Densities of valence states of amorphous and crystalline As₂S₃, As₂Se₃, and As₂Te₃: X-ray photoemission and theory

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The density of valence states (DOVS) of amorphous and crystalline As₂S₃ and As₂Te₃ and of amorphous As₂Se₃ have been investigated with monochromatized x-ray photoemission spectroscopy (XPS). All three compounds exhibit similar XPS spectra consisting of a pronounced peak near the Fermi energy associated with the nonbonding p orbital of the chalcogen atom followed by a shoulder 4 eV wide, ascribed to the bonding p orbitals, and lower s bands situated about 13 eV below the top of the valence band. These XPS spectra are well described by DOVS synthesized from those of the constituent elements. The similarity in the DOVS of the crystalline and amorphous forms of As₂S₃ is presumably attributable to the similarity of the local structural configurations of the two forms. In the case of As₂Te₃, where the crystalline and amorphous structures are quite different, the very similar XPS spectra for the two forms are argued to be a consequence of the chemical composition and the maintenance of chemical order in the amorphous state. A band-structure calculation for a model of an isolated arsenic chalcogenide layer is performed using only important nearest-neighbor interactions. The few parameters in the calculation are derived from XPS spectra for the constituent elements and the resulting band structure is in good agreement with the gross features of the XPS DOVS for the arsenic chalcogenides. From this semiempirical band structure, the s-p hybridization is estimated to be about 5%. This s-p interaction, however, is sufficient to shift the s and p energy bands by 1 eV.

I. INTRODUCTION

Much experimental and theoretical work exists concerning the optical and electrical properties of crystalline and amorphous semiconductors containing group-VI elements in twofold coordination.[1] However, little is known about the over-all band structures and densities of states of the V-VI compounds such as the arsenic chalcogenides. Owing in part to their large unit-cell sizes, no band-structure calculations have been carried out for these materials, and experimental studies from which densities of states can be determined directly have not been reported. In the past two years, x-ray and ultraviolet photoemission spectroscopy (XPS, UPS) have been applied to the determination of the density of valence states (DOVS) of various crystalline and amorphous materials.[2-15] The present work is concerned with the determination by such techniques of the DOVS for the amorphous and crystalline forms of the arsenic chalcogenides.

A. Structure of arsenic chalcogenides

Structural measurements can indicate, to some extent, the types of disorder (positional, topological, or chemical) occurring in the amorphous compounds that can lead to differences in the DOVS of the crystalline and amorphous forms.

Crystalline As₂S₃ (orpiment) has a monoclinic structure[16] with eight As atoms and twelve S atoms

in the unit cell (Fig. 1). Each As atom is covalently bonded to three S atoms in a triangular pyramidal unit and each S atom is shared by two As atoms. The resulting network of puckered AsS₃/₂ "molecules" forms a covalently bonded layer. Van der Waals bonding between layers is weak and the crystals cleave readily in a plane containing the a axis and the c axis. The structure of As₂Se₃ is essentially isomorphic with that of orpiment, and it too can be described in terms of AsSe₃/₂ units which form covalently bonded layers. In both materials, the constituent atoms have the same short-range order as in their elemental forms, i.e., all As atoms are threefold coordinated and the chalcogens are twofold coordinated. X-ray-diffraction studies of glassy As₂S₃ and As₃Se₃ have shown that the nearest-neighbor and next-nearest-neighbor coordinations and chemical ordering are the same as in the crystal.[17] In fact, some features of the x-ray-diffraction spectra[18-20] as well as the results of far-infrared spectroscopy,[20] neutron diffraction,[21,22] interband optical absorption, and reflection[23] strongly suggest that vestiges of the crystalline-layer structure are retained in glassy As₂S₃ and As₂Se₃. However, it is difficult to determine other possible changes in the topology by these techniques.

The structure of crystalline As₂Te₃ is not isomorphic with that of the other two arsenic chalcogenides.[24,25] It consists of complex puckered chains or ribbons which are parallel to the binary
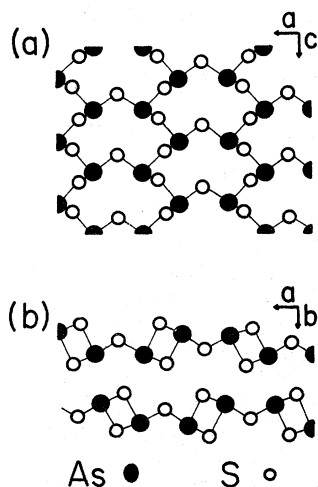
FIG. 1. Schematic of the orpiment (As_2S_3) structure: (a) projection of one layer onto the a-c plane; (b) projection of two layers onto the a-b plane showing separation of the layers.

axis of the monoclinic cell. For present purposes, the most important features of the structure of crystalline As_2Te_3 are that all Te atoms are *three-fold* coordinated while the As atoms occupy both tetrahedrally and octahedrally coordinated sites. Given these essential differences from the orpiment structure, one might expect marked differences in the valence-band electronic structure of crystalline As_2Te_3 relative to those of As_2S_3 and As_2Se_3. On the other hand, x-ray-diffraction studies of rapidly quenched vitreous As_2Te_3 (Ref. 24) indicate that the structure of this glass is comprised of a covalently bonded network of $AsTe_{3/2}$ trigonal units in which threefold coordination of As and twofold coordination of Te prevail, as in As_2S_3 and As_2Se_3. In view of the drastic differences in the coordination of the atoms and the topology of these two forms, it might therefore be anticipated that the valence-band electronic structures of the crystalline and amorphous forms of As_2Te_3 will exhibit substantial differences.

B. Density of states of elements Se and As

Before discussing the DOVS's of the arsenic chalcogenide compounds, it is useful to examine those of some of the constituent elements. It is anticipated that the lone-pair peaks associated with the twofold-coordinated chalcogen will appear in the DOVS of the compounds since their existence depends only upon the twofold coordination.[26-35] Since As is essentially a layerlike material, the behavior of its DOVS upon disordering might, to some extent, reflect the situation occurring in the amorphous chalcogenides. The experimental DOVS's for both the amorphous and crystalline

forms of[35] As and[6] Se are reproduced in Fig. 2.

The DOVS's for both forms of Se exhibit three well-defined peaks, which correspond to the lone pair, bonding p and s bands, occurring at binding energies of 1, 5, and 13 eV, respectively. The experimental density of states for the trigonal form seems to be in agreement with most of the previously computed band structures.[28-34] Since each lone-pair orbital interacts only weakly with orbitals on neighboring atoms, the DOVS associated with the lone-pair band is narrow. Although the bonding p band is repelled 5 eV below the Fermi energy by the antibonding p bands, it is also narrow because the bonding p orbitals on the *same* atom are only weakly coupled to one another. The two peaks observed in the lower band correspond to the bonding and antibonding s levels. In general, the DOVS's of the two forms of Se are quite similar, the most significant difference being the reversal in the relative intensities of the two peaks in the bonding p band. This reversal has been attributed to changes in the interchain interaction[34] and to changes in the average dihedral angle distribution.[28,34]
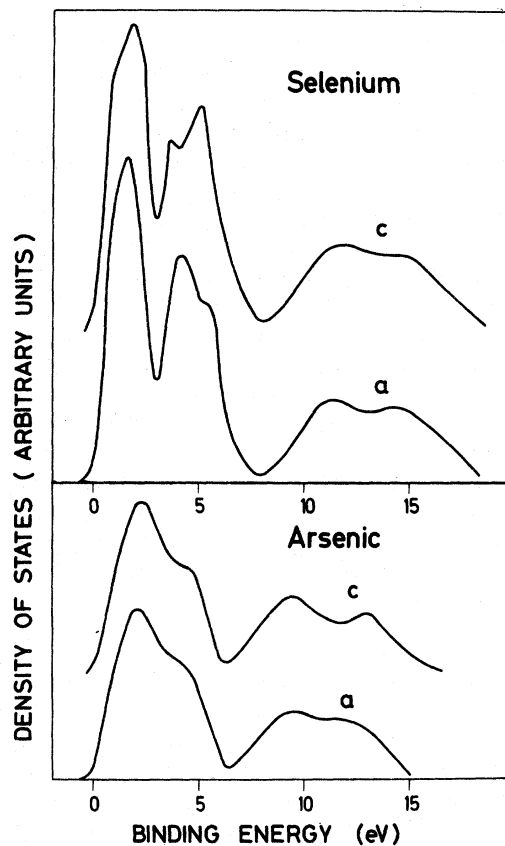

FIG. 2. Experimental densities of valence states for the amorphous and crystalline forms of (a) Se (Ref. 6); and (b) As (Ref. 35).

The DOVS of As consists of two main peaks[4,35]: The peak extending from 0- to 5-eV binding energy has primarily bonding p character, and the broader peak centered about 11-eV binding energy is composed of the bonding and antibonding s-like levels,[36,37] similar to the situation occurring in Se.[6]

The differences in the p-like DOVS of the two structural forms are small; recent high-resolution photoemission experiments[35] show that they are even smaller than indicated in the previous work.[4] In contrast to the situation found in Se, this peak is not expected to have a lone-pair component because the nonplanar threefold coordination of the As atom requires that all three p orbitals participate in the bonding. The first subpeak of the upper p band is probably due to a p band repelled by the lower s orbitals. The differences between the DOVS are, however, quite pronounced for the lower s-like bands. The pronounced two-peak structure observed in the lower s DOVS is greatly reduced in the amorphous form. It has been observed previously that DOVS of amorphous and crystalline Ge behaves in a similar fashion,[4,5] and the interpretation can be extended to As. In the crystal, the two-peak structure occurs because of the presence of six membered rings.[38] The flattening of the two peaks in the amorphous form is believed to be a consequence of the presence of odd-membered rings, which destroy the topological order.[4,38] It is of interest to see whether similar changes occur in the DOVS's of amorphous and crystalline As chalcogenides.

It has been suggested previously that the DOVS's of the amorphous chalcogenides could be synthesized approximately by a linear superposition of the properly weighted DOVS's for the constituent elements.[15] The justification for this synthesis is as follows: The lone-pair peak associated with the chalcogen should be retained in the DOVS of the amorphous compound, independent of the chemical ordering, because it is primarily attributable to the twofold coordination. If each atom satisfies its local valency requirements, its p orbitals interact with similar p orbitals near the same energy independent of the chemical ordering, since the energies of the As and chalcogen p orbitals are nearly at the same absolute energies. However, the lower s orbitals of the As and the chalcogen do not lie at the same energy, but are about 2 eV apart. Thus, the s bands should be sensitive to the chemical ordering as well as to the topology of the structure, and should not be described accurately by the superposition.

C. Valence-band calculations for compounds

Very little theoretical work has been performed on the band structures of the arsenic chalcogenides. Chen has performed molecular-orbital calculations

for the layer structure V-VI compounds As_2Se_3 and As_2S_3.[39] The electronic density of states and band structure were not determined, but only the hybridized basis orbitals and their energies. The energies of these hybridized basis orbitals for the "molecules" $AsS_{3/2}$ and $AsSe_{3/2}$ predict valence-band widths for As_2Se_3 and As_2S_3 which are even smaller than that obtained in Chen's molecular-orbital treatment of Se. This determination of the orbital energies is apparently the only currently available theoretical estimate of the valence-band energies for As_2S_3 and As_2Se_3; no more complete calculations of the electronic structure have been carried out to date.

D. Scope of present work

In this paper, the results of monochromatized XPS studies of the V-VI compounds As_2S_3, As_2Se_3, and As_2Te_3 are presented. A preliminary report of this work has appeared elsewhere.[40] Both the crystalline and amorphous forms of As_2S_3 and As_2Te_3 have been studied, and in the case of As_2Te_3, 21.2- and 40.8-eV UPS measurements have also been carried out. The XPS densities of states have nearly the same form for all of the above-mentioned materials independent of structure. For the two forms of As_2Te_3, this is surprising since the short-range order of the two forms is significantly different. We point out that this similarity is due to certain features occurring in the density of states that depend upon the chemical formula and order and are otherwise insensitive to the details of the structure.

A tight-binding band-structure calculation has been performed for a layer model which simulates isolated layers found in crystalline As_2Se_3 and As_2S_3. The model contains five atoms per primitive cell and 20 basis functions, and retains only the important interactions between nearest-neighbor atoms. Most of the few parameters in the calculation are determined from the experimental density of states for the constituent elements. The resulting band structure for the compound is in good agreement with the photoemission spectra. It is shown that while the composite DOVS constructed from the elements describes the gross DOVS, the band structure of the compound exhibits properties not found in those of the constituent elements.

II. BAND-STRUCTURE CALCULATION

In this section, we outline a simplified tight-binding band-structure calculation on a layer model that approximates the structures of As_2S_3 and As_2Se_3.

Since the interaction between layers arises from the weaker Van der Waals's forces, a reasonable description of the electronic spectra should be obtained by treating a single isolated layer. How-

ever, the unit cell for a single layer still contains 20 atoms because of the puckering of the rings composing the layer. We propose a model layer which has only five atoms per primitive cell and yet retains all the essential features of the true As_2Se_3 layer; that is, it retains the approximate bond angles, nearest-neighbor separations, and coordination numbers. As shown in Fig. 3, the As atoms lie in a single plane with their bonds directed to a plane below containing the Se atoms, which have their bonds directed upward to meet the As bonds. This is in contrast to the true As_2Se_3 layer in which all of the As atoms do not lie in the same plane nor do all of the Se atoms [see Fig. 1(b)].

The structural symmetry of the model layer is quite simple and similar to that of a single As layer in which the atoms are compressed to occupy a single plane. In the layer model, the Se atoms merely serve to connect such an As sublattice. As long as we ignore the translations in the z direction, the symmetry operations of the C_{6v}^4 space group for $k_z = 0$ are identical to those of our model. We refer the reader to Slater[41] for details of the symmetry operations, character tables, compatability relationships, and the reduced zone structure of the C_{6v}^4 space group for $k_z = 0$.

We wish to utilize only the s and p orbitals of the As and Se atoms. A two-dimensional schematic diagram of the 20 orbitals in the primitive cell is shown in Fig. 4. Each of the three large bonds between the As atoms is composed of the several orbitals indicated. The orbitals of the As atom are primed and those of the Se atom are unprimed. The first index on each orbital designates to which of the three large bonds the orbital belongs; the second index, s, 1, 2, or l, corresponds to the s orbital, bonding p orbitals, or the lone-pair orbital, respectively. The s orbitals are represented by circles and the p functions by ovals. The
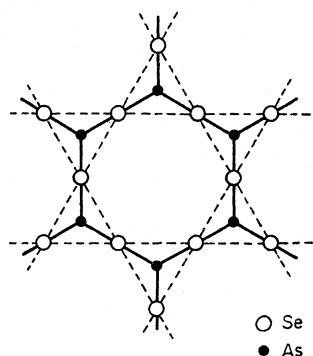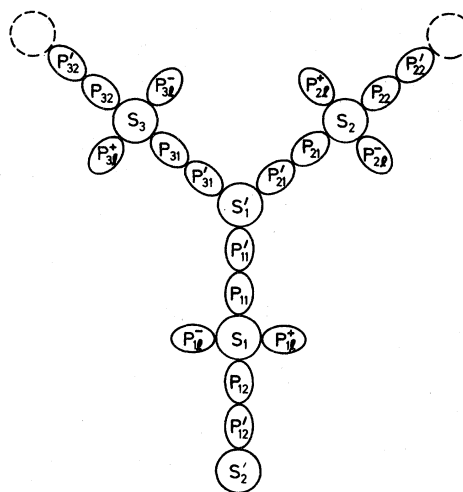
PROJECTION OF As_2Se_3 PRIMITIVE CELL

FIG. 4. Primitive cell of the model As_2S_3 layer with the basis orbitals indicated. The circles designate s orbitals, and the ovals p orbitals.

negative lobes of the bonding p functions, pointing in directions opposite to the nearest neighbors, are ignored. Both the positive and negative lobes of the lone-pair orbitals are shown. Since the lone-pair p orbitals have their nodes in the plane defined by the As-Se-As bond, they interact only weakly with the neighboring orbitals and should give flat bands at the energy of the atomic p level. We do not include these orbitals explicitly in the calculation, but will simply insert them in the calculated band structure.

The full 17×17 Hamiltonian matrix, for a given k value, which includes the nearest-neighbor interactions, can be written in the form

$$H\psi = \begin{pmatrix} H_0 & V_1 & V_3 & S_0 \\ V_1^\dagger & H_0 & V_2 & S_1 \\ V_3^\dagger & V_2^\dagger & H_0 & S_3 \\ S_0^\dagger & S_1^\dagger & S_3^\dagger & H_s \end{pmatrix} \begin{pmatrix} \vec{b}_1 \\ \vec{b}_2 \\ \vec{b}_3 \\ \vec{S} \end{pmatrix} , \quad (1)$$

where

$$H_0 = \begin{pmatrix} E_{p'} & 0 & V_{p'p} & 0 & V_{sp'} \\ 0 & E_{p'} & 0 & V_{p'p} & V_{sp'} \\ V_{p'p} & 0 & E_p & V_{pp} & V_{sp} \\ 0 & V_{pp}' & V_{pp} & E_p & V_{sp} \\ V_{sp'} & V_{sp'} & V_{sp} & V_{sp} & E_s \end{pmatrix} ,$$

FIG. 3. Model-layer approximation for the As_2S_3 structure; the As atoms lie in one plane and the Se atoms in another plane. From A. E. Owen, Contemp. Phys. 11, 227 (1970).

$$V_j = \begin{pmatrix} V_{p'p'} & 0 & 0 & 0 & 0 \\ 0 & V_{p'p'}e^{i f_j} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad ,$$

$$S_j = \begin{pmatrix} V_{s'p'} & 0 \\ 0 & V_{s'p'}e^{-i f_j} \\ V_{s'p} & 0 \\ 0 & V_{s'p}e^{-i f_j} \\ V_{ss'} & V_{ss'}e^{-i f_j} \end{pmatrix} \quad ,$$

$$H_s = \begin{pmatrix} E_{s'} & 0 \\ 0 & E_{s'} \end{pmatrix} \quad ,$$

$$e^{i f_j} = 1 \, , \quad e^{i k_x} \, ,$$

$$\exp[-\tfrac{1}{2}ik_x + \tfrac{1}{2}i\sqrt{3}k_y] \, , \quad \exp(\tfrac{1}{2}ik_x + \tfrac{1}{2}i\sqrt{3}k_y) \, ,$$

for $j = 0, 1, 2, 3$, respectively, and

$$b_j = \begin{pmatrix} P_{j'1} \\ P_{j'2} \\ P_{j1} \\ P_{j2} \\ S_j \end{pmatrix} \quad , \quad \vec{S} = \begin{pmatrix} S_1' \\ S_2' \end{pmatrix} \quad .$$

The model at this point has too many parameters to permit an entirely meaningful fit to the experimental densities of states to be performed and we proceed to reduce their number by retaining only the most important ones. Since the short-range order (coordination number) of each constituent element in the compound is the same as in its elemental form and the ionicity of the compound is small,[42] the interaction parameters for the elements should be approximately valid for the compound. The energies of the p and s levels of As and Se are estimated from the photoemission data of the pure elements in Fig. 2 to be

$$E_p = E_{p'} = 0.0 \, , \quad E_{s'} = -10.0 \text{ eV}, \quad E_s = -13.0 \text{ eV}.$$

In a previous calculation in which a similar basis set was used to fit the experimental DOVS of Se,[28] it was found that for Se, the $(pp\sigma)$ interaction is approximately equal to -4.0 eV and (ss) the interaction is approximately -1.0 eV. Unfortunately the $(ps\sigma)$ interaction could not be obtained directly from the photoemission data, but it was estimated that it had a value between the $(pp\sigma)$ and (ss) interactions and was chosen to be -2.0 eV.[28] Since the atomic potentials of As and Se are similar, on

the basis of Ref. 28 we choose

$$V_{pp'} = -4.0 \text{ eV} \, , \quad V_{ss'} = -1.0 \text{ eV} \, ,$$

$$V_{sp'} = V_{s'p} = -2.0 \text{ eV} \, .$$

The (sp) interactions ($V_{s'p'}$ and V_{sp}) between orbitals on the same atom are neglected since they have been found in Se to be about $\tfrac{1}{4}$ as large as the interactions between orbitals on nearest-neighbor atoms, i.e., $V_{sp'}$ and $V_{s'p}$.

The interaction integrals between p orbitals on the same site, although smaller than the s-p interactions, are important for determining features of the upper p-like bands. In Ref. 28, it was estimated for Se that $V_{pp} = +0.5$ eV. It has been estimated by fitting a similar tight-binding model to the As band structure of Falicov and Golin,[36] that $V_{p'p'} \cong -1.0$ eV. These are our most uncertain parameters since they cannot be fitted directly to the photoemission data as can the parameters $V_{ss'}$ and $V_{pp'}$.

One might argue that the basis set of the model is too crude, although similar basis sets have been successful in describing the valance-band structures of several tetrahedrally coordinated semiconductors. The authors well realize that a weakness of the present calculation lies in the choice of the p interaction parameter. We expect our band structure to be only qualitatively rather than quantitatively correct.

III. EXPERIMENTAL

X-ray-photoemission spectra were obtained for the three V-VI compounds with a Hewlett Packard 5950 spectrometer. This instrument utilizes a monochromatized Al x-ray source and provides a resolution of 0.6 eV. It is equipped with an electron flood gun, which eliminates the charging effects that are usually encountered in photoemission studies of insulating samples such as As_2S_3 and As_2Se_3. Amorphous As_2Te_3 is sufficiently electrically conducting to preclude the occurrence of charging effects. It was therefore possible to study this material in our Vacuum Generators ESCA III system, which is fitted with both an Al x-ray source and a differentially pumped gas-discharge lamp, but currently has no flood gun for use with insulating samples. The XPS data obtained with this instrument have a resolution of 1.5 eV, while the resolution of the UPS data taken with the 21.2-eV He I line is 0.1 eV and with the 40.8-eV He II line is 0.3 eV.

Both evaporated amorphous films and bulk glassy samples of As_2S_3 and As_2Se_3 were used. The thin films were evaporated in the sample-preparation chamber of the HP 5950 on the room temperature gold substrates under a base pressure of 10^{-6} Torr. Immediately after deposition, the films were inserted directly into the measuring chamber where

the vacuum was 2×10^{-9} Torr. Thin platelets of bulk glassy As_2S_3 and As_2Se_3 were also examined; the surfaces of these samples were abraded thoroughly just a few seconds prior to insertion into the 10^{-6}-Torr vacuum of the sample-preparation chamber. These samples were studied both with and without subsequent cleaning by argon ion bombardment. In neither case did the x-ray-photoemission spectra exhibit any traces of contamination by either carbon or oxygen. The thin crystals of As_2S_3 (orpiment) cleave readily because of the layer structure of this material. A thin surface layer was cleaved off these crystals just seconds prior to insertion into the sample preparation chamber. Crystalline surfaces prepared in this manner also showed no signs of contamination by carbon or oxygen.

Clean surfaces of the relatively highly conducting As_2Te_3 were prepared by dc sputtering onto aluminum substrates in a high-purity argon atmosphere at 4×10^{-2} Torr. A base pressure of 5×10^{-6} Torr was maintained during sputtering with a turbomolecular pump. The amorphous form of As_2Te_3 was obtained, when the substrate temperature was held at or below room temperature, as verified by x-ray-diffraction techniques. Crystalline As_2Te_3 films resulted when the substrate temperature was maintained at 150–200 °C. In all cases, the substrate was returned to room temperature before proceeding with the photoemission measurements. Monochromatized XPS spectra were also obtained for a powdered polycrystalline sample of As_2Te_3, which are in good agreement with those for the crystalline-sputtered films.

IV. RESULTS

A. Photoemission spectra

The monochromatized XPS spectra for amorphous As_2S_3, As_2Se_3, As_2Te_3 are shown in Figs.

FIG. 6. XPS spectra of amorphous As_2Se_3 compound with a composite density of states constructed from those of the constituent elements.

5–7, respectively. All of the spectra have been corrected for the contributions from secondary electrons by a straight-line approximation and the zero of binding energy has been defined by extrapolating the steeply rising onset to the background level.

On first inspection, one observes that three major features, labelled I, II, III, are present in the spectra for each of these materials: In each case, the XPS data exhibit a strong leading peak (I) at a binding energy of 1.0–1.5 eV, which is associated with the lone-pair electrons. Peak I is followed by a shoulder (II) at 4.5-eV binding energy, which is associated with the bonding p electrons. Since peaks I and II overlap to some extent, it is diffi-
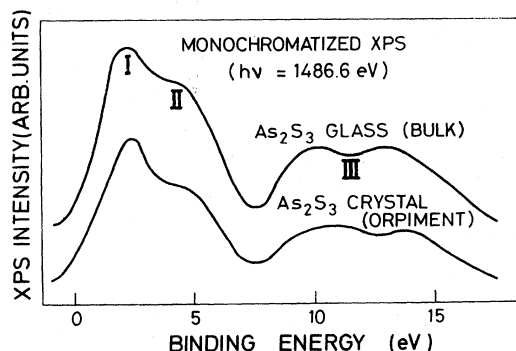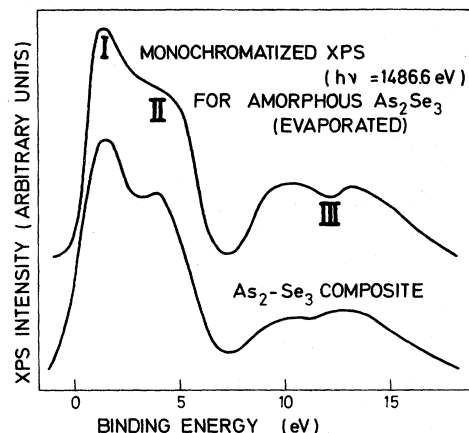

FIG. 5. XPS spectra of amorphous and crystalline (orpiment) As_2S_3. The nonbonding p, bonding p, and s bands are labelled by I, II, and III, respectively.
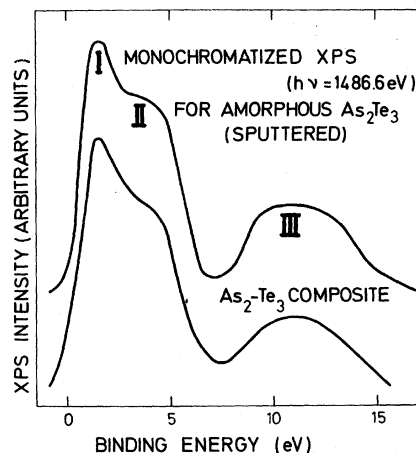

FIG. 7. XPS spectra of amorphous As_2Te_3 compound with a composite density of states constructed from those of the constituent elements.

cult to determine the relative numbers of electrons contained in each. A gap or minimum at 7 eV separates the upper p-like bands from the broad lower s-like band (III). For As_2S_3 and As_2Se_3, the lower s bands exhibit two peaks and extend to 17 eV. This two-peak structure is not observed in the s bands of amorphous As_2Te_3. These data are similar in form to those reported previously for these[14] and other V-VI compounds.[2,3]

Comparison of the XPS data of Figs. 5-7 with those reported previously for the constituent elements As, Se, and Te reveals a remarkable similarity in the form of these spectra. This similarity is graphically illustrated by the composite XPS spectra for As_2Se_3 (Fig. 6) and As_2Te_3 (Fig. 7), which were constructed simply by adding the properly weighted XPS spectra for the amorphous forms of the constituent elements. These fabricated spectra have been positioned in energy so as to provide the best possible alignment of their leading peaks and prominent minima with the experimental XPS spectra. From such a synthesis, it becomes clear that the leading peak in the XPS data of the compounds is due to the lone-pair electrons of the chalcogen. This construction demonstrates that the gross features of the density of valence states are determined primarily by the nearest-neighbor coordination numbers of the constituent atoms, independent of the chemical ordering. This explains the nearly identical XPS spectra
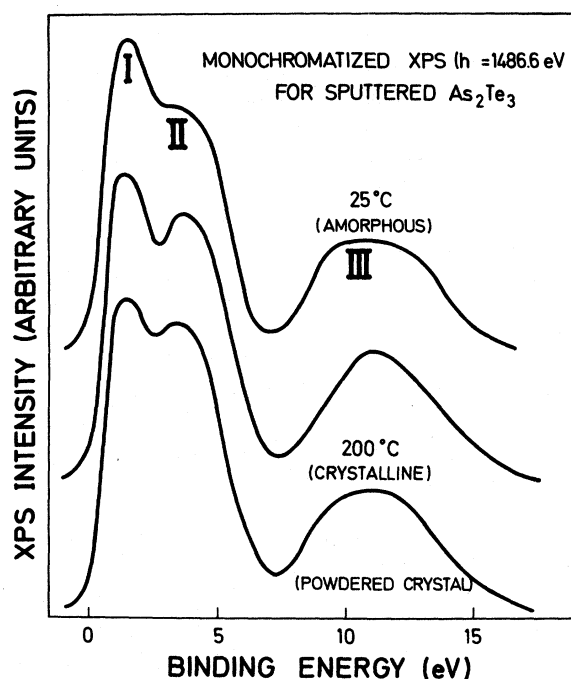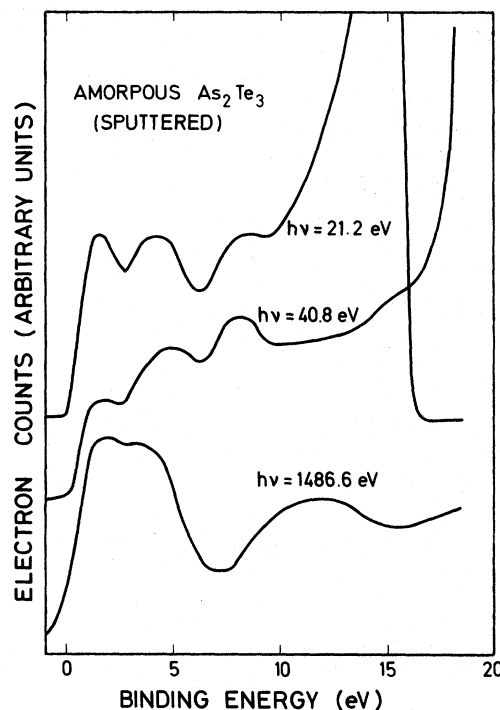

FIG. 9. UPS spectra of amorphous As_2Te_3 for $h\nu = 21.2$ and 40.8 eV, and 1486.6-eV XPS spectrum (nonmonochromatized).

observed for the amorphous and crystalline As_2S_3 (Fig. 5) since x-ray-diffraction studies indicate that the nearest-neighbor coordinations of the orpiment are maintained in glassy As_2S_3.

As mentioned in Sec. I A, the local structural configurations of the As and Te atoms are quite different in the amorphous and crystalline forms of As_2Te_3, and it might be expected that the two forms would exhibit significantly different XPS spectra for amorphous sputtered As_2Te_3, crystalline sputtered As_2Te_3, and powdered polycrystalline As_2Te_3; they are compared in Fig. 8. All of the major features, which have been identified in the XPS spectrum of the amorphous form [the nonbonding p peak (I), the bonding p shoulder (II) and the lower s band (III)] are also observed in the crystalline spectrum, despite the fact that the coordination numbers of both the As and Te atoms are different in the two forms. The only obvious difference between the spectra for the two forms is the apparent increase in the intensity of the bonding p peak (II) relative to that of the nonbonding peak (I) in the crystalline spectrum. The reason for this remarkable similarity of the amorphous and crystalline XPS spectra in As_2Te_3 will be discussed in Sec. V B.

In Fig. 9, the raw UPS data for amorphous sputtered As_2Te_3 are presented along with the raw non-

FIG. 8. XPS spectra of amorphous and crystalline As_2Te_3.

monochromatized XPS data. (UPS data were not
obtained for As_2S_3 and As_2Se_3 because of severe
charging effects encountered with samples of these
insulating glasses.) The 21.2- and 40.8-eV spec-
tra clearly resolve the nonbonding and bonding p-
like peaks seen in the XPS spectra of Fig. 8; these
peaks are superposed on a steeply rising back-
ground of inelastically scattered secondary elec-
trons. The 21.2-eV spectrum also exhibits a weak
peak in the range 7–8 eV, which is probably at-
tributable to slight contamination or Auger elec-
trons, while a somewhat stronger peak at the same
energy in the 40.8-eV spectrum is probably due to
the NVV (31-eV) Te Auger line. Neither of the UPS
spectra show any definite evidence of the lower
s-bands observed in the XPS spectra. Apparently
the photoionization cross section of the s levels is
nearly negligible compared to that of the p levels
at 21.2 eV, while at higher photon energies the two
cross sections are comparable.[43] The interference
of the 31-eV Te Auger transition in the 40.8-eV
spectrum makes it impossible to distinguish any
evidence of the s bands. We should also mention
at this point that no splitting or broadening of the
core-level spectra was observed that would indi-
cate a possible breakdown of the chemical order
in the amorphous form.[7,10]

B. Band structure

In Fig. 10, the results of our band-structure
calculation for the model As_2Se_3 layer are pre-
sented. The full 17×17 matrix was diagonalized
at 20 points on the path in k space and the sym-
metries at the edge of the zone were determined
by inspection of the wave functions. The com-
patibility relationships[41] were used to ensure the
correct connectivity of the lines.

Consistent with our previous observations of
the experimental DOVS, the energy bands of the
model divide into four main groups:

(i) the five lower s bands at $-(10-15)$ eV;

(ii) the six bondinglike p bands at $-(2-5)$ eV;

(iii) the three lone-pair bands at -1.0 eV;

(iv) the six antibondinglike p bands at $3-5$ eV.

The lower s-like bands are computed to be about
5 eV wide, whereas experimentally they are ob-
served to be 10 eV wide. Theory predicts that the
gaps should occur between the As and Se s bands
and between the s and bonding p bands. Both the
width of the lower s bands and the disappearance
of the gaps in the experimental curves are probably
due to the large lifetime broadening of the deeper-
lying levels.

Each bondinglike p band is relatively flat and the
entire set of six bands is distributed over a 2-eV
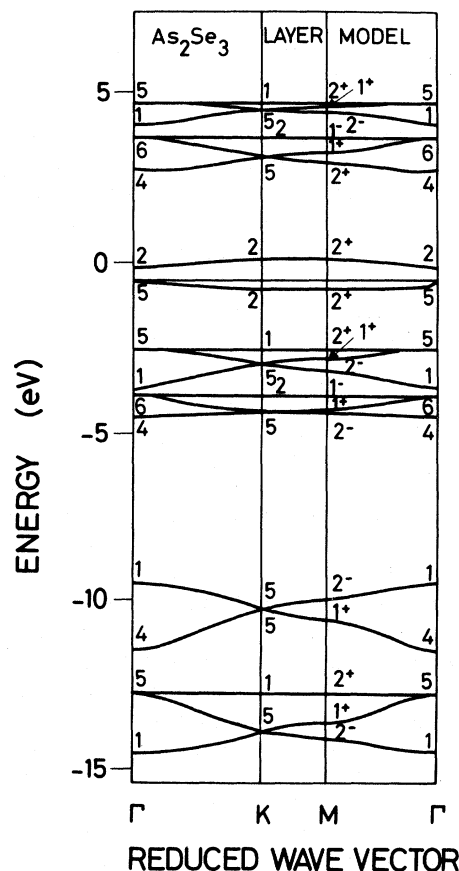energy range, somewhat less than the observed

FIG. 10. Band-structure results for the model layer.

3–4-eV range. Since the bands are more or less
uniformly distributed over this range, no pro-
nounced structure is expected to occur in the bond-
ing p density of states, in accordance with ex-
perimental observation.

Above the bondinglike p bands lie the three flat
lone-pair bands, which were sketched in after the
other bands were calculated. The approximate
shape of the bands was deduced from the follow-
ing considerations. If only the three lone-pair
orbitals are considered, the Γ_2 state having anti-
bonding character should lie higher in energy than
the Γ_5 state having bonding character. Away from
Γ, the Γ_2 state and one of the Γ_5 states have the
same symmetry and repell one another qualitative-
ly as shown.

A band gap of 3 eV occurs between the lone-pair
bands and the antibonding states above, consistent
with the fact that the compound is a semiconduc-
tor.[1,23] Interactions which have not been included
[especially $(pp\pi)$] in the calculation would tend to
broaden the lone-pair and bondinglike p bands so
as to reduce the gap between them and bring the
lone-pair antibondinglike band gap into better

agreement with the observed value of 2 eV. [23]

The p antibondinglike states are perhaps the least well described by the model, since they lie closer in energy to the $4d$ states of the Se and As atoms. It is seen, however, that the antibonding-like states are similar in form to the bondinglike p bands. In fact, by superposing the two sets of bands, one finds that the similarity is remarkable. The over-all agreement of the band structure with the experimental DOVS appears to be quite good, in spite of the simplicity of the model.

V. DISCUSSION

A. Band structure and DOVS

In Sec. IV, we have shown that the gross features of the band structure are in agreement with experiment. It should be pointed out that with the limited interactions included here, it does not make much difference that, unlike the actual crystal structures, all the As atoms are confined to one plane and all the Se atoms are confined to a second plane in the model. In this approximation, the model layer has a band structure identical to that of the true layer. The band structure of the true layer may be found by folding the present band structure to account for the greater number of atoms in the unit cell. To distinguish the model layer from the true layer, more distant interactions would have to be included.

The lowest s bands are probably described best by this calculation. A strong repulsion of the As and Se s levels produces high- and low-lying bands of Γ_1 symmetry which mark the extremities of the s bands. The degree of admixture of these orbitals with one another is about 30%, the lower band being primarily Se-s, and the upper As-s. The lower Γ_1 s band is pushed 3 eV below the energy of the atomic Se-s orbital by the combined repulsion of the As-s and upper p levels. Similarly, the predominantly As Γ_1 s band is pushed upward only 1.1 eV compared to the atomic As-s level as a result of competing repulsion of the p levels above and the s levels below. The twofold degenerate Γ_5 s level (having p like symmetry about the As atom) is pushed 1 eV downward in energy from the atomic value of the Se s orbital by the As p level, the amount of p admixture being about 4%. The Γ_4 s level is primarily As-s; it is pushed 1.2 eV below the atomic As-s level by the interaction with the Se-p levels, the amount of Se p admixture being 12%. Since the total p admixture of the lower s-like bands is about 7% and the photoionization cross section of the s orbital is nearly negligible compared to that of the p orbital for $h\nu < 40$ eV, [43] the lower bands should be nearly invisible in photo-emission experiments performed in this region of energy, similar to the situation found in Se. [6]

The lower s-like DOVS's of both forms of As_2S_3 have a similar two-peak structure. Since the composite density of states (valid for complete phase separation) also shows a similar two-peak structure for As_2Se_3, it is questionable whether the DOVS in this region is sensitive to the chemical disorder. However, in the pure elements, the two-peak structure is due to the topology of the structure, and in the ordered compound we believe that it is due primarily to the chemical order. Any topological disorder might be insufficient to over-power the influence of the chemical ordering in preserving the two-peak structure. For As_2Te_3, in which the As and Te s orbitals are nearly degenerate in energy, the chemical gap disappears and the bands should thus become more sensitive to the topological disorder and other changes in the order. This probably explains why the s DOVS of As_2Te_3 seems to change more with disorder than the s DOVS of As_2S_3 and As_2Se_3.

In the bondinglike p bands extending from -2.5 to -5.0 eV, the As and Se p orbitals are intimately mixed since they lie at nearly the same energy. The ordering of these bands is less certain than that of the s bands, because of their sensitivity to the uncertain V_{pp} and $V_{p'p'}$ parameters as discussed previously. Nevertheless, the over-all width of the bands is in fair agreement with experiment. The bands would be widened if the $(pp\pi)$ interactions were included. We have not done this since this involves the distasteful introduction of more parameters.

Similar to the situation found in pure arsenic, the Γ_1 bondinglike p band is mixed with about 8% As-s. The Γ_6 bonding p level and its partner in the conduction (antibondinglike p) band are unique in that they contain no s orbitals, but are comprised solely of p orbitals. While the Γ_1 level contains a total s admixture of 10%, the upper Γ_5 has about 3% s admixture. The average s admixture of the bondinglike p band at Γ is estimated to be 4%, which is close to the value of 6% estimated for pure Se. [34,35]

In order for a band to have significant dispersion, it is necessary that large interactions exist between neighboring unit cells. The three p orbitals of each As atom interact very strongly with the p orbitals of its three neighboring Se atoms. However, the p orbitals of the same Se atom interact only weakly with one another as in elemental Se. [29] (Although the s-p-interaction integral (2.0 eV) is large, the s orbitals are too far away in energy to cause a significant dispersion of the bands.) Thus, the p orbitals on one As atom are only weakly linked via the p orbitals of the bridging Se atoms to the p orbitals of neighboring As atoms. Hence, to a good approximation, the bondinglike and anti-bondinglike p bands are similar to those of an iso-

lated $AsSe_{3/2}$ molecule. (The s bands are wider than the p bands since the s orbital on one As atom is effectively linked by the Se s orbitals to the s orbitals on other As atoms.)

We wish to stress that the chalcogens play another important role: They localize the p bands onto isolated $As_2Se_{3/2}$ units. (Lucovsky and Martin[44] have pointed out that the vibrational spectra of As_2Se_3 and As_2Te_3 behave as though the molecular units are largely decoupled.) Thus, the p-like bands should be very insensitive to any topological disorder as long as the basic molecular unit is preserved.

We note that the twofold-degenerate levels at Γ each have a flat band for all values of k. The flatness of these bands is due to the limited-range interactions used, and is typical of such models.[38] The orbitals in one cell are connected to neighboring cells by the interactions between As p orbitals on the same atom. The s orbitals of the As atom are not involved in these states. It can be shown that with the interactions included, one linear combination of the two degenerate p-like states valid at Γ can always be found for which the interaction between states in the neighboring cells vanishes. Thus, the bands have no dispersion. These flat bands could be removed, for example, by including $(pp\pi)$ interactions between nearest neighbors.[7]

B. Structure-independent features in DOVS

The DOVS of the amorphous and crystalline forms of As_2Te_3 were found to be essentially identical. This is a surprising result, especially since the short-range order of the two structural forms is significantly different (see Sec. I A). One might expect the lone-pair peak associated with twofold-coordinated Te to disappear in the crystalline form, since it appears that the threefold nonplanar coordination of the Te atom requires that all three of its p orbitals interact with the p orbitals of the neighboring As atoms. As we shall argue below, this peak, common to both structural forms, arises primarily as a consequence of the chemical composition and maintenance of the chemical order, and *does not* depend significantly upon the local-bonding configuration of the atoms nor upon the structural order.

We apply to this case a general argument published elsewhere.[45] Let us reconsider the problem of describing the valence bands of a solid composed of N As_2Te_3 molecules by considering only the s and p orbitals of the constituent atoms. We neglect the interactions between the p and the s orbitals (which are separated by 10 eV) and the interaction between the p orbitals on the same Te atom. The As p orbitals on the same atom can interact with arbitrary strength without affecting the validity of the following arguments. Consider as a basis set for the Hamiltonian of the solid, the functions ϕ_{As}^k,

composed of only As p orbitals, and ϕ_{Te}^l, composed of only the Te p orbitals. The number of each type of function is equal to three times the number of each type of atom. The $6N$ ϕ_{As}^k functions and $9N$ ϕ_{Te}^k functions are assumed to be orthogonal.

For both structural forms, the Te p orbitals interact only with the As p orbitals, and thus, the largest matrix element involved in the electronic structure is between these two basis sets,

$$\langle \phi_{As}^k | H | \phi_{Te}^l \rangle = V_{As,Te}^{kl} \quad .$$

This matrix element includes not only the $(pp\sigma)$, but also the $(pp\pi)$ interaction neglected in the band structure discussed previously. We consider the number of linear combinations of the ϕ_{Te}^k for which this matrix element can be made to vanish for each ϕ_{As}^k. Since the $9N$ ϕ_{Te}^l functions are degenerate in energy, $9N - 6N = 3N$ linear combinations of the ϕ_{Te}^l function can always be found for which V^{kl} vanishes for each of the $6N$ ϕ_{As}^k functions. These $3N$ functions interact with nothing and thus are nonbonding eigenfunctions of the Hamiltonian having pure Te p character and hence the energy of the atomic p level. The remaining Te p states interact with the As p states to form the bondinglike valence band and the antibondinglike conduction bands. Treating the s levels in a similar fashion, we conclude that there are N nonbonding s states having pure Te character. A flat s band was found in our bond structure, but was not obvious in the experimental DOVS, owing to the large lifetime broadening of these lower levels.

The above proof has relied on the fact that there are more Te p orbitals than As p orbitals. Changes in the coordination number and bonding angle cannot alter this fact, but only the detailed nature of the matrix elements, and the detailed nature of the eigenstates. Inclusion of interactions among the p orbitals on the same Te atom and among the p, s, and higher-lying d orbitals would tend to broaden the nonbonding, bonding, and antibonding p bands, but not enough to destroy their basic character, since these interactions are smaller than the large bonding-antibonding and other interactions included in the proof.

Although the peak in the DOVS associated with the nonbonding p band is similar in both structural forms, the nature of the eigenstates in each case is significantly different. For the twofold-coordinated Te in the amorphous form, the interaction of each lone-pair orbital with neighboring p orbitals is very small, and thus, each lone-pair orbital by itself is almost a localized eigenstate of the solid. For the threefold-coordinated Te atom in the crystalline form, each of the three Te p orbitals interacts with equal strength with the p orbitals of the neighboring As atoms. However, the interaction of the nonbonding states vanishes when con-

tributions from *all* of the Te p orbitals are taken into account. The coefficients of the Te p orbitals in the nonbonding state vary from site to site so that contributions to V^{kl} from some Te p orbitals cancel against contributions from other Te p orbitals. Thus, these nonbonding states are delocalized over the unit cell since the cooperative behavior of all of the Te p orbitals in the unit cell is needed to achieve a vanishing net interaction.

The above proof demonstrates that the occurrence of a peak in the DOVS near E_F is not necessarily a consequence of twofold coordination, but can be a consequence of the chemical order. The peak observed in[13,15] a-GeTe must be a consequence of the twofold coordination since the number of Ge and Te p orbitals is equal and hence no peaks due to chemical-ordering effects can occur. Since both the bonding and antibondinglike components of the s levels are filled, most of the cohesive energy of the As chalcogenides comes from the bonding p-like bands. Another constraint on the DOVS is that the center of mass of the bonding p bands must remain at nearly the same energy for both structural forms since the energy differences between any two phases cannot be significantly different. No constraints come to mind that would compel the widths of the bands to be the same.

Thus, with the above constraints imposed, the densities of states of the two forms must be very similar. Any differences are due to the details of the structure.

C. On synthesized DOVS

While the densities of valence states synthesized from those of the constituent elements appear to describe the observed densities of states of the compounds reasonably well, the band structures of the compounds cannot be generated accurately by a similar synthesis. It is apparent that the only feature that can be described well by such a synthesis is the lone-pair band, since it is flat both in the chalcogen element and in the compound. The bonding p bands of the compound are flat as those of Se, rather than broad as those of As, and in this respect, the bands of As_2Se_3 are more similar to those of Se than As. In elemental As, one p-like band (Γ_1) is repelled very strongly upward in energy by interactions between the layers of the crystal structure.[36,37] In the compound, the larger interlayer separation reduces the interlayer interaction and the band derived from a similar As orbital retreats well below the Fermi level. Thus, the bonding p bands, we believe, are about 1 eV narrower in the compound than in As. As a consequence, the relative intensity of the first peak of the synthesized DOVS is probably somewhat greater than that of its counterpart in the experimental DOVS. Because of the overlap of the ex-

perimental lone pair and bonding p densities of states, it is difficult to determine the precise number of electrons involved in each peak.

More failures of the synthesis obviously occur in the description of the lower s bands. The flat s band and the gap occurring between the predominantly As s and Se s bands are features which are not present in the band structures of either Se or As.

The synthesis, however, works reasonably well in describing the positions and widths of features in the DOVS of the compound since the interaction parameters between the constituent atoms are essentially the same as when they are in their elemental forms. However, we feel that such syntheses, while useful superficially, are not entirely meaningful, and they should not be relied upon heavily in the interpretation of XPS results. As we have just shown, important changes in the nature and position of states might be taking place that are not evident from the experimental DOVS alone. Much more meaningful results are obtained if one is first able to fit simple model band structures to the DOVS of the elemental form, and use the deduced parameters to calculate the band structure for the compound.

VI. CONCLUSIONS

Photoemission experiments have shown that the DOVS's of the amorphous and crystalline forms of As_2S_3, As_2Se_3, and As_2Te_3 consist of three reasonably well-separated bands: The lower s bands at 10-15 eV, the bondinglike p bands at 4 eV, and the nonbonding p bands at 1 eV. In the compounds in which the twofold-coordinated chalcogen occurs, the nonbonding peak is associated with the lone-pair p orbital of the chalcogen. In crystalline As_2Te_3, in which twofold coordination does not occur, the nonbonding features result because there are not enough As p orbitals to interact with all of the Te p orbitals.

A band structure computed for the model layer using only p and s orbitals is in fair agreement with experiment. From this band structure, the nature of the eigenstates and the degree of hybridization have been determined. The flat p bands are a consequence of the small interaction between the p levels of the Se atoms that connect the neighboring unit cells. It has also been shown that while density of states constructed from those of the properly weighted constituents give results in fair agreement with experiments, several flaws show up when comparing the band structures of the constituents to the compound.

ACKNOWLEDGMENTS

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