First-principles investigation of the structural and electronic properties of Sr_3Sb_2 in hexagonal phase

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Abstract:

The electronic and structural properties of Sr_3Sb_2 were investigated using the Density Functional Theory (DFT). To solve the equations of Kohen-Sham the method of Full-Potential Linearized Augmented Plane Wave (FP-LAPW) was applied. The lattice parameters, volume modulus and the derivative of the volume modulus were calculated. The band structures were also studied by two different methods of Generalized Gradient Approximation (GGA) and Engle-Vosko Generalized Gradient Approximation (EV-GGA). The results of the calculations by GGA and EV-GGA methods show that this structure is a semi-conductor and predict the energy gap of type Γ→K with a magnitude of 0.412eV and 0.977eV respectively. The effect of pressure on the band structures, the magnitude of the gap, anti-symmetric gap, and the width of the gaps were also studied. With extrapolation of the gap variation with pressure, the metallization pressure was determined which is equal to 19.984GPa. In this work, the electron and hole effective mass were investigated as well by the methods of GGA and EV-GGA.

Keywords: DFT, Sr_3Sb_2, semi-conductor, effective mass, band structure and pressure

I. Introduction

Semi-conductors have been subjects of many research works because of their numerous applications in electronic and optoelectronic devices. Among them, are the compounds formed from the elements on the second and the fifth group of periodic table. These compounds have been investigated by various researchers [1-4]. However, the Sr-Sb compounds have not been studied very well. In view of similar properties between the elements of these two groups, and the similarity between their phase diagrams, it is very likely that the Ca-Sb compound has a formula of Ca_3Sb_2 and a hexagonal and volume-center cubic phase [5, 6]. As we know, Sr_3Sb_2 has not been studied at all. We investigated the structural and electronic properties of the hexagonal phase for this compound. The hexagonal phase of this compound has a similar structure to La_2O_3 with space group of 164. The similarities between the elements of the II and the V groups suggest that this structure is a semiconductor, and because of semiconductors applications, we make use of Density Functional Theory (DFT) to investigate it [7, 8]. This article is organized as follow: in section II we describe the method for calculations, and then in section III the results and discussion will be presented. Concluding remarks are given in the last section.

II. Calculation method

The Density Functional Theory was used to investigate Sr_3Sb_2 compound. The calculations were done using WIEN2k software package [9]. The Muffintin radius for Sr and Sb atoms was selected to be 2.7 $a.u.$ and 2.9 $a.u.$ respectively. The parameter for the expansion of the wave function inside the atomic sphere l_{max} was set to 10. Also the parameters values of K_{max}*R_{MT} and k-point after optimizations were set to 8.5 and 500 respectively where R_{MT} is the smallest atomic sphere radius in the unit cell and K_{max} is the magnitude of the largest K vector. k-point were sampled in the irreducible wedge of the first Brillouin zone hexagonal phases which correspond to 9×9×6 grids in Monkhorst-Park scheme [10]. The calculations were based on FP-LAPW method [9]. To find the interchange-correlation potential, we used the extended slope approximation method (PE GGA) which was introduced by Pedro et. al [11]. It is possible to use different approximation in the calculations. Because the results of calculations for energy by the GGA method are very close to the experimental values, this method is preferred to calculate the parameters which directly come from the energy. The lattice parameter is among those which are calculated directly from energy. The calculated total energies at many different volumes around equilibrium were fitted [Fig. 1] by the Murnaghan equation of state[12]. The results of the works done by researchers show that the GGA method underestimated the magnitude of the energy gap below the experimental value while the value predicted by EV-GGA method is very close to the experimental value [13]. So we were motivated to use the EV-GGA method and the results were compared with the results by the GGA method.

III. Results and Discussion

A. Structural Properties

The Sr_3Sb_2 crystal in hexagonal phase, has 5 atoms per primitive cell. Atoms in hexagonal phase of Sb are located on $\pm(\frac{1}{3},\frac{2}{3},u)$ while those in Sr atoms are distributed into two distinct groups located on $(0,0,0)$ and $\pm(\frac{1}{3},\frac{2}{3},v)$ where parameters u and v are the internal parameters for Sb and Sr atoms respectively [14]. For this phase, two different types of Sr atoms exist labled as Sr1 and Sr2. After the initial location of atoms have been specified, the energy diagram as a function of volume was obtained using Murnaghan equation [12].

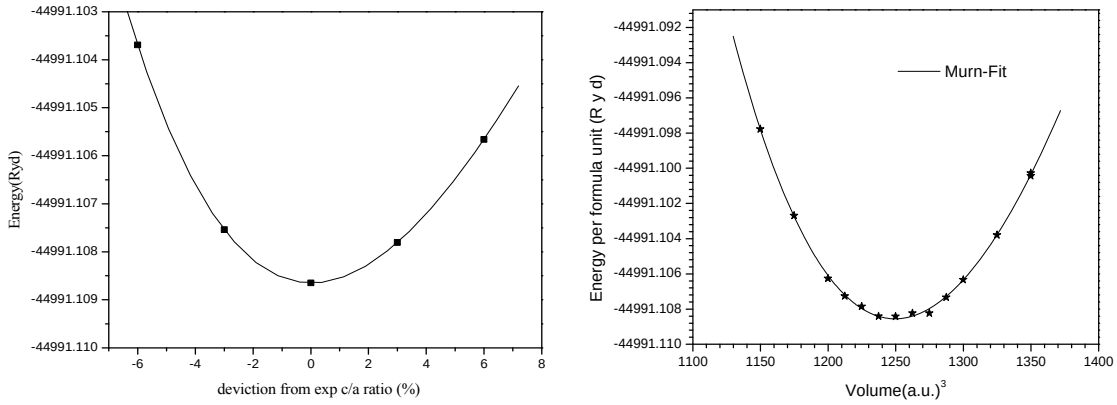

Fig.1. The energy vs. volume, and (right), and the energy vs. the variation percentage in $\frac{c}{a}$ (left) for Sr_3Sb_2 hexagonal phase

The volume of a hexagonal geometric shape is given by $V = \frac{\sqrt{3}}{2}a^2c$, [15] and this contains two unknown. For this reason it is necessary to obtain the optimized ratio for $\frac{c}{a}$ at first, To calculate the optimized value of $\frac{c}{a}$, the energy is calculated with the variation in $\frac{c}{a}$. The minimum value of energy must coincide with zero. In this case the optimized value were obtained which is equal to 1.27198 and then the lattice parameters can be calculated from the energy versus volume diagram. The energy diagrams as a function of volume and the optimized ratio (%) of $\frac{c}{a}$ are shown in Fig.1. It should be mentioned that the internal parameters are contained in the initial locations of the atoms, so these internal parameters are calculated by Holman - Fineman method [16] and the results are given in table 1. In addition to bulk modulus, it is possible to find the derivative of the bulk modulus from the energy versus volume diagram. We also utilized this diagram to find the energy of Sr_3Sb_2 molecule. The Energy of cohesive which is the difference between the energy of solid state and the energy of the free atoms of these atoms, can be easily calculate which for this structure the magnitude of the cohesive energy is 1.053Ryd. The results from the energy versus volume diagram and $\frac{c}{a}$ diagram are presented in table 1

Table 1: The calculated values of lattice parameters, the optimized internal parameters, the volume modulus, the derivative of the volume modulus and the cohesive energy for Sr_3Sb_2 hexagonal phase

	Parameters	Present work
Hexagonal	a, c (a.u.)	10.4299, 13.2666
	u,v	0.2128,0.6864
	B (GPa)	34.2551
	B'	4.4023
	$\lvert E_{coh}\rvert$	1.0532

B. Electronic Properties

Having calculated the optimized values for parameters, the band structures and the density of total and partial states for this structure can be calculated. The gap and band structure were calculated by the methods of GGA and EV-GGA. The results for the band structure show that this structure is a semi-conductor and the magnitude of the gap by GGA method is 0.412eV and by EV-GGA is 0.977eV. The specified gap by these two methods is of the type Γ→K. The magnitude of the anti-symmetric gap and the width of the bands which are labeled as B1 and B2 can be calculated by utilizing the band structures. By anti-symmetric gap we mean the first gap below the Fermi energy and B1 is the width of the band below the Fermi energy, and B2 is the width of the band below the anti-symmetric gap. The results are shown in table 2. The effective mass of electron and the hole can also be calculated by making use of the band structures. The effective mass will be applied in calculating the optical, thermal and conduction properties of matter [15]. The value of m^*/m_e is usually reported in the results of the calculations for the effective mass, where m^* is the effective mass and is calculated by $m^* = \hbar^2/(d^2E/dk^2)$. To calculate the effective mass, from the band structures, we find the energy as a quadratic equation in terms of k and with the help of the quadratic equation the effective mass of the electron and the hole is calculated. The results of these calculations are given in table 3. We should point out that the hole effective mass is calculated at the valence band maximum and the electron effective mass is calculated at the conduction band minimum.

Table 2: The band structures results by GGA and EV–GGA method

Phase	Method	Band gap (eV)	Bandwidths (eV) B1	B2	Anti-Sym-Gap (eV)
Hexagonal	DFT(GGA)	0.412	2.860	0.828	5.222
	DFT(EV-GGA)	0.977	2.588	0.781	5.326

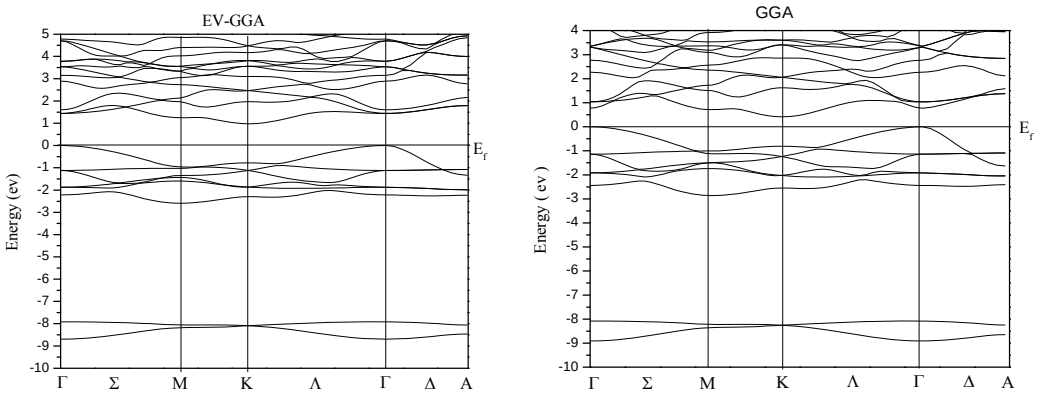

Fig.2. The band structures determined by the GGA (right) and EV-GGA (left) methods

So the electron effective mass were calculated in K→M and K→ Λ paths, and the hole effective mass were calculated in $\Gamma \to \Sigma$, $\Gamma \to \Lambda$ and $\Gamma \to \Delta$ paths. The effect of the pressure on the band structures for this structure were also investigated. An increase in pressure on the structure, is equivalent to a decrease in the volume. The relation between pressure and the initial and final volume of the structure is given by $\mathrm{P(V)} = (B/B')((V_0/V)^{\mathrm{B}'} - 1)$ [17].

Table 3: The electron and hole effective mass determined at the specified paths

Hole	$\boldsymbol{m^*/m_h}$(GGA)	$\boldsymbol{m^*/m_h}$ $(\boldsymbol{EV-GGA})$	Electron	$\boldsymbol{m^*/m_e}$ (GGA)	$\boldsymbol{m^*/m_e}$ $(\boldsymbol{EV-GGA})$
$\boldsymbol{\Gamma \to \Sigma}$	0.882	1.075	K→M	0.542	0.68
$\boldsymbol{\Gamma \to \Lambda}$	0.94	1.116	K→ Λ	0.608	0.714
$\boldsymbol{\Gamma \to \Delta}$	0.28	0.303			

Taking the ratio $\frac{c}{a}$ constant, by decreasing the volume of the crystal, the lattice parameters at different pressures were calculated and with these parameters band structures were obtained, hence the effect of pressure on the main gap, the anti-symmetrical gap, and the width of B1 and B2 bands were studied. The results from the GGA and EV-GGA methods were investigated [Fig. 3]. The separation of sub bands in the B1 band is much greater than the B2 band. This is due to two facts; first the electrons in the far bands to the Fermi energy are more bonded to their nuclei and second the electrons are not allowed to occupy the same quantum state according to the Pauli's exclusion principal. Note that with increasing the pressure, the band widths B1and B2 increase as well. This behavior is observed for both GGA and EV-GGA methods.

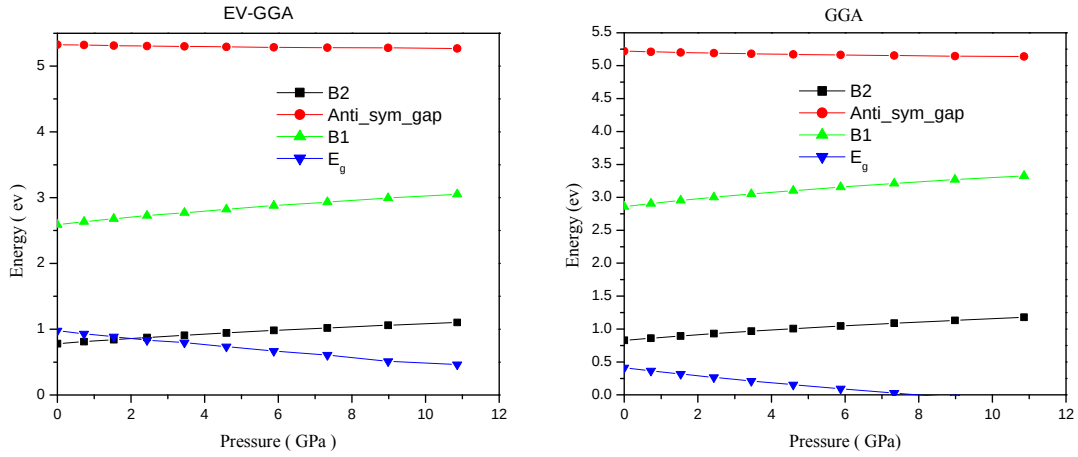

Fig.3. The effect of pressure on the energy gap, anti-symmetric gap, and the width of B1 and B2 bands

With the extrapolation of the energy gap variation with the pressure, one can determine the metallization pressure in both GGA and EV-GGA methods, which these values are equal to 8.0733GPa and 19.984GPa respectively. Finally, the total and partial density of states DOS of this structure were studied using tetrahedral method[18] and the results are shown in the Fig.4.

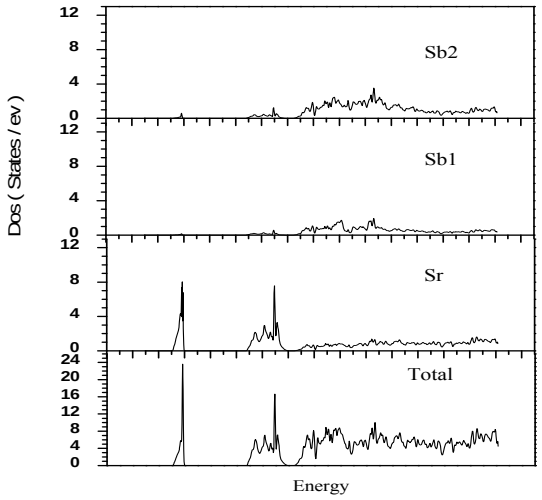

Fig.4. The density of total and partial states corresponding to each atom inSr_3Sb_2compound

IV. Conclusion

In this paper the structural and electronic properties of Sr_3Sb_2 were investigated using DFT. The lattice parameters are equal to a=10.4299a.u., and c=13.2666a.u. To determine the band structures the GGA and EV-GGA methods have been used and the results from other investigations we recarried out on other compounds show that the energy gap from the EV-GGA method is closer to the experimental value. The metallization pressure was also determined from the investigation of the effect of pressure on the band structures which is equal to 19.984GPa. Both methods show Γ→K direction energy gap and density of states confirm semiconducting properties of this compound.

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