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Electronic structures of As_4Se_4 and Se_8

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The valence-band electronic structures of molecular chalcogenide solids are investigated by molecular-orbital method using As_4Se_4 and Se_8 as model systems. The calculated energy levels and the density of states are compared with x-ray-photoemission experimental data. The nature of each state and bands of states is analyzed in terms of atomic orbitals (s or p) and in terms of hybrids (bonding or lone pair). It is found that in the former description the lower and the upper valence bands can clearly be identified as s and p bands, respectively. However, with the physically more meaningful characterization in terms of bonding or lone-pair states, most states are mixtures of the two components. No occupied bands are dominantly bonding or nonbonding.

I. INTRODUCTION

One of the most intriguing questions in the physics of molecular chalcogenide solids is the nature of the valence-band states in these solids. There are six valence electrons in a chalcogen atom (e.g., S and Se), while the coordination number in most chalcogenides is only 2. In contrast, in the well-understood group-IV atoms (e.g., Si and Ge) there are four valence electrons per atom, and the coordination number is 4. It is obvious then, that not all of the valence electrons in a chalcogen atom participate in the bonding. Since it can be expected that the nonbonding electrons and the bonding electrons will contribute differently to the optical and the electrical properties of the solids, it is important to distinguish the energy states of these electrons. In other words, one would like to identify the various valence-band states as belonging to either the bonding or nonbonding electrons.

It has been suggested by Kastner[1] that the valence bands of chalcogenides can be divided into three groups: (i) the s band, having the lowest energy, and occupied by two s electrons; (ii) the lower p band arising from the bonding states and occupied by the two p electrons participating in the bonding; and (iii) the upper p band consisting of the nonbonding or lone-pair states. This is in fact a simplified view of the scheme used earlier by Tutihasi and Chen[2] to interpret the optical properties of trigonal Se, in which the bonding orbitals and the deep-lying "s states" were formed by hybridization of s and p orbitals to account for the bond angle ($\neq 90°$).

Kastner's model lacks quantitative support and has encountered two difficulties. The first is the observation of photodissociation[3] and photocrystallization[4] of chalcogenide solids with the band-gap light. These phenomena are attributed to the breaking of the bonds by the photons. However, according to Kastner's model, the upper valence band is of nonbonding type and hence excitations of electrons from this band should have little effect on the bonding.

The second difficulty is revealed by Nielsen's photoemission experiment on amorphous Se.[5] His experiment with 21.2-eV photons indicates that the entire valence band of amorphous Se extends not more than 9 eV from the top edge, and consists of only two bands. The deep-lying "s band" was not observed. Nielsen's valence-band density of states has been quantitatively interpreted by this author[6] using a semiempirical molecular-orbital theory. The idea is the assertion that the four nonbonding electrons occupy two equivalent orbitals which are hybrids of s and p orbitals, rather than in two orbitals with large energy difference. Because of the hybridization, the nonbonding hybrid has an energy comparable to that of bonding orbital, and hence, the two types of orbitals are intermixed in contributing to the two valence bands observed by Nielsen.

Recently, photoemission experiments with much higher energies (x ray), on various chalcogenide solids have been reported by several groups of investigators.[7-10] A common feature is the discovery of the "s state" in the valence-band density of states, which was missing in Nielsen's data. Since the existence of the s-state band is more in accord with conventional band theory and Kastner's model, Schlüter *et al.*[11] have attempted to fit and interpret the valence-band density of states of trigonal Se and Te by pseudopotential calculations.

Although the existence and/or the interpretation of the s-state band is still subject to some questions,[12] we intend to examine what the semiempirical molecular-orbital theory, which was used to interpret Nielsen's data,[5,6] can tell about these states. In addition, we intend to pursue the role of the bonding and the lone-pair states in the upper valence band.

As_4Se_4 has been chosen as a model system for the following reasons. The solid consists of molecule of finite-number (8) atoms, and therefore, it is easier to apply the molecular-orbital method.

In contrast, As_2Se_3 and amorphous or trigonal Se (chains) consist of molecules infinitely extending in two and one dimension, respectively, and the application of the molecular-orbital theory requires special assumptions. The ring molecule Se_8 has the same advantage, and we shall compare the results of calculations on the two molecules. The intermolecular interactions in the solid state (amorphous or crystalline) are small compared to the intramolecular interactions and therefore the effect of the former will be represented by Gaussian broadening of the molecular energy levels.[6] In addition, As-As bonds exist in As_4Se_4 but not in As_2Se_3. It is conceivable that such like-atom bonds exist abundantly in nonstoichiometric As-Se glasses. Thus, As_4Se_4 appears to be a better model system than As_2Se_3. The molecular-orbital study of the latter has been reported previously.[13]

The molecular-orbital (MO) calculations are carried out with the Wolfsberg-Helmholz approximation.[14] In this method, the off-diagonal elements H_{ij} $(i \neq j)$ of the Hamiltonian matrix are approximated by

$$H_{ij} = \tfrac{1}{2} f S_{ij} (H_{ii} + H_{jj}) \ , \qquad (1.1)$$

where f is a parameter usually having a value between 1 and 2, and S_{ij} is the overlap integral between the basis orbitals i and j. It has been pointed out in a previous paper,[6] that this formula for H_{ij} is not invariant with respect to a unitary transformation of the basis orbitals, e.g., hybridization. In Ref. 6, the agreement with Nielsen's data was obtained only when Eq. (1.1) was applied to the hybrid-orbitals (HO) bases (with equivalent lone pairs). When Eq. (1.1) was applied to the atomic-orbital (AO) bases, a much wider spread in valence band was obtained. It is possible to apply Eq. (1.1) to the AO bases, while expressing the MO's in terms of the more physically intuitive HO's, as long as one performs the necessary transformations. This is done in the present calculations. Thus the same MO can be represented as a linear combination of AO's or as that of HO's. In this way, the composition of the MO can be analyzed in terms of AO (s or p), or in terms of HO (bonding or lone pair).

The MO calculations including the composition analysis for As_4Se_4 are detailed in Sec. II. In Sec. III we present the results of similar calculations for Se_8, and discuss the over-all results with comparison to experimental results.

Our conclusion, in short, is that the compositions of the lower and the upper valence bands, in terms of atomic orbitals, are s and p type, respectively. However, in terms of the more physical hybrid orbitals, both bands contain considerable mixtures of bonding and lone-pair orbitals. Only the empty (conduction) band is almost purely of antibonding type.

II. ELECTRONIC STATES OF As_4Se_4

The molecular structure[15] of As_4Se_4 is shown in Fig. 1. Each As atom (1, 2, 3, or 4) is bonded to two Se atoms (5, 6, 7, or 8) and an As atom, while each Se atom is bonded to two As atoms. The As-As and As-Se bond lengths are 2.564 and 2.388 Å, respectively. The As atoms 1 and 4 lie above the plane (square) formed by the four Se atoms, with the As-As bond parallel to the plane. The As-As bond 2–3 lies below and parallel to the Se plane, and is perpendicular to the As 1-4 bond. Thus the molecular symmetry belongs to the point group D_{2d}. The character table for the irreducible representations of this group can be found in Hamermesh.[16]

The coordinate systems at each atomic site are also shown in Fig. 1. With this choice of the coordinate systems, the As s, p_x, and p_z orbitals transform as the irreducible representations A_1, B_2, and E; the p_y orbitals transform as A_2, B_1, and E. The Se s and p_x orbitals transform as A_1, B_1, and E; the p_y and p_z orbitals transform as A_2, B_2, and E. The linear combinations of atomic or-

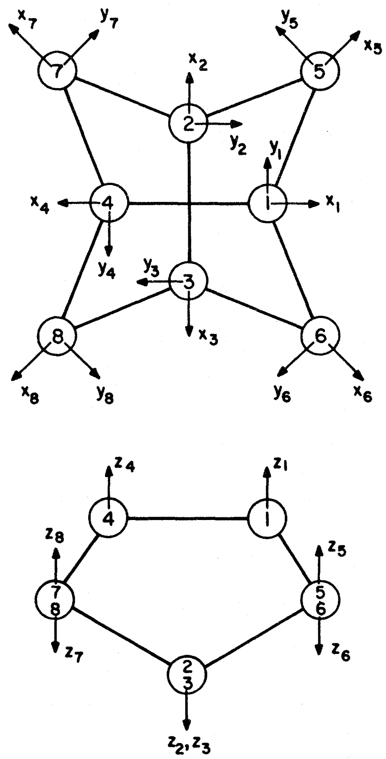

FIG. 1. Molecular structure of As_4Se_4, not to scale. Atoms 1–4 are As, 5–8 are Se. The coordinate axes at each atomic site are shown. The upper and lower figures are for top view and side view, respectively.

bitals which transform according to an irreducible representation are represented by

$$\phi_i=\sum_k a_{ik}\chi_k \, , \tag{2.1}$$

with

$$\langle \phi_i | \phi_i \rangle = \sum_{k,l} a_{ik}a_{il}S_{kl}=1 \, , \tag{2.2}$$

where a_{ik}'s are the coefficients and S_{kl} is the overlap integral between the AO's χ_k and χ_l. The overlap integrals are calculated with the analytic Hartree-Fock wave functions of Watson and Freeman.[17] These overlap integrals are used to form the 32 $\times$32 overlap matrix S.

Let us denote the collection of the 32 symmetry combinations ϕ_i and the collection of the 32 AO's χ_k by column matrices Φ and X, respectively, then

$$\Phi = AX \, , \tag{2.3}$$

where A is the square matrix of the coefficients. Then the group overlap matrix G whose elements are the overlap integrals between ϕ_i's, can be calculated by the matrix multiplication

$$G \equiv \Phi\Phi^\dagger = AXX^\dagger A^\dagger = ASA^\dagger \, , \tag{2.4}$$

where $A^\dagger$ denotes the transpose of A. The group overlap matrix G is block diagonalized within each irreducible representation.

The valence-state energies E_i deduced from the atomic spectroscopic data[18] are used for the diagonal element H_{ii} of the Hamiltonian matrix. Because of the small ionicity of the As-Se bond, the effective charges on the As and Se atoms are not integer multiples of the elemental charge. The valence-state energies of the atomic orbitals of such atoms are obtained by the interpolation

$$E(Q)=E_0+Q(E'-E_0) \, , \tag{2.5}$$

where Q is the ionization state of the atom, and E_0 and E' are the valence-state energies of the neutral and the singly ionized atom, respectively. The latter values can be deduced from the tables of atomic energy levels.[18] For As and Se, the following values are used:

$$\begin{aligned} \text{for As:}\quad & E_s(Q)=-18.20-13.38Q \text{ eV} \, , \\ & E_p(Q)=-9.19-10.52Q \text{ eV} \, ; \\ \text{for Se:}\quad & E_s(Q)=-21.12-8.94Q \text{ eV} \, , \\ & E_p(Q)=-10.82-8.59Q \text{ eV} \, . \end{aligned} \tag{2.6}$$

The ionization state Q is calculated from the coefficients of the occupied MO's. Thus, the calculation must be carried out iteratively until self-consistency in Q is achieved. Define P_{ij} as the contribution of the ith AO to the jth MO,

$$P_{ij}=\tfrac{1}{4}C_{ij}\sum_k C_{kj}G_{ik} \, , \tag{2.7}$$

then

$$Q=N-\sum_j n_j\Bigl(\sum_i P_{ij}\Bigr) \, , \tag{2.8}$$

where N is the number of valence electrons ($N=5$ for As, $N=6$ for Se), n_j is the number of electrons occupying the jth MO, and the i summation is over those ϕ_i's which belong to the atom in consideration. Because of the neutrality of the molecule and the normalization of the MO coefficients, we must have

$$Q(\text{As})=-Q(\text{Se}) \, . \tag{2.9}$$

The off-diagonal elements of the Hamiltonian matrix H_{kl} ($k \neq l$) are calculated from the valence state energy (the diagonal elements) according to Eq. (1.1). The matrix H can also be block diagonalized by the transformation

$$F=AHA^\dagger \, . \tag{2.10}$$

Using the block-diagonalized matrices F and G, the secular equation

$$FC=GCE \tag{2.11}$$

is solved to obtain the MO energies E and the MO coefficients C. The latter are used to calculate Q to examine the consistency of the input and output Q values. The calculations are repeated until the two Q values differ less than $0.01e$. Calculations are carried out with different values of the off-diagonal element parameter f ranging from 1.1 to 1.7.

The MO energies, the irreducible representation of the MO's, and the ionization state Q of As atoms obtained from these calculations are summarized in Table I.

As expected from the covalency of the molecule, the ionization state Q is small (~ 0.08). The value varies only slightly over the range of f values. Because the value of $E'-E_0$ in Eqs. (2.5) and (2.6) is comparable to that of E_0, even this small value of Q affects the results of calculations (especially the MO coefficients) significantly, necessitating the use of self-consistent-charge calculations.

The 44 valence electrons occupy the lower 22 MO's. Although the spread of the unoccupied MO's (23–32), and the gap between the highest occupied (22) and the lowest empty levels vary by a factor of 6 over the range of f values from 1.1 to 1.7 (see Table I), the corresponding change in the spread of the occupied levels is only about 50%. Thus the nature of the occupied MO's, which is our major interest in this paper, is rather insensitive to the f value.

The occupied MO levels can be grouped into an upper band and a lower band. The former lies in the energy range from about -9 to -12 eV and has a high density of states containing 14 MO's(9–22). The lower band lies between -16 and -24 eV and

TABLE I. Molecular-orbital energies and the ionization states Q of As in As_4Se_4, for different values of f.

Mo. No.	Rep.	f 1.7	1.5	1.3	1.1
31,32	E	4.14	−0.61	−4.88	−8.22
30	B_2	2.32	−1.46	−4.97	−7.91
29	A_1	2.10	−1.98	−5.59	−8.38
28	A_2	0.64	−2.42	−5.48	−8.55
26,27	E	−0.44	−3.21	−5.95	−8.54
25	B_1	−0.50	−3.47	−6.18	−8.50
23,24	E	−2.30	−4.61	−6.78	−8.82
22	A_2	−8.63	−9.06	−9.49	−9.90
21	B_2	−9.36	−9.56	−9.74	−9.96
19,20	E	−9.48	−9.67	−9.86	−10.01
18	B_1	−9.77	−9.88	−9.98	−10.05
17	B_2	−9.89	−9.96	−10.03	−10.07
15,16	E	−10.08	−10.15	−10.16	−10.09
14	A_1	−10.14	−10.20	−10.18	−10.02
13	A_1	−11.43	−11.04	−10.56	−10.10
11,12	E	−11.57	−11.24	−10.81	−10.31
10	A_2	−11.77	−11.29	−10.81	−10.33
9	B_2	−12.90	−12.09	−11.29	−10.49
7,8	E	−16.33	−16.42	−17.09	−18.83
6	A_1	−17.34	−17.38	−17.93	−19.33
5	B_2	−20.85	−20.15	−19.74	−19.95
4	B_1	−20.27	−20.06	−20.12	−20.58
2,3	E	−22.13	−21.41	−20.93	−20.80
1	A_1	−24.50	−23.17	−21.92	−20.86
$\Delta^a(23-32)$		6.44	4.00	1.90	0.91
$\Delta\ (22-23)$		6.33	4.45	2.71	1.08
$\Delta\ (1-22)$		15.87	14.11	12.43	10.96
Q (As)		0.077	0.077	0.079	0.083

[a] $\Delta(i-j)=E(j)-E(i)$.

contains only 8 MO's. Assuming that the random intermolecular interactions result in Gaussian broadening of each MO level with the same width ω, the density of states at energy E can be written

$$D(E)=\frac{1}{\sqrt{\pi}\,\omega}\sum_{i=1}^{32}\exp\left(\frac{-(E-E_i)^2}{\omega^2}\right)\ , \tag{2.12}$$

where E_i's are the MO energies. Figure 2 shows a plot of $D(E)$ vs E from − 24 to − 8 eV, with $\omega = 0.75$ eV and the MO energies obtained with $f = 1.4$. This result is in semiquantitative agreement with the experimental data obtained by Liang.[9]

In order to analyze the composition of each MO, we tabulate the quantity P_{ij}, Eq. (2.7) for $f = 1.4$, in Table II. The contributions from the p_x, p_y, and p_z orbitals are lumped together under the column p; and the contributions from the like atoms are also summed up in the same column. (Thus the entries actually represent $4P_{ij}$, and are normalized to unity.) In the lower part of Table II, the contributions (per atom) from each of the three groups: empty levels (23–32), upper occupied levels (9–22) and lower occupied levels (1–8), are listed. One can see that more than 90% of the lower occupied band consists of the As and Se s orbitals. The As p orbitals contribute almost equally to the upper occupied and the empty bands, while the contributions of Se p orbitals to the two bands are in the ratio of 2 to 1.

The above finding seems to confirm the description, by many workers,[1,7–10] of the lower occupied band as the s band, and the rest as p bands. However, this description tells little about the bonding or nonbonding nature of the electronic states. Such information can be obtained by representing MO's with HO's as bases. HO's can be constructed by linear combinations of AO's, so that each HO has an intuitive quantum chemical meaning. For example, the s, p orbitals of the As atom in As_4Se_4 can be hybridized into three bonding hybrids, each having a maximum density in the direction of As-As and As-Se bonds, and a lone-pair hybrid which is occupied by two electrons not shared with the neighboring atoms. Similarly, the s and p orbitals of Se atoms are hybridized into two bonding hybrids and two lone-pair hybrids. The explicit forms of the hybrids can easily be calculated from the molecular geometry and the orthonormalization conditions, and hence there is no reason to make any assumptions and approximations about the compositions of these hybrids. The results for the hybrids in As_4Se_4 are given below:

For As atom:

$$\begin{aligned}
&\text{As-As bonding,}\quad h_1 = 0.5876s - 0.8091x\ ,\\
&\text{As-Se bonding,}\quad h_2,\ h_3 = 0.2583s + 0.1880x\\
&\qquad\qquad\qquad \pm 0.7071y - 0.6308z\ ,\\
&\text{lone pair,}\quad h_4 = 0.7220s + 0.5240x + 0.4519z\ ;
\end{aligned} \tag{2.13}$$

For Se atom:

$$\begin{aligned}
&\text{Se-As bonding,}\quad h_1,\ h_2 = 0.3514s - 0.6138x_1\\
&\qquad\qquad\qquad \mp 0.3554y \pm 0.6112z\ ,
\end{aligned}$$

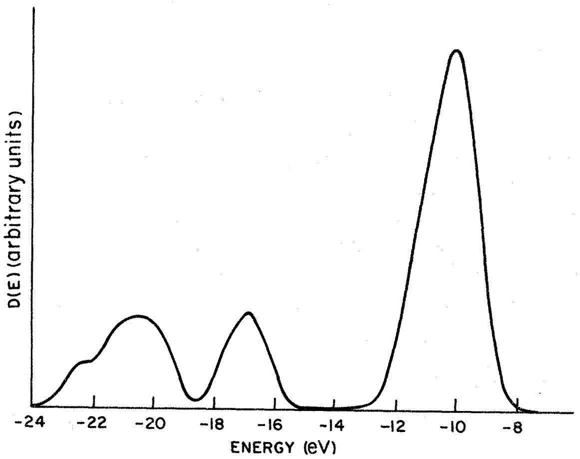

FIG. 2. Valence-band density of states for As_4Se_4, calculated from MO energies with Gaussian width $\omega = 0.75$ eV (parameter $f = 1.4$).

TABLE II. Compositions of As_4Se_4 molecular orbititals in terms of s, p atomic orbitals.

Mo. No.	Rep.	E	As s	As p	Se s	Se p
31, 32	E	−2.82	0.11	0.42	0.03	0.44
30	B_2	−3.27	0.02	0.32	0.00	0.65
29	A_1	−3.86	0.05	0.39	0.05	0.50
28	A_2	−3.95	0.00	0.59	0.00	0.41
26, 27	E	−4.58	0.01	0.88	0.00	0.12
25	B_1	−4.86	0.00	0.76	0.02	0.22
23, 24	E	−5.71	0.00	0.60	0.00	0.40
22	A_2	−9.28	0.00	0.00	0.00	1.00
21	B_2	−9.65	0.00	0.95	0.00	0.05
19, 20	E	−9.77	0.00	0.21	0.00	0.79
18	B_1	−9.94	0.00	0.22	0.00	0.78
17	B_2	−10.00	0.00	0.17	0.00	0.83
15, 16	E	−10.16	0.01	0.48	0.00	0.51
14	A_1	−10.20	0.01	0.80	0.01	0.19
13	A_1	−10.81	−0.01	0.74	−0.01	0.28
11, 12	E	−11.04	0.00	0.35	0.01	0.64
10	A_2	−11.05	0.00	0.40	0.00	0.60
9	B_2	−11.69	0.00	0.55	0.00	0.45
7, 8	E	−16.65	0.64	0.07	0.19	0.10
6	A_1	−17.57	0.46	0.08	0.42	0.04
5	B_2	−19.89	0.98	0.00	0.00	0.02
4	B_1	−20.05	0.00	0.02	0.97	0.00
2, 3	E	−21.14	0.23	0.00	0.77	0.00
1	A_1	−22.53	0.50	−0.01	0.52	−0.01
Sum (23–32)			0.07	1.47	0.04	0.92
Sum (9–22)			0.01	1.48	0.00	2.01
Sum (1–8)			0.92	0.06	0.96	0.06
Sum (1–32)			1.00	3.00	1.00	3.00

lone pairs

$$h_3,\, h_4 = 0.6136s + 0.3513x \pm 0.6113y \pm 0.3555z\,, \tag{2.14}$$

where the x, y, and z coordinates are shown in Fig. 1, and for atoms 6 and 7 the signs of the coefficient of z are reversed.

The MO coefficients C_h with HO bases can be obtained from those with AO base, C, by the matrix multiplication

$$C_h = C B^{-1}\,, \tag{2.15}$$

with

$$Y = BX\,, \tag{2.16}$$

where B is the matrix of coefficients which represents the HO, Y as linear combination of AO, X. It can also be obtained independently by finding the symmetry combinations, block diagonalizing the overlap and Hamiltonian matrices and solving for the eigenvalues and vectors, as outlined above for the case of AO base. In matrix notation the symmetry combinations Φ_y; the group overlap G_y and the Hamiltonian F_y read

$$\begin{aligned} \Phi_y &= AY = ABX\,, \\ G_y &= \Phi_y \Phi_y^\dagger = (AB)S(AB)^\dagger\,, \\ F_y &= (AB)H(AB)^\dagger\,. \end{aligned} \tag{2.17}$$

The MO energies obtained by this second method must be identical to those obtained with AO bases. Since it serves as an independent numerical check, the second method was actually carried out.

With the MO's represented with the hybrids as bases, one can analyze the contributions of the As-As bonds, As-Se bonds, As lone pairs, Se-As bonds, and Se lone pairs. The results are shown in Table III. In the upper part of the table, the entries are again normalized to each orbital, while in the lower part, where contributions to groups of orbitals are listed, the values per atom are given. Again dividing the whole energy levels into three groups, one sees that the empty bands (23–32) consist almost totally of the bonding hybrids (in antibonding states), while the compositions of the occupied bands are mixtures of the bonding and the lone-pair hybrids. Although the highest occupied orbital (22) is mostly of Se lone pair, there exist, within a few tenths eV of it, states with considerable bonding character. It is also noted that in the center (about − 10.5 eV) of the upper occupied band, there are two orbitals (MO Nos. 13, 14) which are largely of As origin. In the observed spectra[7,9] the valley in the upper occupied band of amorphous Se disappears in arsenic chalcogenides. This may be interpreted as the filling of the valley with As orbital dominated states in the latter materials. The calculated density of states for Se_8 (Sec. III, Fig. 3) shows a well resolved doublet for the upper occupied band.

III. ELECTRONIC STATES OF Se_8

The electronic structures of the eight-membered puckered-ring molecules S_8 and Se_8 have been discussed by this author previously.[6,19] The present calculation differs from the previous ones in that the Wolfsberg-Helmholz approximation, Eq. (1.1), for the off-diagonal elements of the Hamiltonian matrix is applied to the AO bases in the present calculation, while it was applied to the HO bases in the previous ones. In addition, the results of the composition analysis for the MO's, as for As_4Se_4 in Sec. II, are reported here. The arrangements of the coordinate axes at each atomic site are the same as the previous one and are shown in Fig. 1 of Ref. 19 and Fig. 2 of Ref. 6. Since Se_8 is a homoatomic molecule, the procedure of self-consistent charge is not necessary. The MO energies and coefficients are solved with both AO and HO as bases. The two bonding and two lone-pair hybrids as combinations of atomic s, p orbitals are given in Ref. 6, Eqs. (4.2)–(4.4). The symmetry combinations of the hybrid orbitals are given in Ref. 19, Table I.

The MO energies obtained with the parameter $f = 1.4$ are shown in the third column of Table IV. As in the case of As_4Se_4, the electronic states can be divided into three groups: empty orbitals (25–32); upper occupied orbitals (9–24); and lower oc-

TABLE III. Compositions of As_4Se_4 molecular orbitals in terms of bonding ($As-As$, $As-Se$, $Se-As$) and lone-pair (As 1p, Se 1p) orbitals.

Mo No.	Rep.	E	As-As	As-Se	As 1p	Se-As	Se 1p
31, 32	E	-2.82	0.18	0.35	0.00	0.48	0.00
30	B_2	-3.27	0.00	0.33	0.02	0.65	0.01
29	A_1	-3.86	-0.02	0.47	0.00	0.55	0.00
28	A_2	-3.95	0.00	0.59	0.00	0.38	0.02
26, 27	E	-4.58	0.60	0.22	0.07	0.10	0.02
25	B_1	-4.86	0.00	0.76	0.00	0.26	-0.02
23, 24	E	-5.71	0.05	0.55	0.00	0.38	0.02
22	A_2	-9.28	0.00	0.00	0.00	0.09	0.90
21	B_2	-9.65	0.15	0.36	0.45	0.04	0.00
19, 20	E	-9.77	0.04	0.06	0.11	0.19	0.61
18	B_1	-9.94	0.00	0.22	0.00	0.55	0.23
17	B_2	-10.00	0.12	0.04	0.02	0.11	0.71
15, 16	E	-10.16	0.00	0.35	0.14	0.25	0.26
14	A_1	-10.19	0.45	0.14	0.23	0.10	0.09
13	A_1	-10.81	0.03	0.30	0.39	0.17	0.11
11, 12	E	-11.04	0.01	0.34	0.00	0.35	0.30
10	A_2	-11.05	0.00	0.40	0.00	0.52	0.07
9	B_2	-11.69	0.29	0.22	0.04	0.18	0.28
7, 8	E	-16.65	0.09	0.06	0.56	0.05	0.24
6	A_1	-17.57	0.34	-0.02	0.21	-0.01	0.48
5	B_2	-19.89	0.45	0.06	0.48	0.02	0.00
4	B_1	-20.05	0.00	0.02	0.00	0.19	0.79
2, 3	E	-21.14	0.03	0.07	0.13	0.22	0.55
1	A_1	-22.53	0.20	0.11	0.18	0.19	0.32
Sum (23–32)			0.41	1.10	0.04	0.94	0.02
Sum (9–22)			0.29	0.79	0.40	0.83	1.18
Sum (1–8)			0.31	0.11	0.56	0.22	0.80
Sum (1–32)			1.0	2.0	1.0	2.0	2.0

cupied orbitals (1–8). Also, the empty orbitals and the gap between the highest occupied (24) and the lowest empty orbitals are very sensitive to the f value while the occupied orbitals are rather insensitive. In spite of the difference in the total number of occupied orbitals between As_4Se_4 and Se_8, the numbers of MO's in the lower occupied group are the same ($=8$) for both molecules. This is understandable because as shown by the composition analysis in columns 6 and 7 the lower occupied band, as in the case of As_4Se_4, is essentially of s character. The p orbitals contribute to the upper occupied band and the empty band in the ratio 2 : 1, as expected. A more interesting analysis is in terms of the bonding and lone-pair hybrids (columns 4 and 5 of Table IV). The empty band is of course mostly of (anti) bonding type. Both the upper (9–24) and the lower (1–8) occupied bands consist of considerable mixtures of the bonding and lone-pair hybrids, nearly in the ratio of 1 : 2.

A feature distinct from As_4Se_4 appears in the plot (Fig. 3) of the density of states $D(E)$. The upper occupied band shows a doublet feature with a valley near -10.8 eV. Although it is impractical to quantitatively fit such calculations to the experimental density of states curves, this feature is in qualitative agreement with the experimental data reported by Shevchik *et al.*[7,10] and Liang.[9] The upper valence band ($E = 0$ to 7 eV) in Se shows a

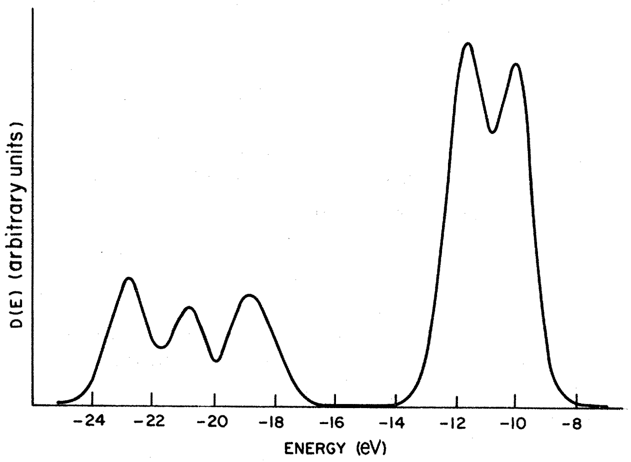

FIG. 3. Valence band density of states for Se_8, calculated from MO energies with Gaussian width $\omega = 0.75$ eV (parameter $f = 1.4$).

TABLE IV. Compositions of Se_8 molecular orbitals, in terms of bonding (bn) and lone-pair (lp) orbitals, and of s, p atomic orbitals.

Mo No.	Rep.	E	bn	lp	s	p
31, 32	E_2	−4.72	0.96	0.04	0.03	0.97
29, 30	E_1	−5.16	0.97	0.03	0.00	1.00
28	B_2	−5.30	0.86	0.14	0.10	0.90
26, 27	E_3	−5.55	0.95	0.05	0.08	0.92
25	A_2	−5.72	1.00	0.00	0.00	1.00
24	A_1	−9.82	0.33	0.67	0.00	1.00
22, 23	E_3	−9.82	0.20	0.80	0.00	1.00
20, 21	E_2	−10.06	0.08	0.92	0.00	1.00
18, 19	E_1	−10.21	0.30	0.70	0.00	1.00
17	B_2	−10.94	0.07	0.93	0.02	0.98
15, 16	E_2	−11.44	0.54	0.46	0.01	0.99
13, 14	E_1	−11.49	0.22	0.78	0.00	1.00
12	B_1	−11.72	1.00	0.00	0.00	1.00
11	A_1	−11.93	0.13	0.87	0.00	1.00
9, 10	E_3	−12.16	0.63	0.37	0.00	1.00
8	B_2	−18.12	0.07	0.93	0.88	0.12
6, 7	E_3	−18.96	0.22	0.78	0.91	0.09
4, 5	E_2	−20.88	0.41	0.59	0.97	0.03
2, 3	E_1	−22.65	0.51	0.49	1.00	0.00
1	A_1	−23.32	0.54	0.46	1.01	−0.01
Sum (25–32)			0.96	0.04	0.04	0.96
Sum (18–24)			0.19	0.69	0.00	0.88
Sum (9–17)			0.50	0.63	0.00	1.12
Sum (9–24)			0.68	1.32	0.00	2.00
Sum (1–8)			0.36	0.64	0.96	0.04
Sum (1–32)			2.00	2.00	1.00	3.00

distinct doublet while for As_2Se_3, As_4Se_4, and As the "doublets" are not resolved. In the composition analysis of Sec. II, we have attributed the disappearance of the valley to the existence of As-orbital dominated states. In Table IV, the compositions of the two subbands, (9–17) and (18–24), of the upper occupied band are also shown. Although the upper subband has a slightly larger lone pair than bonding character, in the ratio of 7:2, it can hardly be regarded as "lone-pair band." The lower subband is nearly half bonding and half lone-pair character.

Two additional features of the experimental density of states curves[9] are qualitatively reproduced in the calculated $D(E)$ plots of Figs. 2 and 3. First, the width of the upper occupied band is narrower in As_4Se_4 than in Se_8. Second, the valley in the lower occupied band is more discernible for As_4Se_4 than for Se_8. In Fig. 3, the lower occupied band appears as a triplet, because of the doubly degenerate E symmetry MO (4, 5) located in the center of the group. At higher ω value (>1 eV) the triplet reduces into a doublet with a shallow valley in between.

The identification of a band as arising from either s or p states is not so interesting, especially in molecular chalcogenides, where the electrons are better characterized by bonding or nonbonding rather than by their orbital angular momenta in the atomic state. Unfortunately, as this analysis shows (Tables II and IV) the s, p classification is the only clear cut one as far as the valence band is concerned. However the separation in energy of the s band from the p band does not mean the s-p hybridization is not extensive, as suggested by some authors,[1,10] at least not in the quantum chemical sense.[20] Strong directed covalent bonds with bond angles not equal to 90° can be formed only by mixing the s and p orbitals. The nonbonding lone pairs, in general, also consist of mixtures of s and p orbitals, because of the orthonormality requirement. In the valence-band density of states, the s and p states are well separated because for the MO's in the upper occupied states ($-9 > E > 13$ eV) the MO coefficients are such that the s components from the bonding and the lone pairs tend to cancel each other, while the MO's in the lower states ($E < -13$ eV) they add up.

As we have shown quantitatively in Tables III and IV, the bonding and nonbonding orbitals are mixed in most of the occupied MO's. There are a few MO's (e.g., MO Nos. 8, 12, 17, and 20, 21 in Se_8, Table IV) which is almost purely of one type. But since the energy levels are so closely located, it is difficult to identify a particular state especially in amorphous solids. In any band of occupied states with a width of 0.5 eV or more, one finds considerable mixture of bonding and lone-pair components.

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[1] M. Kastner, Phys. Rev. Lett. 28, 355 (1972).

[2] S. Tutihasi and I. Chen, Phys. Rev. 158, 623 (1967).

[3] J. S. Berkes, S. W. Ing, Jr., and W. J. Hillegas, J. Appl. Phys. 42, 4908 (1971).

[4] J. Dresner and G. B. Stringfellow, J. Phys. Chem. Solids 29, 303 (1968); J. Feinleib, J. de Neufville, S. C. Moss, and S. R. Ovshinsky, Appl. Phys. Lett. 18, 254 (1971).

[5] P. Nielsen, Phys. Rev. B 6, 3739 (1972).

[6] I. Chen, Phys. Rev. B 7, 3672 (1973).

[7] N. J. Shevchik, M. Cardona, and J. Tejeda, Phys. Rev. B 8, 2833 (1973).

[8] R. A. Pollak, S. Kowalczyk, L. Ley, and D. A. Shirley, Phys. Rev. Lett. 29, 274 (1972); and Phys. Rev. B 8, 641 (1973).

[9] K. S. Liang and A. I. Bienenstock, Bull. Am. Phys. Soc. 19, 213 (1974); K. S. Liang (private communication).

[10] S. G. Bishop and N. J. Shevchik, *Proceedings of the Twelfth International Conference on Physics of Semi-*

conductors, edited by M. H. Pilkuhn (Teubner, Stuttgart, 1974).

[11] M. Schlüter, J. D. Joannopoulos, and M. L. Cohen, Phys. Rev. Lett. 33, 89 (1974).

[12] P. Nielsen, Phys. Rev. B 10, 1673 (1974); *Proceeding of the Fifth International Conference on Amorphous Liquid Semiconductors*, edited by J. Stuke and W. Brenig (Taylor and Francis, London, 1974).

[13] I. Chen, Phys. Rev. B 8, 1440 (1973).

[14] M. Wolfsberg and L. Helmholz, J. Chem. Phys. 20, 837 (1952); M. D. Newton, F. P. Boer, and W. N. Lipscomb, J. Am. Chem. Soc. 88, 2353 (1966).

[15] E. J. Smail and G. M. Sheldrick, Acta Crystallgr. B 29, 2014 (1973).

[16] M. Hamermesh, *Group Theory and Its Application to Physical Problems* (Addison-Wesley, Reading, Mass., 1962).

[17] R. E. Watson and A. J. Freeman, Phys. Rev. 124, 1117 (1961).

[18] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Std. (U.S.) Circ. No. 467 (U.S. GPO, Washington, D. C., 1949).

[19] I. Chen, Phys. Rev. B 2, 1053 (1970).

[20] L. Pauling, *The Nature of the Chemical Bond* (Cornell U.P., Ithaca, N. Y., 1960).