Optoelectronic properties of GaAs and AlAs under temperature effect

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\textbf{A B S T R A C T}

An application study of optoelectronic properties as a function of the temperature for GaAs and AlAs according to our model has been presented using empirical pseudopotential method (EPM). The structural phase transition can be seen easily from behavior of the bonding character. The results are compared with the experimental data with reasonable agreement.

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1. Introduction

The electronic energy bands of semiconductors became the subject of many theoretical and experimental studies within the last few decades \cite{1,2}. The semiconducting compounds have generated considerable interest \cite{3,4} in their electronic structure because of their wide range of device applications. For the tetrahedrally bonded semiconductors such as GaAs and AlAs, the zinc-blend structure (ZB) has the lowest minimum total energy, it is the most stable phase of these compounds at room temperature, at increased temperature, while the volume deformed and the transition to the β-Sn (or NaCl) phase occurs at relatively high temperature.

By controlling the evolution with temperature of the bond character in terms of the band structure, we can attempt to link the effect of temperature to theionicity character. This provides a real picture of the temperature-induced structural phase transitions from the fourfold-coordinated crystal structure (ZB) to the sixfold one. In this context, we have used \cite{5} this process for testing the validity of our model of ionicity.

2. Calculations and results

The band gaps between the first and second valence bands at point X are computed on the basis of the empirical pseudopotential method (EPM). The pseudopotential form factors are found using a nonlinear least-square method \cite{6}, in which all the parameters are simultaneously optimized under a definite criterion of minimizing the root-mean-square deviation. Optical, Ultra Photoemission Spectroscopy (UPS) and X-ray Photoemission Spectroscopy (XPS) data are used. Table 1 gives the adjusted pseudopotential form factors for both room temperature and the transition one.

We have evaluated the ionicity factor $f_i$ from our model \cite{5}, which is based on the difference between the first and second valence bands at point X, according to the formula:

$$f_i = \left[ \frac{E_g}{E_g - 1} \right]^{-0.75} - \left[ \frac{1}{E_g} - 0.66 \right]$$

where $E_g$ is the band gap between the first and second valence bands at point X and 1 equals to 1 eV. The experimental data for the temperature variation of the forbidden energy gap (direct or indirect) are similar for many materials.

Most of these data, found in the literature, were fitted by the formula:

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{(\beta + T)}$$

which contains two fitting parameters $\alpha$ and $\beta$. It was originally given by Varshini \cite{7} using the behavior of $E_g(T)$ in the vicinity of zero temperature and above the Debye temperature as the best way to achieve an empirical fit.

At room temperature, the covalent semiconductors are fourfold-coordinated. The reason that density is so low is that nearest neighbours are bound together overlapping hybridized orbitals, which are well known $Sp^3$ hybrids with tetrahedral direction. Therefore, these covalent compounds can be transformed either through chemical shifts, under pressure, or applied high temperature into a denser structure, which may be ionic or metallic.

The results of our calculations of charge densities at room and high temperature transition are presented in Fig. 1, (the results are...
displayed along (1 1 1) direction). The transition occurs when the Ewald contribution dominates over the covalent electronic contribution. As temperature is raised, the volume is deformed and the strong Sp$^3$ covalent bonding, which characterizes their covalent structures at room temperature, is destroyed, resulting in a new structure. From our viewpoint, this discrepancy at high temperature is an immediate consequence of the difference in the corresponding ionicities. The effect of temperature is to transform the compunds from fourfold coordinated structure to a denser structure which is the β-Sn or NaCl phase, and these transformations correspond to the category with $i_1 < 0.35$ [8] for the first transformation.

In Table 2, we compared the calculated transition (critical) temperature with the experimental one. A good notice, the critical temperature is the value, which separates the decrease and the increase of the ionicity value. The decreasing of the ionic factor under temperature is confirmed by changing the positions of the first and second valence bands at point X as shown in Table 3. The ionicity decreases as temperature increases until a critical value is characterized by a random behavior (Table 2). A new atomic arrangement is more appropriate than the ZB structure. Our critical values of temperature are of the same order as the experimental ones. The calculated ionicity factors are in good agreement with experimental and theoretical ones. Therefore, we may conclude that the sudden variation of the ionic character is an indication of the structural phase transition. In conclusion, the simple method gives easy use for the calculation of the structural phase transition, and confirms its validity for GaAs and AlAs, expecting a new phase transformation for other compounds.

**Table 1**
The adjusted symmetric and antisymmetric form factors (in Ry.) and the lattice constant $a_0$ (in atm. units) at $T=300$ K, for GaAs and AlAs.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp. (K)</th>
<th>$a_0$</th>
<th>$V_3(3)$</th>
<th>$V_3(8)$</th>
<th>$V_3(11)$</th>
<th>$V_{4(4)}$</th>
<th>$V_{4(4)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>300</td>
<td>10.68852</td>
<td>-0.25249</td>
<td>0.0002</td>
<td>0.089</td>
<td>0.03587</td>
<td>0.065975</td>
</tr>
<tr>
<td>AlAs</td>
<td>$T_c$</td>
<td>10.7760</td>
<td>-0.23625</td>
<td>-0.00636</td>
<td>0.06422</td>
<td>0.03165</td>
<td>0.05201</td>
</tr>
<tr>
<td></td>
<td>$T_c$</td>
<td>10.78245</td>
<td>-0.26451</td>
<td>-0.00656</td>
<td>0.08301</td>
<td>-0.00327</td>
<td>0.09453</td>
</tr>
</tbody>
</table>

**Table 2**
The ionicity values are corresponding to the room and critical temperatures (in K). The ionicities are compared to the experimental values and theoretical results.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$i_1$ [cal.]</th>
<th>$i_1$ [exp.]</th>
<th>$i_1$ [theor.]</th>
<th>$i_1$ at $T_c$</th>
<th>$T_c$ (K)$^a$</th>
<th>$T_c$ (K)exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>0.328</td>
<td>0.310</td>
<td>0.310$^b$, 0.316$^b$, 0.312$^b$, 0.313$^b$, 0.325$^b$</td>
<td>0.266</td>
<td>1200</td>
<td>1513$^{3,4}$</td>
</tr>
<tr>
<td>AlAs</td>
<td>0.275</td>
<td>0.274</td>
<td>0.376$^b$, 0.375$^b$, 0.292$^b$</td>
<td>0.193</td>
<td>1500</td>
<td>2013$^{3,4}$</td>
</tr>
</tbody>
</table>

\(^a\) The used data: (a) Ref. [8], (b) Ref. [9], (c) Ref. [10], (d) Ref. [11], (e) Ref. [12], (f) Ref. [13], (g) Ref. [14], (h) Ref. [15], and (i) Ref. [16].

![Fig. 1](image_url) The total valence pseudocarce densities along (1 1 1) direction at $T=300$ K (solid lines), and at $T=T_c$ (dashed lines): (a) GaAs and (b) AlAs.

**Table 3**
The calculated first and second valence energy levels and the heteropolar band gaps at point X for GaAs and AlAs in eV.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp. (K)</th>
<th>$E_1 - E_2$</th>
<th>$E_3 - E_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>300</td>
<td>1.59395</td>
<td>1.83734</td>
</tr>
<tr>
<td>AlAs</td>
<td>$T_c$</td>
<td>-0.97870</td>
<td>2.13858</td>
</tr>
<tr>
<td></td>
<td>$T_c$</td>
<td>-1.66048</td>
<td>1.49353</td>
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</table>

References


