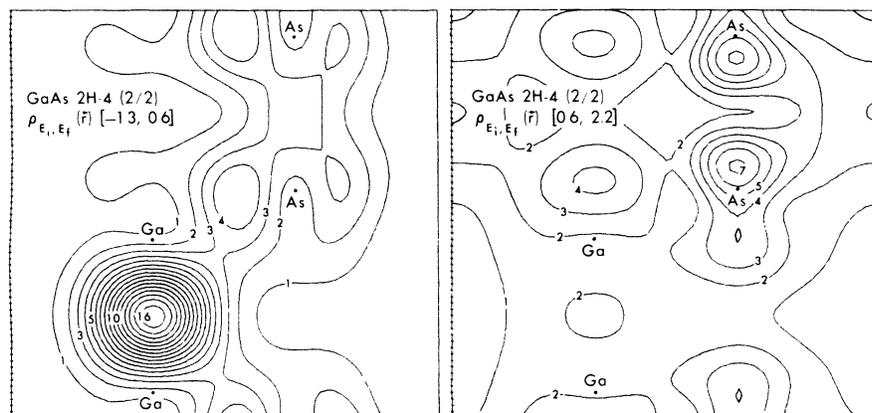


FIG. 7. GaAs 2H-4 (2/2) charge density in the (110) plane for the regions of the density of states in the energy (eV) intervals  $[-1.3, 0.6]$  and  $[0.6, 2.2]$  designated by arrows in Fig. 4(c).

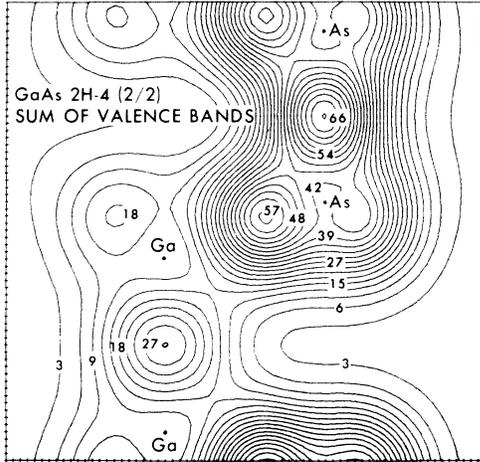


FIG. 8. GaAs 2H-4 (2/2) total charge density in the (110) plane.

### C. Charge densities

As a simple and typical example of what happens to the electrons in a structure with like- and unlike-atom bonds we calculate charge densities in the 2H-4 (2/2) substructure. Information about the distribution of electrons in various regions of the density of states can be obtained from band charge densities  $\rho_n(\vec{r})$  where appropriate and from integrated "energy" charge densities  $\rho_{E_f, E_i}(\vec{r})$  for energies in the intervals  $[E_i, E_f]$ . These charge densities are plotted in terms of contours for the (110) plane of the 2H-4 structure in Figs. 4-7. In Fig. 4 we show the results of  $\rho_n(\vec{r})$  for bands 1 and 2, which represent the s-like region of the density of states. The bonding and antibonding nature of the As s-like states is clearly evident. In Figs. 5-7 we show our calculations for  $\rho_{E_f, E_i}(\vec{r})$  for the intervals (in eV)  $[-7.2, -6.1]$ ,  $[-6.1, -5.0]$ ,  $[-5.0, -3.7]$ ,  $[-3.7, -1.3]$ ,  $[-1.3, 0.6]$ , and  $[0.6, 2.2]$ . These intervals are labeled with arrows and are shown in Fig. 3(c). In Fig. 5 we show the charge density for the middle-peak region which can be approximated by the intervals  $[-7.2, -6.1]$  and  $[-6.1, -5.0]$ . The electronic distributions are very similar for these two regions. The charge is spread out with slightly more charge in the As-As and Ga-As bonds than in the Ga-Ga bond. In Fig. 6 we show the charge density for the interval  $[-5.0, -3.7]$ , which is essentially the lower-energy p-like region. As we see, the electrons are concentrated primarily in the As-As bonds with a small concentration in the Ga-As bonds and a negligible distribution in the Ga-Ga bonds. This region then certainly represents As-As bonding states. In this figure we also show  $\rho_{E_f, E_i}(\vec{r})$  for the interval  $[-3.7, -1.3]$  which represents approxi-

mately the middle p-like region. Now the electrons are almost entirely concentrated in the Ga-As bonds. The contours to the left of the Ga atoms and to the right of the As atoms represent cross-sectional slices of the other diagonal bonds which are not shown in this plane. This region then represents the Ga-As bonding states. In Fig. 7 we show the electronic distribution in the interval  $[-1.3, 0.6]$  which approximates the high-energy region of the p-like states. As we see, the electrons are now concentrated primarily around the Ga-Ga bond so that this region represents the Ga-Ga bonding states. In this figure we also show the hypothetical situation where the conduction-band region  $[0.6, 2.2]$  is filled with electrons. The electrons are now very plane-wave-like but at the same time show a distinct antibonding s-like distribution around the As atoms. Finally, in Fig. 8 we show the charge density obtained by summing over all the filled bands. We notice that we obtain definite bonding character for all the bonds. The strengths of the Ga-As bonds are very close to their strengths in the zinc-blende case. The As-As bonds have a lot of bonding charge which is also quite localized. On the other hand the Ga-Ga bonds are rather weak and less localized.

Let us now return to the question of the gap in the density of states. What we must ask is whether we shall always get a semimetal under disorder (L). From the charge-density calculations we have definite proof that the top of the valence band represents Ga-Ga bondinglike states. In addition the bottom of the conduction band has some antibonding As s-like character. Therefore we would expect a shift in energy of these regions depending on the nearest-neighbor distances of the Ga-Ga and As-As bonds. In our calculations of the 2H-4 and 4H-8 substructures we have always taken the ideal situation where the Ga-Ga nearest-neighbor distance is equal to that of the As-As nearest-neighbor distance, which is in turn equal to the ideal Ga-As nearest-neighbor distance. Since the top of the valence band has much more charge around the Ga atoms than the conduction band has around the As atoms we would expect a larger sensitivity of the gap to changes in Ga-Ga bonding distances. Hopefully by increasing the gap we would also be making the Ga-Ga bonding states more bondinglike in character and more concentrated in the bonds rather than what we obtain in Fig. 7. We find that in the 2H-4 (2/2) substructure the gap increases by about 0.08 eV for every 1% reduction in the Ga-Ga bonding distance. Furthermore this gap increases by only 0.01 eV for every 1% increase in As-As bonding distance. In Fig. 9 we show our results for the density of states of 2H-4 (2/2) with a 10% decrease in the Ga-Ga nearest-neighbor distance and a 3% increase in the As-As bonding

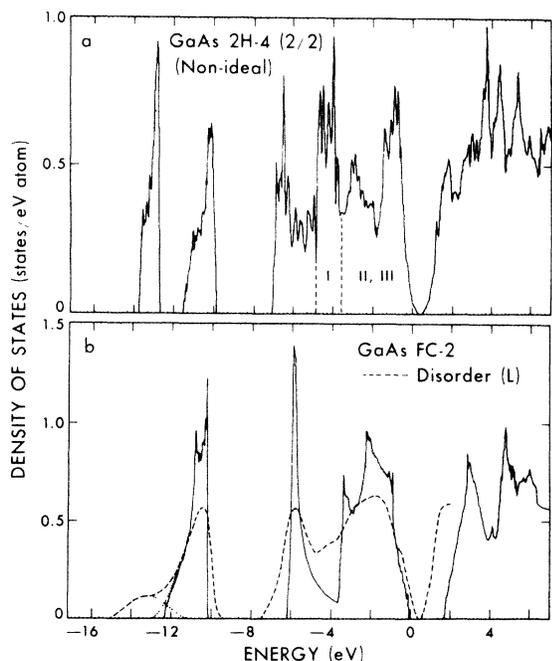


FIG. 9. Density of states of GaAs in the (a) modified  $2H-4$  ( $2/2$ ) and (b) FC-2 structures using the EPM. The modified  $2H-4$  structure was obtained from the ideal  $2H-4$  structure by taking a 10% decrease in Ga-Ga bonding distances and a 3% increase in the As-As bonding distances. This resulted in a merging of regions II and III and the formation of a nonzero energy gap. The dashed curve in (b) represents the consequences of disorder (L) for a III-V compound with 10% like-atom bonds taking GaAs as a prototype as discussed in the text. The dotted line distinguished between the low- and high-energy  $s$ -like peaks.

distance. In this structure we obtain a 0.1-eV gap and at the same time we have the same bulk density as before and negligible changes in the bond angles and Ga-As bonding distances. This result for the gap is very encouraging and we would expect to get similar effects by changing the cation-cation and anion-anion distances in the other structures. The important point to remember is that given a particular configuration of like-atom bonds with particular potentials the cation-cation and anion-anion nearest-neighbor distances would be very important in determining whether a gap could exist. In this structure we also obtain a small shift in the  $s$ -like region due to the decrease in As-As bonding distances. This shift corresponds to about a 0.1-eV change for a 1% change in As-As nearest-neighbor distance.

#### D. Model for disorder (L)

We now have enough knowledge about how disorder (L) affects various regions of the density of states that we could make some definite statements

as to what would be observed in a random-network model with like-atom bonds. We begin by assuming a 10% presence of like-atom bonds, which as Shevchik and Paul<sup>14</sup> have shown would contribute very slightly to the heat of crystallization of the amorphous phase. From stability considerations we would expect the clustering configurations of like atoms to be in the form of chains or rings. However we must also assume the presence of only low-order (one, two, or three) chains of like-atoms since these will affect the possibility of obtaining a nonzero energy gap as is observed experimentally.<sup>16</sup> As we have already seen in Fig. 3(a), fourfold chains of atoms would make a rather large overlap between the Ga-Ga bonding-like states and the conduction band. Thus, without a restriction for low-order chains we would need rather large unrealistic changes in the Ga-Ga bonding distances in order to get a nonzero gap. In this model, with only low-order chains, we simply assume a 10% decrease in Ga-Ga nearest-neighbor distances and a 3% increase in As-As nearest-neighbor distances. This way we would expect to get a nonzero gap as in  $2H-4$  ( $2/2$ ), Fig. 9(a). We should notice also that these changes in nearest-neighbor distances for 5% cation-cation and 5% anion-anion bonds are compatible with some of the RDF's of Shevchik and Paul<sup>14</sup> (e.g., GaP) just in case these RDF's represent systems with disorder (L).

Therefore, based on all these considerations our model for the density of states of an amorphous III-V compound with disorder (L) taking GaAs as a prototype would have the form shown in Fig. 9(b). For comparison we also show the density of states of GaAs in the zinc-blende structure as the solid curve. Let us first concentrate on the  $s$ -like region. As we mentioned earlier there should be a shift in the center of mass of the  $s$ -like states to a lower energy. Along with this is the fact that the highest-energy states of a particular chain tend to overlap with the states of chains of order one. This suggests that we may divide the  $s$ -like region into two main peaks. The first peak is what we may call the lower-energy  $s$ -like peak and would contain all the states except the highest-energy states of all the As like-atom chains of order greater than one. The second peak, which we may call the higher-energy  $s$ -like peak, would contain only the highest-energy states of all the As like-atom chains and would be located around the energy of the states for As chains of order one. By making these simplifications the fraction of like-atom bonds is again given by  $1/2(1+H/L)$ , where  $H$  and  $L$  are the strengths of the higher and lower  $s$ -like peaks, respectively. In addition, as we have already seen the splitting between the higher- and lower-energy peaks will be around 3 eV. Thus for 10% like-atom bonds  $H/L \sim 4$  and we get an  $s$ -

like region as shown in Fig. 9(b). In principle therefore an unfolding of the *s*-like region into two peaks should give us some idea of the fraction of like-atom bonds which are present in an amorphous sample.

In the middle-peak region our calculations can only suggest a general over-all broadening. In particular our results imply an increase in broadening in the amorphous case by about 0.6 eV. In the *p*-like region we should have a shoulder in the lower-energy region representing the As-As bonding states. This should look something like the one in the BC-8 (2, 2/2, 2) substructure but with less strength. In addition we should have a middle *p*-like region which represents Ga-As bonding-like states and is therefore the only part of the density of states whose character is retained under disorder. Its shape is however sensitive to topological disorder so it should look mostly like the middle *p*-like regions in the BC-8 (2, 2/2, 2) or ST-12 (4, 2/5, 1) substructures. Finally the higher-energy *p*-like region representing the Ga-Ga bonding-like states will tend to overlap with the middle *p*-like region in order to obtain a nonzero gap as in Fig. 9(a). From these considerations we propose a *p*-like region as shown in Fig. 9(b) which should be about 5 eV wide. For the bottom of the conduction band we should have a small shift to lower energies as we have observed in all the substructures with like-atom bonds. For our choice of like-atom nearest-neighbor distances in this model, we should have band edges at energies which are similar to those for 2H-4 (2/2) in Fig. 9(a). As we have already seen in Sec. III the effects of disorder (U) on the size of the gap seem to be rather small. In addition the similarity in the overlap of the conduction and valence bands for the 2H-4 (2/2) and BC-8 (2, 2/2, 2) structures suggests that the most important influence on the gap is just the presence of like-atom bonds with or without disorder. Unfortunately, however, although the size of the gap is very sensitive to the cation-cation bonding distances it cannot be used alone as a measure of this bonding distance. This is because the contributions from the anion-anion bonds, even though they are weaker, are not negligible. Nevertheless a measure of the energy between the *s*-like high- and low-energy peaks, together with the size of the gap, may be able to provide some information about both the cation-cation and anion-anion nearest-neighbor distances.

## V. SUMMARY AND CONCLUSIONS

In this paper we have primarily been interested in the structural nature of the amorphous III-V phase. From an experimental point of view the information obtained from optical properties<sup>17</sup> and RDF's<sup>14</sup> is not very sensitive to the microscopic

structural aspects of the amorphous phase. Neither of these experiments, for example, is able to give precise information as to what type of disorder is present in any given III-V sample. In the former case one would need a theoretical model that would have to agree very closely with the experimental optical data in order to get any believable information about the disorder present. And in the latter case the RDF is unfortunately not a sufficient condition for any structure. For example, random-network models (RNM) have been able to fit experimental RDF's rather well. In all these RNM's however we find fivefold and sevenfold rings of bonds. It is quite conceivable, nevertheless, and indeed probable that one could make an RNM with only even-numbered rings of bonds, that would also fit the experimental RDF's. This would then have important consequences related to the type of disorder that would be present in the amorphous phase.

All this suggests that the aforementioned experimental data would in some cases still be consistent with two distinct types of disorder which could exist in an amorphous III-V compound. The first type of disorder, which can be called disorder (U), describes a stoichiometric disordered system of atoms in fourfold coordination with only unlike-atom bonds. In addition we have variations in the bond lengths and angles while keeping all bonds satisfied. The second type of disorder is referred to as disorder (L) and encompasses all the properties of disorder (U) along with the presence of like-atom bonds.

In order to be able to distinguish between these two types of disorder we chose to study their effects on the electronic density of states, which would be quite sensitive to the microscopic structural nature of the amorphous phase. In order to study these effects we have used the concept of a short-range disorder model<sup>5</sup> and we have been particularly interested in the effects caused by the following structural features: (i) topological variations of atoms, (ii) variations in bond lengths and angles, (iii) percentage of like-atom bonds, (iv) clustering configurations of like-atoms, and (v) topological variations of clustering configurations.

Our results for disorder (U) and disorder (L) are shown in Figs. 1(a) and 9(b). For disorder (U) we find that the *s*-like region of the density of states is rather insensitive to the topological arrangement of the atoms. This, however, is not true for the *p*-like region, whose shape is quite sensitive to the local environment of each atom. Furthermore the *s*-like region is influenced by the second-nearest-neighbor distances which are affected by variations in the bond lengths and bond angles. The *p*-like states are also probably affected by deviations in the bond angles which might cause a steepening of the band edge as in the case of amorphous Ge.<sup>5</sup>

The middle-peak region of the density of states seems also to shift slightly to higher energies with the inclusion of disorder. This is perhaps due to the relatively delocalized nature of these states. This region, however, is not at the present clearly understood. Finally, the energy gap does not seem to be very sensitive to the topological properties of the system and is affected only slightly by nearest-neighbor distances. All in all, the effects of disorder (U) on the density of states are rather small.

With disorder (L), however, we obtain some very interesting effects. Our results show that the *s*-like region of the density of states is very sensitive to the types of clustering configurations the like atoms can form. From energy considerations we have preferred clustering configurations in which any given atom does not have more than two like-atom nearest neighbors. This implies that the like atoms can cluster into various configurations of chains. We find that we obtain *N* peaks in the *s*-like region from each group of chains of order *N*. In addition the position in energy of these peaks is not very sensitive to the different topological arrangements of these chains. The center of mass of each set of *N* peaks is shifted to lower energies by an amount approximately equal to the interaction between atoms in a chain. This is similar to the shift observed in the electronic energy of a hydrogen molecule-ion. The effect of this shift is to make the highest-energy peaks of each cluster to chains of order *N* overlap and form one large peak around the energy of the peak for chains of order one. Similarly (particularly true in the case of low-order chains) the rest of the peaks will also tend to overlap into one peak at about 3 eV lower than the first one. The splitting of these two main peaks is found to be insensitive to the percentage of like-atom bonds present. However we have found that the fraction *f* of like-atom bonds can be correlated in a simple and approximate way to strength *L* and *H* of these low-energy and high-energy *s*-like peaks, respectively, by the expression  $f = 1/2(1 + H/L)$ . In Fig. 9(b) we have assumed the presence of 10% like-atom bonds and so  $H/L \sim 4$ .

The *p*-like region of the density of states is also very sensitive to the clustering configurations of the like atoms and broadens into three main re-

gions (I, II, and III) which we call the low-, middle-, and high-energy *p*-like regions. The low and high *p*-like regions represent anion-anion and cation-cation bonding states, respectively. On the other hand, the middle *p*-like region represents cation-anion bonding states and is therefore the only region of the density of states that retains its character under disorder (L). In addition the shape of this region is quite sensitive to the topological arrangement of the atoms. The main effect of the percentage of like-atom bonds on the *p*-like region seems to be just a variation in the strengths of the peaks in these three regions. The width of the *p*-like region is however sensitive to the order of the like-atom chains and to the cation-cation and anion-anion bonding distances. We have found that in order to get a finite energy gap we would need a structure with only low-order chains of atoms ( $\lesssim 4$ ) and cation-cation and anion-anion bonding distances which are smaller and larger, respectively, than the ideal cation-anion bonding distance.

Finally, we should mention that although we used GaAs to study disorder (U) and disorder (L) we would have obtained similar results from any other III-V compound. This is not to say, however, that all the III-V compounds are equally likely to exist in the amorphous phase with disorder (U) or disorder (L). In particular, in the case of disorder (L) we would expect to find only the compounds with the strongest bonding character. Now presumably the bonding charge calculated by Walter and Cohen<sup>13</sup> can be considered a measure of this bonding character. In that case their results would indicate, for example, that InSb and InP are more likely to be found with disorder (L) than GaAs. In any case, if amorphous samples are to be found with disorder (L), it would seem preferable to prepare them at low enough temperatures so that the diffusivity of the atoms is very small.

#### ACKNOWLEDGMENTS

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<sup>1</sup>The references here would be far too numerous to mention so we refer the reader to the following recent review articles: S. C. Moss and D. Adler, *Comments Solid State Phys.* **5B**, 47 (1973); D. Adler and S. C. Moss, *Comments Solid State Phys.* **5B**, 63 (1973).

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