Band structure and optical properties of some quasi-molecular AI_3 (A=Sb, Bi, As)

Husnu Koc[*], Amirullah M. Mamedov[♦]

Physics Department, Cukurova University, Adana, Turkey.

Abstract

We perform first principles density functional pseudopotential calculation for the description of band structure and optical responses a prototypical family of quasi-molecular layered solid of the type AI_3 where $A = Sb, Bi$ and As. Our report on calculation of the anisotropic frequency-dependent optical properties and density of states of these compounds and find excellent agreement with the available experimental data. The optical properties show two main structures that can attributed to transitions between the np-orbitals of A^{3+} -cations and $5s^2 5p^5$ orbitals of I^- -anions.

1. Introduction

The $AI_3 (A = Sb, Bi \, and \, As)$ crystals have received attention in relation to their possible uses for optical information. They posses semiconducting properties with relatively high resistance and photosensivite in the visible and IR region of the spectrum [1-3].

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[*]) For correspondence; Email: hkoc@student.cu.edu.tr.

[♦]) For correspondence; Email: mamedov@cu.edu.tr.

Their energy structure and certain of their physicochemical properties are not sufficiently well understood. One of AI_3 crystals-antimony tri-iodide with hexagonal structure [4] is an important precursor in the synthesis of ferroelectric $SbSI$ [5]. Crystalline SbI_3 exhibits second harmonic generation [2]. This photosensitive film has found applications in solid-state batteries as cathode, high resolution image micro-recording and information storage [6].

SbI_3 belongs to the trigonal system with space group C_{3i}^2. Unlike alkali halides antimony tri-iodide has a rhombohedral crystal structure in which the halogen atoms are in almost perfect hexagonal packing. According to [8] other members of the tri-iodide family have crystallographically equivalent structures. There is clear three-fold coordination and the molecular geometry in the solid is close to that of gas phase AI_3 [8].

The molecular character is lost in BiI_3 which exhibits near-perfect six-fold coordination of the metal. In the three materials there is an iodine sublattice in which iodine atoms exist in well-defined planar double layers [9]. This crystal has [6] AI_3 molecules $(24\ atoms)$ in a unit cell. The lattice constants in the unit cell for all AI_3 are given in table 1. The band structures of some AI_3 have been investigated using semiempirical [8] and ab-initio [7] pseudopotential methods. As we know, no ab initio general potential calculation of the electronic band structure and optical properties of the AI_3 compounds have been reported in detail.

Table 1: Structure parameters of AI_3 materials.

Material	$a(A^o)$	$c(A^o)$	Space Group
SbI_3 Present	7.501	20.603	
SbI_3 [18] Experiment.	7.48	20.90	$C_{3i}^2 - R\overline{3}m$
SbI_3 [19] Experiment.	7.505	20.966	
BiI_3 Present	7.49	19.72	
BiI_3 [18] Experiment.	7.516	20.718	
BiI_3 [19] Experiment	7.526	20.731	$D_{3i}^2 - R\overline{3}m$
AsI_3 Present	7.242	20.32	
AsI_3 [18] Experiment	7.208	21.436	
AsI_3 [19] Experiment.	7.208	21.415	
AsI_3 [20] Experiment	7.193	21.372	
AsI_3 [21] Theory (GGA)	7.248	21.547	
AsI_3 [21] Theory (LDA)	7.031	20.223	$C_{3i}^2 - R\overline{3}m$

    In the present work we have investigated and calculated the electronic band structure and the linear optical properties of the AI_3 compounds using a pseudopotential method based on the density functional theory (DFT) in the local density approximation (LDA) [10]. Firstly, the band structure and the total density of states (DOS) of SbI_3, BiI_3 and AsI_3 were calculated. Then, the linear frequency dependent optical dielectric functions including the self-energy effects and some optical functions were calculated. In the calculations of the optical response, according to the band structure calculated by us, we have chosen a photon energy range of $0-30\ eV$ and seen that a $0-18\ eV$ photon energy range is sufficient for most optical functions.

2. Computational details

SİESTA (The Spanish Initiative for Electronic Simulations with Thousands of Atoms) code [11−13] was utilized in this study to calculate the energies and optical responses. It solves the quantum mechanical equation for the electron within DFT approach in the LDA parameterized by Ceperley and Alder [14]. The interactions between electrons and core ions are stimulated with seperable Troullier –Martins [15] norm-conserving pseudopotential. The basis set is based on the finite range pseudoatomic orbitals (PAO's) of the Sankey-Nicklewsky type [16], generalized to include multiple-zeta decays.

We have generated atomic pseudopotentials separately for Sb, As, Bi and I by using the $5s^2 5p^3$, $4s^2 4p^3$, $6s^2 6p^3$ and $5s^2 5p^5$ atomic configurations, respectively. The cut-off radii for the present atomic pseudopotentials are taken as 2.35, 2.55, 2.70 and 2.85 a.u. for the s, p, d and f channels of Sb, As, Bi and I, respectively.

SİESTA calculates the self-consistent potential on a grid in real space. The fineness of this grid is determined in terms of an energy cut-off E_c in analogy to the energy cut-off when the basis set involves plane waves. Here by using a double-zeta plus polarization (DZP) orbitals basis and the cut-off energies between 50 and 450 Ry with various basis sets, we found an optimal value of around 300, 325 and 200 Ry for SbI_3, AsI_3 and BiI_3, respectively. For the final computations, 25, 16 and 16 k-points for SbI_3, AsI_3 and BiI_3 were found to be adequate for obtaining the total energy with an accuracy of about 1 $meV/atoms$.

First, the equilibrium lattice parameter was computed by minimizing the crystal's total energy calculated for the different values of lattice constant by means of Murnaghan's equation of state (EOS) [17]. The calculated lattice constant are in a good agreement with the experimental values [4 − 8].

3. Results and Discussion

3.1 Electronic Band Structure

The electronic band structures of SbI_3, BiI_3 and AsI_3 single crystals have been calculated along high symmetry directions in the first Brillouin zone (BZ) of the hexagonal system.

The results of the calculations are shown in Fig.1 for SbI_3, BiI_3 and AsI_3 single crystals. In the rightmost panels of this figure, the density of states (DOS) is presented for each crystal. The calculated band gap values of these crystals are given in Table 2.

Table 2: Energy band gap for AI_3 .

Material	$E_g(eV)$
SbI_3 Present	1.7141 indirect-1.740 direct
SbI_3 [22] Experiment.	2.3 direct
	1.93 indirect-1.99 direct
BiI_3 Present	2.0081 indirect
BiI_3 [23] Experiment	2.2 direct
BiI_3 [25] Experiment.	
	1.6350 indirect-1.6510 direct
AsI_3 Present	2.47 direct
AsI_3 [24] Experiment.	

For SbI_3, the maximum of the valence band lies between Γ and A symmetry points, and the minimum of the conduction band locates at A point of the BZ. The band gap of SbI_3 is thus indirect with the value $1.7141\ eV$. The calculated lowest direct gap value is

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1.740 eV are located at the A symmetry point of the BZ. The estimates of the band gap of SbI_3 vary from 1.7141 eV to 1.740 eV (see Table 2).
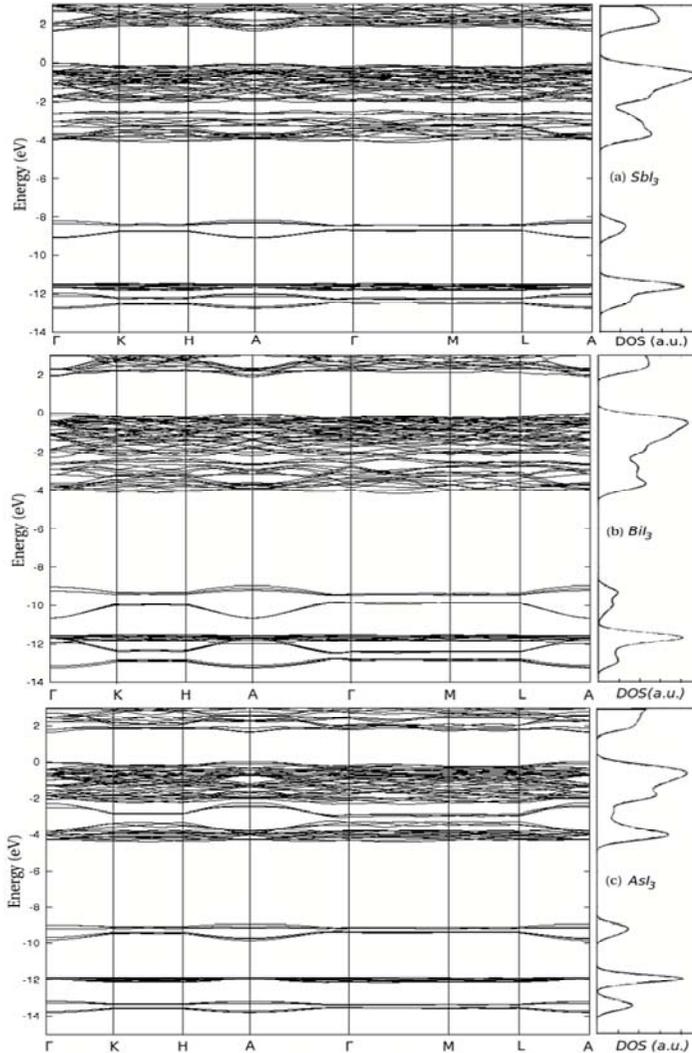
Fig. 1: Energy band structure and DOS (density of states) for AI_3.

As seen from the band structure of BiI_3 in Fig $1(b)$, while the top of the valence band appears nearly midway between Γ and K points, the bottom of the conduction band is located at A of the BZ. The BiI_3 crystal has an indirect band gap with a value $1.93\ eV$. For BiI_3, the lowest direct band gap value obtained is $1.99\ eV$. That means our results obtained are consistent with the experimental result.

The calculated band structure and the corresponding total DOS of AsI_3 are given in Fig$1(c)$. As can be seen from the figure, the band gap has the same character with that of SbI_3, that is, it is an indirect gap. The indirect and direct band gap values of AsI_3 crystal are, $1.6350\ eV$ and $1.6510\ eV$, respectively.

Finally, the band gap values obtained for SbI_3, BiI_3 and AsI_3 are less than their measured values. For all crystal structures considered, the band gap values are underestimated than the experimental values. It is an expected case because of the use pseudopotential method.

3.2 Optical Properties of AI$_3$

It is well known that the effect of the electric field vector, $\mathbf{E}(\omega)$, of the incoming light is to polarize the material. At the level of linear response this polarization can be calculated using the following relation [26]:

$$P^i(\omega) = \chi_{ij}^{(1)}(-\omega,\omega).E^j(\omega), \tag{1}$$

Where $\chi_{ij}^{(1)}$ is the linear optical susceptibility tensor and it is given by [27]

$$\chi_{ij}^{(1)}(-\omega,\omega) = \frac{e^2}{\hbar\Omega}\sum_{nm\vec{k}} f_{nm}(\vec{k})\frac{r_{nm}^i(\vec{k})r_{mn}^i(\vec{k})}{\omega_{mn}(\vec{k})-\omega} = \frac{\varepsilon_{ij}(\omega)-\delta_{ij}}{4\pi} \qquad (2)$$

Where n, m denote energy bands, $f_{mn}(\vec{k}) \equiv f_m(\vec{k}) - f_n(\vec{k})$ is the Fermi occupation factor, Ω is the normalization volume. $\omega_{mn}(\vec{k}) \equiv \omega_m(\vec{k}) - \omega(\vec{k})$ are the frequency differences, $\hbar\omega_n(\vec{k})$ is the energy of band n at wave vector **k.** The $\vec{r}_{nm}$ are the matrix elements of the position operator and are give by [28]

$$r_{nm}^i(\vec{k}) = \frac{v_{nm}^i(\vec{k})}{i\omega_{nm}}; \quad \omega_n \neq \omega_m \qquad (3)$$

$$r_{nm}^i(\vec{k}) = 0; \quad \omega_n = \omega_m$$

where $v_{nm}^i(\vec{k}) = m^{-1}p_{nm}^i(\vec{k})$, m is the free electron mass, and $\vec{p}_{nm}$ is the momentum matrix element.

As can be seen from eq. (2), the dielectric function $\varepsilon_{ij}(\omega) = 1 + 4\pi\chi_{ij}^{(1)}(-\omega,\omega)$ and the imaginary part of $\varepsilon_{ij}(\omega)$, $\varepsilon_2^{ij}(\omega)$, is given by

$$\varepsilon_2^{ij}(w) = \frac{e^2}{\hbar\pi}\sum_{nm}\int d\vec{k}fnm(\vec{k})\frac{v_{nm}^i(\vec{k})v_{nm}^j(\vec{k})}{\omega_{mn}^2}\delta(\omega - \omega_{mn}(\vec{k})). \qquad (4)$$

The real part of $\varepsilon_{ij}(\omega), \varepsilon_1^{ij}(\omega)$, can be obtained by using the Kramers-Kroning transformation:

$$\varepsilon_1^{ij}(\omega) - 1 = \frac{2}{\pi}\wp\int_0^\infty \frac{\omega'\varepsilon_2^{ij}(\omega')}{\omega'^2 - \omega^2}d\omega'. \qquad (5)$$

Because the Kohn-Sham equations determine the ground state properties, the unoccupied conduction bands as calculated have no physical significance. If they are used as single-particle states in a calculation of optical properties for semiconductors, a band gap problem comes into included in calculations of response. In order to take into account self-energy effects, in the present work, we used the 'scissors approximation' [26].

In the present work, Δ, the scissor shift to make the theoretical band gap match the experimental one, is $0.5859, 0.835, 0.078 \ eV$ for SbI_3, AsI_3 and BiI_3, respectively

The known sum rules [28] can be used to determine some quantitative parameters, particularly the effective number of the valence electrons per unit cell N_{eff}, as well as the effective optical dielectric constant ε_{eff}, which make a contribution to the optical constants of a crystal at the energy E_0. One can obtain an estimate of the distribution of oscillator strengths for both intraband and interband transitions by computing the $N_{eff}(E_0)$ defined according to

$$N_{eff}(E) = \frac{2m\varepsilon_0}{\pi \hbar^2 e^2 Na} \int_0^\infty \varepsilon_2(E)EdE, \qquad (6)$$

Where N_a is the density of atoms in a crystal, e and m are the charge and mass of the electron, respectively and $N_{eff}(E_0)$ is the effective number of electrons contributing to optical transitions below an energy of E_0.

Further information on the role of the core and semi-core bands may be obtained by computing the contribution which the various bands make to the static dielectric constant, ε_0.

According to the Kramers-Kronig relations, one has

$$\varepsilon_0(E) - 1 = \frac{2}{\pi} \int_0^\infty \varepsilon_2(E)E^{-1}dE. \qquad (7)$$

One can therefore define an 'effective' dielectric constant, which represents a different mean of the interband transitions from that represented by the sum rule, equation (12), according to the relation

$$\varepsilon_{eff}(E) - 1 = \frac{2}{\pi} \int_{0}^{E_0} \varepsilon_2(E) E^{-1} dE. \tag{8}$$

The physical meaning of ε_{eff} is quite clear: ε_{eff} is the effective optical dielectric constant governed by the interband transitions in the energy range from zero to E_0, i.e. by the polarizition of the electron shells.

In order to calculate the optical response by using the calculated band structure, we have chosen a photon-energy range of $0-20\ eV$ and have seen that a $0-12\ eV$ photon-energy range is sufficient for most optical functions.

The SbI_3 single crystal has an hexagonal structure that is optically uniaxial system. For this reason, the linear dielectric tensor of the SbI_3 crystal has two independent components that are the diagonal elements of the linear dielectric tensor. We first calculated the real (ε_1) and imaginary (ε_2) parts of the $xx-$ and $zz-$ components of the frequency- dependent linear dielectric function and these are shown in Fig.2. The function ε_1^{xx} is equal to zero at about $3.49\ eV$, $5.61\ eV$, $8.51\ eV$ and $16.77\ eV$, while the other function ε_1^{zz} is equal to zero at about $3.74\ eV$, $5.70\ eV$, $8.43\ eV$ and $16.72\ eV$. The peaks of the ε_2^{xx} and ε_2^{zz} correspond to the optical transitions from the valence band to the conduction band and are in agreement with the previous results. In general, there are various contributions to the dielectric function, but Fig. 2 shows only the contribution of the electronic polarizability to the dielectric function. Fig. 2 shows also that except for a narrow photon-energy region, between 0.5 eV and $2.0\ eV$, the ε_1^{xx} and ε_1^{zz} increase with increasing photon energy, which is the normal dispersion. In the range between $2.2\ eV$ and $4.0\ eV$ ε_1^{xx} and ε_1^{zz} decrease with increasing photon energy, which is the characteristics of an

anomalous dispersion. Furthermore as can be seen from Fig. 2, the photon –energy range up to $1.5 \, eV$ is characterized by high transparency, no absorption and a small reflectivity. The $1.7 - 4.0 \, eV$ photon energy range is characterized by strong absorption and appreciable reflectivity.

Our calculation for BiI_3 and AsI_3 show us the results very close to SbI_3 results and they are presented in Fig. 2

The calculated effective number of valence electrons (N_{eff}) and the effective dielectric constant (ε_{eff}) are given in Fig. 3. The effective number of valence electron per unit cell, N_{eff}, contributing in the interband transitions, reaches saturation value at about $16 \, eV$. This means that deep-lying valence orbitals do not participate in the interband transitions (see Fig. 1)

The effective optical dielectric constant, ε_{eff}, shown in Fig. 3, reaches a saturation value at about $10 \, eV$. The photon-energy dependence of ε_{eff} can be separated into two regions. The first is characterized by a rapid rise and it extends up to $4 \, eV$. In the second region the value of ε_{eff} rises more smoothly and slowly and tends to saturation at the energy $10 \, eV$. this means that the greatest contribution to ε_{eff} arises from interband transitions between $2 \, eV$ and $8 \, eV$
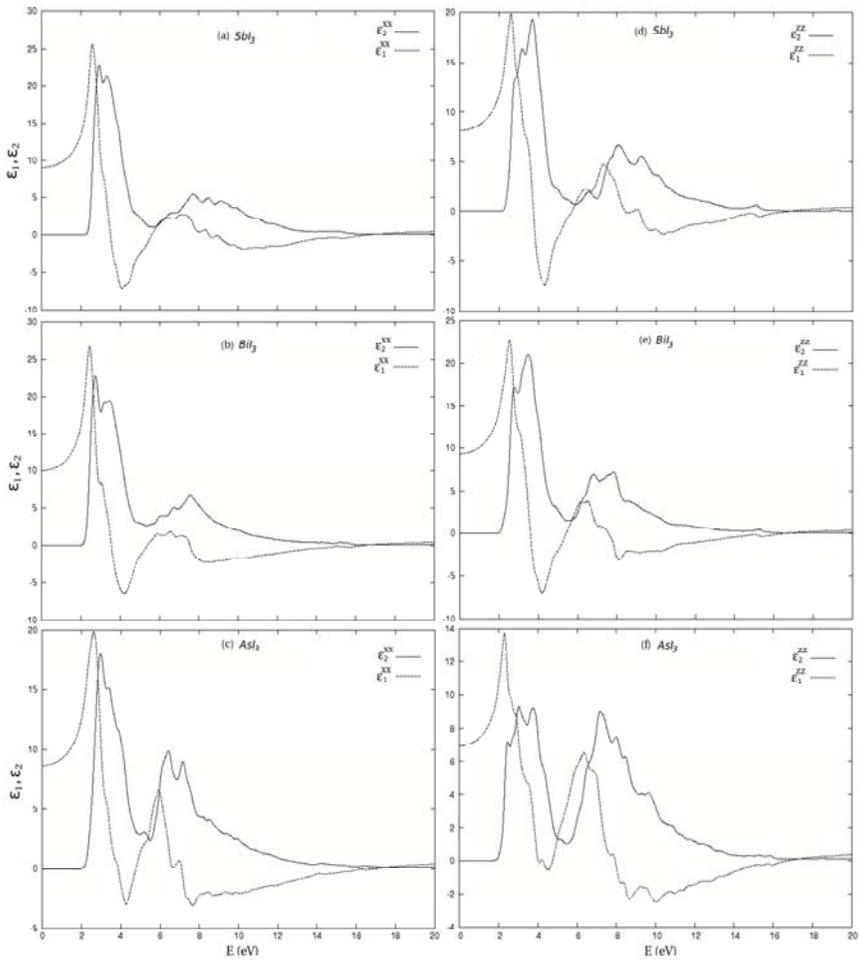
Fig. 2. Energy spectra of dielectric function $\varepsilon = \varepsilon_1 - i\varepsilon_2$ for SbI_3, BiI_3 and AsI_3
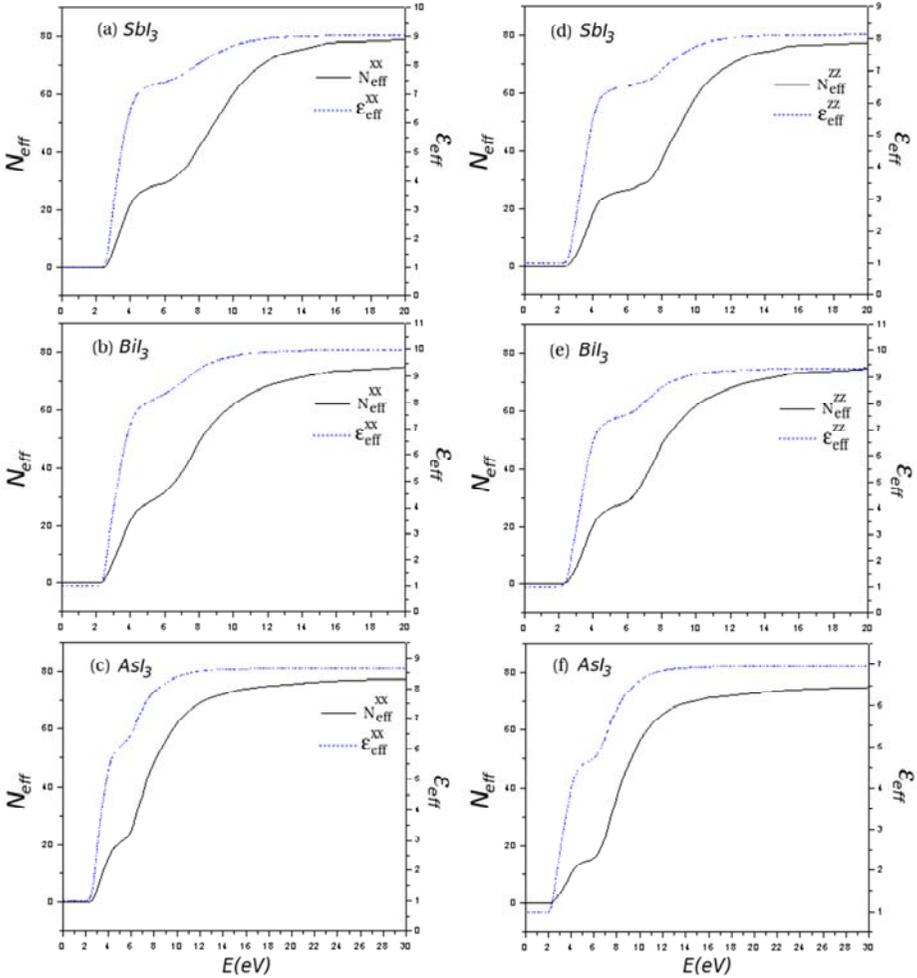
Fig. 3: Energy spectra of N_{eff} and ε_{eff} for AI_3

4. Conclusions

In present work, we have made a detailed investigation of the electronic structure and frequency-dependent linear optical properties of the $AI_3 (A = Sb, Bi, As)$ single crystals using the density functional methods. The task of this work was to apply the density-functional methods to a complex crystals like the AI_3. It is seen that

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all AI_3 single crystals have the indirect forbidden gap. The obtained band gap values are in agreement with the previous results.

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