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Electronic structure of tin monosulfide

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ABSTRACT

The band structure of three-dimensional and two-dimensional tin monosulfide was calculated by the density functional method in LDA and LDA+U approximations. Group-theoretical analysis of the electronic band structure of SnS crystallized in the orthorhombic structure with space group $D_{2h}^{16} - Pcmn$ is carried out, the symmetry of wave functions of the valence band and the bottom of the conduction band is found. The selection rules for direct and indirect optical transitions at different incident light polarization are determined. The group-theoretical analysis of energy states of the three-dimensional and two-dimensional SnS structures explains the formation of the band structure including the Davydov splitting. The calculated total density of states is compared with the known experimental XPS and UPS spectra, providing the assignment of their main features.

1. Introduction

Tin monosulfide (SnS) belongs to $A^{IV}B^{VI}$-type layered semiconductors, crystallized in orthorhombic structure [1,2]. It opens possibilities for practical applications of SnS layered crystals and thin layers, in particular, creation of solar cells [3–5], Schottky barriers [6,7], photovoltaic detectors [8], effective thin-film thermoelements [9] and SnS_2/SnS heterostructures by optical contact bonding and by plasma-enhanced chemical vapor deposition [10,11]. This stimulates further studies of its physical properties, but understanding of their nature is impossible without detailed investigation of electronic structure.

Up to the present time, calculations of SnS band structure were performed by various semiempirical quantum chemical methods [12–21]. A significant disadvantage of these calculations is arbitrary choice of the setting and the notation system of crystal axes within the D_{2h}^{16} space group by different author groups ((*Pmnb*) [12,14], (*Pcmn*) [13,19], (*Pnma*) [15,18,20], (*Pbnm*) [21]) and matching them to the Brillouin zone. It complicates the interpretation of experimental optical and photoelectrical spectra by the available SnS band calculations. Along with the theoretical studies, detailed experimental investigation of the features of SnS electronic states by ultraviolet and X-ray photoelectron [15,22–26], X-ray emission [24], electron energy loss [27], and inverse photoemission [26] spectroscopies were performed.

This paper presents calculations of energy band structure, total and local partial densities of states as well as spatial distribution of valence electronic charge density of orthorhombic SnS by the first-principle density functional theory (DFT) method. The group-theoretical analysis performed enabled us to determine the symmetry of wave functions in a number of high-symmetry points of the Brillouin zone, to find the structure of valence band representations and to determine the actual Wyckoff positions in orthorhombic SnS. The information about the symmetry of wave functions enabled us to establish the selection rules for optical dipole transitions.

2. Crystal structure of tin monosulfide

Under normal conditions, tin monosulfide crystallizes in the orthorhombic structure of GeS-type (B16) which is a binary analogue of black phosphorus structure. Different groups of authors (in different studies) used arbitrary choice of setting within the D_{2h}^{16} space group ((*Pcmn*) [28], (*Pmcn*) [29], (*Pbnm*) [2,9,30], (*Pnma*) [31,32]) and system of crystallographic axes for the description of the orthorhombic SnS crystal structure. One of possible reasons for this is the fact that some space groups have identical X-ray extinction laws for the determination of single crystal structure by diffraction methods [33]. Only 61 out of the total 230 space groups can be uniquely identified by X-ray diffraction. In other cases, from two to six possibilities of space groups of crystal symmetry can exist. For the D_{2h}^{16} space group six settings are possible: *Pnma* (a, b, c), *Pmnb* ($a, b, c \to b, a, -c$), *Pbnm* ($a, b, c \to c, a, b$), *Pcmn* ($a, b, c \to -c, b, a$), *Pmcn* ($a, b, c \to b, c, a$), *Pnam* ($a, b, c \to a, -c, b$). As real SnS crystals grow from the gas phase in the form of thin plates with natural (001) faces where the $\boldsymbol{a}$ and $\boldsymbol{b}$ axes are in the layer plane and the $\boldsymbol{c}$ axis is perpendicular to the (001) plane, then in order to describe the anisotropy of their physical properties one should choose the *Pcmn* ($c > a > b$) setting as the most correct one, essentially simplifying the interpretation of the optical, electrical, photoelectrical

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and other experimental data. Therefore, we used the crystal structure description and performed the electronic structure calculation of orthorhombic SnS with the *Pcmn* setting (D_{2h}^{16}) with the following experimental unit cell parameters: a=4.334 Å, b =3.987 Å, c=11.2 Å [2].

The electronic configuration of valence electrons of a tin atom is $4d^{10}5s^{2}5p^{2}$ and that of a sulfur atom is $3s^{2}3p^{4}$. In SnS compound, sulfur is a more electronegative element, drawing off two electrons from the tin atom, which leads to the electronic configuration of $3s^{2}3p^{6}$ for S and $5s^{2}5p^{0}$ for Sn. Thus, the oxidation state of tin in SnS is +2. In this state two 5*p*-electrons participate in the formation of a chemical bond while two 5*s*-electrons form an electron lone pair. This electronic lone pair is not directly involved in the chemical bond formation, but it significantly affects the non-symmetric arrangement of sulfur atoms around the tin atom, which finally leads to the formation of distorted [SnS_5•E•] ψ-octahedra where •E• is the electron lone pair. These edge-connected coordination ψ-octahedra of Sn atoms form corrugated double-layer packets in the XY plane (Fig. 1). The bond between the Sn and S atoms in the double-layer packets has a predominantly covalent character. The bonding between the double-layer packets is weak due to van der Waals forces. The primitive unit cell contains eight atoms and includes two nonequivalent double-layer packets (Fig. 2c).

Since the electron lone pairs of the tin atoms are located near the edges of the double-layer packets and directed toward the interlayer van-der-Waals gap, then the nearby edges of the neighboring double-layer packets are strongly negatively recharged (the chalcogen anions repel the ψ-electron pairs) which leads to the formation of quite perfect cleaved (001) faces normal to the crystallographic **c** axis.

3. Calculation method

The energy band structure calculations are performed within the DFT [34,35] using the ABINIT (basis set of plane waves) [36,37] and SIESTA (basis set of linear combination of atomic orbitals) [38,39] software packages. For the calculations we used first-principal atomic normconserving pseudopotentials [40,41] for the following electronic configurations: [Kr] $5s^{2}5p^{2}$ (for Sn atoms) and [Ne] $3s^{2}3p^{4}$ (for *S* atoms). The specified states belong to the valence shells while [Kr] and [Ne] – to the core. The relaxation procedure of the crystal cell geometry (with the conservation of the overall crystal symmetry) was performed to minimize of the total energy E_{tot} and to achieve zero values of the forces acting on the ions.

Calculations from the first principles within the density functional theory in the local density approximation (LDA) for the exchange-correlation potential are known to give underestimated band gap values. The underestimation of the band gap can be corrected by relevant calculations in LDA+U [42,43] using local self-excited Coulomb potentials (U) for the selected bands. It combines the account of electronic correlations with the Hubbard-like model [44] for a subset of states in the system. This approximation describes half-integer or double populations of these states with two parameters being introduced: U related to the force of local Coulomb interaction (U=3 eV in these calculations) and J regulating the exchange interaction force (J=0.1U).

4. Group-theoretical analysis of symmetry of wave functions for tin monosulfide

While the energy band structure of the crystal is being calculated, the symmetry properties play an important role. Based solely on the system symmetry properties, the group theory enables one to carry out the classification of electronic and vibrational states of the crystal as well as to determine the degeneracy of the system energy levels.

Besides, using the group theory one can determine the selection rules for the matrix elements which are significant for the calculation of transition probabilities. In the quantum-mechanical approach, the symmetry of a system is understood as invariance of motion equations that describe the system relative to a set of transformations that are a consequence of the object symmetry in its general sense [45]. The main theorem says that the energy (considered as a quasimomentum function in the Brillouin zone) is characterized by the symmetry of the entire point group of a crystal. Any transformations (for example, the crystal rotation around an axis) which keep the crystal invariable will also transform the $E(k)$ function into itself. This property can be used to classify the energy levels and the wave functions that correspond to the different points of the Brillouin zone as well as to find out the dispersion laws in their vicinity [46]. The symmetry of the calculated band spectra was described on the basis of the calculated wave functions and using the projective operator method. In order to analyze the topology of the tin monosulfide energy band spectra, we performed the symmetry analysis of the valence band states in the high symmetry points and directions of three-dimensional and two-dimensional Brillouin zones of an orthorhombic lattice (Fig. 2a, b). The corresponding unit cells are shown in Fig. 2c, d.

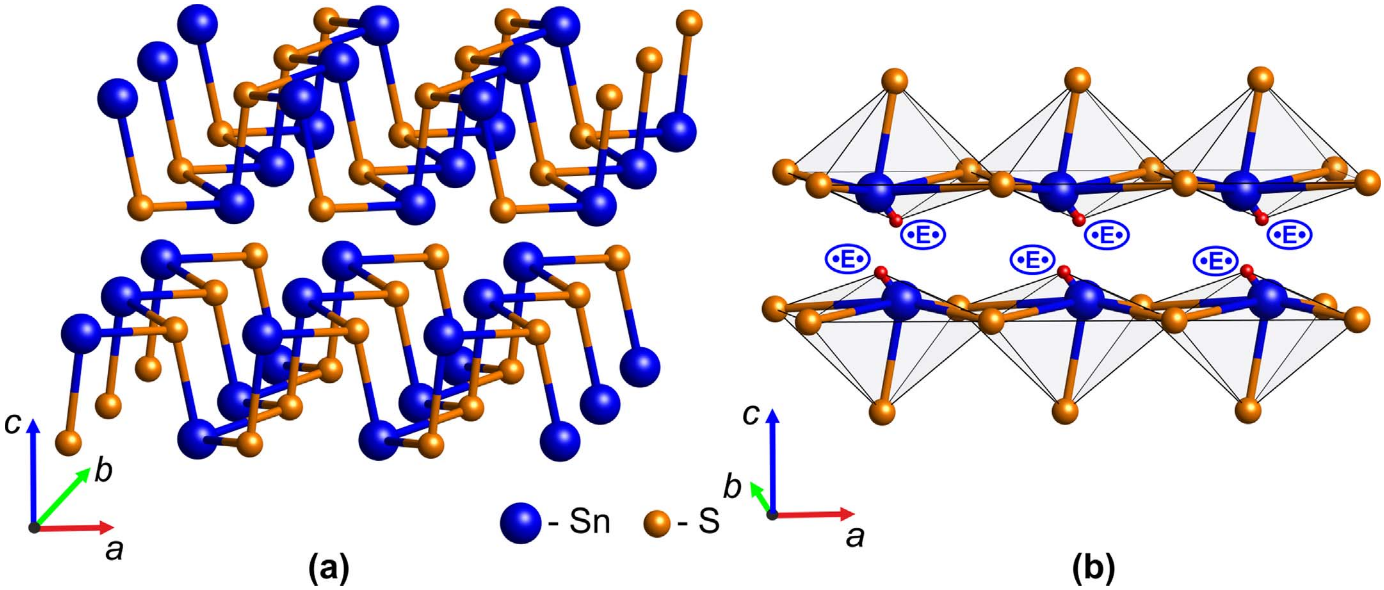

Fig. 1. Crystal structure (a) and packing of ψ-octahedra [SnS_5•E•] (b) of the SnS orthorhombic phase (•E• is an electron lone pair).