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Investigation of the electronic structure of the SbSeBr cluster

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Abstract: The energy levels of valence bands (VB) in SbSeBr crystals were calculated for investigation of the photoelectron emission spectra of $A^5B^6C^7$ – type crystals. The molecular model of this crystal was used for calculation of VB by the Density Functional Theory (DFT) and Unrestricted Hartree – Fock (UHF) methods. The molecular cluster consisting of 20 molecules of SbSeBr was used for calculations of averaged total density of states including atom vibrations. The spectra of averaged total density of states from VB in the SbSeBr cluster were compared with experimental photoelectron emission spectra from VB of $A^5B^6C^7$ – type crystals. The results of comparison clarify that the atomic vibrations are one of possible reasons for the smoother appearance of the experimental X-ray photoelectron spectrum (XPS).

1. Introduction

A great interest in $A^5B^6C^7$ – type ferroelectrics is caused by the fact that they possess semiconductor properties [1, 2]. These ferroelectrics are characterized by a number of unique properties, e.g. SbSI has the largest piezomodulus among the compounds of its class. The temperature of the phase transition T_C depends on the composition of the mixture. The piezomodulus and piezoactivity are sensitive to the external pressure and also depend on the composition. Such a combination of unique properties opens up wide possibilities to employ it in practice. Besides the practical use, $A^5B^6C^7$ – type crystals are interesting objects of fundamental research. There is a very strong electron–phonon interaction in $A^5 B^6 C^7$ – type crystals, which affects density of states of VB and also optical and electrical properties. A very strong reverse phenomenon exists in these crystals. Ferroelectric properties and the phase transition temperature T_C [3, 4] depends on electronic structure of these crystals. Therefore, a phase transition exists in SbSI, and SbSBr crystals but does not exist in SbSeI, SbSeBr, BiSI, BiSeI, BiSBr, BiSeBr crystals. SbSeBr does not have ferroelectric phase transition, but it possesses semiconductor properties.

The aim of our work is to investigate the electronic structure of the VB of SbSeBr crystals. We provide a theoret-

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ical investigation of the electronic structure, the influence of atomic vibration on electronic structure of VB using Unrestricted Hartree – Fock (UHF) and Density Functional Theory (DFT) methods. The theoretical *total-* and *l-* density of states (*total-DOS*, *l-DOS* (*l-DOS* is a sum of *s-DOS* and *p-DOS*)) of VB are compared with the experimental X-ray photoemission spectra (XPS) of $A^5B^6C^7$ – type crystals.

We present the results of our theoretical investigations in the following sections:

Section 2 – the methods for investigation of the electronic structure of molecular cluster.

Section 3 – the theoretical investigation of VB energy levels and *total-* and *l* – density of states of SbSeBr molecular cluster by UHF and DFT methods when all atoms of a cluster are in their equilibrium positions.

Section 4 – investigation of vibration spectrum and the mean square amplitudes of atoms of the normal modes of SbSeBr crystals. In this section we have investigated the averaged total density of states of SbSeBr molecular cluster influenced by all normal vibrations. The results were compared with experimental XPS of BiSI, SbSI and SbSeI.

2. *Ab initio* calculation of the energy levels

The method of calculation is based on Unrestricted Hartree–Fock (UHF) equations. The UHF method as well as the binding energy calculations is described in [5, 6]. The authors of work [7] found that DFT (B3LYP functional) method provide a rather accurate description of the band gap and electronic structure of semiconductors. We also prove the same calculation using the Density Functional Theory – DFT (B3LYP functional) method [8]. We have chosen B3LYP from 21 DFT functionals in order to match BiSI, SbSeI and SbSeBr molecular clusters theoretically calculated forbidden energy gaps with experimental energy gaps.

The calculations were performed by GAMESS program [9] using Computer Cluster of Laboratory of Solid State Optic in Vilnius Pedagogical University. The energy levels of VB were calculated by UHF and DFT (B3LYP) methods by GAMESS program. We used HW basis sets (Hay/Wadt valence basis: implies 3-21G) with pseudopotentials.

The theoretical calculations explain qualitatively the experimental values obtained by XPS. The theoretical UHF and DFT calculations show the ionization potential with the zero in the range of the conduction band, while the experimental binding energies refer to the Fermi level with

the calibration accuracy of ± 0,3. The Fermi level in electronic SbSeI and SbSeBr structure lies at the bottom of the conduction band. In order to compare the experimental and theoretical binding energies and to refer to the Fermi level we have decreased the calculated ionization potential by a work function.

3. Model of SbSeBr crystal structure and calculated energies of valence bands

The SbSeBr crystals consist of chains of atoms in paraelectric phase and belong to Pnam space group. All atoms in SbSeBr crystals lie on mirror planes normal to the $\vec{c}$-axis. A projection of the crystal structure of SbSeI and SbSeBr on the (001) plane is shown in Fig. 1. It contains double chains [(SbSeBr)∞]2 consisting of two chains related by a twofold screw axis and linked together by a short and strong Sb-Se bonds. Weak van der Waals – type bonds bind the double chains. The weakly bonded double chains may be considered as non-interacting and one double chain may be taken as a molecular model of the SbSeBr crystals for the binding energies calculation. The double chain is formed by many simplified unit cells. One of such simplified unit cell consists of six atoms (Fig. 1a).

Therefore, the calculations of energy levels of VB were performed using the molecular cluster model of one SbSeBr crystal chain (Fig. 1c), which consists of atoms separated by dashed line shown in Fig. 1a.

For calculation of electronic structure of SbSeBr clusters we used the coordinates of atoms from Table 1, [10, 11].

Table 1. Atomic coordinates of SbSeBr cluster when *m* changes from 0 to 9.

Parameters of unit cell	$a = 8.3$ Å	$b = 10.2$ Å	$c = 4.0$ Å
Atoms	x (Å)	y (Å)	z (Å)
Sb3	3.152	6.469	$3.012 + mc$
Sb4	5.168	3.762	$1.004 + mc$
Se3	5.500	5.600	$3.012 + mc$
Se4	2.820	4.632	$1.004 + mc$
Br1	4.272	8.430	$1.004 + mc$
Br2	4.049	1.802	$3.012 + mc$

We found that the energy levels only slightly change with the increase of the number of molecules in SbSeBr cluster. It means that the model of even twenty SbSeBr molecules
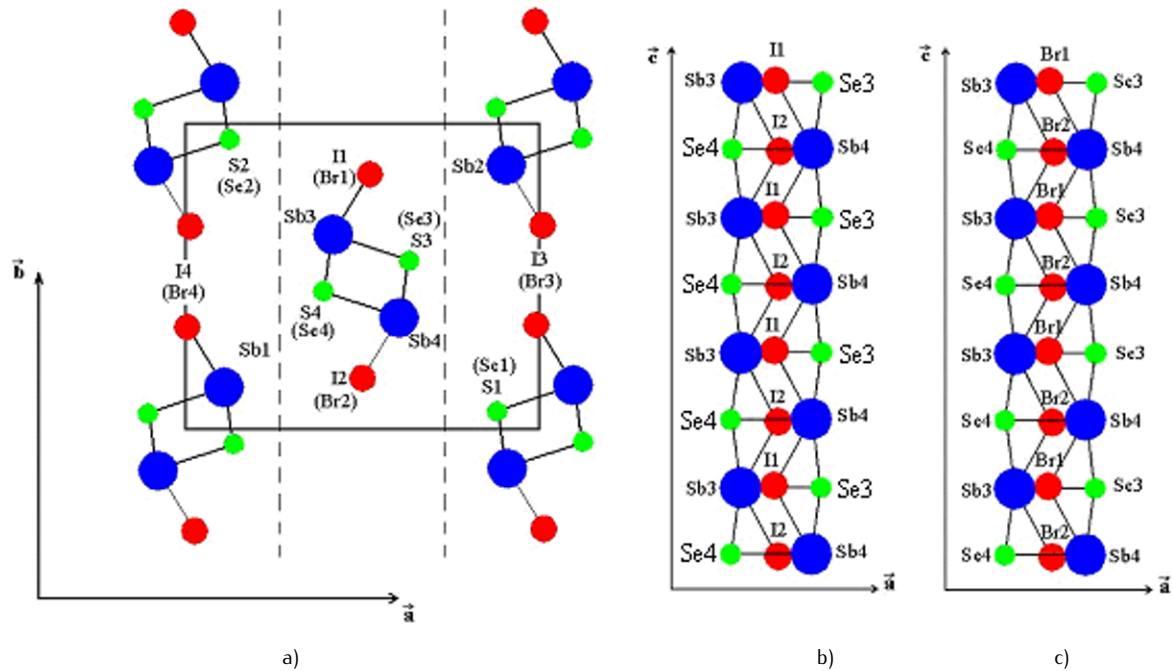
Figure 1. Crystal structure of SbSeI and SbSeBr projected on the $\vec{a}-\vec{b}$ plane (a). Simplified unit cell is separated by the dashed lines. One double chain of SbSeI (b) and SbSeBr (c) molecular clusters in projection on the $\vec{a}-\vec{c}$ plane.

is enough to describe qualitatively the electronic spectrum of the crystal.

In our work we have calculated the theoretical partial density of states of VB of Sb, Se, I, and Br atoms and total- and l – density of states of SbSeI, and SbSeBr molecular clusters (Figs. 2–3). The total- and l – density of states were calculated from the partial electronic densities of states weighed with atomic photoemission cross–sections [12]. The total – density of states is

$$total - DOS = \sum_i (l - DOS(E))_i \qquad (1)$$

$$= \sum_i \left(\left(\frac{dN}{dE} \right)_s \sigma_s + \left(\frac{dN}{dE} \right)_p \sigma_p \right)_i,$$

where σ_s is the photoemission cross–section of s states i–atoms, σ_p is the photoemission cross–section of s states i–atoms. $\left(\frac{dN}{dE} \right)_{s,p}$ – partial density of states of VB of Sb, Se, I, and Br atoms. For finding photoemission cross–sections σ_s, σ_p from Tables [12] we have used experimental X–ray photons energy 1486,6 eV (the X–ray photoemission spectra were obtained with monochromatic Al K_α radiation at room temperature using spectrometer with energy resolution about 0.3 eV) [13–15].

The spectrum of l –DOS(E) has been convoluted with Gaussian function [16]

$$g(E) = \frac{1}{\sqrt{2\pi}\sigma} \sum_i \exp \left(\frac{(E - E_i)^2}{2\sigma^2} \right),$$

where σ is half–width of Gaussian function (σ=0.3 eV). The calculated total – DOS spectra (Fig. 2) is the approximation of the theoretical photoemission spectra of SbSeBr molecular cluster (PES).

We compared the total density of states of VB of SbSeBr (Fig. 2 and Fig. 3a) molecular cluster of 20 molecules with experimental XPS of the VB of SbSI, SbSeI and BiSI crystals (Fig. 3b) because all A^5 B^6 C^7 – type crystals consist of the chains of atoms along z ($\vec{c}$) axis with the same structure of a unit cells (Fig. 1a, b) and theoretical total density of states of these crystals are very similar (Fig. 3a).

As it is seen from Figs. 2, 3a and Fig. 3b the experimental X–ray photoelectron emission spectrum (XPS) of SbSI, SbSeI and BiSI crystals differs from theoretical total density of states spectrum of SbSeBr cluster. The peaks which are visible in the theoretical total density of states spectrum of SbSeBr and SbSeI (Figs. 2, 3a) clusters do not get distinct shapes in the XPS of SbSI, SbSeI and BiSI (Fig. 3b). We obtained theoretical results in the
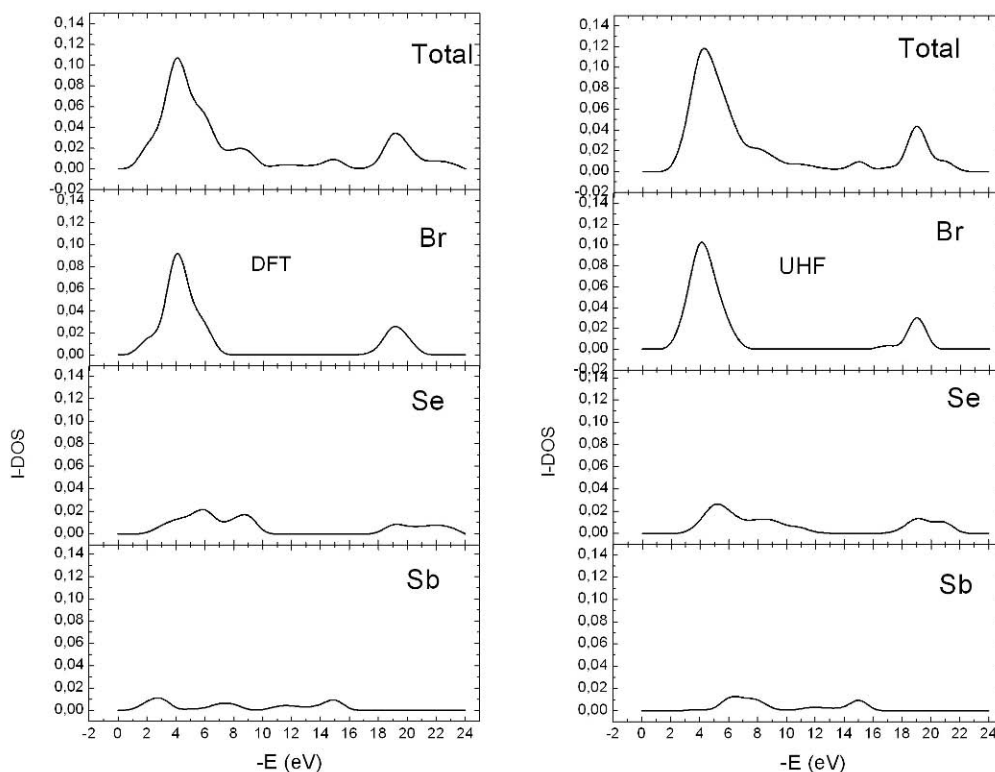
Figure 2. Total and *l* - density of states (*l-DOS* is a sum of *s-DOS* and *p-DOS*) of SbSeBr molecular cluster calculated by DFT (B3LYP functional) and UHF methods.

case when atoms are not oscillating. But the results obtained during the experiment include thermal oscillations of atoms. Therefore, we have to present theoretical results taking into account the normal coordinates of atom oscillations.

4. Influence of normal vibrations on total density of state of VB

The influence of normal vibrations on the total density of state of VB may be explored after the calculation of normal coordinates of SbSeBr crystal. The unit cell of a SbSeBr crystal in the $x - y$ plane is sketched in Fig. 1a. A simplified unit cell containing 6 atoms (Sb3, Sb4, Se3, Se4, Br1 and Br2) is outlined in a dashed line. In this simplified unit cell, we can distinguish a chain of atoms directed along the z ($\vec{c}$) axis. For this specific part of the chain, transformed into a cycle by applying the Born–Karman boundary conditions, we can apply the following

expression for the dynamic matrix along the z ($\vec{c}$) axis (with the wave vector $\vec{k} = 0$), which has off – diagonal terms [18]

$$D_{\alpha\beta}^{ij} = -\frac{C_{\alpha\beta}^{ij}}{\sqrt{M_i M_j}}, \qquad (2)$$

and diagonal terms

$$D_{\alpha\beta}^{ii} = \frac{\sum_j C_{\alpha\beta}^{ij}}{M_i}, \qquad (3)$$

where α, $\beta = x, y, z$, $C_{\alpha\beta}$ is force constant, M_i and M_j are the masses of corresponding atoms, i, j are atoms of simplified unit cell: where $i = $ Sb3, $j = $ Br1, Se3, Se4; $i = $ Sb4, $j = $ Br2, Se3, Se4.

The force constants were calculated using *GAMESS* program for the chain consisting of 20 molecules. Table 2 presents the force constants inside the chain of two combined molecules.

Table 2. Force constants between atoms $C_{\alpha\beta}^{ij}$ along z ($\vec{c}$) axis and in x-y plane calculated by DFT approach.

Atoms		Force constants $C_{\alpha\beta}^{ij}$ [10^4dyn/cm]				
i	j	C_{xx}	C_{yy}	C_{zz}	C_{xy}	C_{yx}
Sb3 (Sb4)	Br1 (Br2)	1.556	1.579	2.111	0.395	0.217
Sb3 (Sb4)	Se4 (Se3)	1.169	4.405	5.169	1.307	0.034
Sb3 (Sb4)	Se3 (Se4)	19.566	2.419	0.186	7.978	6.412
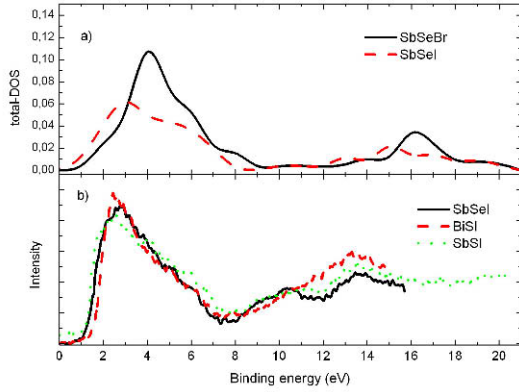
Figure 3. a) Total density of states of SbSeI and SbSeBr molecular clusters calculated by DFT (B3LYP functional), b) XPS of the VB of BiSI [13], SbSeI [14] and SbSI [15, 17] crystals, T = 308 K.

After diagonalization of the dynamic matrix, the obtained diagonal elements yield eigenvalue normal mode frequencies ω_n, and the diagonalization matrix provides eigenvectors, that give the amplitudes of normal coordinates as functions of atom displacements Q_i along $x(\vec{c})$ axis which are presented in Table 3. After diagonalization of the dynamic matrix in $x - y$ ($\vec{a} - \vec{b}$) plane we obtained the frequencies ω_n and the amplitudes of normal coordinates which are presented in Table 4.

The expression of experimental mean- square amplitude $\langle u^2(i)\rangle$ in region of high temperature is given by [19, 20]

$$\langle u^2(i)\rangle = \frac{1}{M_i N_i}\sum_n \frac{k_B T}{\omega^2(n)} = C_i \sum_n \frac{1}{\omega^2(n)}, \qquad (4)$$

where $\omega(n)$ is the frequency of n mode (Tables 3, 4), i is the type of atom, N_i is the number of atoms in unit cell, M_i is the mass of $i-$atom, and $C_i = \dfrac{k_B T}{M_i N_i}$ is the coefficient which depends on temperature.

Table 3. Amplitudes of normal coordinates of SbSeBr crystals along z ($\vec{c}$) axis.

Q_i	Sb3	Sb4	Se3	Se4	Br1	Br2
ω_n[cm^{-1}]						
201	0.491	0.491	–0.496	–0.496	–0.113	–0.113
200	0.491	–0.491	0.496	–0.496	–0.115	0.115
108	–0.216	0.216	0.347	–0.347	0.577	–0.577
107	0.205	0.205	0.336	0.336	–0.587	–0.587
21	0.461	–0.461	–0.365	0.365	0.393	–0.393
0	–0.466	–0.466	–0.375	–0.375	–0.377	–0.377

The mean–square amplitude of i – atom in n – mode is

$$\langle u^2(n, i)\rangle = C_i \frac{1}{\omega^2(n)}. \qquad (5)$$

The total densities of states l–DOS for each normal mode n have been calculated using coordinates of atoms $R(n, i) = (-1)^k\sqrt{\langle u^2(n, i)\rangle} + R_0(i)$, where $R_0(i)$ is the co-ordinates of $i-$atoms in their equilibrium position, and $\sqrt{\langle u^2(n, i)\rangle}$ is the displacements of $i-$atoms from their equilibrium positions in $n-$ mode (5), k =1 when amplitude of normal coordinate of the $i-$th atom $Q_i < 0$ (Tables 3, 4) , and $k = 2$ when $Q_i > 0$.
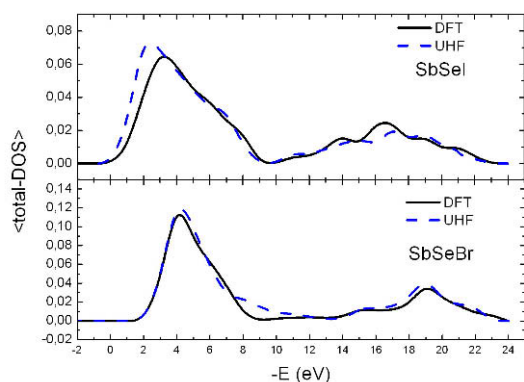
The averaged total density of states for one mode is

$$\langle total - DOS\rangle = \frac{1}{n}\sum_{i=1}^{n}(total - DOS)_i, \qquad (6)$$

where n = 15 is the number of normal modes, with 5 modes in z ($\vec{c}$) direction, (see Table 3), and 10 modes in the $x - y$ plane, (see Table 4). The experimental XPS data of SbSI, SbSeI and BiSI crystals (Fig. 3b) is more similar to averaged total density of states spectrum of SbSeBr and SbSeI molecular cluster (Fig. 4) than to a total density of states of SbSeBr and SbSeI molecular clusters (Figs. 2, 3a). These results indicated that atomic vibration is one of possible reasons for the smoother appearance of the experimental XPS.

Table 4. Amplitudes of normal coordinates of SbSeBr crystals in x–y plane.

ω_n [cm^{-1}]	Q_i	Sb3 x	Sb3 y	Sb4 x	Sb4 y	Se3 x	Se3 y	Se4 x	Se4 y	Br1 x	Br1 y	Br2 x	Br2 y
288		−0.421	0.161	−0.418	0.162	0.507	−0.206	0.505	−0.202	0.013	−0.002	0.013	−0.002
282		−0.425	0.125	0.426	−0.128	0.507	−0.211	−0.509	0.210	0.014	−0.001	−0.014	0.001
131		0.101	0.493	−0.098	−0.489	0.147	0.461	−0.148	−0.467	−0.036	−0.104	0.035	0.103
128		−0.163	−0.449	−0.183	−0.474	0.193	0.470	0.173	0.444	0.050	0.105	0.054	0.111
80		0.416	−0.230	−0.408	0.225	0.419	0.012	−0.412	−0.015	−0.328	0.022	0.322	−0.020
72		0.183	0.109	0.197	0.101	0.221	0.244	0.235	0.243	−0.396	−0.420	−0.413	−0.423
69		0.094	0.141	−0.094	−0.115	−0.053	−0.259	0.061	0.300	−0.380	−0.541	0.351	0.475
60		0.161	−0.212	0.159	−0.211	0.116	−0.245	0.114	−0.245	−0.391	0.454	−0.386	0.453
44		0.190	−0.127	−0.187	0.126	0.171	−0.013	−0.169	0.012	0.484	−0.438	−0.476	0.433
36		−0.390	−0.341	0.318	0.363	−0.072	0.402	0.013	−0.384	−0.232	−0.213	0.191	0.223
0		−0.147	−0.442	−0.147	−0.442	−0.119	−0.356	−0.119	−0.356	−0.119	−0.358	−0.119	−0.358
0		0.433	−0.172	0.433	−0.172	0.348	−0.139	0.348	−0.139	0.351	−0.140	0.351	−0.140

Figure 4. Averaged total density of states of SbSeI and SbSeBr molecular clusters calculated by DFT (B3LYP functional) and UHF methods.

5. Conclusions

For the investigation we used a molecular cluster model of the SbSeBr crystal. For approximation of the deep VB levels we used the UHF and DFT methods. This molecular model was used for the calculation of total density of states of the cluster. The spectrum of total density of states of SbSeBr cluster differs from experimental X-ray photoelectron spectrum (XPS) of $A^5B^6C^7$ – type crystals. The spectrum of averaged total density of states of SbSeBr cluster containing all normal modes of oscillation is more

similar to the experimental XPS of $A^5B^6C^7$ – type crystals. The comparison of results clarifies that atomic vibrations are one of possible reasons for the smoother appearance of the experimental XPS.

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