PHYSICAL REVIEW B VOLUME 19, NUMBER 8 15 APRIL 1979

Electronic structure of defects in amorphous arsenic

W. B. Pollard and J. D. Joannopoulos

Department of Physics and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 30 October 1978)

The cluster–Bethe-lattice method, self-consistent pseudopotentials, and tight-binding Hamiltonians are used to study the electronic structure of various possible defects in amorphous As. The electronic densities of states of isolated twofold coordinated As atoms, fourfold coordinated As atoms, "intimate valence alternation pairs," and vacancies are calculated. The origin, character, and localization of the resulting gap states are discussed. It is found that isolated fourfold coordinated As atoms give rise to states in the gap that are nondegenerate, fairly localized, and predominantly p-like in character. Moreover, our investigation indicates that the character and localization of the gap states arising from the "valence alternation pair" are consistent with the properties of optically induced paramagnetic states observed in amorphous As, while the electronic gap states of the vacancy defect may be consistent with the recently observed thermally generated paramagnetic states in this material.

I. INTRODUCTION

Recent experimental optical-absorption,[1] electron-spin-resonance (ESR),[2] and field-effect measurements[1] on amorphous arsenic (a-As) have been interpreted in terms of theoretical models which envisage the presence of various structural defects in the amorphous network.[3-7] These defects are associated with atoms in the glass which assume atypical bonding configurations, and can be broadly classified as bonding coordination defects (BCD). More recently, Nemanich *et al.*[8] have reported possible spectroscopic evidence for the existence of fourfold (tetrahedral) and twofold coordinated sites in a-As. However, there does not exist a realistic theoretical description of the vibrational or electronic excitations of these defects. It is the purpose of this work to examine the electronic structure and properties of BCD's in a-As. Specifically, we will focus upon twofold and fourfold coordinated As atoms, as well as vacancies and "intimate valence alternation pairs".[6]

In order to probe the electronic structure of these defects, we employ the cluster–Bethe-lattice method (CBLM),[9,10] self-consistent pseudopotentials calculations,[11] and simple-tight-binding Hamiltonians. The basic idea behind the CBLM is that the electronic behavior of the defect in the amorphous network can be simulated by attaching Bethe lattices[9] (an infinite network of atoms with coordination 3 that contains no closed rings of bonds) to the surface bonds of the defect. Further, since the electronic density of states (DOS) of a Bethe lattice is generally smooth and featureless, all of the structure in the local DOS at the defect site can be attributed to the properties of the defect alone.

The interactions within the Bethe lattice are described by a tight-binding Hamiltonian which contains nearest-neighbor s, p, and s-p interactions. We fit this Hamiltonian to the results of a self-consistent pseudopotential calculation for As in the A-7 structure.[11] (The values of the interactions are given in Table I.) In Fig. 1(a), we show the theoretical (pseudopotential) DOS spectrum of A-7 As (solid line) along with the experimental x-ray photoelectron (XPS) spectrum[12] (broken line) for A-7 As. The corresponding tight-binding DOS is shown in Fig. 1(b). The top of the valence band is taken to be the zero of energy. The s-like states lie in a band centered about -12.0 eV, while the regions between 0.0 and ∓ 6.0 eV are composed of p-like bonding and antibonding states, respectively. The pseudopotential DOS bandwidths and the separation of the s- and p-like bands are found to be in good agreement with the XPS results, as well as the optical studies on A-7 As.[13] On the other hand, the tight-binding DOS reflects the inclusion

TABLE I. Empirical tight-binding parameters (in eV) which describe the interactions about the threefold and fourfold coordinated As sites (for nearest neighbors only), and between the dangling orbitals at vacancy sites in a-As.

		Threefold coordinated sites			
E_s	E_p	$V_{pp\sigma_1}$	$V_{pp\pi_1}$	$V_{sp\sigma_1}$	$V_{ss\sigma_1}$
-11.34	0.0	2.42	-1.05	-1.25	-1.34
		Fourfold coordinated sites			
E_s	E_p	$V_{pp\sigma_1}$	$V_{pp\pi_1}$	$V_{sp\sigma_1}$	$V_{ss\sigma_1}$
-9.41	-0.25	2.41	-0.60	-1.39	-1.52
		Vacancy sites			
···	···	$V_{pp\sigma_2}$	$V_{pp\pi_2}$	$V_{sp\sigma_2}$	$V_{ss\sigma_2}$
···	···	1.25	-0.29	-0.60	-0.42

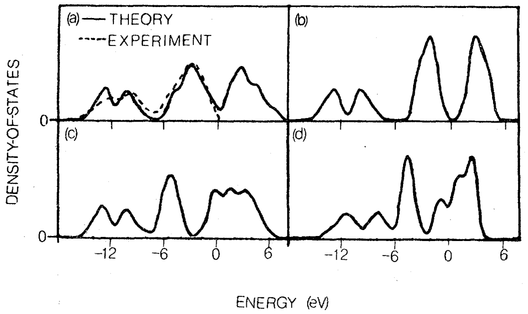

FIG. 1. Theoretical DOS of crystalline As. (a) DOS of As in the A-7 structure calculated from self-consistent pseudopotential (solid line) and experimental photoemission spectrum (broken line, Ref. 12); (b) tight-binding DOS of A-7 As; (c) and (d) pseudopotential and tight-binding DOS spectra, respectively, of As in the diamond structure.

of only nearest-neighbor interactions (e.g., narrower bandwidths). These, however, are the most important interactions in determining the amorphous DOS.[9,14] Further, the same interaction parameters can also be used to study the twofold coordinated and vacancy defects. This is clear from all the work that has been done on surfaces and vacancies in crystalline semiconductors using both self-consistent pseudopotentials[15,16] and tight-binding[17] Hamiltonians. This may not be the case for the fourfold tetrahedrally coordinated defect sites where the nature of the bonds are now different.

To gain some insight into the nature of the bonding about a fourfold tetrahedrally coordinated As site, we perform a self-consistent pseudopotential calculation for As in the diamond structure.[11] In Figs. 1(c) and 1(d), we show DOS spectra for As in this structure calculated from pseudopotential and tight-binding Hamiltonians, respectively (again only nearest-neighbor interactions are included in the tight-binding fit). The states at the bottom of the valence band (~−16.0−12.0 eV) are mostly s-like in character, while those in the region between −12.0 and −8.0 eV are a mixture of s- and p-like states. The band centered around −5.0 eV is composed of states of p-like character. The uppermost part of the valence band (~−2.0−~0.0 eV), on the other hand, is composed of a mixture of s- and p-like antibonding states.

In modeling the fourfold coordinated defect, we note that the local environment about the defect site is similar to that about an As site in the diamond structure. Moreover, as is evident from the pseudopotential DOS of Fig. 1, the bonding about the tetrahedrally coordinated As atom is significantly different from that about a threefold coordinated As atom. However, the nearest neighbors of the fourfold defect will have a lower coordination than the corresponding sites in the diamond structure. These modifications in bonding and coordination about the defect site cause charge rearrangement effects to be important and impose requirements of self-consistency upon a calculation of the defect's electronic states. The tight-binding parameters which describe the interactions about the fourfold coordinated site must therefore be determined in a self-consistent iterative scheme. The iterative procedure that we employ is similar to that used in the study of surfaces in semiconductors, and is described in detail elsewhere.[18,19] Briefly, the method involves treating the intra-atomic tight-binding parameters as functions of the electronic charge and charge configuration about the defect site. The charges themselves are in turn functions of the calculated eigenvalues and eigenvectors. The secular equation is then solved iteratively until the atomic charges are consistent with the tight-binding parameters.

We initially assume that the interactions about the defect site can be described by the tight-binding parameters for As in the diamond structure. The resulting atomic charges and modification of the intra-atomic tight-binding parameters are calculated. These new parameters are then used as input in the next iteration. This process is repeated until self-consistency is achieved. The results of the calculation are shown in Table I.

From the above models we obtain tight-binding Hamiltonians that are realistic enough to describe the main features of the crystalline structures, and yet tractable enough to model the bonding about defects in the amorphous phase as well. The format of the paper is as follows. In Sec. II, we examine the electronic properties of isolated defects, specifically, twofold and fourfold coordinated As atoms. In Sec. III, we focus upon more complicated defect structures and study the electronic structure of vacancies and a nearest-neighbor fourfold and twofold coordinated defect configuration. Finally, in Sec. IV, we discuss our results in light of recent experimental measurements on a-As.

II. ISOLATED DEFECT SITES

A. Twofold coordinated sites

Before examining a specific defect structure, it is necessary to consider the DOS of the threefold coordinated Bethe lattice. This is shown in Fig. 2(a). As expected, the bands in the spectrum are smooth and featureless. Moreover, there is now an energy gap of approximately 1.5 eV (the valence- and conduction-band edges are taken to be $E_v \sim -0.70$ eV and $E_c \sim 0.80$ eV, respectively). The atomic level of the *p* states has been taken as the zero of energy. Finally, note that the band gap and bandwidths are in fair agreement with experimental measurements on amorphous As.[12,13]

Consider now a cluster of seven atoms containing a twofold coordinated As atom with Bethe lattices attached to the surface bonds. The average DOS for the cluster is shown in Fig. 2(b). The predominant feature seen in the spectrum is a sharp state centered at midgap. The state is *p*-like in character and contains a single electron as expected. The localization of this dangling bond state can be examined by studying the local DOS of atoms Nos. 1, 2, and 3 separately. These are shown in parts (c), (d), and (e) of Fig. 2. One finds that nearly 56% of this state is localized on the dangling *p* orbital of the twofold site. The remainder of the state is smeared out over the four second-nearest neighbors, and is absent in the local DOS of the first-nearest neighbors. This oscillation of electron density from site to site results from even and odd combinations of the dangling bond state at the different layers of atoms. A similar behavior is also observed with respect to the resonance in the *s*-like band. Further, we find that each site of the cluster is neutral. This, along with the localization of the dangling bond state, implies that if an additional electron is transferred to this state, the extra charge would be localized mainly around atoms Nos. 1 and 3 with roughly $-0.56e$ on the former and $\sim -0.11e$ on each of the latter.

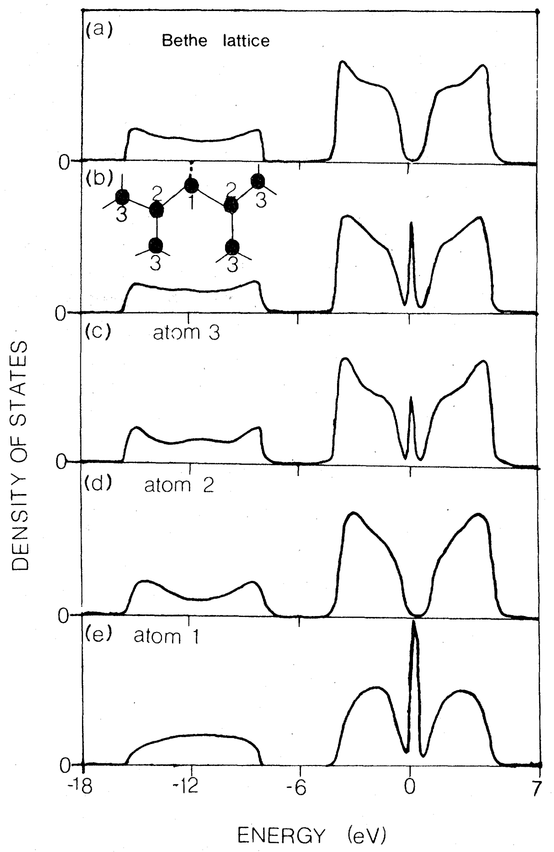

FIG. 2. (a) Electronic DOS of the As Bethe lattice; (b) the average DOS of a cluster of seven atoms containing a twofold coordinated As site with Bethe lattices attached to atoms No. 3; (c)–(e) The local DOS about atoms Nos. 3, 2, and 1, respectively.

Finally, a few remarks should be made concerning relaxations. The most probable relaxation would involve the strengthening of the back bonds of atom No. 1 and can be modeled by increasing the interaction parameters for these bonds. This will lower the energy of the system, delocalize the state from atom No. 1, but will not alter the position of the state in the gap. Only self-energy changes, which do not seem to play an important role in relaxations at surfaces of semiconductor systems,[16,17] would shift the position of the dangling bond state.

B. Fourfold coordinates sites

Using the model described in Sec. I for a fourfold coordinated defect, we calculate the average DOS of a 13-atom cluster containing a fourfold coordinated As atom with Bethe lattices again attached to the surface bonds. The results are shown in Fig. 3(a). Three features are directly attributable to the defect: the sharp states at ~ -7.7 and ~ 0.50 eV, and a resonance centered about -4.0 eV.

First, the state centered at -7.7 eV is *s*-like in character and arises from interactions between the *s* orbital on the defect and those of its four nearest neighbors. The local DOS in Figs. 3(b), 3(c), and

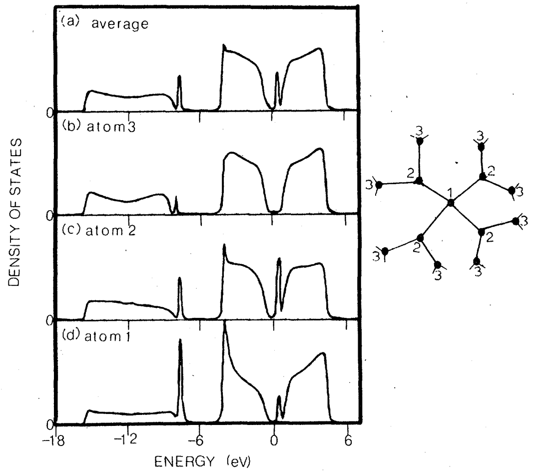

FIG. 3. (a) Average DOS of a cluster of 13 atoms containing a fourfold coordinated As site with Bethe lattices attached to atoms No. 3; (b)–(d) The local electronic DOS about atoms Nos. 3, 2, and 1, respectively.

3(d) indicate that this state is localized primarily on the defect with about 10% on each of its nearest neighbors.

Second, the resonance at −4.0 eV and the state at 0.5 eV arise from the interactions between the four tetrahedral bonds. These states correspond respectively to states of T_2 (triplet) and A_1 (singlet) symmetry with respect to the defect center. Specifically, the T_2-like states are made from *p*-like orbitals on the central and surrounding atoms. These states are concentrated predominantly on the defect site. The A_1-like state, on the other hand, projects on the *s* orbital of the fourfold site and the *p* orbitals (directed along the bonds) of the four neighboring sites. It has ~92% *p*-like character and ~8% *s*-like character.

The nature of the bonding about the fourfold site creates a small net charge transfer. We find that the central atom No. 1 has a charge of about $-0.16e$ with atoms No. 2 each having a charge of about $+0.04e$. Further, our investigation indicates that including reconstructions (which would break the perfect tetrahedral symmetry of the fourfold defect) will only appreciably affect the T_2-like states. The position in the gap and nature of the A_1-like state would remain essentially unchanged. Finally, we note that the Fermi energy of the average DOS of the cluster lies at ~0.5 eV. Hence, a fourfold coordinates site gives rise to a state in the gap that contains a single unpaired electron, and *unlike an* As *impurity in* Ge, it is localized roughly over only five atoms. This is important in light of recent ESR measurements on *a*-As.[2] We will discuss this point further in Sec. IV.

III. DEFECT COMPLEXES

A. "Intimate valence alternation pairs"

In Sec. II, we concentrated upon isolated defects. It is more likely, however, that defects in the amorphous network possess more complicated structures. In this light, we now examine a defect complex which consists of *nearest-neighbor* twofold and fourfold coordinated As atoms. This configuration is analogous to the proposed intimate valence alternation pairs (IVAP) for the chalcogenide glasses.[6]

In order to investigate the electronic structure of this defect configuration, we apply the procedure outlined in Sec. I for the fourfold defect to a cluster of 14 As atoms which contains an IVAP. The Bethe lattice is again attached to the surface bonds. The resulting DOS spectra are shown in Fig. 4. The average DOS spectrum shown in 4(a) resembles a composite of Figs. 2(b) and 3(a). However, there are some rather subtle differences in the electronic states. For instance, the dangling bond state is now more localized on the twofold site [atom No. 3, Fig. 4(d)]. This is evident from the small amount of dangling-bond character in Fig. 4(b) (atom No. 1). The character and localization of the A_1-like state, on the other hand, is for the most part unchanged.

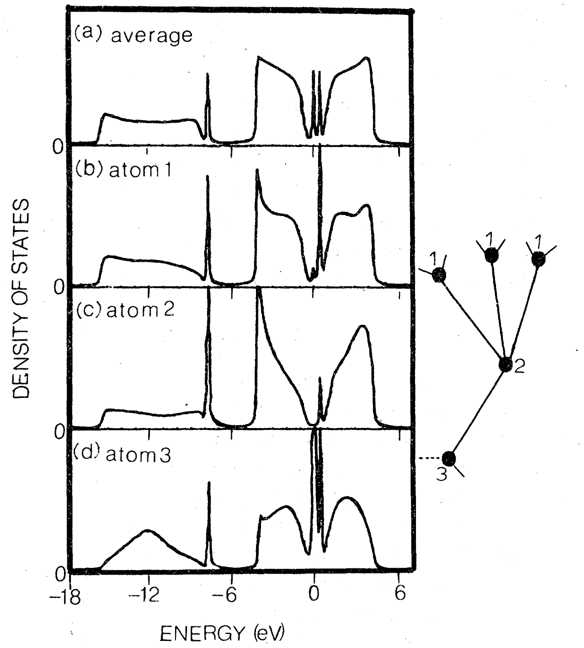

FIG. 4. Electronic DOS for atoms in a cluster containing nearest-neighbor fourfold (atom No. 2) and twofold (atom No. 3) coordinated As atoms ("valence alternation pair") with Bethe lattices attached outside. The average DOS of the atoms in the cluster is shown in (a). The local DOS about atoms Nos. 1, 2, and 3 are shown in (b), (c), and (d), respectively.

It may now be possible for the unpaired electron in the A_1-like state to transfer into and fill the dangling-bond state which lies 0.5 eV lower in energy. We find, in fact, that the position of the dangling-bond state in the gap is essentially unchanged by the charge-transfer process. This is easily understood since the extra Coulomb repulsion between the two electrons in the same vicinity (that tends to push this state up in energy) is for the most part canceled by the electrostatic Madelung energy arising from the net charges on the atomic sites. In particular, the change transfer leads to net static charges of approximately $+0.14e$ and $-0.11e$ for atoms Nos. 2 and 3, respectively. Atom No. 1 is almost neutral with a total charge of $-0.03e$. This has implications with regard to the infrared and Raman activities of this defect and is discussed further in Sec. IV.

Relaxation effects associated with the charge-transfer process are also important in determining the position of the dangling-bond state and have not been included here. We expect that such effects may tend to move this state slightly above midgap. The presence of a filled state (at $T = 0\,^{\circ}\mathrm{K}$) above midgap would be consistent with the n-type behavior of a-As. Finally, it should be noted that nearest-neighbor defect pairs should be more stable in a-As than in the amorphous chalcogenides. This is reasonable given the greater rigidity of the As structure to dihedral angle rotations that would result in the annihilation of such pairs.

B. Vacancies

Another type of defect complex which may exist in amorphous As is a vacancy. Recently,[20] the transfer of charge between dangling orbitals at vacancies has been suggested as the mechanism responsible for the rather unusual properties of thermally activated paramagnetic centers in this material. Hence, it is instructive to investigate the electronic behavior of such a defect. Further, in order to probe the effects of local structure upon the vacancy's electronic states we consider three different structural models for a neutral vacancy.

The first model we consider is the ideal vacancy. We model this structure by removing an atom from the Bethe lattice and allowing the three dangling orbitals to couple weakly through second-neighbor interactions (see Table I). The average DOS for the atoms surrounding the vacancy is shown in Fig. 5(a). The interactions between the dangling orbitals give rise to a state at -0.6 eV of A (singlet) symmetry and a state at 0.5 eV of E (doublet) symmetry. A study of the local densities of states shown in Figs. 5(b)–5(d) indicates that about 65% of the electronic density is localized on the dangling orbitals that point toward the vacancy's center. The remainder of the electronic density is spread out over more distant atoms. The main difference between the localization of the A- and E-like states is that the E-states contain some antibonding character and are therefore more localized around the vacancy atoms. Finally, since this doubly degenerate state at low temperatures will contain an electron, one expects, in analogy with the behavior of vacancies in crystalline solids, that this situation is unstable with respect to (Jahn-Teller-like) distortions.

To study the effects of such distortions, we consider a relaxation of the vacancy. Since there are more back bonds than dangling bonds, a reasonable relaxation of the vacancy would involve a symmetric motion of the atoms away from the vacancy's center, and thereby increase the strength of the backbonds and lower the energy of the system. This relaxation can be modeled by introducing a 20% increase in the interactions between the atoms at the vacancy and their nearest neighbors. This is typical of relaxations at the surfaces of semiconductors.[17] We also include a corresponding 20% decrease in the interactions between the dangling orbitals. The resulting DOS spectra are shown in Fig. 6. We note that the system has lost energy by shifting bonding electrons to lower energies. The

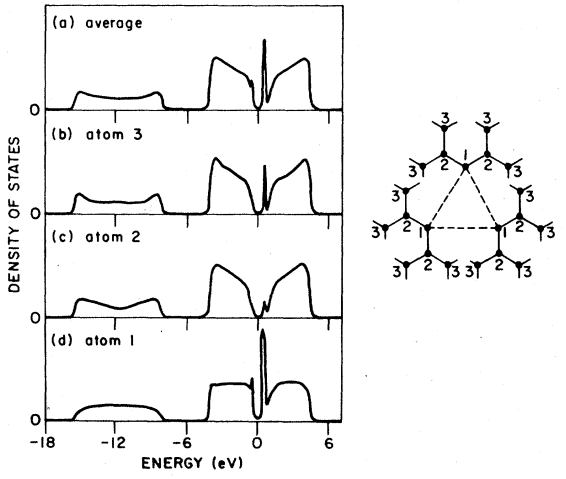

FIG. 5. DOS spectra for atoms surrounding an "ideal" vacancy in the Bethe lattice. (Note right-hand side of figure; the dashed lines schematically indicate the interactions between the dangling orbitals at the vacancy.) In (a), the average DOS for the atoms surrounding the vacancy is shown. In (b)–(d), the local DOS about atoms Nos. 3, 2, and 1 are shown, respectively.

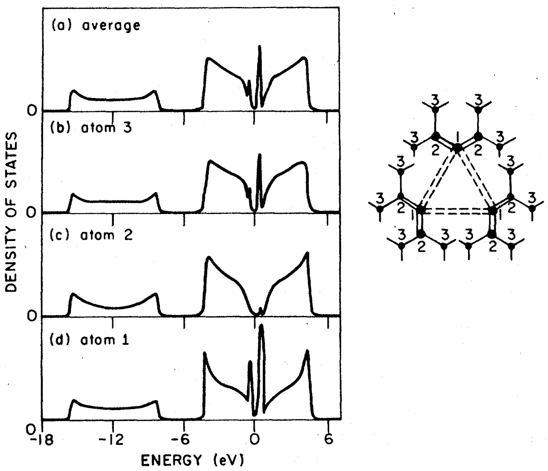

FIG. 6. DOS spectra for a symmetrically relaxed vacancy in the Bethe lattice (the double lines are meant to indicate the modification of the bonds caused by relaxation). The average DOS is shown in (a) with the local DOS shown in (b)–(d), as in Fig. 5.

weakened interactions between the dangling orbitals causes the A- and E-like states to move deeper into the gap. The E-like states, however, remain degenerate with this symmetric relaxation.

Let us now consider a reconstruction in which the symmetry of the system is broken. This is accomplished by having two of the atoms at the vacancy form a weak bond, leaving the third atom with a dangling orbital. The interactions between the dangling orbital and weak bond, however, can not be neglected. We model this structure by keeping the interaction between the relaxed dangling orbital with the atoms forming the weak bond the same as in Fig. 6. The weak bond is modeled by increasing the interactions between the two unrelaxed atoms in Fig. 5 by 50%. The results for this structural model are shown in Fig. 7. The degeneracy of the E-like state has now been lifted. The state splits into two states labeled e_1 and e_2 in the average DOS [Fig. 7(a)] and centered at 0.3 and 0.70 eV, respectively. The e_2 state lies in the conduction-band tail and is the antibonding counterpart of the A-like state (−0.6 eV). This state is localized primarily on the two weakly bonded vacancy atoms. The e_1 state, on the other hand, is concentrated predominantly on the relaxed dangling orbital of the unbonded vacancy atom. The interactions between this orbital and the atoms forming the weak bond causes some of the character of the e_1 state to be found on the bonded atoms. At low temperatures the A-like state is filled, the e_1 state is half filled, and the e_2 state is empty. This is precisely what one would expect for any vacancy in a-As whether or not weak bonds are formed, as long as the dangling bonds are not equivalent. If this vacancy were now to capture an electron (in analogy to the V^- center in Si)[21] it would become a charged spinless defect with a very small electronic activation energy. This is important in understanding the thermally activated ESR signal observed in a-As as discussed in Sec. IV.

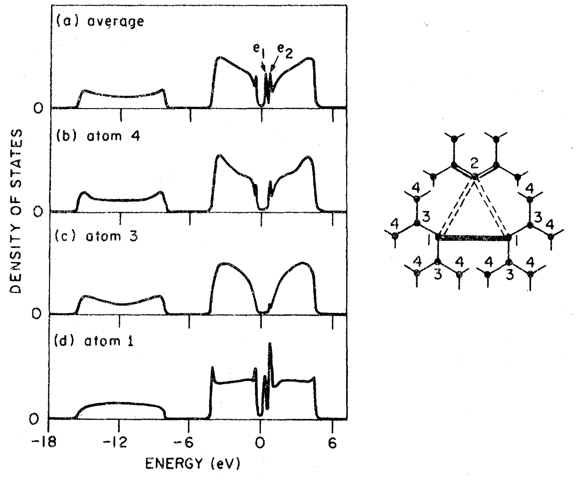

FIG. 7. Electronic DOS of the reconstructed vacancy in the Bethe lattice (schematically depicted on the right with the "distorted" bond between two of the atoms at the vacancy site represented by a heavy line). The average DOS of this configuration is shown in (a) with the states resulting from the splitting of the E state labeled e_1 and e_2 (see text for details). The local DOS about the two bonded atoms (atoms No. 1) is shown in (d). The local DOS about their first and second nearest neighbors are shown in (c) and (b), respectively. The local DOS about atom No. 2 and its neighbors are basically the same as in Fig. 6.

IV. DISCUSSION AND CONCLUSIONS

In the previous sections, we have investigated the electronic structure of various possible defects in a-As as manifested in their DOS spectra. Although the simple models that we have assumed for the BCD's and vacancies are not expected to exhaust all of the possible defect configurations, we believe that those considered here are the ones most likely to occur given the structure and methods of preparation of a-As. Hence, it is instructive and interesting to examine the roles that these defects may play in the optical and thermal excitations of the glass. One of the more sensitive experimental probes of the states involved in such excitations is electron-spin resonance (ESR).[2,21]

Recently, ESR stimulated by illumination with band-gap light ($h\nu \sim 1.1$ eV) at low temperatures has been observed in a-As. The ESR linewidth is found to be consistent with an electron in a p orbital localized over about three atoms.[2] The one-electron states responsible for the paramagnetic signal may result from the NIVAP (non-nearest-neighbor valence alternation pair).[22,23] This can be seen as follows. The free electrons and holes created by photon excitation are captured by an A_1-like state (which is empty) and a dangling bond state (which is filled with two electrons), respectively. This leads to a neutral NIVAP with a single paramagnetic electron in both the A_1 and the dangling bond states. As we pointed out previously, both of these states are predominantly p-like in character ($\gtrsim 90\%$) and are *localized* over only about four atoms in reasonable agreement with the experimental observation.

Unlike the chalcogenide glasses, a-As also exhibits an ESR signal in the dark.[20] A comparison of this ESR signal with the optically induced ESR signal indicates that two different and distinct types of paramagnetic defect centers are involved.

Moreover, the former centers can be thermally excited and are characterized by very small activation energies (~10–30 meV). At low temperatures (~4 °K), the density of the thermally generated centers is on the same order of magnitude as that of the optically induced centers. At high temperatures (~300 °C), the density of these centers increases by an order of magnitude. The paramagnetic spin in this case is thought to be localized on a single As atom and is predominantly p-like in character.

In analogy with the ESR signal of electron irradiated As at room temperature, it has been proposed[20] that the thermally generated spins result from vacancy defects. These are similar in structure to the reconstructed vacancy described in Sec. III. The proposed model[20] assumes that two of the atoms at the vacancy form a weak *distorted bond* while the dangling *orbital* on the remaining atom becomes diamagnetic by either accepting or giving up an electron. The free spins which give rise to the ESR signal result from the breaking of the distorted bond. This would only be possible, however, if the interactions between the dangling orbitals were very weak. Our calculations show that the interactions are fairly strong and result in bonding-antibonding splittings of about ~1.0 eV.

Nevertheless, the thermally generated signal may still be understood in terms of transitions at a vacancy with the following argument. The dangling bond-like state of the reconstructed neutral vacancy (labeled e_1 in Fig. 7) accepts an additional electron forming a V^- center in analogy with Si.[21] This creates a filled band of states which are separated from the empty antibonding-like e_2 states by only a few meV (since we expect the correlation energy to be small in this case). The ESR signal then results from transitions between e_1 and e_2 states. Further, the e_1 and e_2 states (as is evident from the DOS spectra of Fig. 7) are localized primarily within two atoms, thus accounting for the observed increased localization of the thermally induced spin.

Finally, a few comments should be made concerning the implications of the electronic structure results for the vibrational excitations of the various defects considered here. The absence of charge transfer at the twofold site indicates that the infrared and Raman activities are determined primarily by dynamical rather than static charge effects. On the other hand, the small yet non-negligible charge transfer in the fourfold site and IVAP may indicate that static as well as dynamical charges are necessary. A theoretical study of the infrared and Raman activities of BCD's is now underway and will be published shortly.[24]

---

*Supported in part by NSF-DMR 76-80895.

[1] J. C. Knight, Solid State Commun. 16, 515 (1975); J. C. Knight and J. E. Mahan, 21, 983 (1977).

[2] S. G. Bishop, U. Strom, and P. C. Taylor, Solid State Commun. 18, 573 (1976); Phys. Rev. B 15, 2278 (1977).

[3] D. W. Bullett, Phys. Rev. B 14, 1683 (1976).

[4] E. A Davis and G. N. Greaves, Proceedings of the Sixth International Conference on Amorphous and Liquid Semiconductors (Elec. Phenom., 212, Nauka, Leningrad (unpublished).

[5] P. W. Anderson, Phys. Rev. Lett. 34, 953 (1975).

[6] M. Kastner, D. Adler, and H. Fritzsche, Phys. Rev. Lett. 37, 1504 (1976).

[7] R. A. Street and N. F. Mott, Phys. Rev. Lett. 35, 1293 (1975).

[8] R. J. Menanich, G. Lucovsky, W. B. Pollard, and J. D. Joannopoulos, Solid State Commun. 26, 137 (1978).

[9] W. B. Pollard and J. D. Joannopoulos, Phys. Rev. B 17, 1770 (1978).

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

[11] W. B. Pollard and J. D. Joannopoulos (unpublished).

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

[13] G. N. Greaves and E. A. Davis, Philos. Mag. 31, 265 (1976).

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

[15] J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. B 14, 4724 (1976).

[16] S. G. Louis, M. Schlüter, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B 13, 1654 (1975).

[17] K. C. Pandey and J. C. Phillips, Phys. Rev. Lett. 32, 1433 (1972).

[18] C. Calandra, F. Manghi, and C. M. Bertoni, Journal of Phys. C 10, 1911 (1977).

[19] H. Basch, A. Viste, and H. B. Gray, J. Chem. Phys. 44, 10 (1966).

[20] P. C. Taylor, E. J. Friebel, and S. G. Bishop, Solid State Commun. 28, 247 (1978).

[21] G. D. Watkins, Inst. Phys. Conf. Ser. No. 23, Chap. I (1975).

[22] M. Kastner and H. Fritzsche, Philos. Mag. B 37, 199 (1978).

[23] D. Adler and E. J. Yoffa, Can. J. Chem. 55, 1920 (1977).

[24] W. B. Pollard and J. D. Joannopoulos (unpublished).