XPS of incommensurate and electronic structure of thallium chalcogenides

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Abstract. The paper presents the X-ray photoelectron spectra (XPS) of the valence band (VB) and of the principal core levels (CL) for the TlInS2 and TlInSe2 single crystals. The XPS were measured with monochromatized Al Kα radiation in the energy range of 0 - 1400 eV at different temperatures. The resolved splitting of XPS in the incommensurate phase of the ferroelectric semiconductor TlInS2 single crystal was obtained. The VB is located from 0.6 to 10 eV below the Fermi level. Experimental energies of the VB and CL are compared with the results of quantum mechanical \textit{ab initio} calculations of the molecular model of the TlInSe2 crystal. The electronic structure of the VB and CL is described theoretically by quantum-mechanical Hartree-Fock calculations. The surface and bulk atoms influence the shape of the VB and CL, which is crystallographic plane dependent. The chemical shifts in the both crystals for the Tl, In, S and Se states are obtained.

1. Introduction

Low-dimensional chalcogenides are characterized by a “friable” crystal lattice of a complicated chemical bonding. The structural anisotropy affects lattice and electronic properties. Many of them possess various phase transitions, extreme dielectric and electronic properties [1]. TlInS2 is the layer-structured ferroelectric semiconductor. At temperature $T_i \approx 215$ K this crystal undergoes a second order phase transition from the paraelectric $C\bar{2}c$ phase to an incommensurate (IC) phase and at $T_c \approx 195$ K a first order lock-in phase transition from the IC to a ferroelectric phase [2]. The ferroelectric phase transition is related to a strongly overdamped soft ferroelectric mode which softens down to 106 GHz near $T_i$ [1]. The soft mode makes the main contribution ($\Delta \varepsilon = 500$) to a high static dielectric permittivity. Within the incommensurate phase the soft mode splits into a phason and an amplitudon.

The TlInSe2 is a ternary chain crystal. The chain character of its structure derives from the presence of two inequivalent cation sites. In is in a tetragonal site, while Tl is in an octahedral site. The In and Se atoms form covalent chains along the [001] axis. These chains are held together by weaker ionic bonds through the octahedrically coordinated Tl atoms. Such chains form a tetragonal lattice of the space group $D_{4h}^{18}$ (I4/mcm). The crystal exhibits many nonlinear effects which attract the interest for technological applications [3, 4].

Electronic structure of TlInSe2 was studied by synchrotron radiation photoemission [5]. The CL of Tl 5d and In 4d are included into VB. However, due to the lack of theoretical calculations of VB structure and CL energies, the width of VB and its electronic structure remain unclear.
We investigated the electronic structure of TlInSe$_2$ together with theoretical ab initio calculations in greater detail. In literature, there were some indications that at about 370 K a phase transition exists as in other monoclinic ternary thallium chalcogenides [1]. Therefore, XPS were measured at room temperature and at 393 K. The splitting of XPS in the incommensurate phase of the ferroelectric semiconductor single crystal TlInSe$_2$ was first obtained in [6].

The organisation of the paper is as follows. A brief description of the experimental details is given in Section 2. In Section 3, a molecular model of the TlInSe$_2$ crystal and a method of ab initio calculations of the photoionization energies are presented. Section 4 presents experimental results of XPS in TlInSe$_2$ crystal. In Section 5, the electronic structure of TlInSe$_2$ crystal is discussed. Finally, conclusions are given in Section 6.

2. Experiment

The crystals were grown from the melt by the Bridgman technique. The XPS of the VB and principal CL were measured with monochromatic Al K$_\alpha$ radiation (1486.6 eV) using PHI 5700/660 Physical Electronics Spectrometer. The photoelectron spectra as a function of kinetic energy were analysed in the range of 0 – 1400 eV by a hemispherical mirror analyser. The measurements were performed on the (010) (broken lengthwise) and (001) (broken crosswise) crystal surfaces. The crystal was cleaved in situ under ultrahigh vacuum conditions, at a pressure of the low $10^{-10}$ Torr range, to obtain a clean surface. The working pressure was sufficient to keep the sample free of detectable contamination for the duration of the experiment. The only contaminant was found to be carbon. No other spectral features showing non-stoichiometry or impurities have been found. The size of the X-ray spot was about several square microns. The 45$^\circ$ angle between the sample and X-ray incident beam was used to analyse the XPS. The sample charging was negligible. For calibration, the carbon C 1s (284.5 eV) peak was applied.

3. Molecular model of TlInSe$_2$ crystal and ab initio calculation of the energy levels

The electronic structure of the VB and CL was calculated by the method based on Hartree-Fock (HF) matrix equations solution, in the Linear Combinations of Atomic Orbitals (LCAO) approach for the molecular orbitals.

![Figure 1. The TlIn$_4$Se$_{16}$ cluster as a molecular model of the crystal.](image-url)
For the theoretical *ab initio* calculation of energy levels the molecular model of the crystal is needed. The model must be a cluster composed from the even number of molecules. The interaction between the clusters should be weak.

Figure 1 shows a cluster of the TlInSe$_2$ crystal structure on the xy plane. The unit cell is shadowed. The calculated bond strengths and atom’s Löwdin charges are shown in the picture. They are different in different planes from surface and reveal in the VB and CL electronic structure. It came out that the stable UHF solution gives the quasi-two-dimensional $z = 1/4c$ plane model. The irreducible cluster of this model is TlIn$_4$Se$_{16}$. View of the selected cluster TlIn$_4$Se$_{16}$ of the crystal is framed by octagon. Such a cluster was used for theoretical calculations. The cluster has odd number of electrons. For the chosen model we used Unrestricted Hartree-Fock (UHF) method.

The molecular orbital $\phi_i^\alpha$ (MO) can be expanded as a linear combination of atomic orbitals $\chi_{\mu}$ $(AO)$, however, the MO with spin $\alpha$ is not equal to MO with spin $\beta$:

$$
\phi_i^\alpha (\vec{r}) = \sum_{\mu=1}^{M} C_{i\mu}^\alpha \chi_{\mu} (\vec{r}),
\tag{1}
$$

$$
\phi_i^\beta (\vec{r}) = \sum_{\mu=1}^{M} C_{i\mu}^\beta \chi_{\mu} (\vec{r}),
\tag{2}
$$

where $\mu$ is the number of the AO, or the set of quantum numbers $nlm$. The coefficients $C_{i\mu}^\alpha$ and $C_{i\mu}^\beta$ in Eqs. (1,2) and state energies $\varepsilon_\alpha$ and $\varepsilon_\beta$ are obtained by solving UHF matrix equations

$$
F^\alpha C^\alpha = SC^\alpha \varepsilon_\alpha, \tag{3}
$$

$$
F^\beta C^\beta = SC^\beta \varepsilon_\beta, \tag{4}
$$

The diagonal matrix $\varepsilon$ gives the energies of MO levels. The method of finding Fock’s matrix elements $F_{\mu\nu}^\alpha$ and overlap integrals $S_{\mu\nu}$ are shown in [7].

The coefficients $C_{i\mu}$ allow to calculate the electronic structure of molecules and to interpret the experimental results. They also allow us to find the matrix of the electron distribution density, which is given by

$$
P_{\mu\nu}^\alpha = \sum_{i=1}^{N_\alpha} C_{i\mu}^\alpha C_{i\nu}^\alpha, \tag{5}
$$

$$
P_{\mu\nu}^\beta = \sum_{i=1}^{N_\beta} C_{i\mu}^\beta C_{i\nu}^\beta. \tag{6}
$$

Here $N_\alpha$ and $N_\beta$ are the number of electrons with spin $\alpha$ and $\beta$, respectively. Equations (3) and (4) are solved by Fock’s matrix $F$ diagonalisation. The orthogonalisation of this matrix was proposed by Löwdin in a following way

$$
C = S^{1/2}C_0, \tag{7}
$$

As Fock’s matrix elements in equations (3 and 4) nonlinearly depend on unknown coefficients $C_{i\mu}$ UFR equations are solved by the iterations.

According to Löwdin the density matrix $P$ has to be renormalized in a way

$$
P = S^{1/2}PS^{1/2}. \tag{8}
$$

Having MO coefficients $C$ (equations 1 and 2), one can find bond strengths $P_{AB}$ between the atoms $A$ and $B$

$$
P_{AB} = \sum_{\sigma=A,B} \sum_{\lambda=\alpha, \beta} (P_{\sigma\lambda}^\alpha + P_{\sigma\lambda}^\beta), \tag{9}
$$
and the charge of the atoms:

$$q_\alpha = Z_\alpha - \sum_{\mu=A} (P_{\mu \alpha}^\alpha + P_{\mu \beta}^\beta).$$

(10)

Knowing the MO coefficients $C_0$ from equation (7), one can evaluate the contribution of A atom electrons for $\varepsilon_i$ state

$$p_{\alpha i} = \sum_{\mu A} C_{\alpha \mu}^2.$$

(11)

The UHF method was realized with the GAMESS program [8]. In our model (figure 1), the calculations have shown that Löwdin charges of atoms are: Tl$^{+0.79}$, In$^{+0.24}$, and Se$^{-0.47}$. The charges of atoms in our model differ from the supposed in [5]. Tl is in an octahedral site, while In is in a tetragonal site and covalently bound with 2 bulk (Se$_b$) and 2 surface (Se$_s$) atoms. The charge of surface Se$_s^{+0.24}$ atoms is not compensated by electropositive Tl atoms and it distorts VB. The calculated bond strengths and atoms’ charges are also shown in figure 1. The bonds of the surface Se atoms in the cluster are broken therefore their charges and bond strengths are decreased.

4. Splitting of XPS in the incommensurate phase of TlInS$_2$

Figure 2 shows the spectrum of the spin-orbit doublet of Tl 4f. In the paraelectric phase (300 K), the peaks of Tl 4f$_{7/2}$ and 4f$_{5/2}$ are situated at 118.8 and 122.8 eV, respectively. The binding energy, $E_b$, in TlInS$_2$ increases by about 0.8 eV in comparison with $E_b$ in pure Tl ($E_b = 118$ eV for 4f$_{7/2}$ and $E_b = 122$ eV for 4f$_{5/2}$). However, in the incommensurate phase the spectrum lines of the each spin-orbit components split into two components. They are clearly seen in the deconvoluted spectrum. At the temperature 195 K, the IC phase still exists and the ferroelectric phase already appears. As a result, the resolved splitting starts to decrease. Most probable, that the strong electric field on the crystal surface in the “domains” of opposite charge, caused by the frozen wave of displacements, modulates the energy of the emitted photoelectrons resulting in the apparent resolved splitting of the core levels.

Similar splitting of XPS of about 1 eV in the IC phase has been observed for the In 3d and S 2p spin-orbit doublets. XPS measurements also revealed the chemical shift of Tl states of +0.8 eV and In states of +0.5 eV to higher binding energy and the S states of −2.8 eV to lower binding energy. These shifts suggest charge transfer from Tl and In to S.

Figure 2. XPS of the spin-orbit doublet of the Tl 4f in the paraelectric (300 K) and IC (210÷195 K) phases.
5. Electronic structure

Figure 3 presents form and electronic structure of TlInSe$_2$. The top of the figure represents the density of states (DOS). In the middle panel of the figure, intensity of the DOS and MO of Tl, In and Se atoms on states are shown (see also table 1). Experimental XPS is the integral picture of all electronic states. At the bottom of the figure, the approximation of TlInSe$_2$ bands spectra of three different clusters, Tl$_4$In$_6$Se$_{16}$ (underpart), Tl$_3$In$_6$Se$_{24}$ (middle part), and Tl$_7$In$_{10}$Se$_{40}$ (upper curve), by the Gaussian broadening method and their comparison with experimental XPS are presented.

The VB is located from 0.6 to about 10 eV below the Fermi level. The electronic structure of VB is calculated from equations (3 and 4). It consists of two bands - intensive $sp$- and less intensive $s$ bands. At higher energies the VB overlaps with the Tl 5$d$ and In 4$d$ core level energies which Kilday et al. [5] included into VB.

The VB electronic structure is seen also from table 1 in which an analysis of the contribution of atom’s electrons for $\epsilon_i$ state is calculated. Se bulk (73%) and surface (21%) atom’s degenerate 4$p$ states (MO 409) form sharp left side (near to $E_F$) of the $sp$-band. In 5$s$ and surface Se 4$p$ states form right side (MO 377, 381) of $sp$-band. Tl 6$p$ states form the middle part of $sp$- band, while bulk (MO 365) and surface (MO 361, 357) Se 4$s$ states form $s$-band. Surface Se 4$p$ states (MO 414-417) form $p$-band of CB.

The calculated binding energies are close to experimental [7]. Figure 4 shows the spectrum of the Tl 4$f$ spin-orbit doublet (overlapping by the In 4$s$) from the broken lengthwise (010) and crosswise (001) planes. The peaks of Tl 4$f_{5/2}$ are situated at about 118.5 (crosswise) and 118.3 eV (lengthwise), respectively.

Figure 3. Electronic structure of VB of TlInSe$_2$ crystal.
Table 1. Population (in%) of VB levels in TlIn₄Se₁₆ cluster. Seₐ and Seₛ are bulk and surface atoms. VB binding energies are negative, while CB positive.

| ε[eV] | MO  | Tl | In | Seₐ | Seₛ |
|-------|-----|----|----|-----|-----|
|       | CB(p) |    |    |     |     |
| 0.9   | 417  | 4  | 6  | 19  | 71  |
| 0.7   | 414  | 0  | 4  | 5   | 91  |
| 0.5   | 411  | 1  | 7  | 71  | 21  |
| 0.7   | 409  | 0  | 6  | 73  | 21  |
| 1.1   | 404  | 0  | 4  | 90  | 6   |
| 1.4   | 401  | 1  | 6  | 83  | 10  |
| 1.6   | 397  | 2  | 16 | 74  | 8   |
| 1.8   | 394  | 7  | 7  | 72  | 14  |
| 2.2   | 391  | 0  | 25 | 58  | 17  |
| 2.5   | 386  | 0  | 14 | 3   | 83  |
| 2.5   | 385  | 27 | 5  | 65  | 3   |
| 2.7   | 381  | 0  | 3  | 2   | 95  |
| 2.9   | 377  | 0  | 6  | 4   | 90  |
| 3.4   | 373  | 0  | 34 | 14  | 52  |
|       | VB(sp) |    |    |     |     |
| 6.0   | 369  | 0  | 8  | 91  | 1   |
| 6.4   | 365  | 0  | 7  | 89  | 4   |
| 7.0   | 361  | 0  | 4  | 0   | 96  |
| 7.7   | 357  | 1  | 5  | 5   | 89  |

The electronic structure measurements revealed the chemical shift of Tl states of +0.8 eV and In states of + (0.1 - 0.6) eV to a higher binding energy, and Se states of – (2.2 - 2.0) eV to a lower binding energy. This shift suggests a charge transfer from Tl and In to Se. The chemical shifts in both crystals are comparable. As the result, the both crystals possess similar ionicity, however, the TlInSe₂ has no phase transitions and is not a ferroelectric one.

The crosswise spectra of In and Se spin-orbit doublets are wider than of the lengthwise spectra. This indicates the stronger interactions and higher bond strengths along the [001]-axis (chain axis). But only Tl 4f spin-orbit doublet is split in two components as in an incommensurate phase of ferroelectric TlInS₂. All the lengthwise spectra from the (010) plane are similar at room temperature and 393 K. They show that there is no phase transition (as was supposed in literature) which would change the interactions in this temperature range.

Figure 4. XPS of Tl 4f/2 and 4f5/2 spin-orbit doublet.
6. Conclusions
XPS studies revealed the apparent splitting of the core levels in the IC phase of the TlInS$_2$ crystal. Thus, XPS are sensitive to the incommensurate modulation of the crystal structure in ferroelectrics.

The form and electronic structure of the valence band of the TlInSe$_2$ crystal was studied experimentally and calculated by solving the UHF matrix equations. Only quasi-two-dimensional molecular cluster perpendicular to the c-axis is stable to UHF equations.

The VB is composed from the s- and sp-bands. Bulk and surface S(Se) 4s states form the s-band. S(Se) 4p, In 5s and 5p, Tl 6s and 6p states form the sp-band: S(Se) 4p states form sharp left side while In 5s and surface S(Se) 4p states form right side. S(Se) 4p surface states form the conduction band.

Theoretically all the CLs are split due to electron-electron interaction. Experimentally only Tl 4f (broken crosswise) doublet is split as if surface and bulk atoms were in different valence state.

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