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# Effects of Disorder on the Electronic Density of States of III-V Compounds*

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Abstract

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 stoichoimetric system with four fold 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 amorphous GaAs, for each type of disorder, which we believe would be consistent with the present experimental radial distribution 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.[1] 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) photo emission spectroscopy.[2-4] The differences observed between the crystalline and amorphous density of states spectra has proven to be valuable in probing the

the structural nature of amorphous Ge and Si.[5,6] In particular these calculations indicate that these differences are associated with the presence of five and seven fold 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 four-fold 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. In general if we let $N_{III-III}$, $N_{V-V}$, $N_{III}$ and $N_V$ be the total number of type III-III bonds, type V-V bonds, type III atoms and type V atoms respectively, then we have:

$$\frac{N_{III-III}}{2} + \frac{N_{III-V}}{4} = N_{III} \qquad (1)$$

$$\frac{N_{V-V}}{2} + \frac{N_{III-V}}{4} = N_V \qquad (2)$$

so that the difference in percentage of type III-III and type V-V bonds is equal to the difference in percentage of type III and type V atoms.

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 our knowledge there have been as yet no published experimental XPS or UPS spectra on amorphous III-V compounds.

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

(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.[5,6] 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 and the empirical pseudopotential method (EPM).[7] The tight binding scheme will be used to easily discern 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 these 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 section II we shall give a description of the crystal structures studied and the notation that we shall use describing their topological properties. In section III we shall discuss the methods of our calculations. In sections IV and V we shall present and discuss the results of our calculations for disorder (U) and disorder (L) respectively. Finally in section VI 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 strucrures 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 sub-groups depending upon the number of like-atom bonds for each atom.

This is of interest since it characterizes 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 atom nearest neighbors. The method used to investigate the total energy per atom of these structures is described in section III.

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

$$\left(N^1_{Ga}, N^2_{Ga}, \ldots N^M_{Ga} / N^1_{As}, N^2_{As}, \ldots N^L_{As}\right) \qquad (3)$$

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

$$\frac{\sum_{i=1}^{M} (N^i_{Ga}-1)}{2\sum_{i=1}^{M} N^i_{Ga}} = \frac{N_T-2M}{2N_T} \qquad (4)$$

where $N_T$ is the total number of atoms in the primitive cell.

Since we are dealing with stoichiometric structures an equivalent expression to equation (4) could be obtained by replacing $N^i_{Ga}$ by $N^i_{As}$. In equation (4) we are assuming finite chains of like-atom bonds. In the case of rings or infinite chains we can use equation (4) but we must replace $N^i_{Ga}-1$ by $N^i_{Ga}$, where $N^i_{Ga}$ would represent the number of like-atoms of the ith ring or infinite chain in the primitive cell. We could also make this explicit in the notation (3) by placing an R (ring) or I (infinite chain) after the number $N^i$. The number of atoms in the structure that have zero like-atom neighbors is just given by the total number of one-link chains (i.e. $N^i = 1$). The number of atoms that have one like-atom neighbor is given by twice the total number of finite chains of order greater than one. Finally the number of atoms in the structure with two like-atom neighbors is given by the total number of atoms in finite chains of order greater than two minus twice the number of finite chains of order greater than two plus the total number of atoms in rings or infinite chains.

As an example let us find what information we can obtain about two substructures of the ST-12 structure if they are designated by (5,1/4,2) and (3,3/4I,1,1) respectively. In the first structure we have two Ga atom chains of order five and order one and two As atom chains of order four and order two. In the second structure we have two Ga atom chains of order three, an infinite As atom chain with four

atoms in a primitive cell and two one As atom chains. The fraction of like-atom bonds in both structures is 1/3. In the first (second) structure there is one (two) atom(s) with zero like-atom nearest neighbors, six (four) atoms with one like-atom nearest neighbor and five (six) atoms with two like-atom nearest neighbors.

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 $(N^1_{Ga}\ldots N^M_{Ga}/N^1_{As}\ldots N^L_{As})$ 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 (see section III) 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 wurtzite-like 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 zincblende 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 (zincblende). 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) sub-structure 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[8] 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 A 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 zincblende structure. There are also two types of bond angles approximately equal to 118° and 100° respectively. An interesting feature of the BC-8 structure is that although it only has even numbered rings of bonds we <u>cannot</u> create any substructures with a total of zero like-atom bonds. 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 thirty two substructures. This group

can be divided further into two subgroups containing twenty four 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 neighbor 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 thirty two which is of the type (4/4). These two structures will be studied using the tighting 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 sixteen atoms. All the BC-8 substructures can therefore be obtained from the SC-16 structure. The purpose and usefulness of the SC-16 structures 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 described in section III. 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° to 119°.

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[8] structure is a simple tetragonal unit cell with twelve 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 A and c = 6.955 A 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 zincblende structure. The bond angles however range from 20% less 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.

(1) twenty four substructures with four atoms having two like-atom nearest neighbors and eight atoms with one like-atom nearest neighbor.

(2) forty eight 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.

(3) one hundred and forty four 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.

In the first subgroup the substructures are all of type (3,3/3,3) while in the second subgroup we can find substructures of types (5,1/5,1), (3,3/4I,1,1) and (4I,1,1/3,3). Finally in the third subgroup we find four types of substructures (5,1/3,3), (3,3/5,1), (4,2/5,1) and (5,1/4,2). We have chosen one distinct substructure from each of these eight types. 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. Calculations

In this section we shall describe the calculational methods used to study the various crystals mentioned in section II. In particular we shall discuss the EPM and the tight binding model used to calculate the band structures, the model used to calculate total energies, the relaxation process, and the charge density scheme.

Once the band structure is known the density of states can be obtained using the following expression:

$$N(E) = \frac{1}{NN_a} \sum_{\underset{\sim}{k}} \sum_{n} \delta(E - E_n(\underset{\sim}{k})) \qquad (5)$$

where $N_a$ is the number of atoms in the primitive cell, N is the number of primitive cells, n is the band index and N(E) is normalized to the number of states per atom. The method used to evaluate the integral in equation (5) is due to Gilat and Raubenheimer.[9] The energy derivatives required by this method were obtained using $\underset{\sim}{k}\cdot\underset{\sim}{p}$ perturbation theory.

### A. EPM

The Empirical Pseudopotential Method (EPM) has been discussed extensively in an article by Cohen and Heine.[7] The EPM essentially entails removing the large potential of the core along with the many oscillations of the wave functions in the core. The valence pseudowavefunction, $\psi_{\underset{\sim}{k}}(\underset{\sim}{r})$, is then in essence the true valence wavefunction minus the core states and satisfies the Schroedinger equation:

$$\left[\frac{p^2}{2m} + V(\underset{\sim}{r})\right] \psi_{\underset{\sim}{k}}(\underset{\sim}{r}) = E(\underset{\sim}{k})\psi_{\underset{\sim}{k}}(\underset{\sim}{r}) \qquad (6)$$

where $V(\underset{\sim}{r})$ is the pseudopotential and the $E(\underset{\sim}{k})$ are the eigenvalues of the real valence electron wavefunctions. The weak periodic pseudopotential $V(\underset{\sim}{r})$ can now be expanded in a small number of plane waves:

$$V(\underset{\sim}{r}) = \sum_{\underset{\sim}{G}} V(\underset{\sim}{G}) e^{i\underset{\sim}{G}\cdot\underset{\sim}{r}} \quad \text{for} \quad |\underset{\sim}{G}| \leq |\underset{\sim}{G}_o| \tag{7}$$

where $|\underset{\sim}{G}_o|$ represents some cutoff reciprocal lattice vector. In the case of two types of atoms $V(\underset{\sim}{G})$ can be written as:

$$V(\underset{\sim}{G}) = S^S(\underset{\sim}{G})V^S(\underset{\sim}{G}) + iS^A(\underset{\sim}{G})V^A(\underset{\sim}{G}) \tag{8}$$

where $S^S$ and $S^A$ are the symmetric and antisymmetric structure factors and $V^S$ and $V^A$ are the symmetric and antisymmetric form factors given by:

$$S^S(\underset{\sim}{G}) = \frac{1}{n} \sum_{\lambda} e^{-i\underset{\sim}{G}\cdot\underset{\sim}{\tau}_\lambda} \tag{9a}$$

$$S^A(\underset{\sim}{G}) = -\frac{i}{n} \sum_{\lambda} P_\lambda \, e^{-i\underset{\sim}{G}\cdot\underset{\sim}{\tau}_\lambda} \tag{9b}$$

$$V^S(\underset{\sim}{G}) = \frac{n}{\Omega} \int \frac{1}{2} \{v_1(\underset{\sim}{r})+v_2(\underset{\sim}{r})\} \, e^{-i\underset{\sim}{G}\cdot\underset{\sim}{r}} d^3\underset{\sim}{r} \tag{10a}$$

$$V^A(\underset{\sim}{G}) = \frac{n}{\Omega} \int \frac{1}{2} \{v_1(\underset{\sim}{r})-v_2(\underset{\sim}{r})\} \, e^{-i\underset{\sim}{G}\cdot\underset{\sim}{r}} d^3\underset{\sim}{r} \tag{10b}$$

where n is the number of atoms in the primitive cell of volume $\Omega$, $v_1(\underset{\sim}{r})$ and $v_2(\underset{\sim}{r})$ are atomic potentials, $\tau_\lambda$ is the position of the $\lambda$'th atom in the primitive cell and $P_\lambda$ is +1 or -1 if $\lambda$ denotes an atom of type 1 or type 2. Here we have assumed that the form factors are independent of energy, and, since the atomic potentials are taken to be

spherical, the form factors are functions of $|\underset{\sim}{G}|$ only. In zincblende structures Cohen and Bergstresser[10] used only three symmetric and three antisymmetric form factors to obtain a good agreement of calculated optical properties with experiment. Once one has a good set of form factors, the atomic potentials can be obtained in principle from Eqs. (10a) and (10b). If one now assumes that the atomic potentials do not change very much from one type of crystal structure to the next, the form factors can be used for a variety of crystalline structures. In this sense the EPM is extremely useful. The procedure[11] essentially involves obtaining a continuous $V^S(|\underset{\sim}{q}|)$ and $V^A(|\underset{\sim}{q}|)$ by a suitable interpolation scheme and reading off the $V^S(|\underset{\sim}{G}|)$ and $V^A(|\underset{\sim}{G}|)$ for the set of $\underset{\sim}{G}$ spanning the reciprocal lattice of the particular structure.

In our calculations we have interpolated the form factors obtained by Cohen and Bergstresser[10] for GaAs since in this reference $V^S$ was constrained to be the Ge potential. For other form factors[12] the qualitative features in the density of states are the same and we only get small shifts in the energies of the peaks.

For good convergence in the 2H-4 structure we used 50-60 plane waves as a basis set along with another 140 plane waves through a perturbation scheme developed by Löwdin.[13] We calculated $E(\underset{\sim}{k})$ in 1/24 of the Brilluoin zone (BZ) at 144 grid points. For the 4H-8 structure we used approximately 70 plane waves as a basis set with about

200 additional plane waves through perturbation theory. We diagonalized our Hamiltonian in 1/24 of the BZ at 144 grid points for the (2,1,1/2,1,1) structure and at 62 grid points for the (1,1,1,1/1,1,1,1) structure. In the case of BC-8 we used 60 plane waves as a basis and an additional 140 plane waves through the Löwdin scheme. We used 1/8 of the BZ with a grid of 154 points. For the ST-12 structure we used about 70 plane waves as a basis set and another 270 plane waves through perturbation theory. The Hamiltonian was diagonalized in 1/2 of the BZ at 192 grid points. Finally for SC-16 we used about 85 plane waves as a basis set along with approximately 235 more plane waves through the Löwdin scheme. The eigenvalues were obtained in 1/2 of the BZ at 256 grid points.

B. Tight Binding Model

In our tight binding calculations we have taken the model used recently by Weaire and Thorpe.[14] The Hamiltonian can be written as:

$$H = \pm V_o \sum_{i,\ell} |\phi_{i\ell}\rangle\langle\phi_{i\ell}| + V_1 \sum_{i,\ell\neq\ell'} |\phi_{i,\ell}\rangle\langle\phi_{i,\ell'}| + V_2 \sum_{i\neq i',\ell} |\phi_{i,\ell}\rangle\langle\phi_{i',\ell}| \qquad (11)$$

where the $|\phi_{i\ell}\rangle$ represent localized orthonormal basis functions which can be taken as ($SP^3$) hybridized directed orbitals (four to each atom). The subscripts i and $\ell$ label a particular atom and the orbitals of that atom respectively. The first

term in this Hamiltonian is a diagonal term which is taken to be $+V_o$ or $-V_o$ depending on whether the states are associated with group V atoms or group III atoms. The second term represents an interaction $V_1$ between different basis functions on the same atom and the last term is an interaction $V_2$ between basis functions along the same bond. We have thus ignored the differences in the interactions of basis functions on different atoms and along the different types of bonds and we have assumed equal bond lengths and an ideal tetrahedral arrangement of atoms. We used $V_o = 3.2$ eV, $V_1 = -2.7$ eV and $V_2 = -6.1$ eV which are the same values as those used by Weaire and Thorpe for their calculation of GaAs in the zincblende structure.[14]

The most prominent features of this tight binding model are an inadequate conduction band because of the limited number of basis functions, a relatively good description of the s-like states, and for the case of structures with all or no bonds that are like-atom bonds, a delta function peak in the density of states at the top of the valence band. This peak contains pure p-like bonding states with a degeneracy of one state per atom. This is interesting because it says that to first order with nearest neighbor interactions which are independent of the dihedral angle the p-like states are not disturbed by topological differences. This is a fact that is supported to some degree by experiment.[4] However if we introduce the possibility of having like and unlike-atom bonds in our structures it is no longer true that the delta

function will contain one state per atom. It would therefore be of interest to obtain an expression for the degeneracy of the delta function depending upon the type of like and unlike-atom bond configurations that exist in a particular structure. One thing this will give us is an idea of how much of the density of states of zincblende is preserved under disorder (L).

Consider first the case where we have only one type of bond in the structure, then there are three p-like functions that can be formed on each atom from the four hybrids. Therefore there are 3N pure p-like functions that can be formed in a system of N atoms. However there is one constraint per bond if we wish to make pure p-like bonding or antibonding states. Thus as Weaire and Thorpe[15] have shown there are 2N independent constraints and therefore 3N-2N = N degenerate pure p-like bonding (or anti bonding) crystalline states. These states are then responsible for the delta function peak with one state per atom. In the case of a structure with both like-atom and unlike-atom bonds we must be a bit more careful. We must now distinguish the p-like functions among bonds of type III-III, V-V and III-V. That is, we are interested in the p-like functions of a certain type (i.e. III-III, V-V or III-V) which can be made from the hybrids along bonds of that type. The number of such functions that can be made on a certain atom given the configuration of nearest neighbor atoms is shown in Table I. Therefore, given a structure with a particular

distribution or arrangement of atoms, we can use Table I to find the total number of p-like functions of a particular type. Once this is known the total number of bonding (or antibonding) p-like states of a certain type that can be made is just given by this number minus the total number of constraints for bonds of that type. But the number of constraints of a particular type is just equal to the number of bonds of that type. Therefore the degeneracy of the delta function $D^X$ representing bonding (or antibonding) p-like states of type X (where X represents the three distinct combinations of III and V) is given by:

$$D^X = 3N_4{}^X + 2N_3{}^X + N_2{}^X - N_B{}^X \tag{12}$$

Here $N_I{}^X$ represents the number of atoms with I bonds of type X, and $N_B{}^X$ is the total number of bonds of type X. If we now express $N_B{}^X$ in terms of the $N_I{}^X$ we get:

$$D^X = N_4{}^X + \frac{1}{2} N_3{}^X - \frac{1}{2} N_1{}^X \tag{13}$$

This expression is quite useful since it tells us immediately that for the structures we are studying there will be no delta function in the density of states representing like-atom (L) bonding states. This is because we chose our structures to have $N_4{}^L$ and $N_3{}^L$ equal to zero due to stability requirements. This suggests therefore that in the amorphous case the like-atom bonding state regions in the density of states will be quite sensitive to different types of clustering configurations. On the other hand equation (13)

also tells us that in the structures we are studying we will definitely have a delta function peak in the density of states representing unlike-atom (U) bonding states as in the case of zincblende whose degeneracy will be given by $D^U = N_4{}^U + \frac{1}{2} N_3{}^U$. One might thus suggest that there will be a region of the p-like states in the density of states of zincblende whose character will be relatively unaffected by disorder. In other words the nature of the unlike-atom bonding states in the amorphous density of states should be very nearly the same as that of the zincblende p-like states. We shall examine this again in Section V.

C. Stability and Relaxation

In the process of selecting and studying various distinct substructures from substructures with similar like-atom bond clustering configurations it was useful to use stability as a final criterion. To calculate the energy U of a particular configuration of atoms which has both ionic and covalent character we must have a short range contribution and a coulomb contribution. For the short range energy we take a repulsive term due to the interaction between the ionic cores and an attractive term to take account of the covalent bonding nature of the atoms. With a small extension of the work of Keating[16] and Martin[17] he can get the following approximate but simple expression for U when expressed relative to the cohesive energy of the zincblende structure.

$$V = \frac{1}{2} \sum_{s=1}^{n} \sum_{i=1}^{4} f_{s,i} \Delta r_{s,i} + \frac{3}{16} \sum_{s=1}^{n} \sum_{i=1}^{4} \alpha_{s,i} \frac{[\Delta(\underset{\sim}{r}_{s,i} \cdot \underset{\sim}{r}_{s,i})]^2}{(r^o_{s,i})^2}$$

$$+ \frac{3}{8} \sum_{s=1}^{n} \sum_{\substack{i,j \\ j>i}} \beta_{s,i,j} \frac{[\Delta(\underset{\sim}{r}_{s,i} \cdot \underset{\sim}{r}_{s,j})]^2}{(r^o_{s,i} r^o_{s,j})} + \frac{1}{2} \sum_{s=1}^{n} \frac{(e^*)^2}{\varepsilon r_o} (\alpha_s{}^M - \alpha_{ZB}{}^M) \tag{14}$$

Here U is the energy per primitive cell. The sum over s is over atoms in the primitive cell, the sums over i and j are over the bonds i and j of a particular atom s, $f_{s,i}$ is a parameter describing the linear term of the repulsive ion core potential, $\alpha_{s,i}$ and $\beta_{s,i,j}$ are essentially bond stretching and bond bending force constants respectively, and $r^o_{s,i}$ is one of the three equilibrium nearest neighbor bond lengths (since we can have like and unlike atom bonds). For the coulomb part of the energy we assume rigid point ions with charges $\pm e^*$ which are the effective charges on the atoms which interact via a screened coulomb potential with the electronic dielectric constant $\varepsilon$, $\alpha_s{}^M$ is the Madelung constant of a particular atom s; $\alpha_{ZB}{}^M$ is the Madelung constant of the zincblende structure and $r_o$ is the equilibrium nearest neighbor distance for atoms in the zincblende structure. For simplicity we take all the $\alpha_{s,i} = \alpha$ and all the $\beta_{s,i,j} = \beta$ and we also assume that the $f_{s,i} = f$. The condition that the zincblende structure be in equilibrium requires $f = -\frac{1}{4} \alpha_{ZB}{}^M (e^*)^2/\varepsilon r_o{}^2$ and we can take $e^*$ to be the dynamic effective charge. Then we have from Martin[17] for GaAs in the zincblende structure: $\alpha = 41.2 \times 10^3$ dyn/cm,

$\rho = 8.95 \times 10^3$ dyn/cm, $r_o = 2.44$ A and $(e^*)^2/\varepsilon = 0.441\ e^2$ which, along with the $r^o_{s,i}$ equal to twice Paulings covalent radii for Ga and As, are the values we assumed for the parameters used in Eq. (13) to study our various GaAs structures.

Equation (13) works fairly well in comparing the differences in cohesive energy of various substructures of the same basic structure. In particular the most important term in Eq. (13) for structures with like-atom bonds is the coulomb term. For example the Madelung energy per primitive cell of the ST-12 substructures which have 33-1/3% like-atom bonds can vary by more than 10 eV. In addition the largest Madelung energy of these ST-12 substructures is only 20% smaller than the Madelung energy of GaAs in the zincblende structure. On the other hand with our approximations the short range energy term will vary only by about 0.1 eV and if we take the $\beta_{s,i,j}$ and the $\alpha_{i,j}$ not all equal respectively we would expect a variation by not more than 1 eV.

We selected one substructure to study with the tight binding model from each set of substructures with similar like-atom clustering configurations. The selection of one substructure out of a particular set was carried out in two simple steps. First we found the particular atom A in the primitive cell with the <u>least</u> binding energy for each substructure in the set. Secondly we picked the substructure with the <u>largest</u> binding energy for the atom A as our choice for that particular set.

We chose one substructure from each of the five basic structures to study with the EPM. The selection was carried out in a similar fashion as we just described above. In addition we allowed the energies of these substructures to relax to a local minimum. The procedure was similar to that used by Henderson and Ortenburger[18] and consisted of moving each atom by a small random amount. If the energy was lowered the move was accepted, if not then it was rejected. This process was carried out about 2000 times until a local minimum in the cohesive energy was reached. The consequences of this relaxation were to lower slightly the energy of the substructure and to add a small randomness to the distribution of bond angles and bond lengths.

D. Charge Density Scheme

Charge density calculations are particularly useful in studying the nature of the like-atom bond. They can also give us information about the distribution of electrons in various regions of the density of states and therefore now like-atom bonds affect these various regions.

We can obtain a charge density $\rho(\underset{\sim}{r})$ using the wavefunctions $\psi_{n,\underset{\sim}{k}}(\underset{\sim}{r})$ that we get from our EPM calculations. Since the wavefunctions are known as a function of band index n or energy E we can postulate a "band" charge density $\rho_n(\underset{\sim}{r})$ or an average "energy" charge density $\rho_E(\underset{\sim}{r})$. In the former case we would have

$$\rho_n(\underset{\sim}{r}) = e \sum_{\underset{\sim}{k}} \psi^*_{n,\underset{\sim}{k}}(\underset{\sim}{r}) \cdot \psi_{n,\underset{\sim}{k}}(\underset{\sim}{r}) = \sum_{\underset{\sim}{k}} \rho_n(\underset{\sim}{k},\underset{\sim}{r}) \qquad (15)$$

and in the latter

$$\rho_E(\underset{\sim}{r}) = e \sum_n \sum_{\underset{\sim}{k}} \delta(E_n(\underset{\sim}{k})-E)|\psi_{n,\underset{\sim}{k}}(\underset{\sim}{r})|^2 = \sum_{\underset{\sim}{k}} \rho_E(\underset{\sim}{k},\underset{\sim}{r}) \qquad (16)$$

where the $E_n(\underset{\sim}{k})$ are the one electron valence energies. Therefore in principle in order to obtain $\rho_n(\underset{\sim}{r})$ or $\rho_E(\underset{\sim}{r})$ it is necessary to integrate $\rho_n(\underset{\sim}{k},\underset{\sim}{r})$ or $\rho_E(\underset{\sim}{k},\underset{\sim}{r})$ over the entire BZ. There is however a method to obtain $\rho(\underset{\sim}{r})$ without having to sum over all the $\underset{\sim}{k}$ points in the BZ. The idea here is to find just a few $\underset{\sim}{k}$ points whose charge density will give a good approximation to the total charge density. Baldereschi[19] first proposed this and obtained one representative $\underset{\sim}{k}$ point which gave an approximate total charge density for compounds in an FCC lattice. Chadi and Cohen[20] using wavefunctions expanded in terms of Wannier functions, obtained three representative $\underset{\sim}{k}$ points whose weighted sum of charge densities gives better agreement than the Baldereschi point. In addition Joannopoulos and Cohen[21] have presented a simple method of obtaining the same conditions for the $\underset{\sim}{k}$ points without using any wavefunctions and this method is valid for any periodic function of $\underset{\sim}{k}$. If we define $\hat{\rho}(\underset{\sim}{k},\underset{\sim}{r})$ in the following way:

$$\hat{\rho}(\underset{\sim}{k},\underset{\sim}{r}) = \sum_T \rho(T\underset{\sim}{k},\underset{\sim}{r}) \qquad (17)$$

where {T} represents the set of point operations for the lattice, then $\hat{\rho}(\underset{\sim}{k},\underset{\sim}{r})$ has the symmetry of the lattice in addition to being a periodic function of $\underset{\sim}{k}$. Fourier

transforming gives:

$$\hat{\rho}(\underset{\sim}{k},\underset{\sim}{r}) = \sum_{|\underset{\sim}{\ell}|} \hat{\rho}(|\underset{\sim}{\ell}|,\underset{\sim}{r}) \sum_{T} e^{i\underset{\sim}{k}\cdot T\underset{\sim}{\ell}} \tag{18}$$

$$\hat{\rho}(\underset{\sim}{k},\underset{\sim}{r}) = \sum_{|\underset{\sim}{\ell}|} \hat{\rho}(|\underset{\sim}{\ell}|,\underset{\sim}{r})\xi(\underset{\sim}{k},|\underset{\sim}{\ell}|) \tag{19}$$

where $\hat{\rho}(o,\underset{\sim}{r})$ is the total charge density in question. Now $\hat{\rho}(\underset{\sim}{k},\underset{\sim}{r})$ is a slowly varying function of $\underset{\sim}{k}$ so that we would expect the $\hat{\rho}(\underset{\sim}{\ell},\underset{\sim}{r})$ to decrease in magnitude as $|\underset{\sim}{\ell}|$ increases. The object then is to find a $\underset{\sim}{k}_o$ that will make as many of the $\xi(\underset{\sim}{k}_o,\underset{\sim}{\ell})$ equal to zero as possible for small $|\underset{\sim}{\ell}|$. For the case of more than one $\underset{\sim}{k}_o$ equation (19) becomes

$$\sum_i \alpha_i\hat{\rho}(\underset{\sim}{k}_i,\underset{\sim}{r}) = \sum_i \alpha_i\hat{\rho}(o,\underset{\sim}{r}) + \sum_{\ell} \hat{\rho}(\underset{\sim}{\ell},\underset{\sim}{r}) \sum_i \alpha_i\xi(\underset{\sim}{k}_i,\underset{\sim}{\ell}) \tag{20}$$

with $\sum_i \alpha_i = 1$ and with $\{\alpha_i\}$ and $\{\underset{\sim}{k}_i\}$ chosen in such a way as to make as many of the $\sum_i \alpha_i\xi(\underset{\sim}{k}_i,\underset{\sim}{\ell})$ equal to zero as possible up to some large $|\underset{\sim}{\ell}_{max}|$. Chadi and Cohen[22] have recently developed a scheme to generate a series of larger and larger special $\underset{\sim}{k}_i$ point sets along with weighting factors $\alpha_i$ which give $\sum_i \alpha_i\xi(\underset{\sim}{k}_i,\underset{\sim}{\ell}) = 0$ for all $|\underset{\sim}{\ell}|$'s up to larger and larger values of $|\underset{\sim}{\ell}_{max}|$ respectively.

Although a one or two point scheme works very well in obtaining the <u>total</u> charge density it is rather inadequate for calculating the $\rho_n(\underset{\sim}{r})$. On the other hand the Chadi and Cohen[22] ten (for FCC) or twelve (for 2H-4) point scheme is excellent for the <u>total</u> charge density and works very well

for the $\rho_n(\underset{\sim}{r})$. In our calculations we have taken the 2H-4 (2/2) structure as a simple typical example of a structure with like-atom bonds and we have used the Chadi and Cohen twelve point scheme to calculate $\rho_n(\underset{\sim}{r})$. In addition we have calculated $\rho_{E_f,E_i}(\underset{\sim}{r})$[23] which is defined by:

$$\rho_{E_f,E_i}(\underset{\sim}{r}) = \int_{E_i}^{E_f} \rho_E(\underset{\sim}{r})dE \qquad (21)$$

for various intervals $[E_i,E_f]$.

IV. 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

(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 zincblende 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.

The tight binding model is not very useful in studying these structures with disorder (U) since we could tell 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 Fig. 1(a)-(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[24] we know that the region of the density of states (Fig. 1) from about -10 eV 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 on the Ga atoms and in the bond. 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 eV 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 eV and -3.5 eV. What we are 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 stack randomly 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 steeping of the band edge by the introduction of states at the top of the valence band around 0.5 eV. This is caused by the derivations of the bond angles from the ideal tetrahedral angle which produce the same effects as in Ge. Secondly we notice that the p-like region also gets broadened. This is caused by the rather large distribution of first nearest neighbor distances in the SC-16 structure as we discussed in section 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.

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.[25] 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 dotted 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. Secondly we would probably get slight shift of the main peak in the middle-peak region to higher energies as in the case of SC-16. And 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[25] than in the SC-16 case.

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

## V. Results for Disorder (L)

In a recent communication[26] we described the gross 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

(v) topological variations in clustering configurations

The first two features were discussed in section IV and are overshadowed for the most part by features (iii) to (v). In what follows, we shall concentrate primarily on the effects of (iii) to (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 2H-4, 4H-8, BC-8, and ST-12 structures mentioned in section II.

In Fig. 2 (a)-(f) we show the densities of states for the 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) structures using the tight binding model. The valence band is mostly at negative energies 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 is obtained from Eq. (13) and the discussion in section II. For example for ST-12 (3,3/3,3) we have $N_4^U = 0$, $N_3^U = 8$, and $N_1^U = 0$ so that the degeneracy of the delta function is $D^U = 4$. The fraction of like-atom bonds for each structure is given by equation (4). 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%, 37-1/2%, 33-1/3% and 33-1/3% 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 Nth 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

chain-like behavior. Nevertheless they are sensitive to the Ga atom clustering configurations as can be seen by an examination of the wavefunctions in this region. Furthermore an examination of the wave functions in the p-like region can give us the nature of the bonding states in the low and high energy regions with respect to the delta function. However the fact that the lower and higher energy peaks in the p-like regions are actually mostly As-As and Ga-Ga bonding states respectively is very easily observed in Fig. 3 (a)-(c). Here we have plotted the density of states of ST-12 (5,1/3,3), ST-12 (4,2/5,1) and ST-12 (3,3/4I,1,1). These substructures all have 33-1/3% like-atom bonds but they are of particular interest since each structure has its Ga and As atoms in different types of clustering configurations. In the density of states for ST-12 (5,1/3,3) we notice three peaks in the s-like region which is consistent with the As atoms forming chains of order three. If we were now to make bonding states that were almost exclusively of As-As bonding character we would expect two peaks in the p-like region. This is exactly what is observed in the lower energy region of the p-like states. On the other hand at the high energy side of the delta function we can distinguish four peaks and this is consistent with Ga like-atom bonding states caused by the Ga-Ga bonds forming chains of order four. For the ST-12 (4,2/5,1) structure we notice that the s-like region has essentially five peaks with a small splitting of the middle

peak. This splitting is due to a difference in environment between the As atoms in the chains of order five and order one. In the p-like region we can have the Ga-like atom bonding states giving three or four peaks while the As-like atom bonding states should give four peaks. From Fig. 3 (b) we notice that both the lower and higher energy peaks are four and so it is rather difficult to distinguish visually the difference between the chains of bonds. Finally in the density of states for ST-12 (3,3/4I,1,1) we see the effects of an infinite (or for that matter, a very long) chain of As atoms. The s-like region has one slightly split peak near the middle which is caused by two chains of As atoms of order one. Superimposed on this is essentially the familiar one dimensional type of density of states which can be obtained by taking only nearest neighbor interactions in an infinite linear chain of atoms. The width of this s-like region is the largest broadening that we would expect to get from any of the other substructures. The effects of an infinite chain of As-As bonds is shown in the lower energy region of the p-like states. We notice that its width is large enough to mix in with the states in the middle peak 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. In Fig. 4 (a)-(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 33-1/3%, 25%, 25% and 12-1/2% 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. 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 six peaks also found in the tight binding case (Fig. 3(b)). However a comparison of the s-like region in Fig. 3(b) with that of Fig. 4(a) shows that the latter peaks using the EPM are not symmetrically situated around the s-like peak of As atoms in chains of order one. 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 shows that the s-like region is relatively insensitive to the topological variations of the atomic chain-like configurations. We also notice that the higher energy s-like peak for both substructures lies very closely 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[26] 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 now to assume that the amorphous phase with disorder (L) would tend to favor like-atoms clustering in chains or 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 2 direction) unlike-atom

bonds. Therefore since the 2H-4 (2/2) structure has only diagonal unlike-atom bonds this anisotropy in the strength of 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. 4(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 overall 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 antibonding like 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 be 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 has some very serious consequences.

We have found that all our EPM calculations related to disorder (L) yield semimetals. Experimentally[27] a large decrease in the gap has been found for amorphous III-V compounds and our results are consistent with Connell's[27] 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. This way we can explore further some of the speculations that we have been making regarding the character of various regions of the density of states and we can get some idea of the nature of the like-atom bond. As a simple and typical example we shall take the 2H-4 (2/2) substructure. Some information about the distribution of electrons in various regions of the density of states can be obtained from band charge densities $\rho_n(\underset{\sim}{r})$. Charge density contours for $\rho_n(\underset{\sim}{r})$ for bands 1 to 10 in the (110) plane of the 2H-4 structure are shown in Figures 5 to 9. In Fig. 5 we show the s-like region where the bonding and antibonding nature of the As s-like states is clearly evident. In Fig. 6 we have what is essentially the middle peak region. The electrons here are mostly spread out around the Ga and As atoms with electrons in the Ga-Ga, Ga-As and As-As bonds. In particular band 3 has more electrons in the As-As bond

and around the Ga atoms than band 4, while band 4 has more electrons in the Ga-As bond. In addition there seems to be slightly more change around the Ga atoms than the As atoms. In Fig. 7 we have the charge density for band 5 which should represent approximately the lower energy region of the p-like states. As we see the electrons are concentrated primarily on the As-As bonds with a small concentration in the Ga-As bonds and negligible distribution in the Ga-Ga bonds. In this same figure we show band 6 which is effectively the first half of the middle p-like region. Now the electrons are primarily concentrated in the Ga-As bonds with a small concentration in the As-As bonding region. Similarly band 7 in Fig. 8 which is essentially the other half of the middle p-like region has its electrons almost completely occupying the Ga-As bond. 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. In this same figure we show band 8 which approximately represents the states in the high energy region of the p-like states. As we see the electrons are now primarily concentrated around the Ga-Ga bond with negligible distributions around the As atoms. Finally in Fig. 9 we show the distribution of electrons in the hypothetical situation where the first two conduction bands are completely filled. The electrons are now very plane-wave like but at the same time are primarily concentrated on the As atoms in an

antibonding like configuration.

These charge densities confirm our earlier speculations about the distribution of electrons in certain regions of the density of states. Furthermore similar results can be obtained by examining an integrated "energy" charge density $\rho_{E_f,E_i}(\underset{\sim}{r})$ for various intervals $[E_i,E_f]$. In Figs. 10-12 we show our calculations of $\rho_{E_f,E_i}(\underset{\sim}{r})$ for the 2H-4 (2/2) substructure 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 shown in Fig. 4(c). The middle peak region can be also approximated by the intervals [-7.2,-6.1] and [-6.1,-5.0]. The charge density for these cases is shown in Fig. 10. We notice immediately that although the general appearance of the electronic distributions are the same as bands 3 and 4 there are some interesting differences. Unlike bands 3 and 4 the charge density in these two energy intervals are almost identical. In going from the low energy interval to the higher energy interval we observe a very slight increase in charge around the Ga-Ga and Ga-As bonds with a corresponding reduction in charge around the As-As bonds. Furthermore although the electronic distribution in band 3 is very similar to that of the low energy interval, the charge density of band 4 is quite different in that it lacks As-As bonding character.

This suggests that band 4 has a rather large overlap with the higher bands presumably in the Ga-As bonding region.

As we have already mentioned it is rather difficult to characterize the middle peak region but generally speaking the electrons are spread out around both types of atoms and in all three types of bonds. In Fig. 11 we show the charge density for the interval [-5.0,-3.7] which is essentially the lower energy p-like region. This electronic distribution represents the As-As bonding states and agrees well with the charge density of band 5. In this figure we also show $\rho_{E_f,E_i}(\underset{\sim}{r})$ for the interval [-3.7,-1.3] which represents approximately the middle p-like region. We notice that the charge is mainly concentrated in the Ga-As bonds and looks mostly like the charge density for band 7. This region then represents the Ga-As bonding states. In Fig. 12 we show the electronic distribution in the interval [-1.3,0.6] and [0.6,2.2]. In the former case we have essentially the Ga-Ga bonding states and this agrees very closely with the results for band 8. In the latter case we have the hypothetical case of a filled conduction band energy interval. We notice that again we obtain plane wave like behavior but at the same time a distinct antibonding s-like distribution around the As atoms. Finally in Fig. 13 we show the charge density obtained by suming 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 zincblende 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 bonding like 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 bonding like in character and more concentrated in the bonds rather than what we obtain in Figs. 8 and 12. 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. 14(a) 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 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 only very small changes in the bonds angles and Ga-As bonding distances. This result on the gap is very encouraging and we would expect to get similar effects by changing the Ga-Ga and As-As distances in the other structures. The important point to remember is that given a particular configuration of like-atom bonds the Ga-Ga and As-As nearest neighbor distances would be critical in determining whether a gap could exist or not. 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.

At this point we 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[25] 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[28] of like-atoms since these will affect the possibility of

obtaining a non-zero energy gap as is observed experimentally.[27] As we have already seen in Fig. 4(a), four-fold 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 non-zero 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 non-zero gap as in 2H-4 (2/2) Fig. 14(a). We should notice also that these changes in nearest neighbor distances for 5% Ga-Ga and 5% As-As bonds are compatible with the RDF's of Shevchik and Paul[25] 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 GaAs compound with disorder (L) would have the form shown in Fig. 14(b). For comparison we also show the density of states of GaAs in the zincblende 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. 14(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 overall 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 moddle 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 non-zero gap as in Fig. 14(a). From these considerations we propose a p-like region as shown in Fig. 14(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. 14(a). As we have already seen in section IV 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 Ga-Ga bonding distances it cannot be used alone as a measure of this bonding distance. This is because the contributions from the As-As 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 Ga-Ga and As-As nearest neighbor distances.

## VI. Summary and Conclusions

In this paper we have been primarily interested in the structural nature of the amorphous III-V phase. From an experimental point of view the information obtained from optical properties[29] and RDF's[25] 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 five and seven fold 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 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

four fold 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[5] 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

(v) topological variations of clustering configurations

Our results for disorder (U) and disorder (L) are shown in Figs. 1(a) and 14(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 affected by deviations in the bond angles which cause a steepening of the band edge as in the case of amorphous Ge.[5] 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 of chains of order N to 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 the 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. 14(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 regions (I, II and III) which we call the low, middle and high energy p-like regions. The low and high p-like regions represent As-As and Ga-Ga bonding states respectively. On the other hand, the middle p-like region represents Ga-As 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 Ga-Ga and As-As 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 Ga-Ga and As-As bonding distances which are smaller and larger respectively than the ideal Ga-As 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[24] 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.

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Table I

The number and type of p-like functions that can be made for a certain atom given the configuration of nearest neighbor atoms.

| Number of unlike-atom nearest neighbors | Number of p-like functions of type III-V | Number of p-like functions of type III-III or V-V |
|---|---|---|
| 4 | 3 | 0 |
| 3 | 2 | 0 |
| 2 | 1 | 1 |
| 1 | 0 | 2 |
| 0 | 0 | 3 |

## Figure Captions

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) as described in the text.

Fig. 2. Density of states of GaAs in the (a) 2H-4 (1,1/1,1), (b) 2H-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.

Fig. 3. Density of states of GaAs in the (a) ST-12 (5,1/3,3), (b) ST-12 (4,2/5,1) and (c) ST-12 (3,3/4I,1,1) structures using the simple tight binding model discussed in the text. The convention is the same as in Fig. 2.

Fig. 4. 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.

Fig. 5. GaAs 2H-4 (2/2) charge density in the (110) plane for bands 1 and 2.

Fig. 6. GaAs 2H-4 (2/2) charge density in the (110) plane for bands 3 and 4.

Fig. 7. GaAs 2H-4 (2/2) charge density in the (110) plane for bands 5 and 6.

Fig. 8. GaAs 2H-4 (2/2) charge density in the (110) plane for bands 7 and 8.

Fig. 9. GaAs 2H-4 (2/2) charge density in the (110) plane for bands 9 and 10.

Fig. 10. 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. 11. GaAs 2H-4 (2/2) charge density in the (110) plane for the regions of the density of states in the energy intervals [-5.0 eV, -3.7 eV] and [-3.7 eV, -1.3 eV] designated by arrows in Fig. 4(c).

Fig. 12. GaAs 2H-4 (2/2) charge density in the (110) plane for the regions of the density of states in the energy intervals [-1.3 eV, 0.6 eV] and [0.6 eV, 2.2 eV] designated by arrows in Fig. 4(c).

Fig. 13. GaAs 2H-4 (2/2) total charge density in the (110) plane.

Fig. 14. 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 non-zero energy gap. The dashed curve in (b) represents the consequences of disorder (L) with 10% like-atom bonds as discussed in the text. The dotted line distinguishes between the low and high energy s-like peaks.

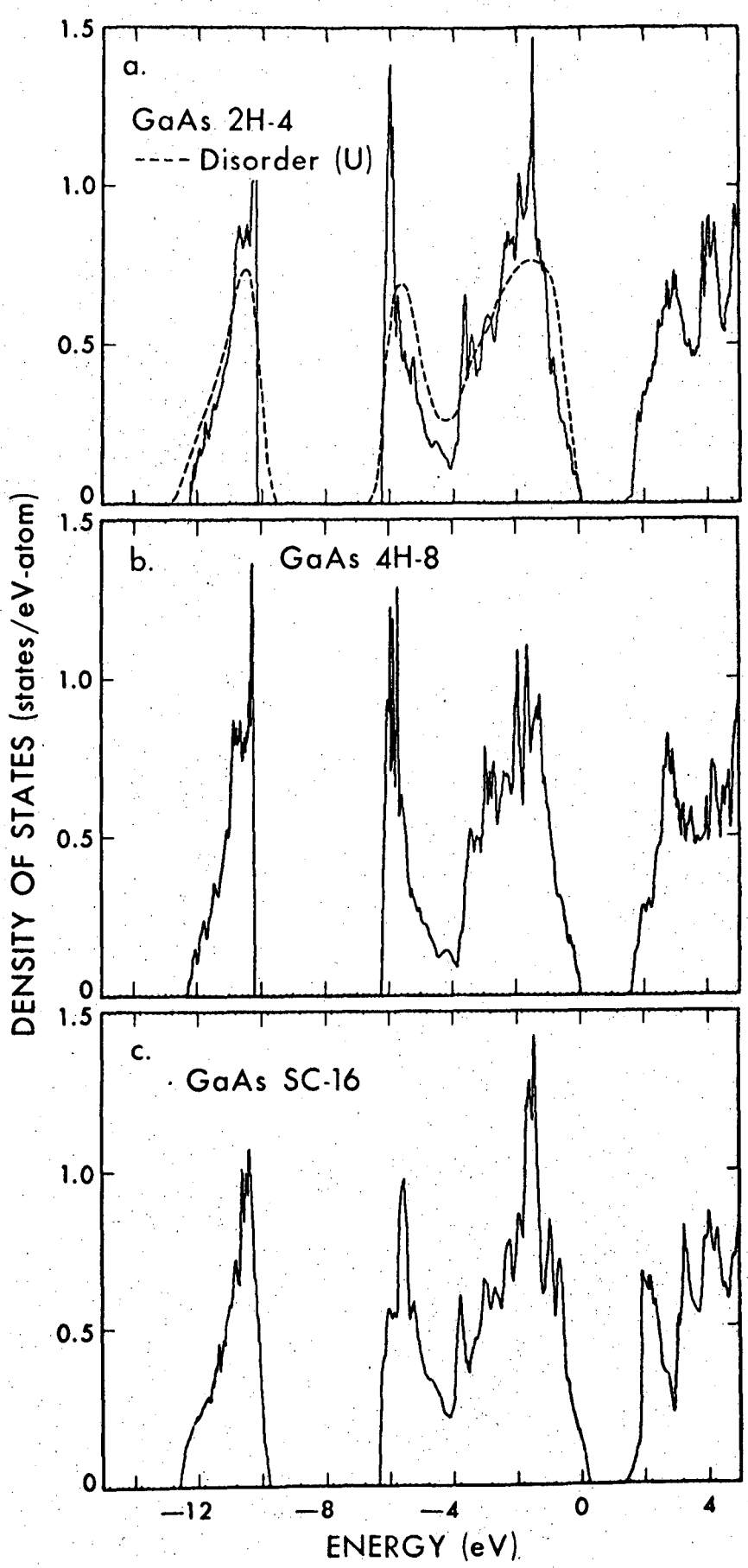
a.
GaAs 2H-4
---- Disorder (U)
b.
GaAs 4H-8
c.
GaAs SC-16
DENSITY OF STATES (states/eV-atom)
ENERGY (eV)
1.5
1.0
0.5
0
−12
−8
−4
0
4

Fig. 1

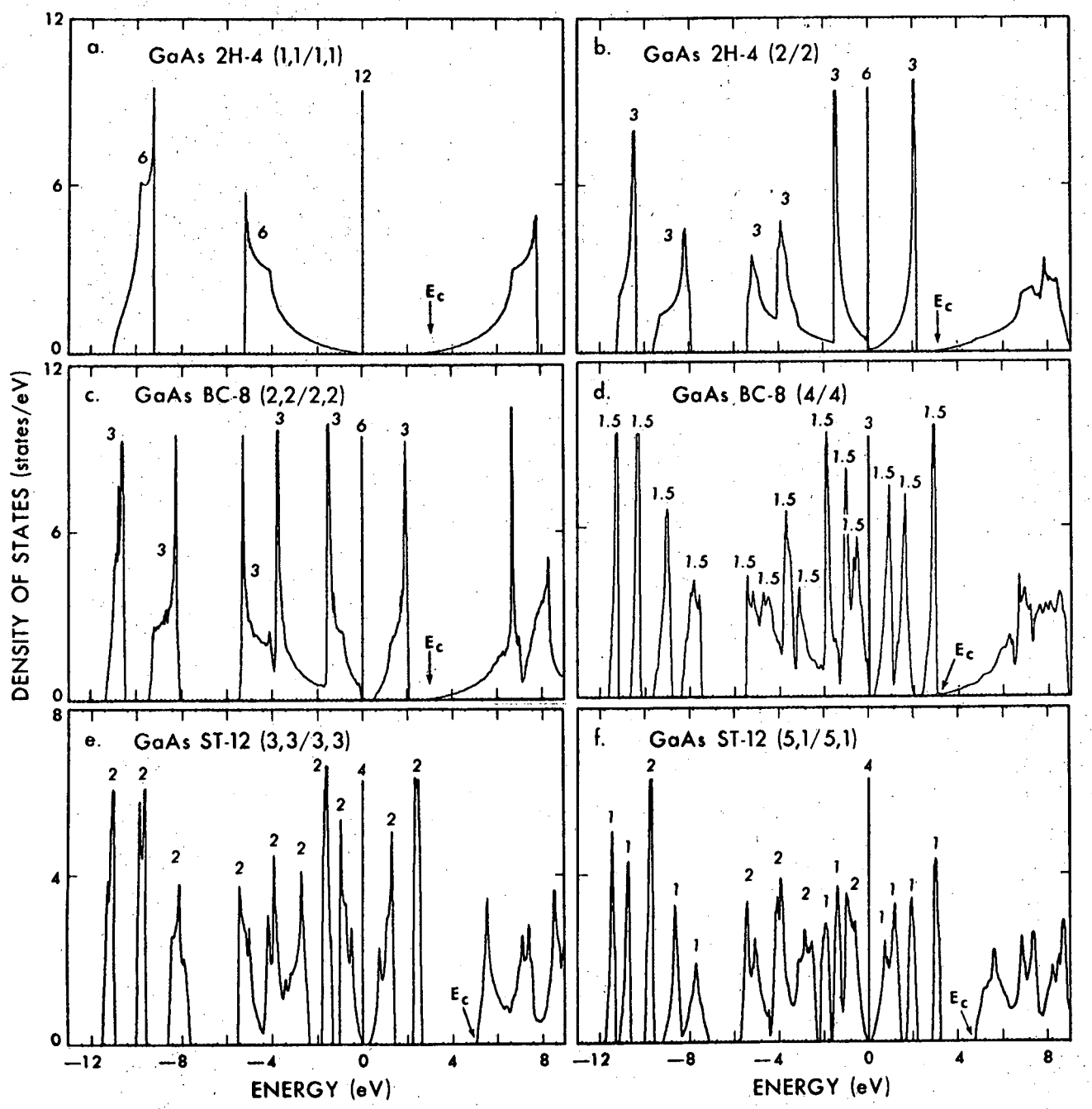
a. GaAs 2H-4 (1,1/1,1)
b. GaAs 2H-4 (2/2)
c. GaAs BC-8 (2,2/2,2)
d. GaAs BC-8 (4/4)
e. GaAs ST-12 (3,3/3,3)
f. GaAs ST-12 (5,1/5,1)
DENSITY OF STATES (states/eV)
ENERGY (eV)
$E_c$

Fig. 2

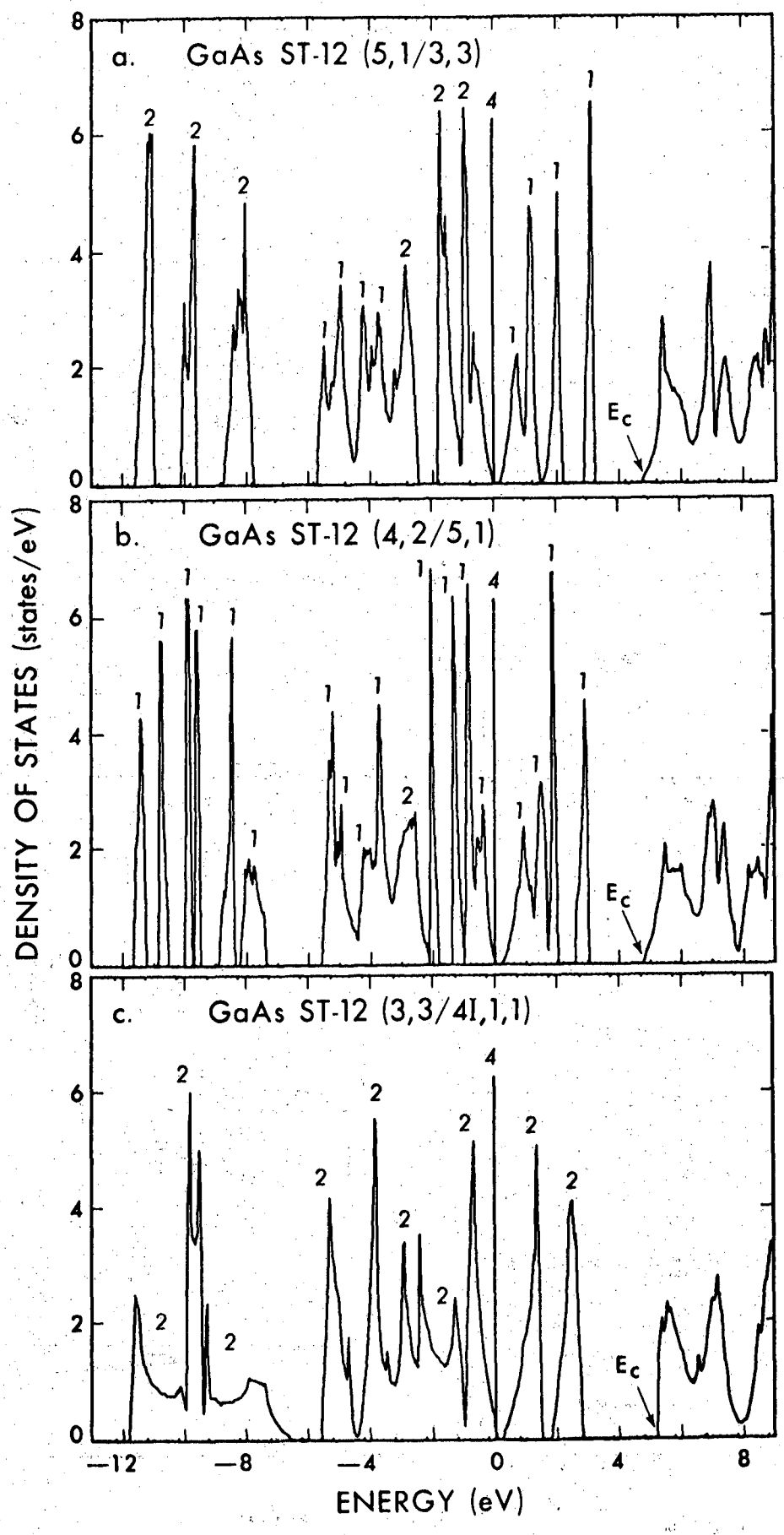
a. GaAs ST-12 (5,1/3,3)
b. GaAs ST-12 (4,2/5,1)
c. GaAs ST-12 (3,3/4I,1,1)
DENSITY OF STATES (states/eV)
ENERGY (eV)
$E_c$
0
2
4
6
8
−12
−8
−4
0
4
8

Fig. 3

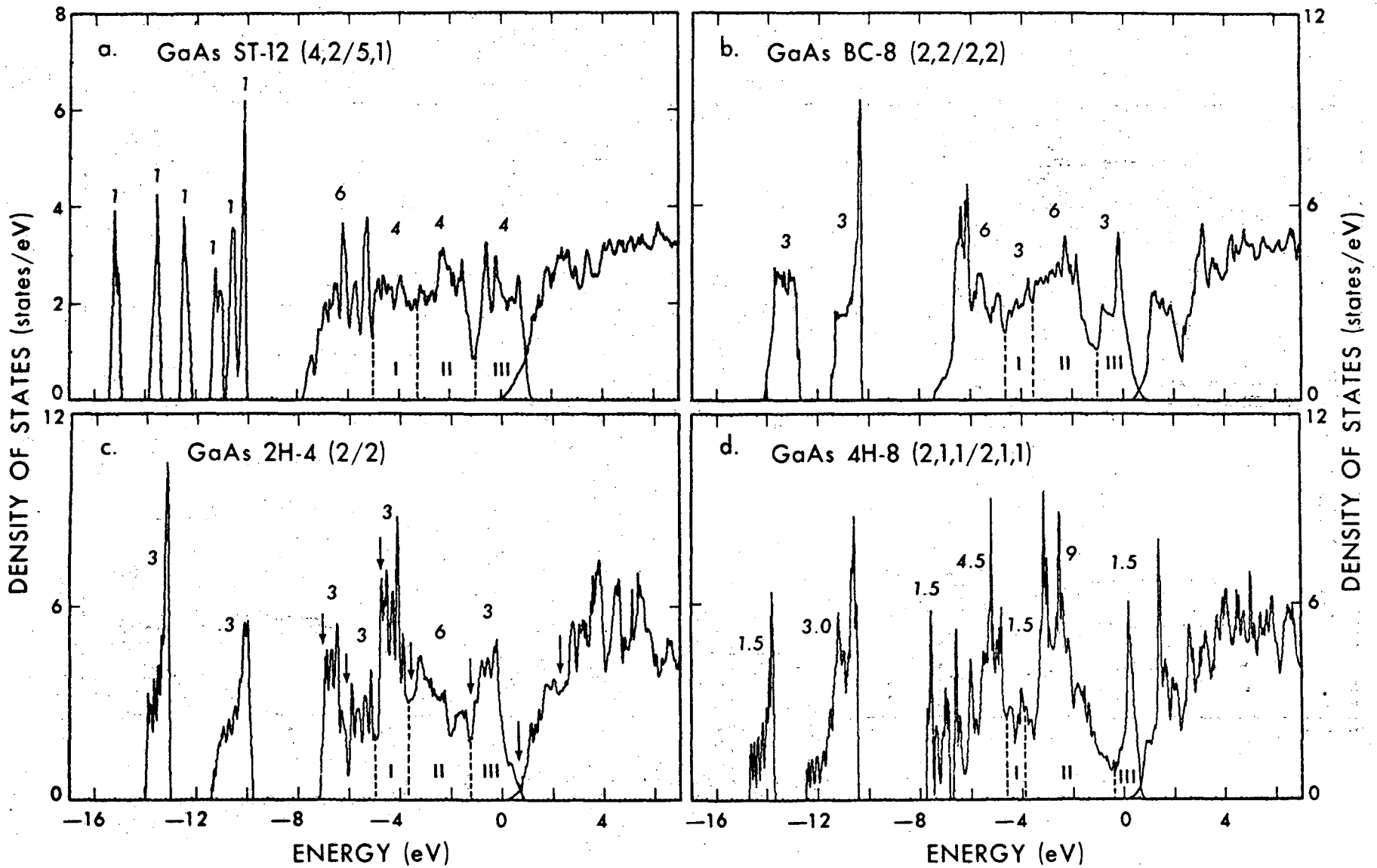
a. GaAs ST-12 (4,2/5,1)
b. GaAs BC-8 (2,2/2,2)
c. GaAs 2H-4 (2/2)
d. GaAs 4H-8 (2,1,1/2,1,1)
DENSITY OF STATES (states/eV)
ENERGY (eV)
I
II
III

Fig. 4

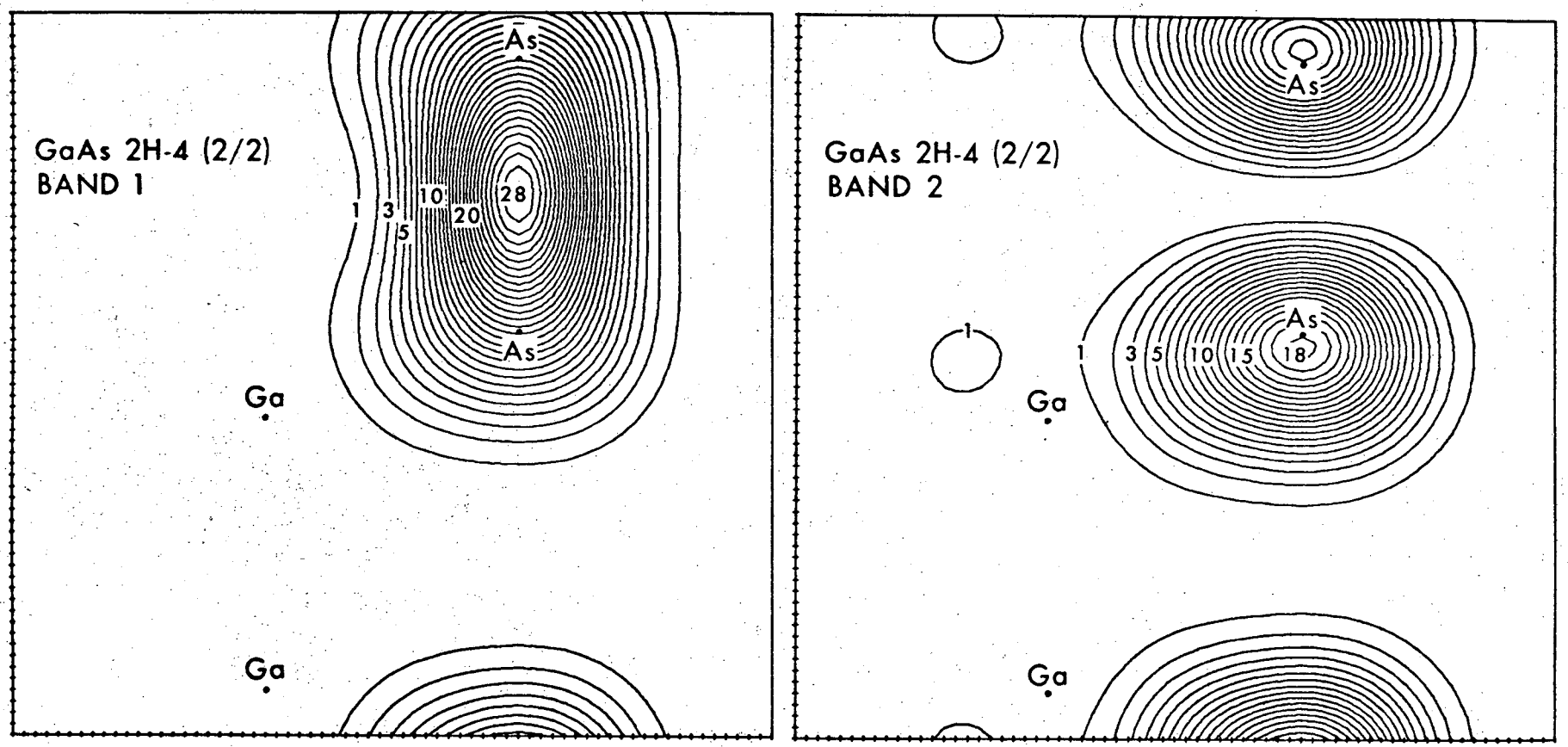
GaAs 2H-4 (2/2)
BAND 1
As
As
Ga
Ga
1
3
5
10
20
28
GaAs 2H-4 (2/2)
BAND 2
As
As
Ga
Ga
1
1
3
5
10
15
18

Fig. 5

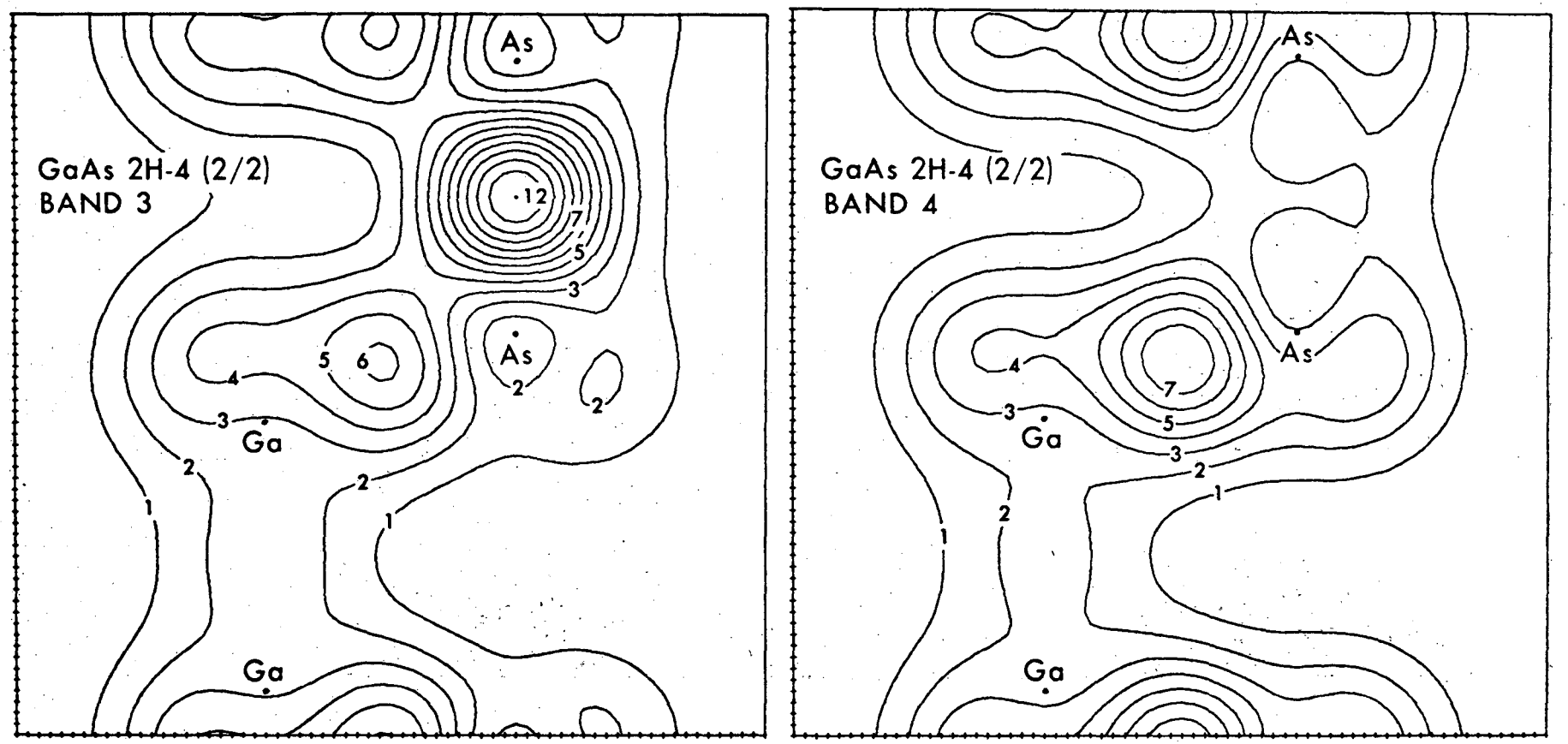
GaAs 2H-4 (2/2)
BAND 3
As
As
Ga
Ga
12
7
5
3
6
5
4
3
2
2
2
1
1
GaAs 2H-4 (2/2)
BAND 4
As
As
Ga
Ga
7
5
4
3
3
2
2
1
1

Fig. 6

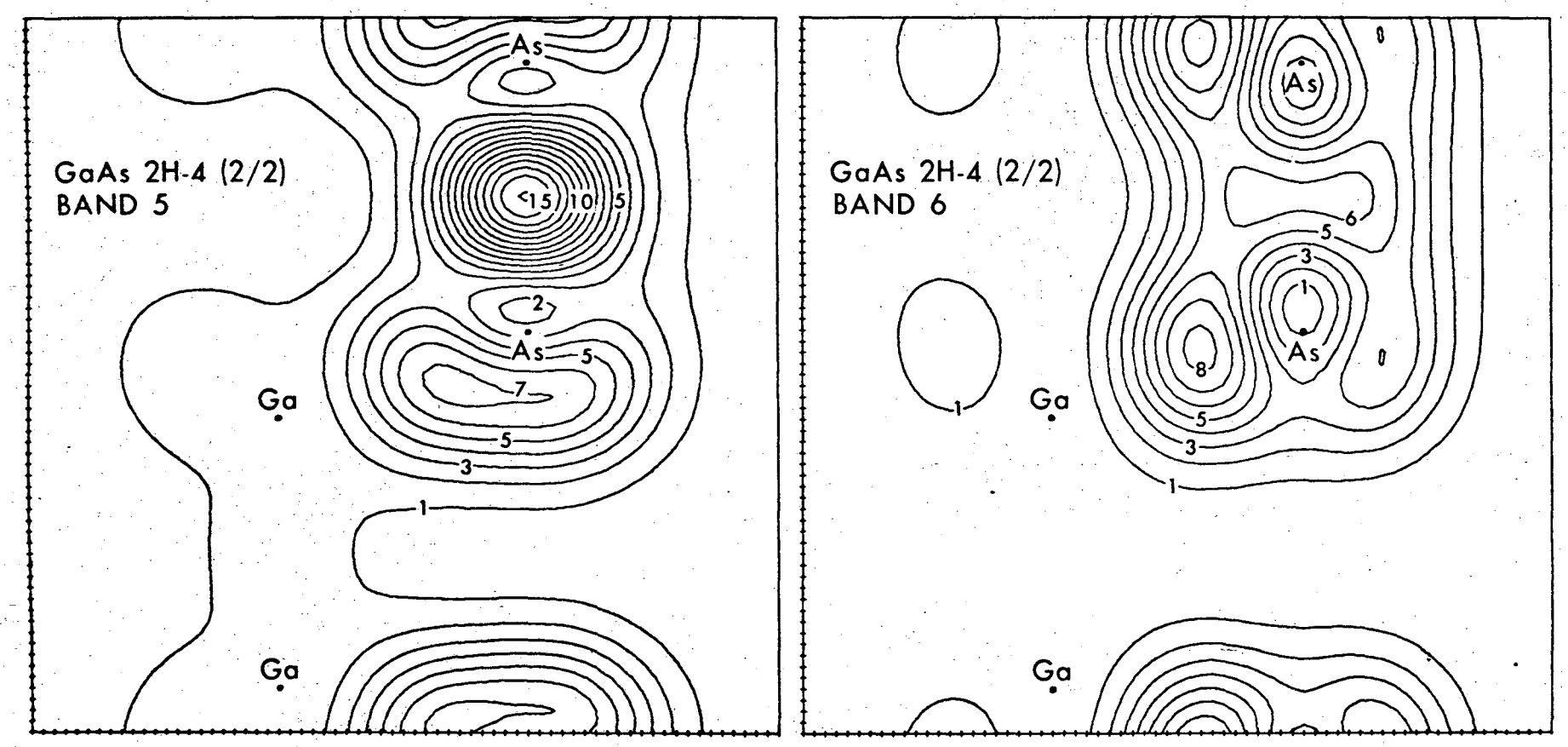
GaAs 2H-4 (2/2)
BAND 5
As
15
10
5
2
As
5
7
5
3
1
Ga
Ga
GaAs 2H-4 (2/2)
BAND 6
As
0
6
5
3
1
As
0
8
5
3
1
1
Ga
Ga

Fig. 7

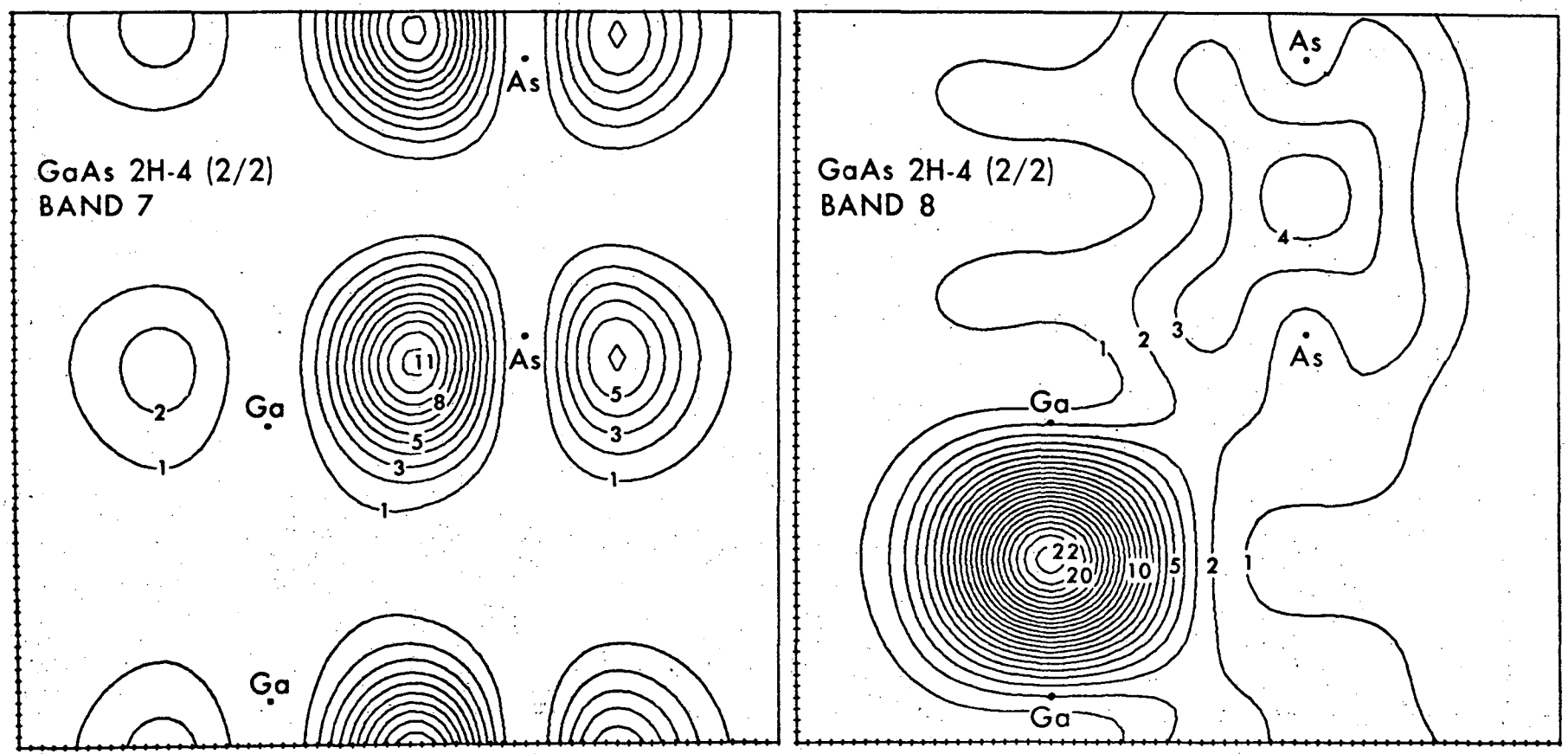
GaAs 2H-4 (2/2)
BAND 7
As
As
Ga
Ga
11
8
5
3
1
2
1
5
3
1
GaAs 2H-4 (2/2)
BAND 8
As
As
Ga
Ga
4
3
2
1
22
20
10
5
2
1

Fig. 8

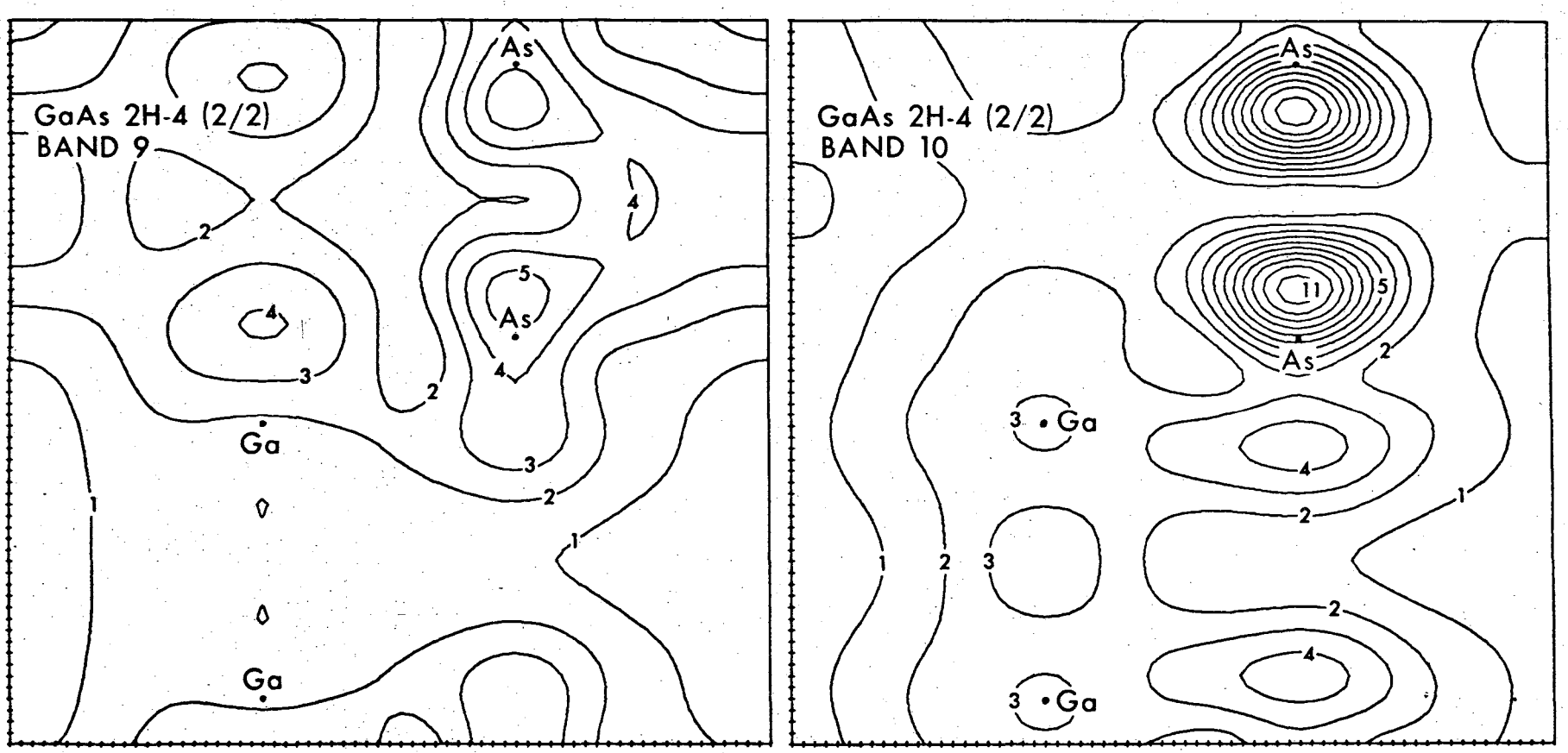


Fig. 9

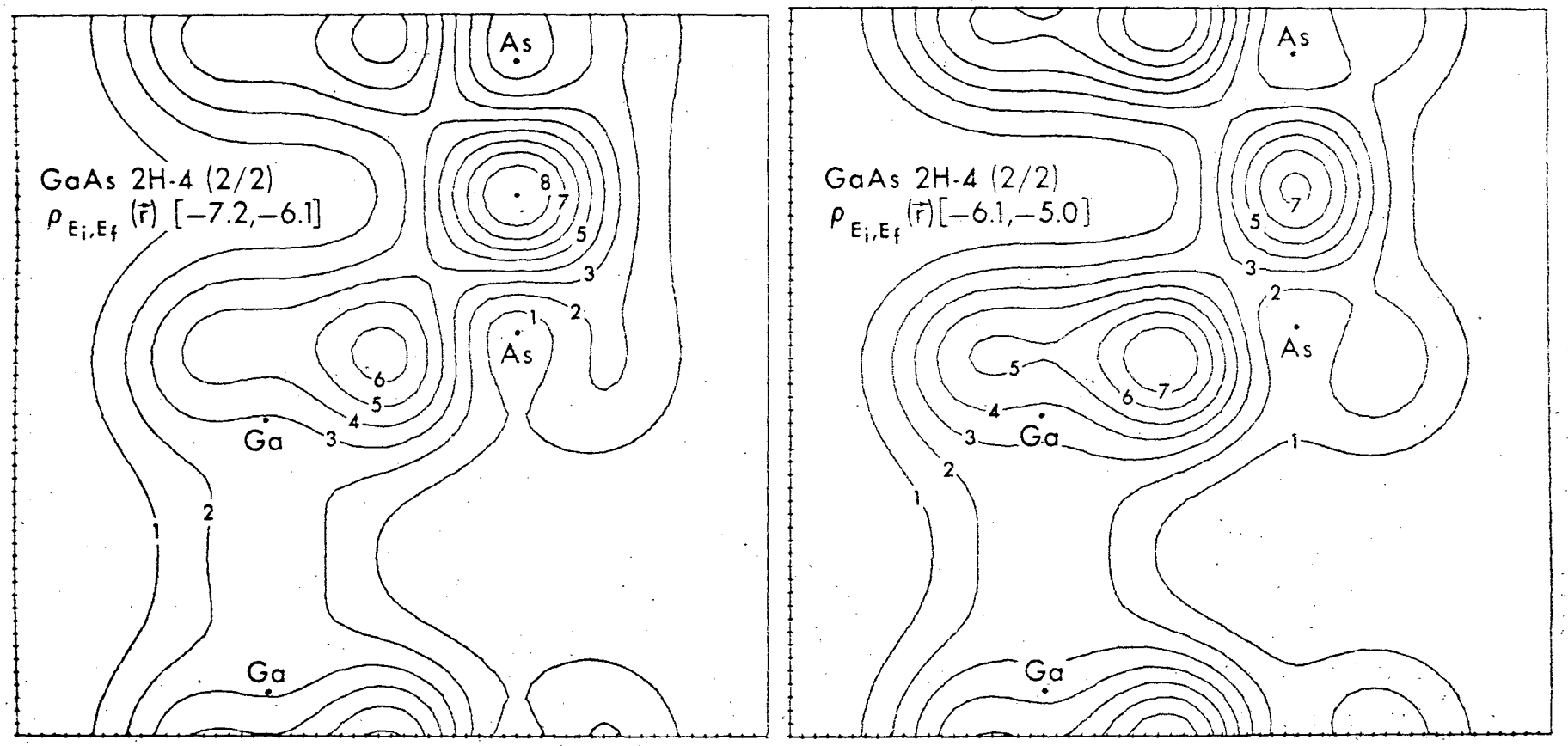
GaAs 2H-4 (2/2)
$\rho_{E_i,E_f}(\vec{r})$ [−7.2,−6.1]
As
As
Ga
Ga
GaAs 2H-4 (2/2)
$\rho_{E_i,E_f}(\vec{r})$[−6.1,−5.0]
As
As
Ga
Ga

Fig. 10

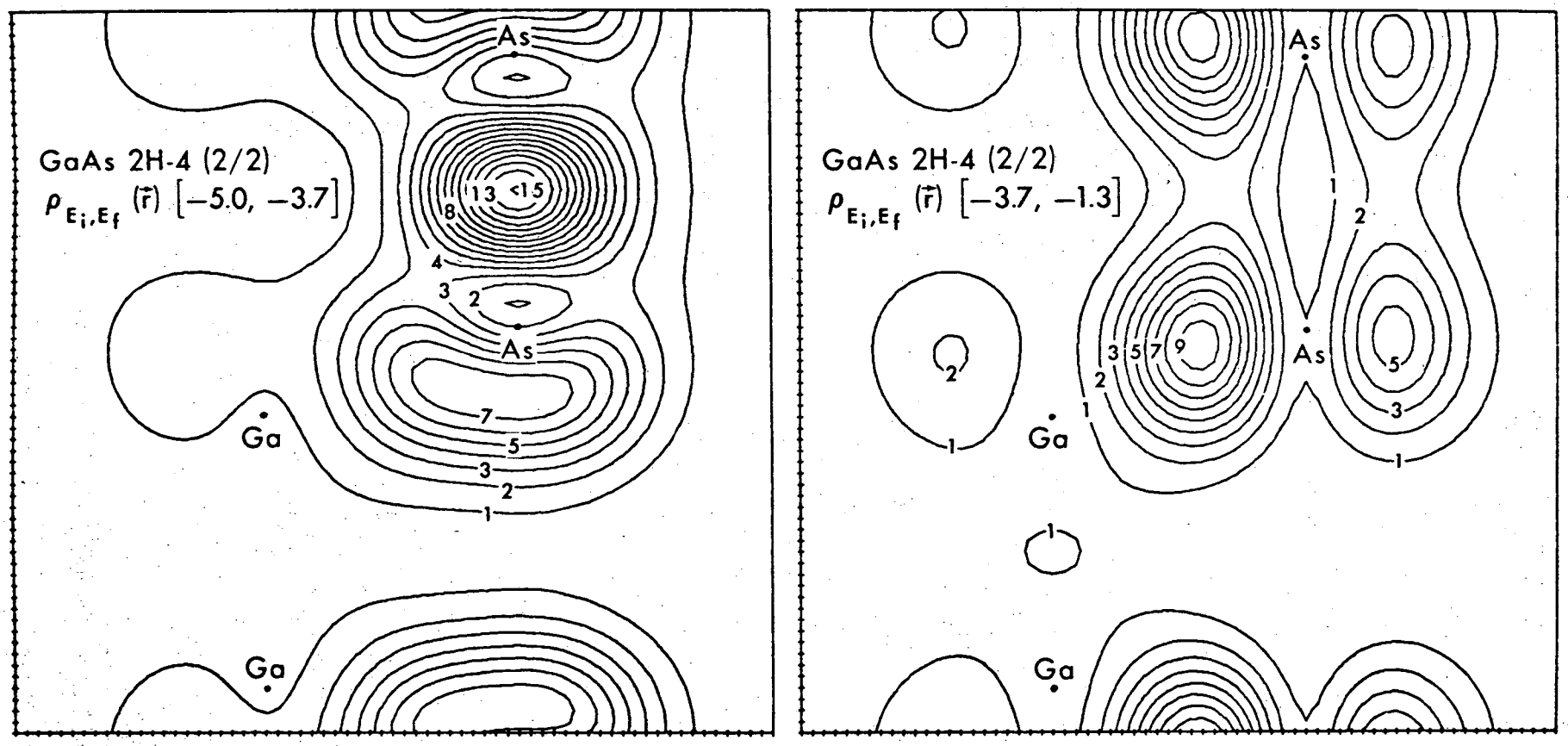
GaAs 2H-4 (2/2)
$\rho_{E_i,E_f}(\vec{r})$ [−5.0, −3.7]
As
As
Ga
Ga
13
<15
8
4
3
2
7
5
3
2
1
GaAs 2H-4 (2/2)
$\rho_{E_i,E_f}(\vec{r})$ [−3.7, −1.3]
As
As
Ga
Ga
1
2
3
5
7
9
2
2
1
5
3
1
2
1
1

Fig. 11

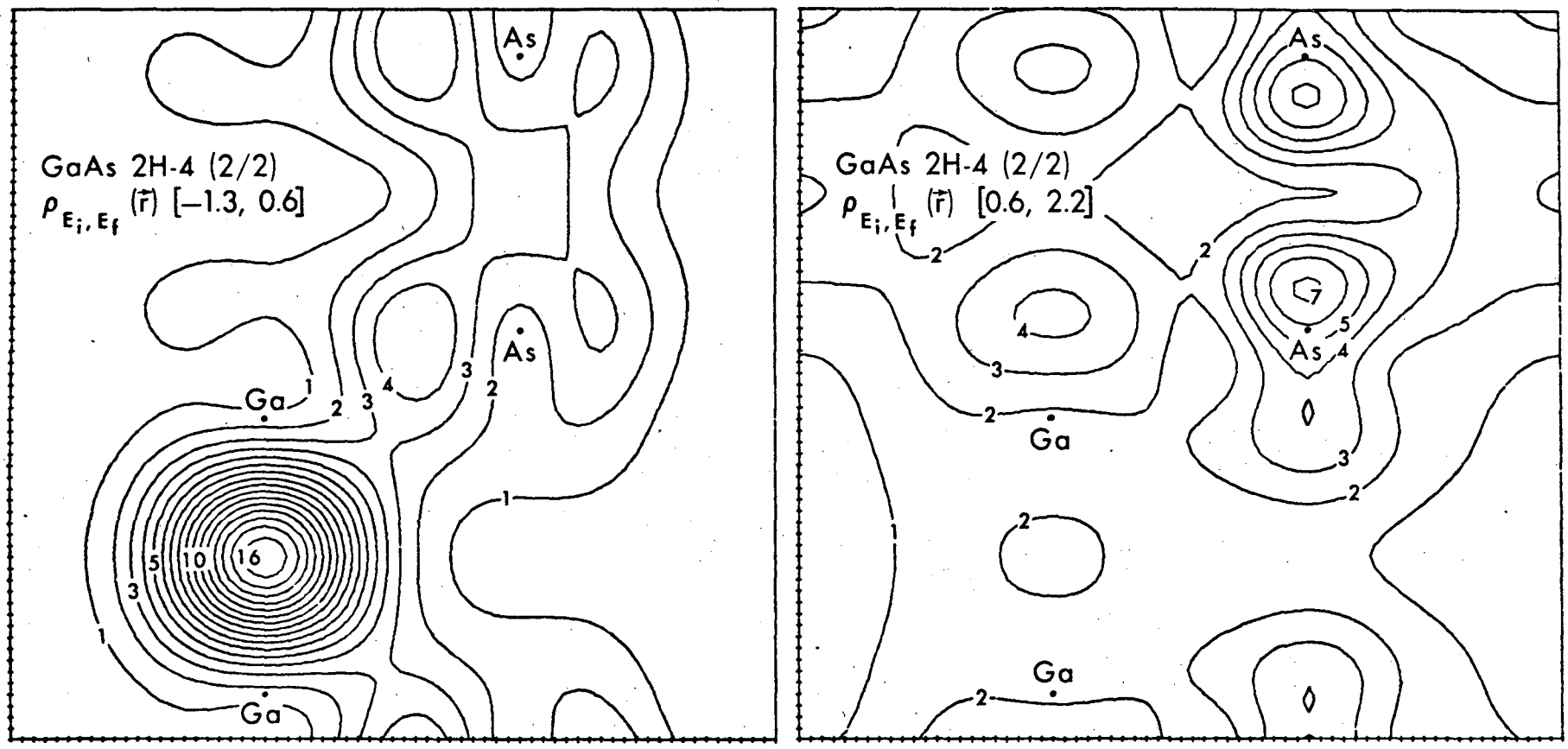
GaAs 2H-4 (2/2)
$\rho_{E_i, E_f}(\vec{r})$ [−1.3, 0.6]
As
As
Ga
Ga
1
2
3
4
3
2
1
5
10
16
3
1
GaAs 2H-4 (2/2)
$\rho_{E_i, E_f}(\vec{r})$ [0.6, 2.2]
As
As
Ga
Ga
2
2
4
3
2
5
4
3
2
2
1
2

Fig. 12

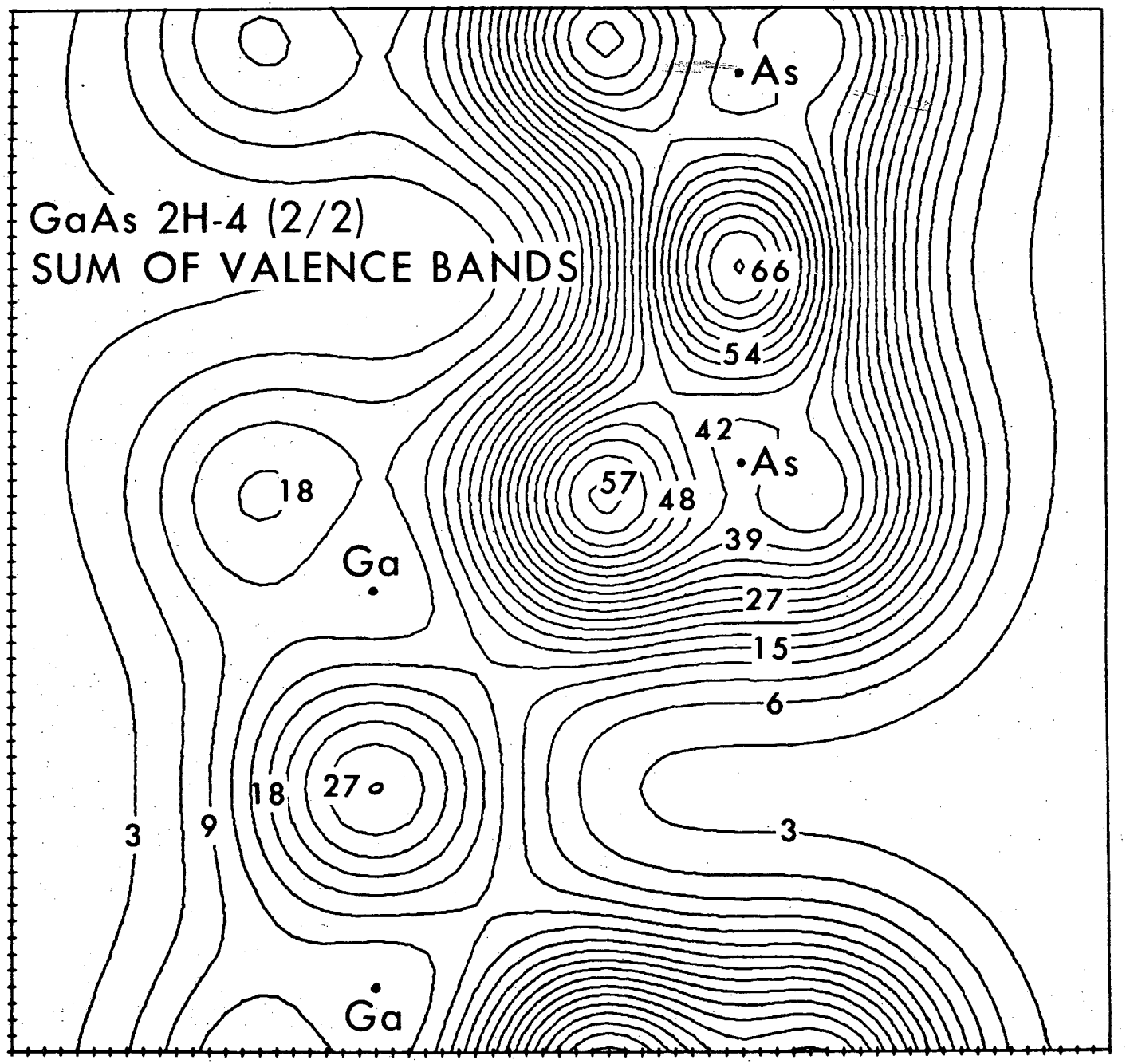
GaAs 2H-4 (2/2)
SUM OF VALENCE BANDS
As
66
54
42
As
57
48
39
27
15
6
3
18
Ga
27
18
3
9
Ga

Fig. 13

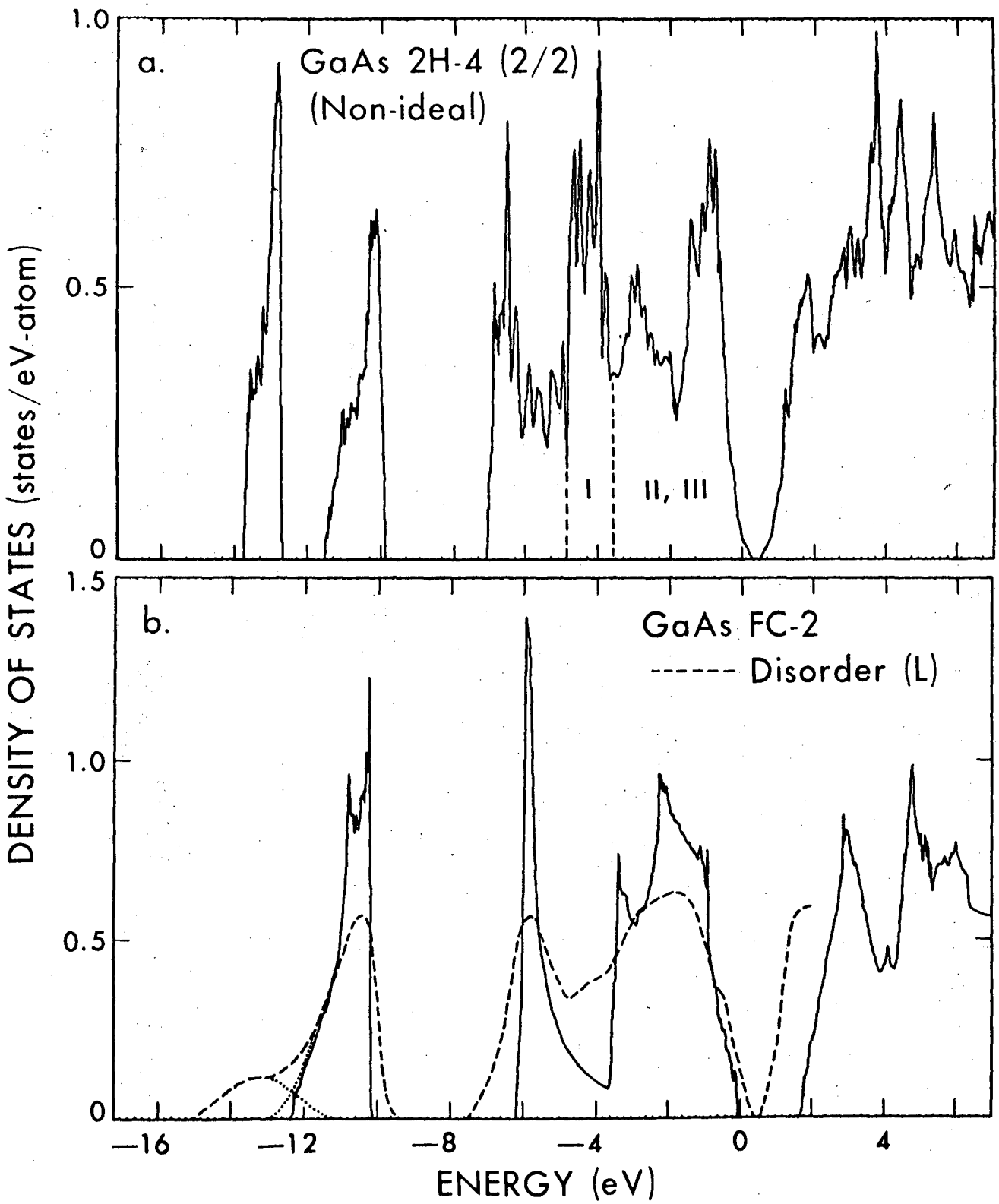
a.
GaAs 2H-4 (2/2)
(Non-ideal)
I
II, III
b.
GaAs FC-2
Disorder (L)
DENSITY OF STATES (states/eV-atom)
ENERGY (eV)
1.0
0.5
0
1.5
1.0
0.5
0
−16
−12
−8
−4
0
4

Fig. 14

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