

Charge density of $\text{Ga}_x\text{Al}_{1-x}\text{Sb}$

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Abstract. Charge density calculations and electronic band structures for $\text{Ga}_x\text{Al}_{1-x}\text{Sb}$ with $x = 1.0, 0.5$ and 0.0 are presented in this work. The calculations are performed using the empirical pseudopotential method. The charge density is computed for a number of planes, i.e. $z = 0.0, 0.125$ and $0.25A_0$ by generating the potential through a number of potential parameters available in the literature. The virtual crystal approximation was applied for the semiconducting alloy. The characteristics of the band structure and charge density are observed to be affected by the potential parameters. Calculated band gaps and the nature of gaps are in good agreement with the experimental data reported. The ionicity is also reasonably in good agreement with other scales proposed in the literature; however the formulation needs to be improved. The present work also demands indirect experimental band gap for the alloy.

Keywords. Semiconducting alloys; III–V compounds; empirical pseudopotential method; electronic band structure; charge density.

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1. Introduction

The moderate energy gaps in III–V antimonide semiconductor alloys, GaSb and AlSb, have device applications in blue and ultraviolet wavelengths and in making double heterostructures [1]. There is growing interest in these compounds to make GaAlSb avalanche photodiodes having specific applications in the infra-red region [2]. The optical properties of these alloys can be tailored by varying the metallic constituents. Electron charge densities and energy band structure of these materials are of importance to look into possibilities of making devices to confine electrons in one or two dimensions. GaSb and AlSb form a 6.1 \AA family of lattice-matched semiconducting compounds and alloys to make heterostructures having applications in photodiodes, heterostructure field effect transistors (HFET) and resonant tunneling diodes (RTD) [3]. To study these semiconducting compounds, empirical pseudopotential method (EPM) is highly suitable, compared to the local density approximation (LDA) based methods as LDA underestimates the energy gap [4] and quasi-particle method is very time consuming [5]. On the other hand, EPM [6,7] is rapidly converging, reliable and less time consuming. Interestingly, the EPM has rarely been applied to unravel band gaps and ionicity in semiconducting alloys

and to our knowledge no such study has been performed for $\text{Ga}_x\text{Al}_{1-x}\text{Sb}$ with a view to explore band widths, charge density and the ionicity. In this work therefore electronic structure and charge density of the $\text{Ga}_x\text{Al}_{1-x}\text{Sb}$ has been undertaken.

2. Empirical pseudopotential method

EPM [6,7] involves fitting of atomic form factors to the experimental data. The crystal potential $V(\mathbf{r})$ is then generated by superposition of atomic potentials:

$$V(\mathbf{r}) = \sum_{\mathbf{R}, \boldsymbol{\tau}} V_a(\mathbf{r} - \mathbf{R} - \boldsymbol{\tau}) \quad (1)$$

where the summation extends over the lattice vector \mathbf{R} , basis vector $\boldsymbol{\tau}$, and the number of atoms in the primitive cell. In the reciprocal space the crystal potential can be written as

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_a(\mathbf{G}) S(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}} \quad (2)$$

where the structure factors are given by

$$S(\mathbf{G}) = (1/N_a) \sum_{\boldsymbol{\tau}} e^{-i\mathbf{G} \cdot \boldsymbol{\tau}} \quad (3)$$

where N_a is the number of basis atoms and $V_a(\mathbf{G})$ is the form factor for the atomic potential.

For zinc-blende structures if the origin is taken half way between the two FCC lattices then $\boldsymbol{\tau} = \pm(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})a$ and for $A^N B^{8-N}$ compounds like AlSb and GaSb the form factors can be simplified to

$$V(\mathbf{G}) = V^S(\mathbf{G}) \cos(\mathbf{G} \cdot \boldsymbol{\tau}) + iV^A(\mathbf{G}) \sin(\mathbf{G} \cdot \boldsymbol{\tau}), \quad (4)$$

where

$$V^S(\mathbf{G}) = \frac{1}{2}[V_A(\mathbf{G}) + V_B(\mathbf{G})]$$

and

$$V^A(\mathbf{G}) = \frac{1}{2}[V_A(\mathbf{G}) - V_B(\mathbf{G})]$$

and $V^S(\mathbf{G})$ and $V^A(\mathbf{G})$ are the symmetric and antisymmetric form factors respectively. The pseudowavefunction $\Psi_{n,\mathbf{k}}(\mathbf{r})$ is then a solution of the Schrödinger equation with the potential $V(\mathbf{r})$. In the local EPM [6], $\Psi_{n,\mathbf{k}}(\mathbf{r})$ is given by

$$\Psi_{n,\mathbf{k}}(\mathbf{r}) = \sqrt{\frac{1}{\Omega}} \sum_{\mathbf{G}} C_{n,\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}}, \quad (5)$$

where $C_{n,\mathbf{k}}(\mathbf{G})$ is the coefficient of the plane wave for a given reciprocal vector \mathbf{G} and Ω is the volume of the unit cell. The charge density can be calculated as

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$$\rho_{\mathbf{k}}(\mathbf{r}) = \sum_n |\Psi_{n,\mathbf{k}}(\mathbf{r})|^2. \quad (6)$$

The charge density calculated over a dense grid of points can then be used to evaluate the total charge density.

To compute band structure and charge density for the alloys virtual crystal approximation (VCA) has been applied. Unlike metallic alloys the approximation has worked reasonably well to examine band gaps, effective masses and bowing in other III–V and II–VI ternary and multi-component semiconductor alloys [8–10].

Si and Ge are presumed to be perfectly covalent bonded semiconductors and the heteropolar gap in the two materials is found to be zero. A number of empirical scales have been suggested on this basis [11–13] to compare the nature of bonding in semiconductor compounds. The ionicity for GaSb, $Ga_{0.5}Al_{0.5}Sb$ and AlSb have been calculated using the following relation [13]:

$$f_i = \left[\left(\frac{E_g}{E_g - 1} \right)^{-1} - 0.75 \right] - \left[\frac{1}{E_g} - 0.66 \right], \quad (7)$$

where E_g is the heteropolar gap.

3. Potential parameters and computational details

To calculate the band structure the potential parameters proposed by Cohen and Bergstresser (CB) [14] and Zaoui *et al* (Z) [11] have been used. Henceforth, the EPM calculation using CB parameters shall be referred as CBC and due to Z shall be referred as ZC for the sake of discussion. The lattice constant for the alloy was generated using the Vegards' law [15] and the potential was generated using virtual crystal approximation [8–10]. The lattice constants for GaSb, $Ga_xAl_{1-x}Sb$ and AlSb were 6.118, 6.127 and 6.135 Å respectively. The basis set of about 350 plane waves was constructed to describe the solids. The charge density was calculated for a number of high symmetry \mathbf{k} -points. The total charge density was found to be normalized.

4. Results

4.1 Electronic band structure and charge density of GaSb

In figures 1a and 1b the electronic band structures for GaSb have been plotted employing the potential parameters of CB and Z respectively. The charge density calculations are performed for a number of x - y planes for the three materials. In figures 2a and 2b the charge density calculated at the Γ point and $z = 0.0$ plane for GaSb using the potential parameters of CB and Z have been plotted. Charge density plots obtained at $z = 0.125A_0$ are shown in figures 3a and 3b. Figures 3, 4, 5 and 6 are drawn on the scale shown with figure 4b whereas remaining contour plots are drawn on another scale shown with figure 2b. The charge density curves at $z = 0.0$ and 0.25 for GaSb with CB parameters are plotted on the same scale in figures 4a and 4b. These figures are on the same scale as figures 3a and 3b.

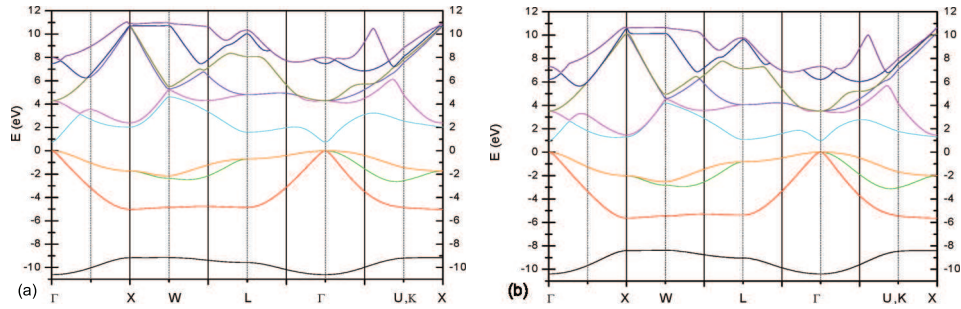


Figure 1. The band structures of GaSb using (a) CB parameters and (b) Z parameters.

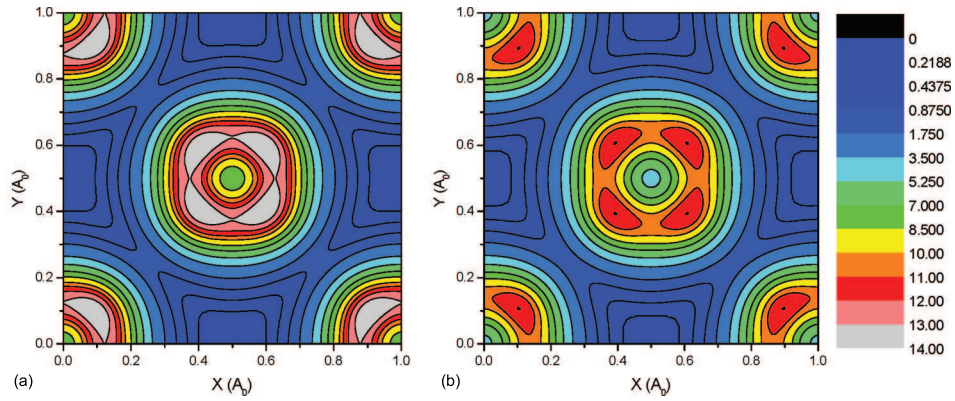


Figure 2. The charge density plots of GaSb with (a) CB parameters and (b) Z parameters for $z = 0.0$ plane at Γ point. The scale is also shown with 2b. The multiplying factor is 0.001.

4.2 Electronic band structure and charge density of $Ga_{0.5}Al_{0.5}Sb$

The crystal potential for the alloy has been generated under the virtual crystal approximation [8–10]. The potential is local in nature and no spin orbit effects are considered. The band structures of the alloy from the two parameters are plotted in figures 7a and 7b.

4.3 Electronic band structure and charge density of $AlSb$

The crystal potentials for AlSb were generated from the potential parameters of CB and Z which are local in nature without spin orbit effects. The band structures obtained are plotted in figures 8a and 8b.

Charge density of $Ga_xAl_{1-x}Sb$

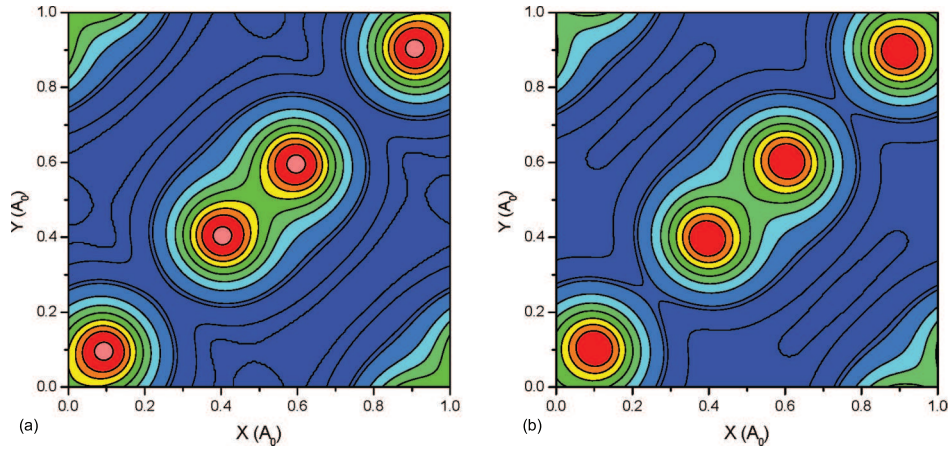


Figure 3. The charge density plots of GaSb with (a) CB parameters and (b) Z parameters for $z = 0.125$ plane at Γ point.

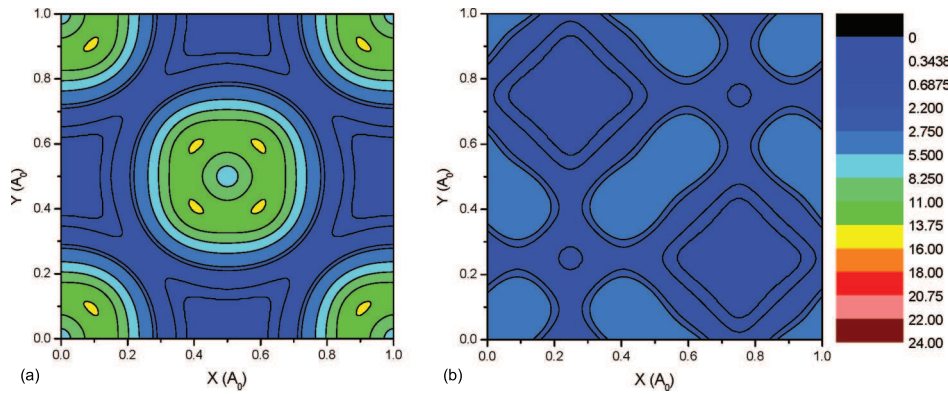


Figure 4. Charge density plots for GaSb obtained using CB parameters at Γ point (a) for $z = 0.0$ and (b) for $z = 0.25$ units. The scale is also shown with 4b. The multiplying factor is 0.0005.

5. Discussion

5.1 Energy bandwidths and gaps

Table 1 summarizes the valence bandwidths along different high symmetry directions for GaSb, $Ga_{0.5}Al_{0.5}Sb$ and AlSb obtained from the parameters of CB and Z. From table 1 and the band structures plotted it is obvious that along the symmetry directions involving Γ point the bandwidths are larger and parameter dependent. Moreover, the ZC gives larger bandwidths compared to the CBC. The parameter dependence is larger for the low lying valence states than the upper states. The difference in the widths predicted by the two parameters is maximum for GaSb and

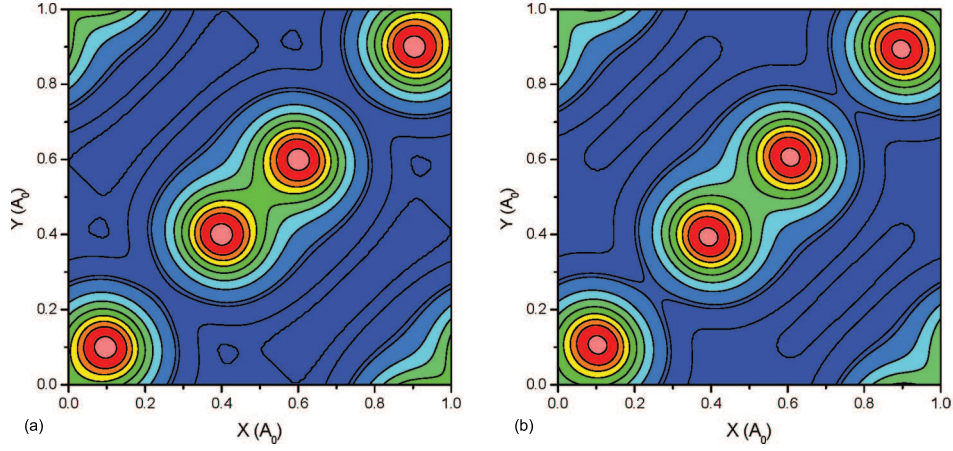


Figure 5. The charge density plots of $\text{Ga}_{0.5}\text{Al}_{0.5}\text{Sb}$ with (a) CB parameters and (b) Z parameters for $z = 0.125$ plane at Γ point.

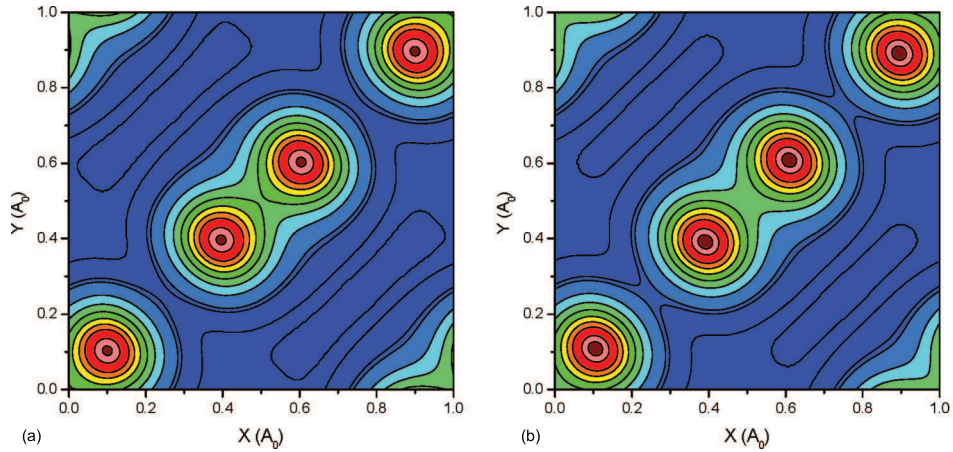


Figure 6. The charge density plots of AlSb with (a) CB parameters and (b) Z parameters for the $z = 0.125$ plane at Γ point. The scale is shown with figure 4b.

minimum for the AlSb . On the other hand, the bandwidths are relatively lower for the symmetry directions not involving the Γ point.

The band gaps for the three materials are summarized in table 2. For GaSb , one observes that the band gap predicted by ZC is larger than the CBC. The experimental gap reported by a number of workers varies in the range 0.72–1.00 eV which is in good agreement with all the calculations presented in table 2. Moreover, the direct band gap observed from all the calculations is well in accordance with the measurements [13,16]. For AlSb , one observes that the band gaps predicted by CBC and ZC are well within the experimental data. Interestingly, the nature of the gap predicted by ZC is indirect whereas CB calculation predicts it to be direct.

Charge density of $Ga_xAl_{1-x}Sb$

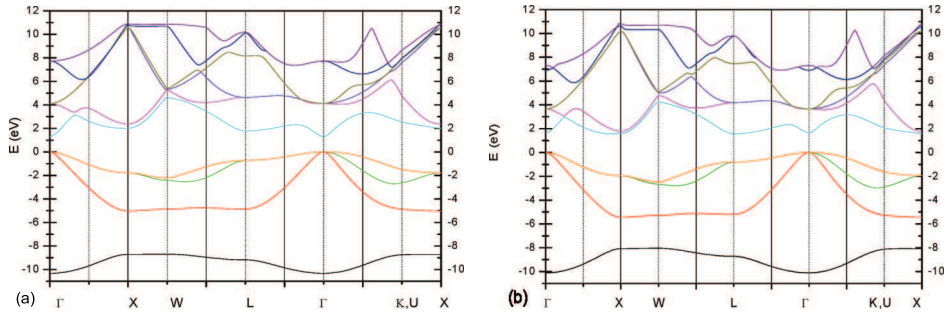


Figure 7. The band structures of $Ga_{0.5}Al_{0.5}Sb$ with (a) CB parameters and (b) Z parameters.

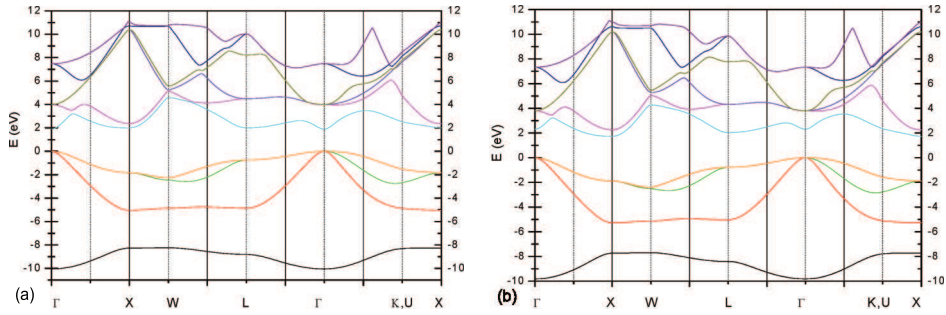


Figure 8. The band structures of $AlSb$ with (a) CB parameters and (b) Z parameters.

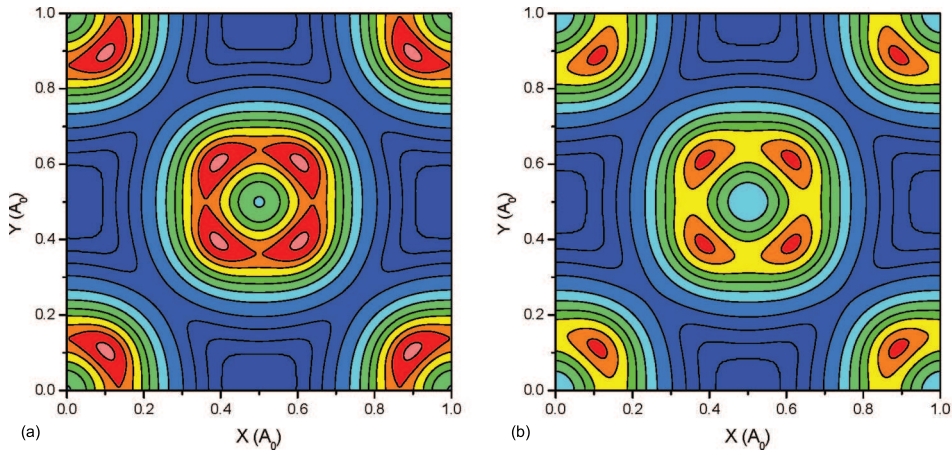


Figure 9. The charge density plots of $AlSb$ with (a) CB parameters and (b) Z parameters for $z = 0.0$ plane at Γ point. The scale is shown with figure 2b.

The experiments have however shown indirect band gap in $AlSb$ indicating good agreement both quantitatively and qualitatively with the Z parameter-based calculations. This discrepancy in CBC may be attributed to the potential parameters

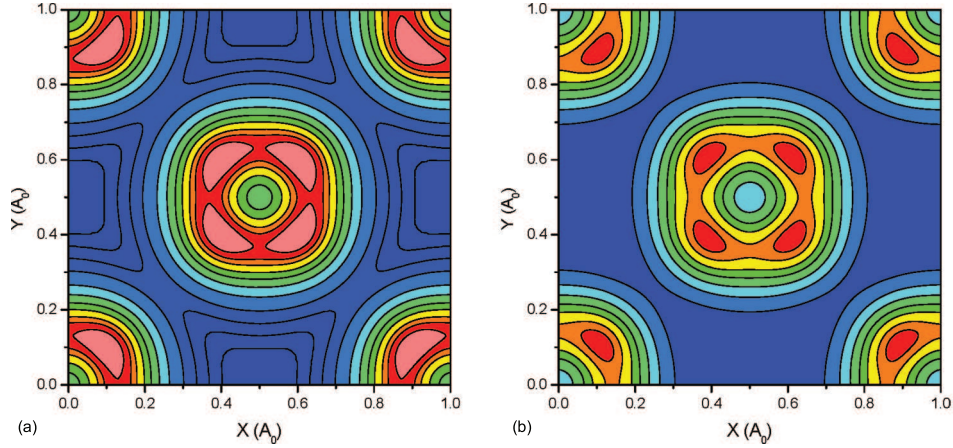


Figure 10. The charge density plots of $\text{Ga}_{0.5}\text{Al}_{0.5}\text{Sb}$ with (a) CB parameters and (b) Z parameters for $z = 0.0$ plane at Γ point. The scale is shown with figure 2b.

determined from the poorly resolved experimental data whereas other parameters are deduced from better resolution. Regarding the $\text{Ga}_{0.5}\text{Al}_{0.5}\text{Sb}$ alloy one observes that CBC shows the gap to be direct whereas the ZC shows the gap to be indirect having minimum in conduction band at the L point. The indirect nature and the magnitude of the gap is reasonably in agreement with the experimental data [16]. It is however worth mentioning that the experimental results are not clearly indicative of the minimal point of the conduction band which may be at L or X [16]. Our calculation suggests L to have minimum in the conduction differing with X by less than 0.02 eV. Thus our calculation based on virtual crystal approximation has been able to unravel the bands reasonably well for the alloy. The calculation however strongly demands experimental data for further verification on the alloy.

The ionicity, evaluated from eq. (7) while calculating the heteropolar gap from CBC, ADC [13] and ZC-based EPM results, are presented in table 2. The ionicity results reported by other workers are also included in table 2 for comparison. One observes that all results show GaSb to be more ionic than AlSb, whereas ADC do not show appreciable differences for the three materials. Moreover, the ionicity predicted by CBC results are larger than the ADC- and ZC-based results and show largest differences with all the scales except that of Louis and Yndurain [17].

It is worth emphasizing that the Al-Douri *et al* [13] and Zaoui *et al* [11] have suggested separate scales of ionicity for semiconducting compounds. From the table it is clear that ionicity factors computed through eq. (7) from the heteropolar gap, deduced from ZC, for GaSb and AlSb (see column IV) differ from the scale of Zaoui *et al* (column V) suggesting inadequacy of the two formulations. It demands improved formulation to the ionicity scale for semiconducting compounds. The efficient way however could be to examine the charge distribution using contour plots as discussed in the following section.

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Table 1. Valence bandwidths (in eV) for $Ga_xAl_{1-x}Sb$. IV band is the top valence band. The first line for each band corresponds to calculation from CB parameters and the second line to the Z parameters. Negative values show upward trends.

| Band | Material | Symmetry directions | | | | | |
|------|----------------------|------------------------|-------------------|-------------------|------------------------|------------------------|-------------------|
| | | $\Gamma \rightarrow X$ | $X \rightarrow W$ | $W \rightarrow L$ | $L \rightarrow \Gamma$ | $\Gamma \rightarrow K$ | $U \rightarrow X$ |
| I | GaSb | -1.451 | -0.017 | 0.429 | 1.037 | -1.422 | -0.028 |
| | | -1.982 | -0.0305 | 0.652 | 1.360 | -1.937 | -0.044 |
| | $Ga_{0.5}Al_{0.5}Sb$ | -1.614 | -0.020 | 0.494 | 1.141 | -1.582 | -0.032 |
| | | -2.035 | -0.034 | 0.680 | 1.388 | -1.989 | -0.045 |
| | AlSb | -1.778 | -0.0254 | 0.563 | 1.240 | -1.741 | -0.036 |
| | | -2.085 | -0.037 | 0.709 | 1.413 | -2.038 | -0.047 |
| II | GaSb | 5.008 | -0.155 | -0.0008 | -4.852 | 4.864 | 0.144 |
| | | 5.622 | -0.168 | -0.073 | -5.380 | 5.450 | 0.172 |
| | $Ga_{0.5}Al_{0.5}Sb$ | 5.019 | -0.159 | -0.003 | -4.858 | 4.869 | 0.150 |
| | | 5.440 | -0.156 | -0.084 | -5.200 | 5.275 | 0.165 |
| | AlSb | 5.031 | -0.162 | -0.0087 | -4.861 | 4.875 | 0.156 |
| | | 5.271 | -0.144 | -0.100 | -5.028 | 5.113 | 0.158 |
| III | GaSb | 1.724 | 0.633 | -1.660 | -0.697 | 2.558 | -0.834 |
| | | 2.009 | 0.810 | -1.992 | -0.827 | 3.023 | -1.014 |
| | $Ga_{0.5}Al_{0.5}Sb$ | 1.777 | 0.634 | -1.689 | -0.723 | 2.618 | -0.841 |
| | | 1.947 | 0.707 | -1.854 | -0.801 | 2.890 | -0.943 |
| | AlSb | 1.825 | 0.633 | -1.712 | -0.746 | 2.671 | -0.846 |
| | | 1.885 | 0.617 | -1.726 | -0.775 | 2.762 | -0.878 |
| IV | GaSb | 1.724 | 0.422 | -1.448 | -0.697 | 1.436 | 0.288 |
| | | 2.009 | 0.525 | -1.707 | -0.827 | 1.687 | 0.321 |
| | $Ga_{0.5}Al_{0.5}Sb$ | 1.777 | 0.431 | -1.486 | -0.723 | 1.483 | 0.294 |
| | | 1.947 | 0.519 | -1.665 | -0.801 | 1.634 | 0.314 |
| | AlSb | 1.825 | 0.440 | -1.519 | -0.746 | 1.526 | 0.299 |
| | | 1.885 | 0.511 | -1.620 | -0.775 | 1.579 | 0.305 |

5.2 Charge density distribution

As inferred earlier, the energy gap evaluated using ZC are in better agreement with the experimental data and therefore the charge density derived from the ZC are considered for further discussion. The parameter dependence shall be briefly outlined in the end.

In figure 2b the charge density calculated at the Γ point and $z = 0.0$ plane for GaSb has been plotted using the potential parameters of Z. Similarly, the charge densities for AlSb and $Ga_{0.5}Al_{0.5}Sb$ at $z = 0.0$ are plotted in figures 9b and 10b respectively. The scale of all these curves is shown with figure 2b. Figures 2b, 10b and 9b show the $z = 0.0$ plane where the cations sit at the corners and the centre of the plane. Compared to AlSb the charge on this plane is larger by 5.1% for GaSb and is 2.5% for $Ga_{0.5}Al_{0.5}Sb$ indicating localization of charge in the plane as one

Table 2. The ionicity and the energy gap E_g at Γ point for $\text{Ga}_x\text{Al}_{1-x}\text{Sb}$.

| (a) The ionicity (f_i) for semiconducting $\text{Ga}_x\text{Al}_{1-x}\text{Sb}$ | | | | | | |
|---|-------|---------|-------|-------------------------|---------------|-------------------------|
| | CB | AD [13] | Z | Zaoui <i>et al</i> [11] | Phillips [12] | Louis and Yndurain [17] |
| GaSb | 0.429 | 0.239 | 0.195 | 0.264 | 0.261 | 0.409 |
| $\text{Ga}_{0.5}\text{Al}_{0.5}\text{Sb}$ | 0.367 | 0.249 | 0.150 | — | — | — |
| AlSb | 0.293 | 0.253 | 0.099 | 0.245 | 0.250 | — |

| (b) The band gap E_g (eV) for $\text{Ga}_x\text{Al}_{1-x}\text{Sb}$ | | | |
|---|---------|--------------------|---------------------------|
| Parameters | CB | Zaoui <i>et al</i> | Experiment |
| GaSb | 0.75(d) | 0.99(d) | 1.00 [13] 0.72(d) [16] |
| $\text{Ga}_{0.5}\text{Al}_{0.5}\text{Sb}$ | 1.31(d) | 1.57(i) | 1.30(i) [16] |
| AlSb | 1.89(d) | 1.73(i) | 2.10 [13] 1.50(i) [16] |

d stands for direct gap and i stands for indirect gap.

adds Ga into AlSb. The planes plotted in figures 3b, 5b and 6b show the planes intersecting the bond direction, i.e. $z = 0.125$. These figures depict lower charge sharing in GaSb, which increases on adding Al. Quantitatively, the charge density is lowered by 1.5% and 0.7% respectively for the GaSb and $\text{Ga}_{0.5}\text{Al}_{0.5}\text{Sb}$ alloy in the bond intersecting plane compared to AlSb. It points that charge density increases in the bond intersecting plane on adding Al into GaSb. Interestingly the charge density is maximum (9.5%) in AlSb at the closest distance between the bonding atoms and the density decreases on adding Ga as visually obvious from the figures representing the $z = 0.125$ plane. Similar observations are clearly visible from figures where charge density plots obtained using CB parameters are drawn. The results are albeit, quantitatively different.

In order to examine the relative charge density in the $z = 0.0$, 0.125 and 0.25 planes, the charge density curves plotted in figures 4a, 3a and 4b for GaSb are now compared. Figure 4a represents the plane containing Ga atoms, whereas 3a represents the bond intersection plane and 4b shows the plane having Sb atoms of GaSb. Figures 4b and 3a show that the charge is minimum around Sb anion being nearly half the charge density shown by the other two planes wherein the total charge density is nearly equal. On comparing figures 3a and 4a it is clear that charge is more distributed and less intense in the cation plane than the bond intersecting plane which has localized charge density due to bonding. Similar observations are also clearly visible for other materials both from CB and Z parameter-based calculations.

6. Conclusions

Charge density calculations and electronic band structures for $Ga_xAl_{1-x}Sb$ with $x = 1.0, 0.5$ and 0.0 are performed using the empirical pseudopotential method. The CBC and ZC are performed to compute charge density for a number of planes, i.e. $z = 0.0, 0.125$ and $0.25A_0$. To generate the potential for alloy the virtual crystal approximation was applied. The EPM is quite successful in evaluating the energy gaps which are in agreement with the measurements for GaSb and AlSb. Calculations based on CB parameters show larger deviations compared to the other parameters namely Z and AD.

It is also observed that the EPM provides strong basis for band engineering in semiconducting alloys by predicting the band gap and its nature well in good accordance with the available measurements. From the charge density analysis, it appears that participation of Sb is more than Ga in bond formation. However, a number of calculations are required for more accurate assertion together with the highly reliable experimental data. The formulae for ionicity do not give systematic in the trends of the ionicity for $Ga_xAl_{1-x}Sb$. More calculations for different values of x would be fruitful to examine it more critically.

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References

- [1] I Vurgaftman, J R Meyer and L R Ram-Mohan, *J. Appl. Phys.* **89**, 5815 (2001)
- [2] X-C Cheng and T C McGill, *J. Appl. Phys.* **86**, 4576 (1999)
- [3] H Kroemer, *Physica* **E20**, 196 (2004)
- [4] M S Hybertsen and S G Louie, *Phys. Rev. Lett.* **55**, 1418 (1985)
- [5] A Rubio, J L Corkill, M L Cohen, E L Shirley and S G Louie, *Phys. Rev.* **B48**, 11810 (1993)
- [6] M L Cohen and J R Chelikowsky, *Electronic structure and optical properties of semiconductors* (Springer-Verlag, Berlin, 1989)
- [7] K B Joshi and B K Sharma, *Proc. Natl. Acad. Sci. India* **76(A)**I, 79 (2006)
- [8] N Bouarissa, *Euro. Phys. J.* **B32**, 421 (2003)
- [9] F Long, P Harrison and W E Hagston, *J. Appl. Phys.* **79(9)**, 6939 (1996)
- [10] W J Fan, M F Li, T C Chong and J B Xia, *J. Appl. Phys.* **79(1)**, 188 (1996)
- [11] A Zaoui, M Ferhat, B Khelifa, J P Dufour and H Aourag, *Phys. Status Solidi* **B185**, 163 (1994)
- [12] J C Phillips, *Bonds and bands in semiconductors* (Academic, San Diego, 1973)
- [13] Y Al-Douri, R Khenata, Z Chelahi-Chikr, M Driz and H Aourag, *J. Appl. Phys.* **94**, 4502 (2003)
- [14] M L Cohen and T K Bergstresser, *Phys. Rev.* **141**, 789 (1966)
- [15] L Vegard, *Z. Phys.* **5**, 17 (1921)
- [16] F Hermann, C D Kuglin, K F Cuff and R L Kortum, *Phys. Rev. Lett.* **11**, 541 (1963)
- [17] E Louis and F Yndurain, *J. Phys. C: Solid State Phys.* **7**, L303 (1974)