The pressure effect of the bulk modulus seen by the charge density in CdX compounds

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Abstract

An application study of the bulk modulus as a function of hydrostatic pressure for CdS, CdSe, and CdTe has been presented. This factor has been calculated by means of our recent model. The structural phase transition can be seen easily from behaviour of the bonding character. The results are compared with the theoretical and experimental data and are in reasonable agreement.

Keywords: Semiconductor; Bulk modulus; Phase transition

1. Introduction

The electronic properties of binary compounds have attracted considerable theoretical interest. The problems of random systems have proved formidable. Many attempts [1] to attack them have been made using a variety of different models. A comparison between the experimental and theoretical results may permit a test of different competing theoretical approximations. The transition from the co-ordinated number \( N_c = 4 \) to 6 is well demonstrated by the use of a computational method based on total energy calculations [2–5].

The most remarkable aspects of tetrahedral co-ordinated structures are low density. Therefore, it is not surprising that these \( A^\times B^{\times -N} \) semiconductors can be transformed under pressure to structure with high density. These higher density structures are either an insulating structure of the NaCl-type, or metallic one of the white-Sn-type. These two structures are approximately sixfold co-ordinated and both are about 20% more dense than the tetrahedral one.

For the tetrahedral bonded semiconductors such as CdS, CdSe, and CdTe, the zinc-blend structure (ZB) has the lowest minimum total energy. It is the most stable phase of these compounds at ambient pressure, and as pressure applied, the volume decreases and the transition to the \( \beta \)-Sn (or NaCl) phase occurs at relatively low pressure. The investigation of chemical trends in solid-state properties appears thus as an extremely useful part of new materials research. This is especially interesting when one tries to gain some information about the many properties of the group of binary compounds under pressure.

Based on measurements of the area of the cation side of the total valence pseudo-charge density, our group [6] established a new empirical formula for the calculation of the bulk modulus \( (B_0) \) of a specific class of materials. The theory yields a formula with three attractive features. Only the pseudo-potential form factors are required as input, the computation of \( B_0 \) itself is trivial and the accuracy of the results reaches that of ab initio calculations.

It seems more fundamental to relate the high pressure behaviour of the compounds to the type of bonds between the nearest atoms. By controlling the evolution with pressure of the bond character in terms of the band structure, an attempt to link the effect of high pressure to the bulk modulus is happened. This provides a real picture of the pressure-induced structural phase transitions from the fourfold co-ordinated crystal structure (ZB) to the sixfold one. In this context, this process is used for testing the validity of our model [6] of bulk modulus. The aim of this paper is to extend this method for calculating the phase transition from the zinc-blend structure \( (N_c = 4) \) to the insulating rocksalt structure of NaCl \( (N_c = 6) \) or into a white-Sn-like structure \( (N_c = 6) \) for II–VI compounds (CdS, CdSe, and CdTe).

2. Calculations and results

The cation part of the electronic pseudo-charge density is computed on the basis of the empirical pseudo-potential
Table 1
The adjusted symmetric and anti-symmetric form factors (Ry), and the lattice constant \(a_0\) (a.u.) at \(P = 0\) and \(P_t\) for CdS, CdSe, and CdTe.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>(a_0)</th>
<th>(V_s(3))</th>
<th>(V_s(8))</th>
<th>(V_s(11))</th>
<th>(V_a(3))</th>
<th>(V_a(4))</th>
<th>(V_a(11))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS</td>
<td>0</td>
<td>11.021</td>
<td>-0.24</td>
<td>0.03</td>
<td>0.03</td>
<td>0.04</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>(P_t)</td>
<td>10.0376</td>
<td>-0.30376</td>
<td>0.00340</td>
<td>0.00341</td>
<td>0.21495</td>
<td>0.18462</td>
</tr>
<tr>
<td>CdSe</td>
<td>0</td>
<td>11.4324</td>
<td>-0.23</td>
<td>0.01</td>
<td>0.01</td>
<td>0.19</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>(P_t)</td>
<td>10.691</td>
<td>-0.25800</td>
<td>-0.03948</td>
<td>-0.02809</td>
<td>0.18141</td>
<td>0.16302</td>
</tr>
<tr>
<td>CdTe</td>
<td>0</td>
<td>12.11491</td>
<td>-0.2</td>
<td>0.0</td>
<td>0.04</td>
<td>0.15</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>(P_t)</td>
<td>10.9635</td>
<td>-0.27047</td>
<td>0.00659</td>
<td>0.03556</td>
<td>0.10624</td>
<td>0.11499</td>
</tr>
</tbody>
</table>

Fig. 1. The total valence pseudo-charge densities along \(\langle 111\rangle\) direction at \(P = 0\) kbar (solid line), and at \(P = P_t\) (dotted line): (a) CdS, (b) CdSe, and (c) CdTe.
method (EPM). The pseudo-potential form factors are found using a non-linear least-square method [7–10], in which all the parameters are simultaneously optimised under a definite criterion of minimising the root-mean-square deviation. Optical, ultraviolet photoemission spectroscopy (UPS), and X-ray photoemission spectroscopy (XPS) data are used. Table 1 gives the adjusted pseudo-potential form factors for both ambient pressure and the transition one.

The bulk modulus $B_0$ is evaluated from our recent model [6], according to the following formula:

$$B_0 = [2400 - 1000\lambda](S_c + 1) \quad (1)$$

where $S_c$ is the cation part of the charge density and $\lambda$ is the parameter separating the weak ionic elements from the strongly ionic ones. $\lambda = 0$ for group IV, $\lambda = 1$ for III-V, and $\lambda = 1.5$ for II-VI semiconductors.

It was one of the successes of the dielectric theory established by Phillips and van Vechten [11] that it was made possible to ascribe in a systematic manner, an ionicity value ($f_i$) to each compound. This ionic character obeys the equation $f_i + f_h = 1$, where $f_h$ is the covalent character. In addition, a specific critical value of ionicity $f_i = 0.785$ was found to provide a complete separation between $N_c = 4$ and 6 structures. At normal pressure, the covalent semiconductors are fourfold co-ordinated. The reason that density is so

![Fig. 2. The total valence pseudo-charge densities in (1 1 0) plane $P = 0$ kbar. (a) CdS, (b) CdSe, and (c) CdTe.](image)
low is that nearest neighbours are bound together overlapping hybridised orbitals, which are well-known sp^3 hybrids with tetrahedral direction. Therefore, these covalent compounds can be transformed either through chemical shifts or under pressure into a denser structure, which may be ionic or metallic. Consequently the first-order phase transformations as a result of the change of the nature of the binding and structure energies are established. It was noticed that as the ionicity increases, the bulk modulus decreases which in role reflects the hardness of the material. This picture is essentially consistent with the present results. The reduction of bond charge is related to the band structure term. In an AB compounds, this terms gets larger because it is proportional to both the symmetric and anti-symmetric form factors. Figs. 1-3 present the results of calculations of charge densities at ambient and high pressure transition (the results are displayed along ⟨111⟩ direction and in the ⟨1 1 0⟩ plane).

The transition occurs when the Ewald contribution dominates over the covalent electronic contribution. As pressure is applied, the volume decreases and the strong sp^3 covalent bonding, which characterised their covalent structure at normal pressure, is destroyed, resulting in a new structure. From this viewpoint, the discrepancy at very high pressure is an immediate consequence of the difference in the corresponding bulk moduli. The effect of hydrostatic pressure is to transform the compounds from fourfold co-ordinated

![Fig. 3. The total valence pseudo-charge densities in ⟨110⟩ plane P = P_f: (a) CdS, (b) CdSe, and (c) CdTe.](image-url)
Table 2
The calculated bulk modulus at 0 and at the critical transition pressure (kbar) to NaCl phase (CdS, CdSe, and CdTe) a

<table>
<thead>
<tr>
<th>Compound</th>
<th>$B_0$ calculated at $P = 0$</th>
<th>$B_0$ experimental b</th>
<th>$P_t$ calculated at $P = P_t$ (kbar)</th>
<th>$P_t$ theoretical d (kbar)</th>
<th>$P_t$ experimental d (kbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS</td>
<td>66</td>
<td>60</td>
<td>65</td>
<td>40</td>
<td>44.8</td>
</tr>
<tr>
<td>CdSe</td>
<td>60</td>
<td>60</td>
<td>59.1</td>
<td>20</td>
<td>23.3</td>
</tr>
<tr>
<td>CdTe</td>
<td>56</td>
<td>47</td>
<td>55</td>
<td>30</td>
<td>28.0</td>
</tr>
</tbody>
</table>

a The latter are compared to the theoretical and experimental values.
b [12].
c The used data.
d [4].

structure to a denser structure which is the $\beta$-Sn or NaCl phase, these transformations correspond to the category with $f_e < 0.35$ for the first transformation. In Table 2, we observe good agreements with experimental values of CdS, CdSe, and CdTe.

A good notice, the critical pressure is the value which separates the decrease and the increase of the bulk modulus value. The bulk modulus is defined as the derivative of pressure $P$ with respect to volume $V$, $B = -V(\partial P/\partial V)$. The decreasing of the bulk modulus under pressure is confirmed by the fact that the charge density moves gradually towards the bond centre as displayed in Figs. 1–3.

The bulk modulus decreases as pressure increases until a critical value characterised by a random behaviour (Table 2). A new atomic arrangement is more appropriate than the ZB structure. As a consequence, a fluctuation of the bulk modulus appears. The critical values of pressure are of the same order as the experimental ones.

In conclusion, the simple method gives easy use for the calculation of the structural phase transition and confirms its validity for II–VI compounds, expecting a new phase transformations for other compounds.

References

Erratum


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The publisher regrets that in the printing of the above article (in page 3, Eq. 1), an error was inadvertently introduced. We regret any embarrassment caused to those concerned. The corrected text is printed below.

\[ B_0 = (2400 - 1000\lambda)(S + 1)^{-2.2} \]

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