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F M Gashimzade, D G Guliev, D A Guseinova and V Y Shteinshrayber

Institute of Physics, Academy of Sciences of the Azerbaijan SSR, Prospekt Narimanova 33, 370143 Baku, USSR

Abstract. The band structures of GeSe, GeS, SnSe and SnS layered semiconductor compounds have been calculated by the EO LCAO method in a single-layer approximation. The Madelung energy of electron in the field of all lattice ions was taken into account. The results of band-structure and density-of-states calculations are in good agreement with earlier calculations carried out by the pseudopotential method. It is shown that, unlike Ge chalcogenides, the minimal energy gap for Sn chalcogenides is situated on the symmetry line $\Lambda(k, 0, 0)$ and not on $V(0, 0, k)$. The effective masses of electrons and holes near band extrema have been calculated.

1. Introduction

GeSe, GeS, SnSe and SnS layered compounds crystallize in a parameter structure with the D_{2h}^{16} space group of orthorhombic symmetry. Macroscopic crystals are very aniso-tropic and can be easily cleaved along the layers' planes. The unit cell of the crystal contains four molecules, the sites of the atoms being as follows [1]:

$$\pm(\tfrac{1}{4}, y, z); \pm(\tfrac{1}{4}, \tfrac{1}{2} + y, \tfrac{1}{2} - z). \qquad (1)$$

The means of the parameters for these four compounds are given in table 1 [1, 2]. The structure consists of two layers, each of them containing two double-corrugated planes of cation and anion atoms. Two nearest neighbours of the cation (anion) are situated on these corrugated planes, and the third nearest neighbour is situated on the next corrugated plane (010) (figure 1). The first model of the chemical bond in A⁴B⁶ ortho-rhombic crystals was suggested in [2] on the basis of their structural analogy with elements in group V of the periodic system (As, Sb and Bi). According to [1] the bonds in these crystals are formed from three hybridized p functions of each atom with a small contribution from s functions in the bond. The values of ionicity in A⁴B⁶ layered crystals were determined by various methods in [3–6]. The layered structure of A⁴B⁶ crystals is revealed also by the energy spectrum of electrons. The band structure of GeSe and SnSe calculated by the pseudopotential method [7] shows a typical double arrangement of valence bands, which is the result of the layered structure of the crystals. This is extremely striking for lower valence bands, which are assumed to originate from the s states of

Table 1. Characteristics of GeSe-type crystal structure. a, b, c are lattice constant; y_1, z_1, y_2, z_2 are positional parameters for cation and anion, respectively; h, l, l_1, h_1 are distances to the nearest neighbours in lattice; α is the angle between horizontal bonds; β_a and β_c are the angles between horizontal and vertical bonds at the anion and cation, respectively.

	GeSe	GeS	SnSe	SnS
a (Å)	3.82	3.64	4.19	3.99
B (Å)	10.79	10.47	11.57	11.20
c (Å)	4.38	4.30	4.46	4.34
y_1	0.879	0.878	0.882	0.882
y_2	0.148	0.151	0.145	0.150
z_1	0.106	0.127	0.103	0.115
z_2	0.503	0.499	0.479	0.478
h	2.54	2.44	2.77	2.62
l	2.58	2.45	2.82	2.68
l_1	3.30	3.26	3.35	3.27
h_1	3.39	3.32	3.39	3.47
α	96°	96°	96°	96°
β_a	103°40′	105°30′	101°40′	103°40′
β_c	91°	90°30′	89°	88°20′

anions and cations. The splitting within each pair of bands does not exceed several tenths of an electronvolt.

If the interlayer interaction is neglected, then the dispersion along the direction perpendicular to the layer vanishes. Also each pair of bands degenerates into single band. Therefore, the band structure of A^4B^6 layered crystals may be considered as quasi two dimensional, confirming experiments on angle-resolved photoemission for GeS crystals [3, 8]. According to [8], almost all valence bands can be traced over the whole Brillouin zone (BZ). Also, for two energies of incident photons $h\omega = 16.8$ eV and $h\omega = 21.2$ eV, the same points occur, which determine the dependence $E(k_\parallel)$ ($k_\parallel$ is a component of the wavevector parallel to the layer planes). This is almost impossible for three-dimensional bands because of restrictions related to energy and momentum conservation laws. For two-dimensional systems this restriction becomes weaker and, as a result, transitions over the whole BZ and with various excitation energies become possible.

As was mentioned above, the band structure for these compounds was calculated by the pseudopotential method [2, 7, 9]. The necessity for a new calculation arose because in [2, 9] the calculated width of the valence band (almost 20 eV) does not correspond to the results of photoemission spectra. Also, the minimal gap for all four A^4B^6 layered crystals, according to their calculations, is situated at the same symmetry line that contradicts experimental data. The question about the origin of the bands was also interesting.

In this paper we have calculated the band structure for all four A^4B^6 layered compounds in the core of the single-layer model by the LCAO method. The essence of the LCAO method is that the Bloch functions are constructed as a linear combination of atomic orbitals. The advantage of this method compared, for example, with the pseudopotential method is that interlayer interaction can be easily involved or neglected. Also the equivalent orbitals (EO) LCAO method is better adjusted for analysis of the origin of the band states, appreciating naturally the origin of chemical bond in the crystals considered.

The EO LCAO method makes it possible to connect wavefunctions with the value of effective charge on the atoms. So it gives the theory a self-consistent character, in the
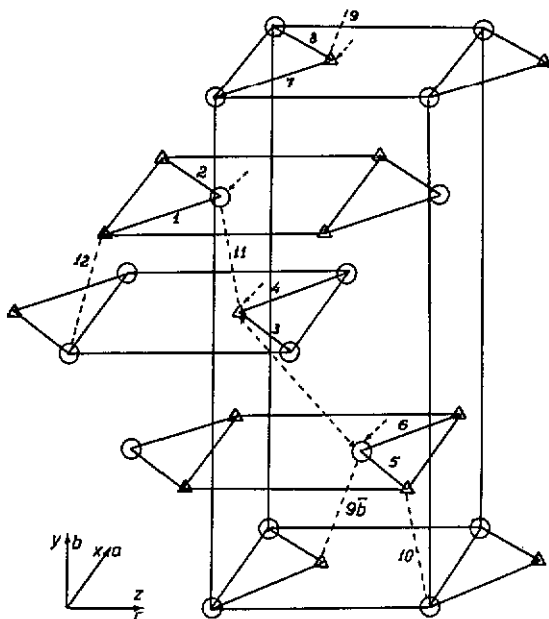
Figure 1. Unit cell of GeSe-type compounds: $\triangle$, Ge; $\bigcirc$, Se.

sense that Z (the effective charge on the atoms) determines both the potential in the crystal Hamiltonian and the form of the Bloch functions. Also the EO corresponds to the bonds in classical structural theory, and the method makes it possible to draw ample empirical material accumulated in the framework of structural chemistry.

For layered compounds A^4B^6, to the abbreviation EO one must add the term 'modified', because for these compounds not all orbitals are equivalent (e.g. 1, 2, 3, 4 and 11, 12 in figure 1). However, for further simplification, we omit the word 'modified'.

The standard LCAO method was used earlier for GeSe band-structure calculations [10]. Yet, in that paper the picture of the band structure was not determined and the extent to which it agrees with that calculated by the pseudopotential method is not clear. Also, the absence of a gap in the density-of-states spectrum shows that the accuracy of calculations in [10] was not sufficient.

Usually, the tight-binding method poorly describes the conduction band. Still, it is possible to improve the results of this method, using the successive semi-empirical approach, which allows us to compensate the non-accuracy of this model and gives a correct description of the energy level structure.

2. The band-structure calculation

2.1. Bloch functions of electrons; bonding and anti-bonding orbitals; orbitals of the lone pair

Let us write the Bloch functions of electrons in crystal as

$$\Psi_k(r) = \sum_R \sum_{j=1}^{16} C_j(k)\varphi_j(r - r_j - R) \exp[ik(r_j + R)] \tag{2}$$

where j is the composite index, which denotes the number and the site of the localized orbital within the unit cell, and R is the lattice translation.

In a single-layer model we have six bonding and six anti-bonding orbitals (figure 1) and four orbitals of the lone pair, two by two on Ge and Se atoms. Four s-type functions and 12 p-type functions were taken as a basis on which the following localized orbitals were constructed:

$$\chi_1^{A,B} = (1/\sqrt{2}l_x)(\sqrt{2l_x^2-1}S_{A,B} \pm l_x P_x^{A,B} \pm l_y P_y^{A,B} \pm l_z P_z^{A,B})$$
$$\chi_2^{A,B} = (1/\sqrt{2}l_x)(\sqrt{2l_x^2-1}S_{A,B} \mp l_x P_x^{A,B} \pm l_y P_y^{A,B} \pm l_z P_z^{A,B})$$
$$\chi_3^{A,B} = (1/\sqrt{2}l_x)(\sqrt{2l_x^2-1}S_{A,B} \mp l_x P_x^{A,B} \mp l_y P_y^{A,B} \pm l_z P_z^{A,B})$$
$$\chi_4^{A,B} = (1/\sqrt{2}l_x)(\sqrt{2l_x^2-1}S_{A,B} \pm l_x P_x^{A,B} \mp l_y P_y^{A,B} \pm l_z P_z^{A,B}) \tag{3}$$
$$\chi_{11,12}^A = \sqrt{(2l_x^2-1)/[2l_x^2-1+(l_y h_y - l_z h_z)^2]}\{[(l_y h_y - l_z h_z)/\sqrt{2l_x^2-1}]$$
$$\qquad \times S_A \pm h_y P_y^A + h_z P_z^A\}$$
$$\chi_{11,12}^B = \sqrt{(2l_x^2-1)/[2l_x^2-1+(l_y h_y + l_z h_z)^2]}\{-[(l_y h_y - l_z h_z)/\sqrt{2l_x^2-1}]$$
$$\qquad \times S_B \mp h_y P_y^B - h_z P_z^B\}$$
$$\chi_{13,16}^A = N_{13}^A(S_A \pm \mu_y P_y^A + \mu_z P_z^A)$$
$$\chi_{14,15}^B = N_{14}^B(S_B \mp k_y P_y^B + k_z P_z^B)$$

where

$$\mu_{y,z} = \frac{l_{y,z}(l_y h_z + l_z h_y) - l_x^2 h_{z,y}}{\sqrt{2l_x^2-1}(l_y h_z + l_z h_y)} \qquad k_{y,z} = \frac{\pm l_{y,z}(l_y h_z - l_z h_y) - l_x^2 h_{z,y}}{\sqrt{2l_x^2-1}(l_y h_z - l_z h_y)}$$

$$N_{13}^A = \frac{1}{\sqrt{1+\mu_y^2+\mu_z^2}} \qquad N_{14}^B = \frac{1}{\sqrt{1+k_y^2+k_z^2}}.$$

Here, the functions χ_i^A and χ_i^B are constructed so that they form the orbitals, directed along the bonds, i.e. towards the nearest neighbours of the given atom (cation A or anion B); l_x, l_y, l_z and h_y, h_z are projections of horizontal and vertical bonds, respectively, on coordinate axes; $s_{A,B}$, $p_x^{A,B}$, $p_y^{A,B}$, $p_z^{A,B}$ are s, p_x, p_y, p_z-type functions of cation A and anion B, respectively.

Let us define bonding and anti-bonding EOs, respectively, as

$$\varphi_i^{(+)} = [1/(1+\lambda^2)](\chi_i^B + \lambda\chi_i^A) \tag{4}$$
$$\varphi_i^{(-)} = [1/(1+\lambda^2)](\lambda\chi_i^B - \chi_i^B) \tag{5}$$

where λ characterizes the bond polarity extent and is expressed through effective charge for A^4B^6 compounds as

$$\lambda^2 = (2-Z)/(4+Z). \tag{6}$$

Equation (6) is obtained in the following way. The effective charge of atom Z_A is equal to the charge of atomic core $\xi_A = 4$ minus the effective number N_A of valence electrons:

$$Z_A = \xi_A - N_A. \tag{7}$$

Considering equations (4) and (5) we obtain

$$N_A = 2[3\lambda^2/(1+\lambda^2) + 1]. \tag{8}$$

Here, the first term in the square brackets is a population of two horizontal (of φ_1- and

φ_2-type) and vertical (of φ_{11}-type) orbitals descending from the atom A, and the second term is the contribution of orbital of lone pair (φ_{13} type). Substituting (8) into (7) we obtain equation (6). Naturally, that for orbitals of lone pairs φ_i coincides with the corresponding χ_i, i.e. $\lambda = 0$.

2.2. *Matrix elements of the Hamiltonian; Coulomb and resonance integrals*

Electron spectrum is obtained from the set of equations

$$[H_{ij} - E(k)\delta_{ij}]C_j(k) = 0 \qquad i = 1, \dots, 16 \tag{9}$$

where

$$H_{ij} = \sum_R \int \exp[ik \cdot (r_j - r_i + R)] \, \varphi(r - r_i) H(r) \varphi(r - r_j + R) \, dr. \tag{10}$$

For single-layer model we restrict our calculations considering only the first neighbours ($l \leqslant 2.58$ for GeSe). Matrix elements (10) are expressed through so-called Coulomb and resonance integrals:

$$\langle \varphi_i^+ | H | \varphi_j^+ \rangle = [1/(1 + \lambda^2)][\lambda^2 \langle \chi_i^A | H | \chi_j^A \rangle + \lambda(\langle \chi_i^A | H | \chi_j^B \rangle + \langle \chi_i^B | H | \chi_j^A \rangle) + \langle \chi_i^B | H | \chi_j^B \rangle]$$

$$\langle \varphi_i^- | H | \varphi_j^- \rangle = [1/(1 + \lambda^2)][\langle \chi_i^A | H | \chi_j^A \rangle - \lambda(\langle \chi_i^A | H | \chi_j^B \rangle$$
$$+ \langle \chi_i^B | H | \chi_j^A \rangle) + \lambda^2 \langle \chi_i^B | H | \chi_j^B \rangle]$$

$$\langle \varphi_i^+ | H | \varphi_j^- \rangle = [1/(1 + \lambda^2)][\lambda(\langle \chi_i^B | H | \chi_j^B \rangle$$
$$- \langle \chi_i^A | H | \chi_j^A \rangle) + \lambda^2 \langle \chi_i^A | H | \chi_j^B \rangle - \langle \chi_i^B | H | \chi_j^A \rangle]. \tag{11}$$

Integrals of $\langle \chi_i^A | H | \chi_j^A \rangle$ and $\langle \chi_i^B | H | \chi_j^B \rangle$-type are called Coulomb integrals. These integrals define the factors before the matrix elements. Let us denote these coefficients in the following way. A_1 and A_2 are the self-bonding Coulomb integrals for horizontal $(1, 2, 3, 4)$ and vertical $(11, 12)$ bonds, respectively (the numbers in parentheses denote the numbers of interacting bonds) (figure 1); $B_1(1-2)$ and $(3-4\bar{a})$, $B_2(1-2a)$ and $(3-4)$ are resonance interaction integrals for the first-neighbour horizontal bonds through the anion and the cation, respectively. $B_3(1-11)$ and $B_4(1-12)$ are similar integrals for vertical bonds. $C_1(1-1a)$, $C_2(1-3)$, $C_3(1-4)$, $C_4(11-12)$, $C_5(1-11\bar{a})$ and $C_6(1-12a)$ are resonance interaction integrals through horizontal and vertical bonds. R_1 and R_2 are resonance interaction integrals between the orbitals of the lone pair, localized on cations and anions, respectively, and horizontal bonds. R_3 and R_4 are similar interaction integrals for vertical bonds. R_5 and R_6 are Coulomb interaction integrals for orbitals of lone pairs localized, respectively, on cations and anions. R_7 and R_8 are resonance interaction integrals for orbitals of lone pairs through horizontal and vertical bonds, respectively.

The Coulomb integrals $\tilde{\alpha}_s$ and $\tilde{\alpha}_p$ were calculated from the following formulae:

$$\tilde{\alpha}_s = \alpha_s + M \qquad \tilde{\alpha}_p = \alpha_p + M. \tag{12}$$

Here M is the energy of an electron in the Madelung potential field of all lattice ions in the site of a given ion. The values of α_s and α_p, depending on the effective charge Z, are expressed through orbital ionization potentials α_s^0 for neutral atoms and α_s^1 for ionized atoms as follows:

$$\alpha_s^A(Z) = \alpha_s^A(0) + [\alpha_s^A(1) + \alpha_s^A(0)]Z_A \tag{13}$$

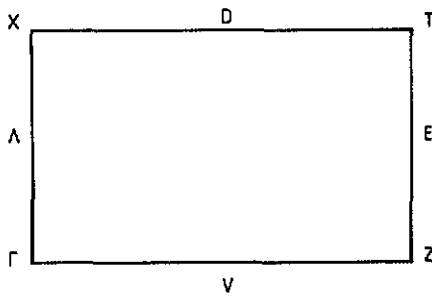and similarly for α_p. The data for corresponding atoms were taken from table 3 of [11].

Figure 2. Two-dimensional BZ of GeSe-type compounds.

The Madelung potential M on the site of the ith atom is calculated by the Ewald method [12].

The values of the four resonance integrals β_{ss}, β_{sp}, β_{pp} and β_π were taken from [10]. Choosing the value of charge we consider the following. In [11] for A^2B^6 and A^3B^5 compounds the values of effective charges were chosen as 1 and 0.5 respectively. One could suppose that for A^4B^6 compounds the value of effective charge is about 0.5. Using this value one obtains lowered values of the gap. So we changed the values of the charges to obtain better agreement with experiment. The following values of effective charges were obtained: GeSe, 0.3; GeS, 0.23; SnSe, 0.37; SnS, 0.3. In [6] the following values of ionicity for these compounds are given: GeSe, 0.55; GeS, 0.5; SnSe, 0.69; SnS, 0.61. Comparing these values of ionicity with the effective charges obtained we note some law for transition from one compound to another, changing the metal or the chalcogen.

The calculations show that of all fitting parameters the value of the charge affects most strongly the features of the band structure. Thus, enlarging the charge by 10% results in reducing the gap by 30%. Such a dependence of gap on the effective charge can be followed also on transition from one compound to another.

2.3. Layer symmetry; group theoretical analysis

Between matrix elements there exist connections related to the symmetry transformation for the layer of the crystal considered. Symbolically this transformation may be written as follows:

$$a_{\hat{g}n\hat{g}m}(k) = a_{nm}(\hat{g}^{-1}k) \tag{14}$$

where $\hat{g}n = n'$ and $\hat{g}m = m'$ denote the number of the line and the column obtained as a result of matrix element transformation by the symmetry operation g. The factor group of the space group of a single layer consists of four elements: $\{E/0\}$, identical element; $\{C_{2z}/(0, \frac{1}{2}, \frac{1}{2})\}$, screw axis parallel to crystallographic direction c; $\{\sigma_v^1/(\frac{1}{2}, 0, 0)\}$, reflection plane perpendicular to the crystallographic direction; $\{\sigma_v^2/(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\}$ gliding plane parallel to the layers. Figure 2 represents a two-dimensional BZ constructed on the vectors

$$g_1 = (2\pi/a, 0, c) \qquad g_2 = (0, 0, 2\pi/c).$$

The matrix of the irreducible representations of the wavevector groups for all symmetry points, directions and planes are given in table 2. From this table one can conclude that each state at points X and T, as well as along the line connecting these points, is *twofold degenerate. Moreover, a check using Herring's criterion shows that additional degeneration takes place owing to the time inversion symmetry at two-dimensional*

Table 2. Matrices of wavevector group irreducible representations for all symmetry points and lines of a two-dimensional BZ for A^4B^6 layered compounds ($\omega = \exp(ika/2)$; $\omega' = \exp(ikc/2)$).

	$\{E/(0,0,0)\}$	$\{C_{2z}/(0,\frac{1}{2},\frac{1}{2})\}$	$\{\sigma_v^{(1)}/(\frac{1}{2},0,0)\}$	$\{\sigma_v^{(2)}/(\frac{1}{2},\frac{1}{2},\frac{1}{2})\}$
Γ_1	1	1	1	1
Γ_2	1	-1	-1	1
Γ_3	1	-1	1	-1
Γ_4	1	1	-1	-1
X_1	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&-1\\1&0\end{pmatrix}$
Z_1	1	i	1	i
Z_2	1	$-i$	-1	i
Z_3	1	i	-1	$-i$
Z_4	1	$-i$	1	$-i$
T_1	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}0&-1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}1&0\\0&-1\end{pmatrix}$
V_1	1	ω'	1	ω'
V_2	1	ω'	-1	$-\omega'$
V_3	1	$-\omega'$	-1	ω'
V_4	1	$-\omega'$	1	$-\omega'$
D_1	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}\omega'&0\\0&-\omega'\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&-\omega'\\\omega'&0\end{pmatrix}$
Λ_1	1			ω
Λ_2	1			$-\omega$
E_1	1			$i\omega$
E_2	1			$-i\omega$
H_1	1			ω'
H_2	1			$-\omega'$

the minimal gap is situated at the line Λ, but not at the line Λ, in contrast with GeSe and GeS, which is proved by experimental data [13].

3. Results

3.1. Results of band-structure and density-of-states calculations

The results of band-structure and density-of-states calculations for GeSe, GeS, SnSe and SnS layered semiconductor compounds are given in figures 3–10.

As one can see, we managed to obtain an acceptable width of valence band and gap. The results agree well with the results of calculation by the pseudopotential method [7] and photoemission spectra for these compounds. We should note that for SnSe and SnS the minimal gap is situated at the line Λ, but not at the line V, in contrast with GeSe and GeS, which is proved by experimental data [13].
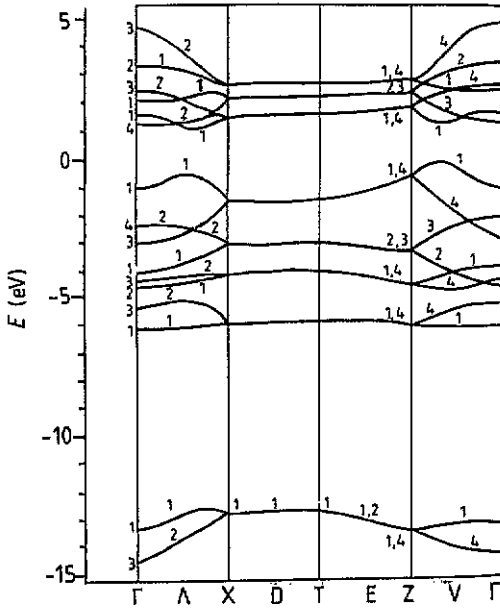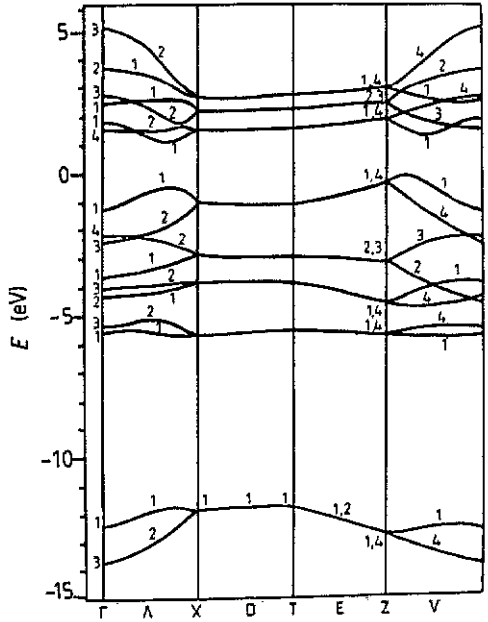
Figure 3. GeSe band structure.
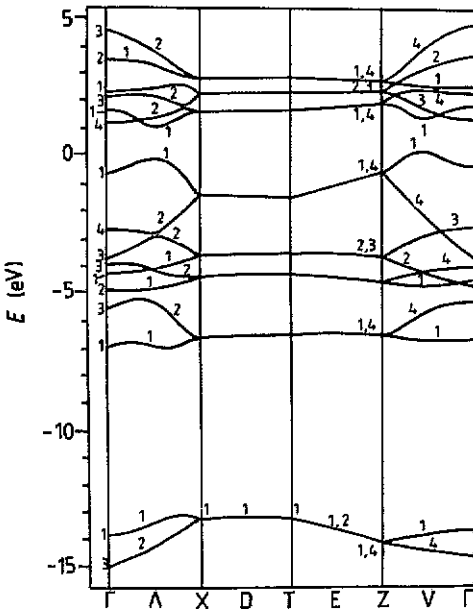
Figure 4. GeS band structure.
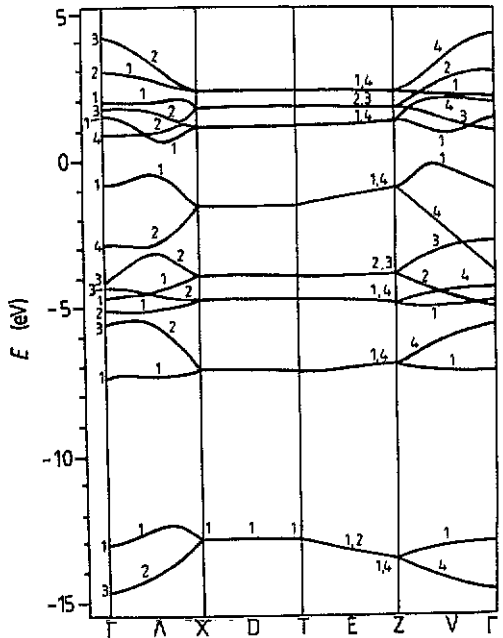
Figure 5. SnSe band structure.
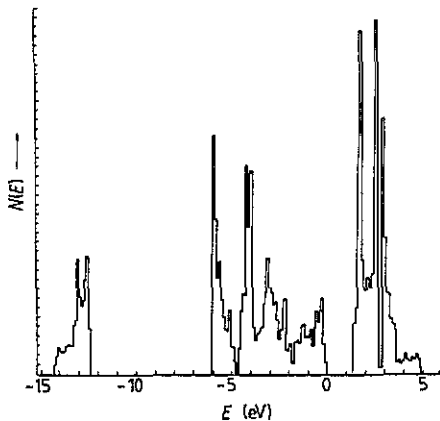
Figure 6. SnS band structure.

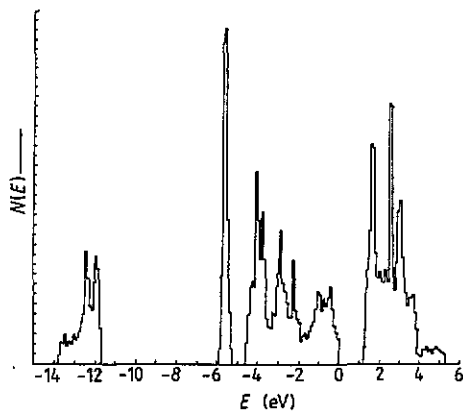**Figure 7.** GeSe density of states.

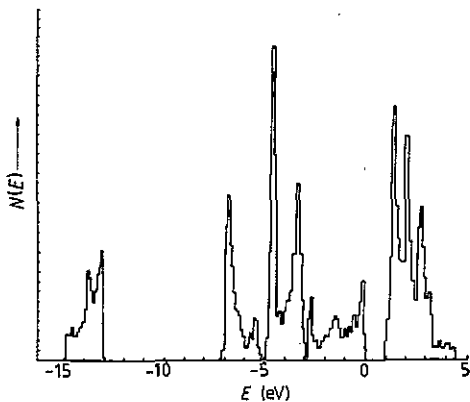**Figure 8.** GeS density of states.

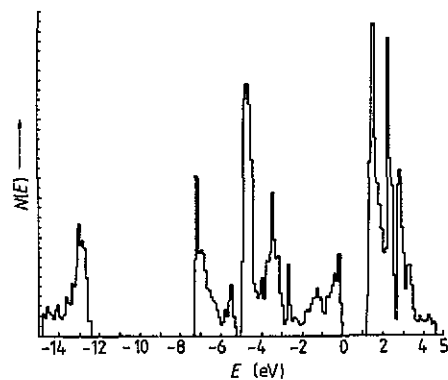**Figure 9.** SnSe density of states.

Figure 10. SnS density of states.

3.2. Analysis of the origin of bands

From the photoemission spectra of these compounds [2, 6, 8, 10, 14] we see that in A^4B^6 layered crystals the valence bands split into three groups. According to our calculations, the lower valence bands are situated near -13 to -14 eV and originate from anion s states (about 92%). The essential contribution gives the orbitals of lone pairs and bonding and anti-bonding states of vertical bonds. The next group of valence bands is situated at -6 to -7 eV and originates from mixing cation (Ge, Sn) s states (about 70%) and anion (Se, S) p states (about 26%). Here the orbitals of lone pairs give the essential contribution. Finally, the group of six upper valence bands originate mainly from the anion p states (about 56%) and to a lesser extent from cation p states (about 37%), while for the six lower conduction bands the situation is vice versa (about 34% and about 59%, respectively). The analysis of the band origin carried out proves the classification of band states given in [15] and is in good agreement with Röntgen and ultraviolet photoemission spectra data. Next we comment on the origin of the highest valence and the lowest

Table 3. Experimental and theoretical values of energy gaps for all four compounds along the symmetry lines Λ and V.

	Experimental		Calculated	
	Λ	V	Λ	V
GeSe	1.90 [18]	1.29 [13]	1.59	1.50
GeS	2.15 [19]	1.65 [18]	1.70	1.52
SnSe	1.05 [13]	1.24 [13]	1.13	1.22
SnS	1.30 [13]	1.60 [13]	1.28	1.33

Table 4. Electron effective masses near the extremes on the Λ and V lines.

	$\lambda(a)$	$\lambda(c)$	V(a)	V(c)
GeSe	0.53	10.19	−2.48	0.31
GeS	0.32	21.76	−1.82	0.29
SnSe	0.34	5.29	−2.86	0.37
SnS	0.46	9.77	−3.42	0.45

Table 5. Hole effective masses near the extremes on the Λ and V lines.

	$\lambda(a)$	$\lambda(c)$	V(a)	V(c)
GeSe	0.33	−7.87	2.29	0.28
GeS	0.41	−8.31	1.61	0.32
SnSe	0.35	−10.87	3.15	0.52
SnS	0.32	−17.64	3.42	0.31

conduction levels. The calculations show that the contribution to the upper valence level from cation states, 90% of which are of the p_y type, is about 96%. The essential contribution gives the anti-bonding states of vertical bonds (about 70%). As for the lowest conduction level, it originates from pure p_x states (64% from Ge(Sn) and 36% from Se(S) atoms).

In table 3 are given experimental and theoretically calculated values of energy gaps on symmetry lines Λ and V for all four compounds.

3.3. Effective masses of holes and electrons

From the calculated band structure we have found the effective masses of holes and electrons near the extreme on the lines Λ and V. The results are given in tables 4 and 5. As one can see from the tables, the effective masses of holes and electrons along the direction perpendicular to the symmetry lines Λ and V are large and sometimes have different signs. Including the interaction with the nearest neighbours, we hope to obtain correct values of effective masses along these directions. The value of the effective masses of holes along the Λ and V directions for GeSe and SnS are in good agreement with experimental data [16, 17].

4. Conclusion

The band structure of A^4B^6 layered semiconductor compounds has been calculated by the EO LCAO method. It is shown that, unlike GeSe and GeS, the minimal energy gap for SnSe and SnS is situated at the symmetry line $\Lambda(k, 0, 0)$ but not on the $V(0, 0, k)$, which is proved by experimental data. From the calculated band structure an analysis of the origin of the electron energy bands has been carried out and the effective masses of holes and electrons near the extreme on the lines Λ and V have been calculated. It is shown that for these compounds the lower valence bands originate from anion s states (about 92%). The next group of valence bands originates from mixing cation s states (about 70%) and anion p states (about 26%). Finally, the group of six upper valence bands originate mainly from the anion p states (about 56%) and to a lesser extent from cation p states (about 37%). The calculation showed that the contribution to the upper valence level from cation states, 90% of which are of the p_y type, is about 96%. The essential contribution gives the anti-bonding states of vertical bonds (about 70%). As for the lowest conduction level, it originates from pure p_x states (64% from Ge(Sn) and 36% from Se(S) atoms).

References

[1] Gashimzade F M and Chartsiev V E 1962 *Fiz. Tverd. Tela* 4 434
[2] Grandke T and Ley L 1977 *Phys. Rev.* B 16 832
[3] Stiles P J and Brodsky M H 1972 *Solid State Commun.* 11 1063
[4] Schiterl D 1974 *Phys. Rev.* B 10 3316
[5] Shalvoy R B, Fischer G B and Stiles P J 1977 *Phys. Rev.* B 15 1680
[6] Kemeny P C, Azoulay J, Cardona M and Ley L 1977 *Nuovo Cimento* B 39 709
[7] Valiukonis G, Gashimzade F M, Guseinova D A, Krivaite G, Kulibekov A M, Orudzhev G S and Sileika A 1983 *Phys. Status Solidi* b 117 81
[8] Chab V and Bartos I 1984 *Phys. Status Solidi* b 121 301
[9] Parke A M and Srivastava G P 1980 *Phys. Status Solidi* b 101 K31
[10] O'Reilly E P 1982 *J. Phys. C: Solid State Phys.* 15 1449
[11] Levin A A 1974 *Vvedenie v Kvantovuy Khimiyu Tverdogo Tela* (Moscow: Khimia) (in Russian)
[12] Simon G and Zeller C R 1974 *J. Phys. Chem. Solids* 35 187
[13] Valiukonis G, Guseinova D A, Krivaite G and Sileika A 1986 *Phys. Status Solidi* b 135 299
[14] Taniguchi M, Chijsen J, Johnson R L and Ley L 1986 *Proc. 18th Int. Conf. on Physics of Semiconductors* vol 2 (Singapore: World Scientific) p 1799
[15] Gashimzade F M, Guseinova D A and Guliev D G 1985 *Fiz. Tverd. Tela* 27 2098
[16] Ishihara Y, Ohno Y and Nakada I 1984 *Phys. Status Solidi* b 121 407
[17] Haas C and Corbey M M G 1961 *J. Phys. Chem. Solids* 20 197
[18] Tyagai V A, Bondarenko V N, Krasiko A N, Bletckan D I and Sheka V I 1976 *Fiz. Tverd. Tela* 18 1433
[19] Logothedis S, Vina L and Cardona M 1985 *Phys. Rev.* B 31 2180