PHYSICAL REVIEW B VOLUME 14, NUMBER 4 15 AUGUST 1976

Electronic structure of arsenic chalcogenides*

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(Received 23 March 1976)

A nonempirical localized-orbital approach is used to calculate the electronic structure of As_2S_3, As_4S_4, As_2Se_3, As_4Se_4, and As_2Te_3 crystals. Contributions of s, $p\sigma$, and p lone-pair orbitals to the various molecular levels are illustrated. Densities of occupied states agree closely with experimental photoemission data. The fundamental absorption edges in As_2S_3 and As_2Se_3 are found to correspond to indirect gaps, but with several other indirect and direct transitions within a few tenths of an eV of the indirect edge, consistent with most of the optical-absorption studies. The method is readily applicable to the electronic structure of fully coordinated random networks but because of the severe self-consistency problems we are unable to tackle problems associated with thermal relaxation at wrongly coordinated atoms.

I. INTRODUCTION

Although the electrical and optical properties of the arsenic chalcogenides and other V-VI compounds have been the subject of a great deal of experimental and theoretical effort,[1-3] we still have comparatively little firm knowledge about electron states in these materials. In the crystalline form unit cells are large, typically containing twenty atoms, and no first-principles band-structure calculations have been performed. However, it is important to have a clear understanding of the electronic structure of such crystals before we can hope to reach any meaningful conclusions about the local bonding structure in the chalcogenide glasses or to interpret the processes involving localized states in these materials.

The techniques of x-ray and ultraviolet photoemission spectroscopy have been used to determine the valence-band density of states of many crystalline and amorphous compounds of this class[4-6] of materials. The present work reports a nonempirical calculation of the electronic structure of several chalcogenides and finds densities of occupied states in very close agreement with the photoemission data. The contributions of s, $p\sigma$, and p lone-pair orbitals to the various molecular levels are illustrated.

The fundamental absorption edges in As_2S_3 and As_2Se_3 are found to correspond with indirect gaps in the band structure; these are complicated by the presence of other indirect and direct transitions within a few tenths of an eV of the indirect edge, consistent with most of the optical-absorption data. Finally, a brief consideration is given to the localized states associated with a few of the types of defects which could occur in these systems and their relationship to the model put forward by Anderson[7] and extended by Street, Mott, and Davis[8,9] to explain some of the properties of amorphous materials.

As_2S_3 occurs as orpiment in a monoclinic structure[10] with eight As atoms and 12 S atoms in the unit cell. Every atom satisfies its normal valence requirements; each S atom is bonded to two nearest-neighbor As atoms with a bond angle close to 90° while As atoms are coordinated to three S atoms in a triangular pyramidal unit. The resulting structural network consists of infinite layers of puckered As-S bonds in a plane containing the a and c axes with weak bonding between the layers. Cleavage in the crystal occurs along planes perpendicular to the b axis. Within the sheets the As_2S_3 molecules form spiral chains parallel to the c axis and there is some similarity to the structure of selenium. As_4S_4 (realgar) is a molecular crystal containing eight atom units[11] in which the atoms retain their expected near-neighbor coordination but each As atom is now bonded to two S atoms and one As atom. As_2Se_3,[12] and As_4Se_4,[13] are isomorphous with orpiment and realgar, respectively.

The structure of crystalline As_2Te_3 is quite different from the other two arsenic chalcogenides[14,15]; all Te atoms occupy threefold coordinated sites while the As sites are either tetrahedrally or octahedrally coordinated. However, it appears that this unusual coordination does not carry over into amorphous As_2Te_3 films.[14] Illustrations of the atomic arrangements in all these crystal structures may be found elsewhere.[4,6,10-16]

The only previous calculations of orbital energies in the orpiment-structure crystals are those of Chen,[16] Bishop, and Shevchik[4] and Gubanov and Dunaevskii.[17] Chen used the extended Hückel parametrization to derive the energies of an appropriate set of hybridized basis orbitals but he did not calculate an electronic density of states. His predicted valence-band widths are much smaller than those observed by photoemission studies.[4]

Bishop and Shevchik[4] applied a very simple tight-binding model to fit their observed photoemission spectra. They simulated an isolated layer of crystalline As_2S_3 or As_2Se_3 by a unit cell containing five atoms and 20 basis functions (s and p orbitals). Orbitals were not permitted to interact beyond nearest neighbors and matrix elements for these interactions were determined mainly from the experimental density of states of the constituent elements. From this model Bishop and Shevchik deduced a band structure in fair agreement with the experimental data (Fig. 1) which feature a broad s band 10–15 eV below the Fermi level, a bondinglike p band at about 4 eV and nonbonding p bands at 1 eV.

Gubanov and Dunaevskii[17] performed an approximate pseudopotential calculation using a modified Lowdin procedure. The great complexity of the structure made the standard pseudopotential method unsuitable, but the perturbation-theory approach of the Lowdin procedure should make it possible to calculate energy levels in a small energy range close to the forbidden gap. A reasonable value of the band gap was obtained, but it is difficult to reconcile the large separation of neighboring valence or conduction bands (comparable to the forbidden gap itself) in their results, which in this respect differ sharply from the results reported here.

Two calculations have recently been reported for the As_4Se_4 molecule. Chen[18] has performed an extended-Hückel-theory calculation. This reproduced three of the four structural features of the valence band[6] x-ray photoemission spectra (XPS) but differed in the bonding character of some of the molecular orbitals compared to the more successful complete-neglect-of-differential-overlap calculations.[6]

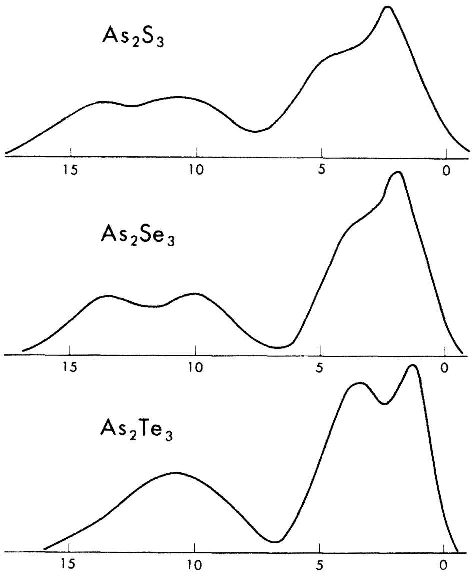

FIG. 1. Valence-band densities of states deduced from XPS spectra (Ref. 4) for crystalline As_2S_3, As_2Se_3, and As_2Te_3.

II. BAND-STRUCTURE CALCULATIONS

A. Method

The method employed is identical to that applied elsewhere to the electronic structure of the group-V[19] and group-VI[20] elements and will not be described in any detail here. A basis of atomic s and p valence level orbitals is used; while this representation should be quite adequate to describe the lower bands we should treat the conduction levels with some caution as in reality these may include appreciable admixture with d states and other high atomic states. The potential at any point in the crystal is approximated as the free atom potential[21] of the nearest atomic site, more distant nuclei being treated as fully screened by the valence electrons.

An isolated atom at site i with Hamiltonian $H_i = T + V_i$ has s and p valence orbitals ϕ_{il}^0 given by

$$H_i\phi_{il}^0 = \epsilon_{il}^0\phi_{il}^0 ,$$

where l labels the angular momentum of the orbital. These free-atom orbitals[21] were used as trial solutions in the pseudopotential equations[23] for the localized orbitals in the solid

$$H\phi_{il} - \sum_{j\neq i}\phi_{jl'}\langle\phi_{jl'}|V_j^i|\phi_{il}\rangle = \epsilon_{il}\phi_{il} , \qquad (1)$$

where V_j^i is the perturbation introduced into the Hamiltonian for the isolated atomic site i by the neighboring atom j. Most of the perturbation from any site will be projected out by orbitals localized on that site so that the unperturbed atomic orbitals and energy levels should form a reasonable approximation to the self-consistent solution for the local orbitals in Eq. (1). We can then expand eigenfunctions ψ_i of the full solid Hamiltonian H in the local basis and, provided only that the local orbitals form a linearly independent set, the one-electron energy levels E_i are determined by the secular equation

$$|(\epsilon_n - E_i)\delta_{mn} + \langle\phi_n|V_n^m|\phi_m\rangle| = 0 ,$$

where suffixes m, n on the orbital now label both the site and angular momentum type. The practicality of this approach for evaluating total energy changes under distortion and hence for discussing relaxation effects in a disordered covalent network has been described elsewhere.[20,23]

B. Band-structure results

In Fig. 2 the calculated densities of states for the molecules As_4S_4 and As_4Se_4 are shown. While it would be quite possible to calculate the densities of states for the full monoclinic crystals by this method, intermolecular interactions between orbitals are so small that we expect the result to be negligibly different from a slightly broadened version of that for the isolated molecule. (An examination of a small number of k points in the crystal Brillouin zone suggested a maximum dispersion in the levels of about 0.2 eV for the valence band and less than 0.1 eV in the conduction band.) For plotting the figures we have used (a) a Gaussian smoothing function of half-width 0.35 eV for valence and conduction levels and (b) a smoothing function of half-width 1 eV applied to the valence band to simulate the experimental XPS resolution. There is almost complete agreement with the XPS data of Salaneck *et al.*[6] The individual levels lie very close to the complete neglect of differential overlap results.[6] In both cases the highest occupied molecular orbital is derived principally from As-As σ-bonding p orbitals; the present calculation may slightly overestimate the splitting off of this state from the rest of the occupied band because we have not included the charge transfer effects which will tend to lower the As $4p$ atomic level relative to the p level of the more electronegative chalcogen. The failure of the extended Hückel calculation[18] to produce any asymmetry in the high-energy peak of the spectrum probably arises partly from an overestimate of such charge transfer effects. A further consideration of the relative As and chalcogen p levels is given below in connection with the magnitude of the band gap.

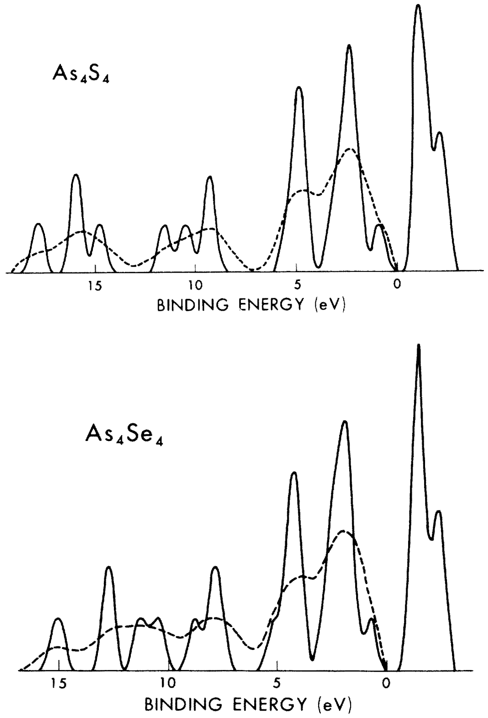

FIG. 2. Densities of states in As_4S_4 and As_4Se_4 calculated using (solid line) a Gaussian smoothing function of half-width 0.35 eV for valence and conduction levels and (broken line) a smoothing function of half-width 1 eV applied to the occupied band to simulate experimental XPS resolution.

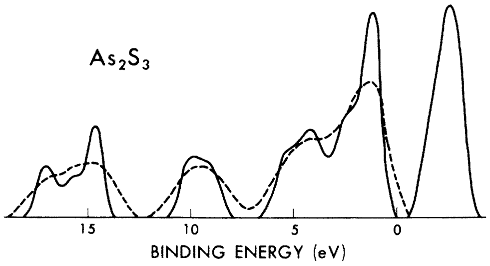

FIG. 3. Density of states in As_2S_3 (orpiment) calculated from a 12-point sampling of the Brillouin zone. The details associated with Fig. 2 apply.

Figures 3, 4, and 5 show the calculated densities of states for crystalline As_2S_3, As_2Se_3, and As_2Te_3, respectively. In these structures, since the crystals do not contain finite molecules we have averaged over a small number of points in the Brillouin zone before applying a smoothing function. For the sulphide and selenide, XPS experiments[4] are hardly able to detect any differences from As_4S_4 and As_4Se_4, respectively, and we do indeed find that for low resolution the differences are very slight. As we mentioned earlier, As_2Te_3 has a quite different crystal structure. The change in local coordination produces distinct alterations in the shape of the lower half of the calculated occupied bands and these results are

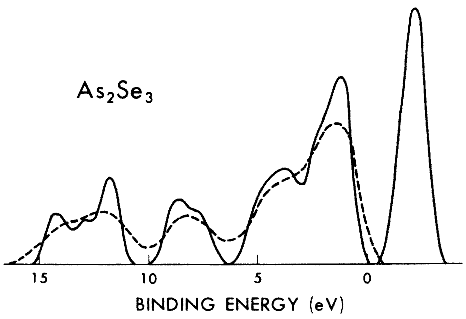

FIG. 4. Calculated density of states in crystalline As_2Se_3. The details associated with Fig. 3 apply.

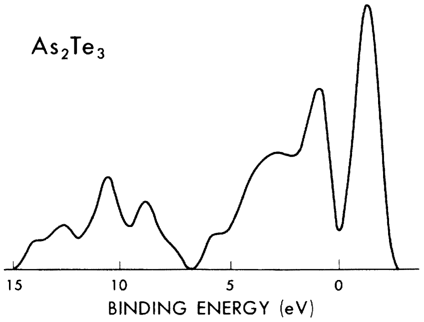

FIG. 5. Density of states in crystalline As_2Te_3 calculated from a 12-point sampling of the Brillouin zone.

again confirmed by the experimental data.[4]

To gain a more physical understanding of the character of the various molecular orbitals, the contributions of the different s and p atomic orbitals as a function of energy are displayed in Figs. 6 and 7. Here we have imposed the artificial normalization condition that

$$\psi_i = \sum a_{in}\phi_n ,$$

with $\sum_n |a_{in}|^2 = 1$ (which, of course, does not mean that the wave function itself is normalized since atomic orbitals on different sites are not orthogonal) and changed from an orthonormal set of p functions on each site to a set which point along the three bond directions for a three-fold coordinated site or along the two bond directions and their common normal, as a nonbonding lone-pair p orbital, for a two-fold coordinated site. In both cases all the states in the lowest 10 eV derive almost entirely from s orbitals, being principally on the sulphur in the lower half and on the arsenic atoms in the upper half of the s band because of the difference in atomic levels. Higher states derive mainly from p orbitals and for states near the valence-band edge the dominant contribution comes from the chalcogens, especially from the chalcogen lone-pair p orbital, as suggested earlier by Kastner.[24] For As_4S_4 the highest occupied state was found to be an As-As bonding state in agreement with Ref. 6.

C. Optical properties

Despite the extensive experimental studies, the nature of the fundamental optical edge in crystalline As_2Se_3 has still not been firmly resolved. Zallen, Drews, Emerald, and Slade[25] conducted optical-absorption experiments down to 10 °K and found thresholds at 2.0 and 2.2 eV which they attributed to direct gap transitions. Other authors[26-29] have reported evidence for indirect transitions. Shaw, Liang, and Yoffe[27] have determined absorption spectra using polarized light at room temperature and at 77 °K. On cooling from 298 °K to liquid-nitrogen temperature the absorption edge sharpens and moves to higher photon energies and in addition structure appears in the curves for $E \perp c$ and $E \parallel c$ at high values for

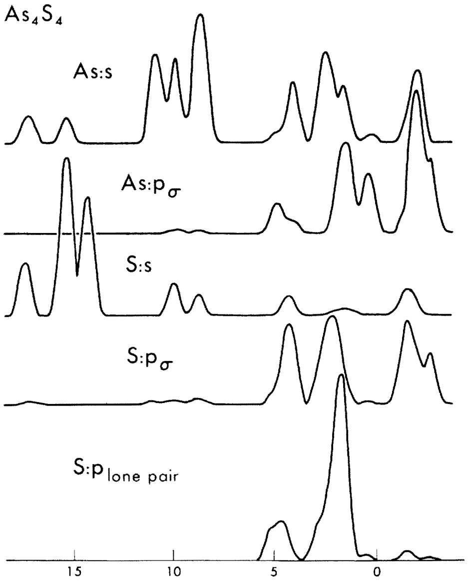

FIG. 6. Calculated density of states in the As_4S_4 molecule decomposed into contributions from s, $p\sigma$, and p lone-pair orbitals.

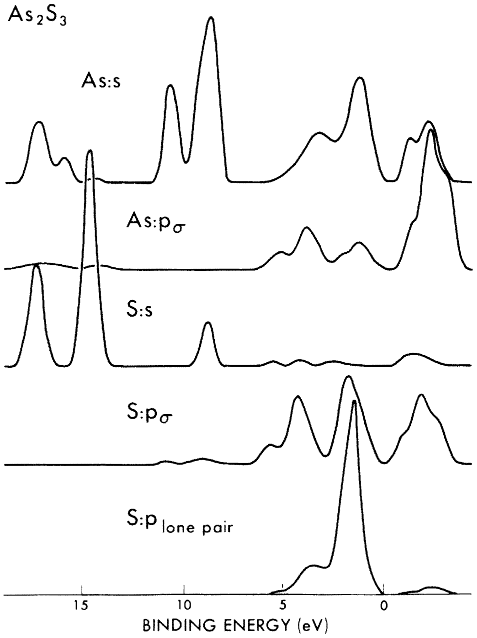

FIG. 7. Calculated density of states at the Γ point in As_2S_3 (orpiment) decomposed into contributions from s, $p\sigma$, and p lone-pair orbitals.

the absorption coefficient α. On cooling to 4 °K there is a further shift of the absorption edge but no appreciable sharpening of the features. Their data suggest that at 77 °K there are indirect gaps at 2.1 eV for $E\perp c$, 2.1 and 2.03 eV for $E \parallel c$, with the first direct gaps at 2.19 and 2.28 eV for $E\perp c$ and 2.26 eV for $E \parallel c$.

Since states near the valence-band edge are predominantly on the chalcogen lone-pair p orbital while states near the conduction-band edge contain roughly equal contributions from the two types of atoms, the magnitude of the calculated gap between occupied and unoccupied states depends quite sensitively on the relative As and chalcogen p levels. For the sulphides the illustrated results were calculated using the Hartree-Fock atomic levels of Clementi[22]: For As, $E_p = -9.9$ eV and for S, $E_p = -11.9$ eV. The calculated energy gap of 1.7 eV in As_2S_3 is a little smaller than its observed value (~2.7 eV). For Se, Ref. 22 gives $E_p = -10.8$ eV and a gap of only 1.0 eV was obtained, which is again about 1 eV less than the experimental gap. The calculated gap increased to 1.6 eV when the Se level was lowered by 1.0 eV and the latter value was used in the figures and in the subsequent discussion. For Te no gap was obtained using[22] $E_s = -19.0$ eV and $E_p = -9.7$ eV, but a gap of about 0.5 eV opens up (Fig. 5) when the chalcogen p level is again lowered by 1 eV. It is unlikely that all of the errors in the calculated gaps arises from differences in the atomic levels of the two atoms however. In the similar calculations for the elemental chalcogens, gaps tended to be about 1 eV too small, perhaps partly because of the crudeness of the local potential which was used and the neglect of the exchange contribution to the gap.[30] Also the repulsive effects discussed in Sec. IV and in Ref. 20 tend to raise the $p\sigma$ orbitals and will thus increase the size of the gap.

Because the number of atoms in the unit cell is

TABLE I. Energies (in eV) of the four highest valence levels and the four lowest conduction levels at various points in the Brillouin zone for As_2S_3, As_2Se_3, and As_2Te_3.

As_2S_3						
(0,0,0)	$(\frac{1}{2},0,0)$	$(0,\frac{1}{2},0)$	$(0,0,\frac{1}{2})$	$(\frac{1}{2},\frac{1}{2},0)$	$(\frac{1}{2},0,\frac{1}{2})$	$(0,\frac{1}{2},\frac{1}{2})$
−8.58	−8.34	−8.50	−8.39	−8.51	−8.37	−8.45
−8.59	−8.56	−8.53	−8.41	−8.59	−8.42	−8.45
−8.73	−8.66	−8.72	−8.45	−8.65	−8.56	−8.46
−8.85	−8.80	−8.88	−8.52	−8.71	−8.70	−8.46
−10.63	−10.69	−10.79	−10.82	−10.76	−10.58	−10.79
−10.73	−10.75	−10.86	−10.82	−10.84	−10.62	−10.79
−10.89	−10.88	−10.88	−10.94	−10.90	−10.66	−10.85
−10.92	−10.89	−10.91	−10.95	−10.90	−10.75	−10.89
As_2Se_3						
(0,0,0)	$(\frac{1}{2},0,0)$	$(0,\frac{1}{2},0)$	$(0,0,\frac{1}{2})$	$(\frac{1}{2},\frac{1}{2},0)$	$(\frac{1}{2},0,\frac{1}{2})$	$(0,\frac{1}{2},\frac{1}{2})$
−8.57	−8.61	−8.54	−8.26	−8.62	−8.20	−8.30
−8.65	−8.65	−8.73	−8.30	−8.69	−8.35	−8.34
−8.87	−8.75	−8.84	−8.36	−8.70	−8.39	−8.38
−8.88	−8.82	−8.86	−8.48	−8.77	−8.49	−8.43
−10.47	−10.59	−10.69	−10.66	−10.69	−10.31	−10.57
−10.57	−10.68	−10.70	−10.70	−10.80	−10.38	−10.57
−10.86	−10.76	−10.81	−10.75	−10.82	−10.43	−10.75
−10.87	−10.81	−10.82	−10.75	−10.85	−10.49	−10.84
As_2Te_3						
(0,0,0)	$(\frac{1}{2},0,0)$	$(0,\frac{1}{2},0)$	$(0,0,\frac{1}{2})$	$(\frac{1}{2},\frac{1}{2},0)$	$(\frac{1}{2},0,\frac{1}{2})$	$(0,\frac{1}{2},\frac{1}{2})$
−8.52	−8.61	−8.28	−8.65	−8.30	−8.66	−8.23
−8.61	−8.61	−8.28	−8.71	−8.30	−8.66	−8.23
−8.84	−8.71	−8.58	−8.78	−8.33	−8.93	−8.36
−9.03	−8.71	−8.58	−8.93	−8.33	−8.93	−8.36
−9.45	−9.47	−9.73	−9.41	−9.65	−9.43	−9.65
−9.54	−9.47	−9.73	−9.48	−9.65	−9.43	−9.65
−9.60	−9.57	−9.90	−9.51	−10.07	−9.62	−9.86
−9.61	−9.57	−9.90	−9.55	−10.07	−9.62	−9.86

so large, the Brillouin zone is narrow and bands are extremely flat. An illustration of the band structure would not be particularly informative and instead we present in Table I the positions of a few of the eigenvalues near to the gap region for several points in the zone. The minimum direct gap occurs at or near Γ. However the maxima in the valence bands occur around the symmetry point $A=(\frac{1}{2},0,\frac{1}{2})$ and the two upper valence bands provide to the conduction-band minimum at Γ indirect gaps which are 0.16 and 0.09 eV smaller than the direct gap. The relative sizes of these gaps are quite consistent with optical data[27] although we have not investigated the transition probabilities for polarized light in more detail.

Optical studies of As_2S_3 suggest an absorption edge similar in complexity to the As_2Se_3 edge but at slightly higher energy. Evans and Young[26] reported an indirect edge with several overlapping absorption bands at 2.9, 3.0, and 3.2 eV ($E \parallel c$) and 3.0, 3.1, and 3.3 eV ($E \perp c$). The calculated results of Table I also predict an indirect gap in As_2S_3 complicated by several indirect and direct transitions within a few tenths of an eV of the fundamental edge.

III. AMORPHOUS NETWORKS AND DEFECT STATES

An "ideal" amorphous semiconductor is generally considered to consist of a collection of atoms connected by a network of covalent bonds in a disordered array such that each atom has its normal coordination of nearest neighbors, i.e., 4 for Si or Ge, 3 for As or Sb, 2 for Se or Te, etc. In addition to x-ray diffraction studies,[31] the chemical shifts observed in electron spectroscopy for chemical analysis experiments[32] provide evidence for such a structure in the chalcogenide glasses. At the composition As_2Se_3 it is found that bonds are predominantly between unlike atoms but the increasing numbers of like-atom bonds can be detected as the composition is varied. These ideal structures will have a definite gap in the one-electron spectrum although a slight tailing of the valence- and conduction-band edges may occur as a result of the small local distortions in bond lengths and angles.

In real amorphous films we might expect that there arise a certain number of defect sites which lack this normal coordination. The way in which adjacent parts of the network have developed may prevent a site from satisfying its valence requirements and we are left with a "dangling bond". The number of such sites will depend on the method of sample preparation and especially on the deposition temperature. Whereas ESR experiments[33] provide firm evidence for such singly occupied states in the group-IV materials, in which they are thought to be associated with divacancies, all the indications are that singly occupied localized states in the gap do not occur in the ground state of chalcogenide glasses. Careful experiments have been unable to detect an ESR signal, low-temperature Curie paramagnetism or variable range hopping in these glasses, yet photoluminescence, photoconductivity, field effect, and drift mobility experiments and the pinned Fermi energy all indicate that these materials do contain a high concentration ($\sim 10^{19}$ eV^{-1} cm^{-3}) of defect states.[34]

Anderson[7] was the first to put forward a model that pins the Fermi energy without producing free spins. He suggested that the network contains more covalent bonding sites than pairs of electrons and that all electrons are paired in bonding states because of an effective attractive Hubbard interaction between up and down spin electrons on the same bond site; the attractive interaction caused by the drawing together of the two atoms in a bond more than compensates for the repulsive Coulomb interaction U. The model has an energy gap for one-electron excitations but the two-electron spectrum extends right down to zero energy. These two-electron excitations are envisaged as new covalent bonds in the structure and while they cannot be excited optically or lead to ordinary electronic conduction they do provide the mechanism for pinning the Fermi energy in the middle of the one-electron gap and lead to a linear term as observed in the specific heat.[35]

Street, Mott, and Davis[8,9] have applied Anderson's concept of an effective attractive interaction of paired electrons to point defects in chalcogenide glasses. They assume that a dangling bond state may be occupied by zero, one or two electrons, labeled D^+, D^0, and D^-, respectively, and that lattice distortion is sufficient to make exothermic the reaction

$$2D^0 \rightarrow D^+ + D^- . \qquad (2)$$

All defect sites are then either positively or negatively charged in the ground state. They find that such a model can provide a unified description of many of the electrical and optical properties of chalcogenide glasses.

A characteristic property of the chalcogens in an amorphous network is the relative ease with which they can change coordination. In the normal lattice each neutral S or Se atom is covalently bonded to two other atoms and has two electrons in a lone-pair state. In a random network it may be energetically favorable for an atom which, because of the local topography, could not otherwise satisfy its normal valence requirements, to approach and bond with an already doubly coordinated chalcogen. The surplus electron may either remain in a state localized around this defect or gain binding energy by pairing with a singly occupied dangling bond electron elsewhere in the network leaving a triply coordinated chalcogen with a positive charge. The driving energy for the process comes from the extra covalent bond which has been formed. Since the bonding in chalcogens comes almost entirely from the overlap of *p* states and the bond angles are quite close to 90° the binding provided by the third bond in the D^+ arrangement can be almost as strong as that from each of the other two; this would not be the case at a group-IV atom where there is no free direction for the extra bond.

Results for various types of unrelaxed defect sites are displayed in Fig. 8. The 80 different electron levels at the zone center were calculated for a periodic arrangement of As_2Se_3 unit cells containing a point defect. Figure 8(a) is for the perfect crystal, in (b) one of the As atoms has been replaced by a Se atom, in (c) a Se atom was replaced by an As atom, and in (d) an As atom was replaced by a Se atom and no interactions were allowed between this atom and one of its three neighbors. Since the two types of atoms are of similar size, (b) and (c) should provide fairly realistic models for a threefold coordinated Se atom and a twofold coordinated As atom, respectively; (d) is a somewhat artificial model for generating a Se atom which is bonded to only one other atom in the lattice. The calculations have not been carried to self-consistency here; the diagonal energies in the tight-binding determinant must vary to some extent according to the local charge on each atom and are thus also a function of the state occupation numbers but for simplicity we have kept the atomic levels constant throughout (−9.90 and −11.79 eV for *p* states, −17.61 and −20.83 eV for *s*-states on As and Se, respectively).

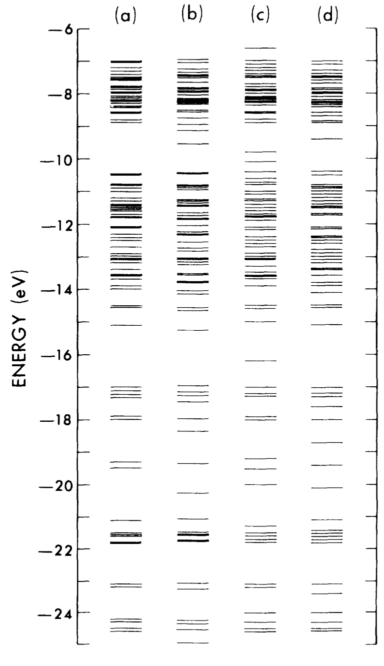

FIG. 8. Electron levels at the zone center calculated for a periodic arrangement of As_2Se_3 unit cells containing a point defect: (a) perfect crystal; (b) Se atom in three-fold site; (c) As atom in two-fold site; (d) Se atom with a dangling bond. The atomic *s* and *p* energy levels are at −17.61 and −9.90 eV for As and at −20.83 and −11.79 eV for Se.

In the perfect crystal there is a gap in the one-electron spectrum between −10.48 and −8.88 eV. New states are introduced within this gap by the presence of defects. The threefold coordinated Se defect had a level at −9.63 eV; this state was comprised almost entirely of antibonding *p* orbitals between the new Se atom and its three neighbors. This level is highly localized because in our model all three of the neighbors are also atoms (a one-dimensional trigonal chain of Se atoms would have its conduction-band edge at −9.58 eV using the present parameters); if some of the neighbors were As atoms the state would grow larger and move closer to the conduction-band edge.

For the doubly coordinated As defect the states at −10.44 and −10.13 eV are comprised principally of the As–As bonding orbitals at the defect. The new level at −9.77 eV is about 50% localized on the As *p* orbital in what would have been the Se lone-pair direction but on the neutral defect is now the As dangling bond.

For the Se dangling bond model, the highest occupied state is at −10.42 eV and shows no noticeable localization on the defect atom. The higher unoccupied levels at −9.4 and −8.9 eV are ~50% localized in Se-Se antibonds on the atom neighboring the defect; these states arise only because our method for the creation of a Se dangling bond automatically creates at the same time Se-Se bonds on an adjacent atom. An alternative method for modeling Se dangling bonds is to compare the results for a finite one-dimensional trigonal chain[20] with those for an infinite chain. Using the same parameters, the infinite chain has a gap in the spectrum between −10.96 and −9.58 eV; a finite (15-atom) chain has levels in the gap at −10.80 and −10.79 eV corresponding to even and odd combinations of the dangling bond states. About 20% of the weight of each state is localized on each of the two end-most atoms at either end of the chain. There are no gap states at the conduction-band edge.

IV. TOTAL ENERGY CONSIDERATIONS

As discussed elsewhere[20] for the elemental group-V and group-VI materials, equilibrium interatomic distances come about as a balance between attractive bonding forces and the repulsive terms characteristic of filled shell systems. The attractive term is essentially the off-diagonal $pp\sigma$ interaction $\langle \phi_{pj} | V_j^i | \phi_{pi} \rangle$ which provides the approximate average lowering of electrons in the bonding p band relative to the lone-pair band. The repulsion comes about because the diagonal energies in the pseudopotential equations are raised as the atoms are brought together. Multiplying (1) on the left by ϕ_{il}^0 we can estimate this repulsion by

$$\epsilon_{il} = \epsilon_{il}^0 + \sum_j \left(\langle \phi_{il}^0 | V_j^i | \phi_{il}^0 \rangle - \langle \phi_{il}^0 | \phi_{jl'}^0 \rangle \langle \phi_{jl'}^0 | V_j^i | \phi_{il}^0 \rangle \right).$$

Between two As atoms or two Se atoms the bonding $pp\sigma$ interactions are approximately 2.1 and 2.4 eV, respectively, at the nearest-neighbor distances. Thus in Se the center of gravity of the bonding band lies just over 2 eV below the lone-pair band and the unoccupied antibonding band lies a similar distance above the highest valence states. With two bonding electrons per atom we should have a cohesive energy of about 5 eV per atom were it not for the repulsive self-energy term which reduces the cohesion by about 60%. A similar balance occurs in As; for both elements the experimental binding energy in the solid is about 2.0 eV per covalent bond and the same will be true of their compounds provided bond length and bond angle distortions are not large. Thus the effective attractive electron-electron interaction U^{eff} in Anderson's model can be as large as the mobility gap in the one-electron spectrum of extended states and in that case the Fermi level may be pinned very effectively near the middle of the one-electron gap and at the same time the optical, conductivity, and photoelectric gaps may be equal.[7]

For the perfect crystal unit cell the sum of the 56 doubly occupied energy levels at Γ, neglecting the diagonal repulsive terms in the atomic levels, is 138.8 eV less than that for the isolated atoms. The difference is equal to 5.8 eV per bond in the attractive part of the binding energy (slightly larger than twice the $pp\sigma$ interaction because the s orbital and second-neighbor interactions also give small contributions to the bonding term). The repulsive terms will reduce this bond energy by about 60%.

An accurate calculation of the energy associated with the creation of a dangling bond is difficult since it would require a very careful treatment of the self-consistent redistribution of charge on the atoms surrounding the defect. However this energy is probably smaller than in the more highly coordinated elements (in silicon, for example, the surface energy is about 1 eV per dangling bond[36]). For the infinite one-dimensional chain of Se atoms the bonding terms were found to give a contribution of $E_1 = 5.7$ eV to the cohesive energy per atom. Since the observed cohesive energy is 2.1 eV, this corresponds to a repulsive term of 3.6 eV between each pair of atoms. For the 15-atom neutral chain the total bonding contribution was found to be only 3.6 eV less than 15 E_1 and in separating a pair of atoms to create two dangling bonds we regain the repulsive interaction between them. Whereas in the infinite chain all bonding and lone-pair states are filled, in the neutral finite chain the creation of two vacant levels 1.0 eV above the atomic p level pushes down the total energy of the occupied levels, regaining part of the energy needed to break a bond. An additional repulsive term arises from the slight charge build-up at the ends of the chain but we conclude that the energy associated with each dangling bond is likely to be less than half the cohesive energy per bond, i.e., less than 1 eV, and that it is quite reasonable to expect that such defects are present in chalcogenide glasses.

No ESR signal is observed and therefore no neutral dangling-bond states can be present at low temperatures. A possible explanation[8,9] is that the reaction (2) is exothermic. Because of the severe self-consistency problems, it is not possible to confirm this hypothesis at the present time. However, the energy needed to place both electrons in the same dangling bond state (the Hubbard U) will be fairly small since the states are not highly localized and if we assume that the network distorts so that the newly formed covalent bond has approximately the same strength as any other bond in the undistorted network, the condition for (2) to be exothermic is simply that U is less than the vacancy creation energy. Under this condition in the ground state some of the defect chalcogens become threefold coordinated positive centers and an equal number become singly coordinated negative centers with paired electrons in the dangling bond state just above the valence-band edge. The strong lattice distortion effects accompanying the different occupation numbers at the defects can explain many of the unusual electrical and optical properties of the glasses.[7-9] In particular, they explain why the Fermi level is pinned although no vertical one-electron transitions can occur between the ground state and states deep in the gap. A state deep in the gap can arise by thermal relaxation after a neutral defect has been produced by optical excitation and it is presumably this state that is responsible for the metastable ESR signal and weak absorption band down to 0.8 eV induced by illumination of As_2Se_3 with band-gap radiation.[37]

Finally, we note that another way to estimate the relative As and Se p levels in the self-consistent system is to use the observed bond strengths. For the three bonds As-As, Se-Se, and As-Se these are 46, 49, and 52 Kcal/mole, respectively.[38] Thus the heteropolar bond strength lies about 0.2 eV above the average of the homopolar bonds. If each bond is made up of hybrids of energies E_A, E_B with an interaction V the bonding and antibonding levels are given by

$$E = \tfrac{1}{2}(E_A + E_B) \pm \tfrac{1}{2}[(E_A - E_B)^2 + 4V^2]^{1/2} .$$

For $E_A - E_B \ll 2V$ the heteropolar contribution to the strength of the doubly occupied bonding level becomes $(E_A - E_B)^2/4V$. As we have shown, $2V \sim 5$ eV which implies a difference in $E_A - E_B$ of about 1.5 eV. Since bond angles at the chalcogens average 90° and those at the As atoms average about 97°, the difference in As and Se p levels may be slightly larger than the energy difference between the bonding hybrids.

V. CONCLUSIONS

Using a very simple tight-binding model and without the need for any empirical fitting of the interactions between near-neighbor atomic orbitals we obtain a description of the electronic structure of crystalline chalcogenides consistent with their experimental properties. In particular we find that the absorption edges of As_2S_3 and As_2Se_3 are made up of several closely spaced indirect transitions. The method is readily transferable to the electronic structure of fully coordinated random networks but because of the severe self-consistency problems we are unable to tackle the problems associated with thermal relaxation at wrongly coordinated atoms.

ACKNOWLEDGMENTS

I would like to thank Professor M. L. Cohen for helpful conversations. Part of this work was done under the auspices of the U. S. Energy Research and Development Administration.

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*Work supported in part by the NSF Grant No. DMR 72-03206-A02.

†Supported in part by the Royal Commission for the Exhibition of 1851.

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