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Density of State Calculations for Tl_3SbS_3 and SbTeI

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Abstract

Based on the full-potential linearized augmented plane waves method (FL-LAPW) with local density approximation (LDA), the partials and totals densities of state of Tl_3SbS_3 and SbT eI are calculated in order to find the semiconductor character via direct or indirect gap. Tl3SbS$_3$ and SbTeI present the most important candidates of the antimony chalcogenides family. Their densities of states curves bring out characteristic features in the valence band a core like peak, at environ 13.00 eV below the valence band maximum, originating mainly from S 3s and I 5s states respectively, and a three-peak structure at the top of the valence band from S 3p and I 5p states hybridized with Sb 5p and Te 5p states. Our results give a good agreement with other theoretical calculations and experimental data.

Keywords: The full linearized augmented plane wave method (FL-LAPW); Density functional theory (DFT); The local density approximation (LDA); Kohn Sham orbitals (KSO)

Introduction

Recently, it has become possible to compute with a great accuracy an important number of electronic structure materials from first-principal calculations. This development in computer simulations has opened up many interesting and existing possibilities in materials sciences. In particular for the materials of columns II -VI, IV-VI and V-VI which are notable for their electronic properties and are the subject of many works [1-3].

Study their ternary combinations as III-IV-VI or III-V-VI is a vast field of research in materials physics. The most common example is the system: Sb_2S_3-Tl_2S that is the result of the ternary $Tl_xSb_yS_z$ compounds, where the compositions take the values: 0.25 of Sb_2S_3 and 0.75 of Tl_2S respectively which leads to a better candidate Tl_3SbS_3.

Tl_3SbS_3 crystallize in rhombohedra structure of R3m space group where Sb presents an environment of six atoms of S three at shorter distances, 2.43115A°, and another three at longer distances, 3.03026A°. SbT eI is an interesting compound for the antimony chalcogenide family. It's present a semiconductor character with an indirect gap and monoclinic structure crystallization of P^{-1} space group. Their calculated energy gaps are in ranging application of optoelectronics [4-9]. Study their properties was necessary to find a technique based on numerical simulation. Among these techniques we find the ab-initio, empirical and the semi empirical methods that became today a tool for the most complex electronic and structural property count. All these methods are based on a minimization of the total energy system.

We will use an ab-initio method because it plays an essential role in determination of the electronic structure. These methods do a rigorous resolution of the standard Schrodinger equation (SE) while calculating all integral of recovery (the integral will be evaluated rigorously and all electrons are, in principle, taken in account) [10,11]. Among these methods, we find the full linearized augmented plane wave method (FL-LAPW) which is based on the theory of functional density (DFT).

In this paper, we present the partials and totals densities of states of Tl_3SbS_3 and SbT eI. In the following section; we expose the method of calculations based on the theory of functional density, and in sec.B we present the main results of this calculation and we discuss it. In the last section, some concluding remarks were described.

Method of Calculations

The functional theory of density (DFT) is a very widely used approach in microscopic studies of physical systems. Even in situations where the two-body elementary interactions are well-known such as in atoms or molecules, or atomic clusters, it is not possible to solve exactly the many body Hamiltonian and it is necessary to use sophisticated many-body techniques to find approximate solutions. This is reason why DFT is quite often employed with great success to describing electronic systems [11]. These calculations are based mainly on the use of many approximations such as the local density approximation (LDA), the approximation of generalized conjugate gradient (GGA) [6].

In this work the atomic positions, the space group and the radii of Muffin are taken into account.

Referring to the theorems of Hohenberg-Kohn (HK) [6], which present the most elementary theorems for this system of particles. The quantum state of the system is no only described by the wave function but by the electronic density.

Then starting from our Hamiltonian which is written as:

$$H_e = -\sum_i \frac{\hbar^2}{2m_i}\Delta - \sum_{i,l} \frac{Z_l e^2}{\left|R_l - R_i\right|} + \sum_{i<j} \frac{e^2}{\left|r_i - r_i\right|}, \tag{1}$$

Where, $-\sum_{i,l} \frac{Z_l e^2}{\left|R_l - R_i\right|}$ is the kinetic energy, $-\sum_{i,l} \frac{Z_l e^2}{\left|R_l - R_i\right|}$ present the potential energy between ions and $+\sum_{i<j} \frac{e^2}{\left|r_i - r_i\right|}$ is repulsive energy from other electrons.

By writing the hamiltonian of Eq. (1) as function as the electronic density, $\rho(\mathrm{r})$, the new form is:

$$H_e = T(\rho(\mathrm{r})) - \mathrm{e}^2 \sum_l \int dr \frac{Z_l \rho(\mathrm{r})}{\left|R_l - r\right|} + \frac{1}{2} e^2 \int dr dr' \frac{\rho(\mathrm{r})\rho(\mathrm{r}')}{\left|r - r'\right|} + E_{xc}(\rho(\mathrm{r})), \tag{2}$$

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With $E_{xc}(\rho(r))$ presents the energy which evaluates all the missing terms during the transformation into integral.

To transform the study of this system with N particles in interaction at the study of a one particle in mean potential created by the N-1 other particles we use the variational principle $\frac{\delta H_e}{\delta\rho(r)} = 0$:

$$V_{KS}(r) = -e^2 \sum_l \frac{Z_l}{|R_l - r|} + e^2 \int dr' \frac{\rho(r')}{|r - r'|} + \frac{\delta E_{xc}}{\delta\rho}, \tag{3}$$

Finally, we obtain the following equation:

$$(T + V_{KS}(\rho(r)))\varphi_i(r) = E_i\, \varphi_i(r), \tag{4}$$

Called also the Kohn-Sham equation. E_i is the eigenstate.

To solve this problem self consistently we will have to write our density $\varphi_i(r)$ as:

$$\rho(r) = \sum_{i \in occu} |\varphi_i(r)|^2, \tag{5}$$

With $\varphi_i(r)$ is the Kohn-Sham orbital (KSO).

In this context, we have used the Wien2k package [12-14] based on the local density approximation (LDA). In order to achieve energy eigenvalues convergence, we expanded the basis function up to $R_{max}K_{max}$=7 where K_{max} is the maximum modulus for the reciprocal lattice vector, and R_{max} is the average radius of the Muffin-Tin (MT) spheres).

Valences densities of state (VDOS)

In attempting to understand the electronic properties of these compounds, one start with Tl_3SbS_3 and we wish this discussion by SbTeI. The calculation is based on the local density approximation (LDA) for exchange correlation potential which permitted us to obtain good densities of state for Tl_3SbS_3 and SbTeI. So the applied data are the atomic positions and the group of space [15] that constitutes the start point that we took in account in this numeric simulation. For each step we have compared, judged and verified the consistency of results found and the validity of our calculations by basing over all applied and theoretical works done by other methods [16]. A Tl_3SbS_3 compound has an indirect gap 1.780 eV [17-19]. Several electronic structure calculations of the SbTeI are available in the literature [17-20]. In the present work, we find for SbTeI also an indirect gap [17-20] 1.009 eV. The Table 1 give the value of predicted and calculated energy gap compared with experimental ones in eV [17-19]. The valence density of states (VDOS) curves exhibit three bands, with a characteristic three peak structure for the upper portion and core-like level for the lower band.

- For Tl_3SbS_3, the upper valence band has a bandwidth of 8.14 eV. Peak A, at E_v=-0.38 eV, originates from S 3p derived states with minor Sb 5p character. Peak B, at E_v=3.078 eV, results from mixed S 3p, Tl 6s and Sb 5p. Peak C, at E_v=7.90 eV, formed by the Sb 5s states. The lowest band D, with a bandwidth of 0.55 eV and centered at E_v=-11.88 eV, is formed essentially from S 3s states. The Figure 1 depicted the DOS curves of Tl_3SbS_3.

Compounds	PEG (eV)	CEG (eV)	EEG (eV)
Tl_3SbS_3	2.210 [19]	1.780	1.800 [9,19]
	1.920 [17,18]		
SbTeI	1.320 [19]	1.009	1.450 [9,19,21]

Table 1: Predicted energy gaps (PEG) and calculated energy gap (CEG) compared with experimental ones (EEG) in eV.

Partial and total density of states of Tl_3SbS_3

- For SbTeI, the upper valence band has a bandwidth of 9.14 eV. Its peak A, located at E_v=1.02 eV, is mostly I 5p with some admixture of the Sb 5p states. Peak B, at E_v=1.72 eV, has some contribution from Te 5p, Sb 5p states in addition to I 5p states whereas peak C results primarily from Sb 5s states and a later peak D is formed principally by I 5s states. It appears at E_v=10.82 eV and has bandwidth of 1.79 eV. For summary the Table 2 gives positions in eV of different peaks deducted by calculation of the density of states of and SbTeI. The Figure 2 depicted the DOS curves of SbTeI.

Conclusion

We have calculated the band structure and the total density of states by using the DFT theory; we remark the following main results:

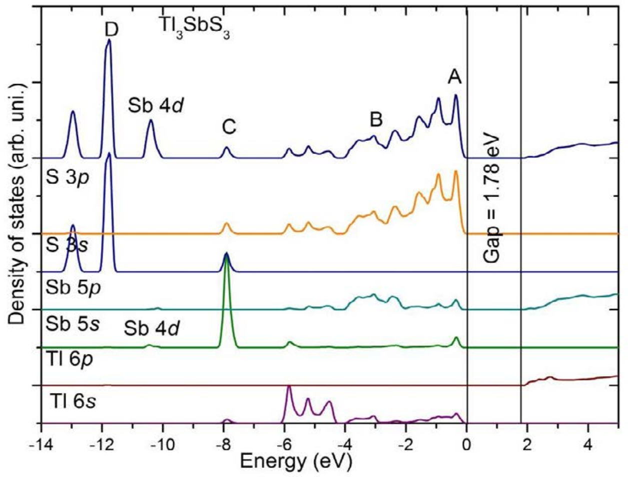

Figure 1: Partial and total density of states of Tl3SbS3.

Compounds	D (eV)	C (eV)	B (eV)	A (eV)
Tl_3SbS_3	-11.88	-7.91	-3.07	-1.38
			-2.80 [4]	-0.80 [4]
SbTeI	-10.82	-8.85	-2.72	-1.02

Table 2: The positions in eV of different peaks deducted by calculation the density of states of Tl_3SbS_3 and SbTeI.

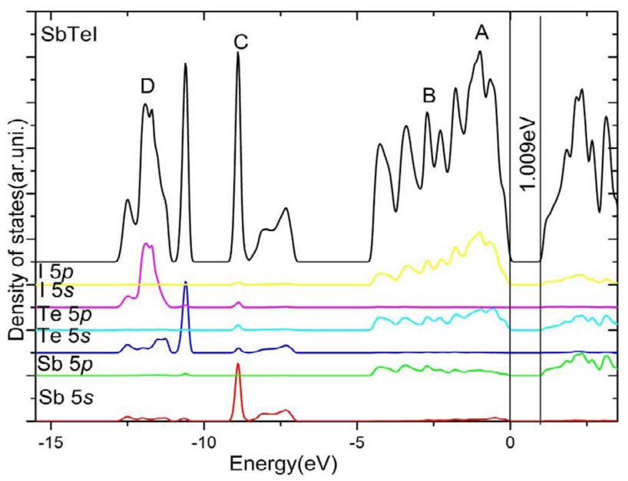

Figure 2: Partial and total density of states of SbTeI.

- The density of states curves bring out three characteristic features in the valence band: a core-like peak, at 13.00 eV below the valence band maximum, originating mainly from S 3s states and I 5s, and three-peak structure at the top of the valence band formed from S 3p and I 5p states hybridized with Te 5p and Sb 5p states. - For Tl_3SbS_3, the strong contribution of S 3p states compared with Sb 5p states, is responsible to form the valence band where their width is about 8.10 eV for our work, 7.50 eV for Lippens work [4] and about 5.00 eV for the experimental data (XPS) and (XES) [5].

- For SbTeI, the strong contribution is affected by the participation of the I 5p states with a weak domination of Te 5p. Its width is around 9.14 eV.

- The value of the calculated energy gap 1.780 eV and 1.009 eV for Tl_3SbS_3 and SbT eI respectively permit them to classify it as important materials for optical applied.

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