

Study of Mechanical properties of Chalcogenide Semiconductor compound Alloy $Cd_{1-x}Hg_xS$ under high pressure

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Abstract

The study of the mechanical properties of Chalcogenide Semiconductor compounds (ChSCs) under high pressure is of significant importance from both the view point technology and basic research. The mechanical properties ChSCs are studied through the stress-strain relationship, which is supposed to be linear for small stress(Hooke's law).The knowledge of elastic constants for such specimens is valuable as these data can be correlated with other physical measurements and thereby provided possible insight into the nature of the atomic forces in solid matter.This strain energy can be interpreted as the atomic vibrations referred to as the equilibrium. Thus, the elastic constants could be directly related to the atomic interaction potential per unit volume in ChSCs.The three-body potential model is found to be satisfactory to a certain extent in explaining some of the physical properties of ChSCs.The success of this TBP model lies in the fact that it takes into account the forces due to the three-body and van der waals(vdw) interactions along with the long-range Columbic and short-range overlap repulsive interactions.. Analysis of the pressure induced mechanical properties is important for understanding the nature of the inter-atomic forces in the crystals. The second order elastic constants and their pressure derivatives at 0K pressure and, $(dC_{ij}/dP)_0$ have been calculated for all the ChSCs taken into considerationIn the present paper, we report the result of our investigations on high pressure and compositional dependence of elastic properties $Cd_{1-x}Hg_xS$.

Keywords: (“Chalcogenide Semiconductor compounds”, $\text{Cd}_{1-x}\text{Hg}_x\text{S}$, High pressure, “Mechanical properties of ChSCs”)

INTRODUCTION

The quest for the nature of inter-atomic interactions in solids is of paramount importance as it leads to an understanding of their thermo dynamical, elastic and numerous other physical properties. Pressure is identified as an attractive thermo dynamical variable to reveal the mechanical properties of most of the solids and alloys. In recent years there has been considerable interest in theoretical and experimental studies of $\text{A}^{\text{N}}\text{B}^{8-\text{N}}$ type crystals with zinc blende structure. In the past few years, many researchers were attracted in knowing the effect of elastic properties of ChSCs at high pressures [1-10]. It is attributed to their high symmetry and simplicity of their ionic bonding (Mujica *et al* 2003). Almost all the $\text{A}^{\text{II}}\text{-B}^{\text{VI}}$ compounds crystallize either in the zinc blended or quartzite structures. The common and dominant feature of these structures is the tetrahedral bonding to four atoms of the other elements. In zinc blende these tetrahedral are arranged in a cubic type structure whilst they are in a hexagonal type structure. Indeed, the centers of similar tetrahedral are arranged in a face-centered cubic (*fcc*) array in the former and a hexagonal closed-packed (*hcp*) array in the latter (Jain 1991). Quite generally at a particular pressure, $\text{A}^{\text{II}}\text{-B}^{\text{VI}}$ compounds are known to undergo a first order phase transition from the *B3* to *B1* as observed in diamond cell by optical (polarized light) and IR microscopy measurement (Piermarini and Block 1975). Arora and co-workers (1988) reported the results of a detailed Raman scattering investigation of the zone-centre optical. In the earlier past, there was an extensive theoretical study and understanding of phase-transition and enharmonic properties of solids by means of different forms of cohesion. The major part of cohesion in these potentials is contributed by long-range Coulomb interactions, which are counter balance, by the short-range overlap repulsion owing its origin to the Pauli Exclusion Principle. Born and Mayer (1932) used overlap repulsion with a lattice sum to describe the cohesion in most of ionic solids. We refer to an earlier work of Tosi and Fumi (1962) and Tosi (1964) who properly incorporated van der Waals interaction along with $d-d (r^{-6})$ and $d-q (r^{-8})$ interactions to reveal the cohesion in several ionic solids. We also quote the work of Singh (1982), who introduced the effects of charge transfer i.e. three-body interactions and followed Hafemeister and Flygare (1965) type overlap repulsion up to second neighbour ions besides short range interactions to discuss the mechanical properties of several solids and alloys. Despite their successes, the basic nature of these interatomic potentials is such that they are inadequate to reveal a consistent picture of the interaction mechanism in ionic solids. The present investigation is organized as follows. We begin with the estimation of van der Waals coefficient from the Slater– Kirkwood variation method with an idea that both the ions are polarizable. elastic constants are deduced within the framework of the Three body model, that incorporates the long-

range Coulomb, van der Waals (vdW) interaction, the short range overlap repulsive interaction up to second neighbour ions within the Hafemeister and Flygare approach and the three-body interaction. After that computed results and numerical analysis are discussed. We aimed at how by minimizing Gibbs free energies of both the phases we trace the results. The results obtained from this method and their comparison is presented. The studies of elastic constants C_{11}, C_{12} and C_{44} and their pressure derivatives at zero pressure and 0°K $(dC_{ij}/dP)_0$ are important to understand the nature of the inter ionic forces in the crystals. Moreover, the study of their variations with respect to pressure can reveal many important features of the short range forces at high pressure. The importance of many body forces [13, 14] can also be estimated by calculating the Cauchy violations. $(C_{11}=C_{44})$ at high pressures. In cubic crystal, $(C_{12}-C_{44}=2P)$ under the hydrostatic pressure P . Thus the application of pressure will be in general increases the many body effects in solids.

METHOD OF CALCULATION

It is well known that pressure causes a change in the volume of the crystal and consequently it alters the charge distribution of the electron shells. As a result of this, a deformation of the overlapping shell takes place that gives rise to charge transfer (or three-body interaction) effects. We begin by writing the Gibbs-free energy

$$G = U + PV - TS, \quad 1$$

To obtain the structural stability condition for a crystal for a particular lattice spacing, r . Here U is the internal energy, which at 0 K corresponds to the cohesive energy, S the vibrational entropy at absolute temperature, T , at 0 K, pressure, P and the volume, V . The Gibbs free energy for zinc blende [ZB] structure ($B3$, real) and rock salt [RS] ($B1$, hypothetical) structure is given by

$$G_{B3}(r) = U_{B3}(r) + 3 \cdot 08Pr^3, \quad 2$$

$$G_{B1}(r') = U_{B1}(r') + 2 \cdot 00Pr'^3, \quad 3$$

With $U_{B3}(r)$ and $U_{B1}(r')$ as the lattice energies for ZB and RS structures. The internal energy consists of the long range Coulomb, modified three-body interaction (Singh 1982), the short-range van der Waals interaction and overlap repulsion effective up to the second neighbour ions. Their relevant expressions are written as:

$$\begin{aligned}
U_{B3}(r) = & -\frac{\alpha_M Z^2 e^2}{r} - \frac{4\alpha_m Z e^2}{r} f(r) \\
& - \sum_{ij} \frac{C_{ij}}{r_{ij}} - \sum_{ij} \frac{D_{ij}}{r_{ij}} + b \sum_{ij} \beta_{ij} \exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) \\
& + b \sum_{ii} \beta_{ii} \exp\left(\frac{2r_i - kr_{ij}}{\rho}\right) + b \sum_{jj} \beta_{jj} \exp\left(\frac{2r_j - kr_{ij}}{\rho}\right),
\end{aligned} \tag{4}$$

$$\begin{aligned}
U_{B1}(r') = & -\frac{\alpha'_M Z^2 e^2}{r'} - \frac{4\alpha'_m Z e^2}{r'} f(r') \\
& - \sum_{ij} \frac{C'_{ij}}{r'_{ij}} - \sum_{ij} \frac{D'_{ij}}{r'_{ij}} + b \sum_{ij} \beta_{ij} \exp\left(\frac{r_i + r_j - r'_{ij}}{\rho}\right) \\
& + b \sum_{ii} \beta_{ii} \exp\left(\frac{2r_i - k'r'_{ij}}{\rho}\right) + b \sum_{jj} \beta_{jj} \exp\left(\frac{2r_j - k'r'_{ij}}{\rho}\right),
\end{aligned} \tag{5}$$

The study of the second order elastic constants (SOEC) [C_{11} , C_{12} , C_{44}], at 0 K is quite important for understanding the nature of the inter-atomic forces in them. Since these elastic constants are functions of first and second order derivatives of the short range potential, their calculations will provide further check on the accuracy of short-range forces in these materials. Following Singh (1982) and subjecting the dynamical matrix within the framework of TBI model to the long wavelength limit, we find the expressions for the SOEC for $B3$ phase as

$$C_{11} = L \begin{bmatrix} 0.2477g + \frac{1}{3} (A_1 + 2B_1) \\ + \frac{1}{2} (A_2 + B_2) + 5.8243Zg_1 \end{bmatrix}, \tag{6}$$

$$C_{12} = L \begin{bmatrix} -2.6458g + \frac{1}{3} (A_1 - 4B_1) \\ + \frac{1}{4} (A_2 - 5B_2) + 5.8243g_1 \end{bmatrix}, \tag{7}$$

$$C_{44} = L \begin{bmatrix} -0.123g + \frac{1}{3} (A_1 + 2B_1) + \frac{1}{4} (A_2 + 3B_2) \\ -\frac{1}{3} \nabla(-7.53912g + A_1 - B_1) \end{bmatrix}. \tag{8}$$

Various symbols appearing in the above equations are associated with the crystal energy and have the following form

$$A_1 = A_{ij} = L' \left(\frac{d^2}{dr^2} U_{ij}^{SR}(r) \right)_{r=r_0}, \quad 9$$

$$A_2 = A_{ii} = A_{jj} = L' \left(\frac{d^2}{dr^2} U_{ii}^{SR}(r) + \frac{d^2}{dr^2} U_{jj}^{SR}(r) \right)_{r=r_0}, \quad 10$$

$$B_1 = B_{ij} = \frac{L'}{a} \left(\frac{d}{dr} U_{ij}^{SR}(r) \right)_{r=r_0}, \quad 11$$

$$B_2 = B_{ii} = B_{jj} = \frac{L'}{a} \left(\frac{d}{dr} U_{ii}^{SR}(r) + \frac{d}{dr} U_{jj}^{SR}(r) \right)_{r=r_0}, \quad 12$$

$$C_1 = C_{ij} = L' a \left(\frac{d^3}{dr^3} U_{ij}^{SR}(r) \right)_{r=r_0}, \quad 13$$

$$C_2 = C_{ii} = C_{jj} = L' a \left(\frac{d^3}{dr^3} U_{ii}^{SR}(r) + \frac{d^3}{dr^3} U_{jj}^{SR}(r) \right)_{r=r_0}, \quad 14$$

$$g = Z + 8f(r), \quad 15$$

$$g_1 = r_0 df(r), \quad 16$$

$$g_2 = r_0 ddf(r), \quad 17$$

$$\nabla = \left[\frac{-7.5391g + (A_1 - B_1)}{-3.141g + (A_1 + 2B_1) + 21.765g_1} \right], \quad 18$$

$$\Omega = -5.0440g + (A_1 + A_2) - 2(B_1 + B_2) + 17.4730Zg_1, \quad 19$$

$$B_T = \frac{1}{3}(C_{11} + 2C_{12}),$$

And

$$S = \frac{1}{2}(C_{11} - C_{12}), \quad 20$$

in terms of the short-range energy

$$U_{ij}^{SR}(r) = b\beta_{ij} \exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) - \frac{c_{ij}}{r_{ij}^6} - \frac{d_{ij}}{r_{ij}^8}, \quad 21$$

With $L = (e^2/4a^4)$ and $L' = (4a^3/e^2)$.

Having discussed the effective inter-atomic potential, we now evaluate various thermo dynamical and elastic properties for which material.

The pressure variation of the second order elastic (SOE) constants can be studied by considering the change in interatomic distance with applied pressure. The equilibrium inter-atomic distance r at a particular applied pressure can be calculated by minimizing the Gibbs free energy, and can be used along with equation (6.1 to 6.7) for two body potentials and eqns. (6.8 to 6.10) for three body interaction potential.

The calculation values of SOE constants for ChSCs are presented in tables. The compositional dependence of the SOEC constants for all the II-VI compounds is given one by one for each material through figures.

RESULTS AND DISCUSSION

Analysis of the pressure induced mechanical properties is important for understanding the nature of the inter-atomic forces in the crystals. The second order elastic constants and their pressure derivatives at 0K pressure and, $(dC_{ij}/dP)_0$ have been calculated for all the ChSCs taken into consideration. The calculated values of C_{11} , C_{12} , C_{44} , Bulk modulus at $P = 0$ Gpa reported in tables from 6.1 to 6.18. As results obtained from TBI model are predicted for Zinc Chalcogenide (ZnS, ZnSe, ZnTe), Cadmium Chalcogenide (CdS, CdSe, CdTe), Mercury Chalcogenide (HgS, HgSe, HgTe), and their solid solutions. We find that the magnitudes of SOEC systematically decrease as the cation radius increase i.e. in the order $ZnX < CdX < HgX$ ($X = S, Se, Te$). This shows that the size of the cation and interatomic distance provide a dominant effect on elastic constants.

All the host binary ZnS, CdS, HgS, ZnSe, CdSe, HgSe, ZnTe, CdTe and HgTe as well as its mixed systems show large values of Cauchy derivations ($C_{11} - C_{44}$) indicating the importance of charge transfer effect in these ChSCs. The present TBI model is therefore more appropriate for the study of elastic properties. The variations of SOEC with composition are shown in figs from 6.1 to 6.18. These figures show that C_{11} and C_{12} , C_{44} monotonically increases/decreases with composition for all the ChSCs. Our TBI results are consistent with the trend shown by all ChSCs. Pressure derivatives of second order elastic constants are important for predicting the high pressure behaviour. We have calculated the values of B' where B is the Bulk modulus [$B = 1/3(C_{11} + 2C_{12})$].

Results for Cd_{1-x}Hg_xS alloys

Table 1 The Computed Elastic parameters C₁₁, C₁₂, C₄₄, bulk modulus (B₀) and Pressure derivative (B₀') for Cd_{1-x}Hg_xS.

Cd _{1-x} Hg _x S	C ₁₁ (Mbar)		C ₁₂ (Mbar)		C ₄₄ (Mbar)		B ₀ (Mbar)		B ₀ '	
	B ₃	B ₁	B ₃	B ₁	B ₃	B ₁	B ₃	B ₁	B ₃	B ₁
0	1.00	1.49	0.33	0.49	0.41	0.62	0.55	0.83	4.75	4.34
0.25	0.95	1.43	0.40	0.60	0.38	0.56	0.58	0.88	4.813	4.43
0.5	0.90	1.36	0.48	0.71	0.34	0.51	0.62	0.93	4.875	4.52
0.75	0.86	1.29	0.55	0.82	0.30	0.45	0.65	0.98	4.938	4.62
1	0.81	1.22	0.62	0.93	0.26	0.40	0.69	1.03	5.00	4.71

In Fig-1-4 for Cd_{1-x}Hg_xS, the variation of second order elastic constants as a function of Mercury composition has been analyzed in two different structural phases i.e. B₃ (original) and B₁ (hypothetical). The Cauchy deviations (C₁₁-C₁₂) indicating the importance of TBI effect in all the host binary chalcogenides as well as its mixed systems. These figures show that for all the chalcogenides C₁₁ and C₄₄ monotonically decreases with concentration while C₁₂ and B₀ increases. The trends of C₁₁ and C₄₄ are more or less similar in nature where the trends for C₁₂ and B₀ are different. The pressure derivative bulk modulus is also following a linear variation as a function of doping concentration. It is also observed that the computed intermediate value of these chalcogenides follows the Vigard's law.

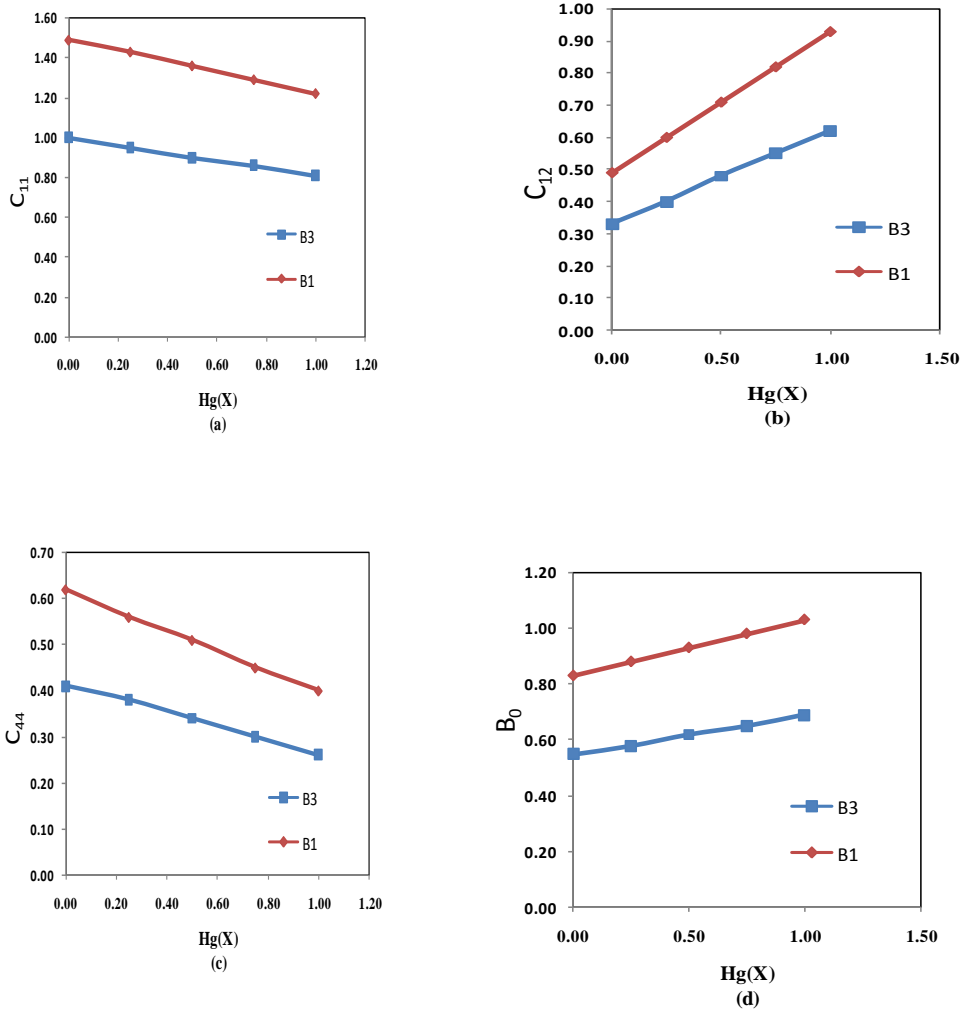


Fig. 1-4. $\text{Cd}_{1-x}\text{Hg}_x\text{S}$, the variation of second order elastic constants as a function of Mercury composition has been analyzed in two different structural phases.

On the basis of an overall discussion, it can be concluded that the description of the elastic properties of cubic Zinc Chalcogenides (ZnS , ZnSe , ZnTe), Cadmium Chalcogenides (CdS , CdSe , CdTe) and Mercury Chalcogenides (HgS , HgSe , HgTe), as well as ternary alloys attained by us is remarkable in view of the inherent simplicity and less parametric nature of the TBI model. The materials covered in this group are primarily Zn, Cd, Hg and S, Se, Te. With all this, TBI can be considered as the triumphant model potential to explain a variety of elastic properties mainly the C_{12} , C_{44} , B_0 , B_0' of these ChSCs.

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