High Pressure Phase Transformation and
dependence of elastic properties of ZnX

* P. Sharma

ABSTRACT

An effective interaction potential (EIOP) is developed to invoke the pressure induced phase transition from zinc blende (B3) to rocksalt (B1) and anharmonic properties in ZnX (X=Se, S, and Te) semiconductors. The effective interaction potential incorporates the long range coulomb interaction, Van der Waals interaction and short range repulsive interaction upto second neighbor ions within the Hafemeister and Flygare approach as well as the charge transfer effects caused by the electron-shell deformation of the overlapping ions. The van der Waals coefficients are computed by the Slater Kirkwood variation method as a first step. Later on, we evaluate second order and third order elastic constants with pressure pointing to the systematic trends in all compounds of zinc blende structure. The vast volume discontinuity in pressure–volume (PV) phase diagram identifies the structural phase transition from zinc blende (B3) to rock salt (B1) structure and is consistent with those revealed from earlier reports.

Keywords: Phase transition; elastic constants

1. Introduction

The quest for the nature of interatomic interactions in solids is of paramount importance as it leads to an understanding of their thermodynamical, elastic and numerous other physical properties. Pressure is identified as an attractive thermodynamical 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 A\(^{8}\)B\(^{6}\)-type crystals with zinc blende structure. It is attributed to their high symmetry and simplicity of their ionic bonding (Mujica et al. 2003). Almost all the A1–B1 compounds crystallize either in the zinc blende or wurtzite structures. The common and dominant feature of these structures is the tetrahedral bonding to four atoms of the other elements.

Quite generally at a particular pressure, All–B1 compounds (herein after ZnX system) 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 coworkers (1988) reported the results of a detailed Raman scattering investigation of the zone-centre optical phonons of the mixed crystal, Zn\(_{1-x}\)Mn\(_x\)Se (0 ≤ x ≤ 0.33). In the earlier past, there was an extensive theoretical study and understanding of phase-transition and anharmonic 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) employed 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) that properly incorporated van der Waals interaction along with d–d (r\(^3\)) and d–q (r\(^4\)) 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 (1985) 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 variational method with an idea that both the ions are polarizable. Later on, the phase transition pressures and elastic constants are deduced within the framework of the Shell 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. The computed results and numerical analysis are discussed in § 3. 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 with experimental results are presented in § 4.

2. The model

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

\[
G = U + PV - TS,
\]

(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 rocksalt [RS] (B1, hypothetical) structure is given by

\[
G_{B3}(r) = U_{B3}(r) + 3.08Pr^3
\]

\[
G_{B1}(r) = U_{B1}(r) + 2.00Pr^3
\]

with \(UB3(r)\) and \(UB1(r)\) 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 overlap repulsion effective up to the second neighbors. Their relevant expressions are written as.
with \( \alpha_i \) and \( \alpha'_i \) as the Madelung constants for ZB (RS) structure, respectively. \( C_{ij} \) and \( D_{ij} \) are overall van der Waals coefficients, \( b_{ij} \) are Pauling coefficients, \( 2e \) the ionic charge, \( b (r) \) the range (hardness) parameters, \( r (r_i) \) the nearest neighbour separations for ZB (RS) structures, \( f (r) \) the three-body force parameters and \( k (k') \) the structure factor for B3 and B1 phases.

The study of the second order elastic constants (SOEC) \( C_{111}, C_{122}, C_{333} \), the third order elastic constants (TOEC) \( C_{1111}, C_{1122}, C_{3333}, C_{1112}, C_{1133} \) and their pressure derivatives at 0 K is quite important for understanding the nature of the interatomic 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 Shell model to the long wavelength limit.

### 3. Results and discussion

The effective interionic potential described in the earlier section for zinc blende (B3) and rocksalt (B1) phases contains three free parameters, viz. the range \( (r) \), hardness \( (b) \) and three-body force parameters, \( f (r) \). While estimating free parameters

Considering pressure and temperature as the external variables (hydrostatic conditions), the free energy of a particular crystal structure at a particular temperature and pressure is obtained by minimizing \( G (P, V, T) \) with respect to \( V \). In an attempt to reveal the structural phase transition of the test material, we minimize the Gibbs’s free energies, \( G_{ZB}(r) \) and \( G_{RS}(r) \), for the equilibrium interatomic spacings \( (r) \) and \( (r') \). As the pressure is increased, \( \Delta G \) decreases and approaches to zero at the phase transition pressure. Beyond this pressure, \( \Delta G \) becomes negative as the phase B1 is more stable. The Gibbs free energy difference, \( \Delta G = G_{RS}(r) - G_{ZB}(r) \), have been plotted as functions of pressure \( (P) \) in figures 4.1(a).

The pressure corresponding to \( \Delta G \) approaching to zero is the phase transition pressure \( (P_t) \) of ZnSe [ZnS, ZnTe] and is about 13.5 [15, 9] GPa. The estimated value of \( P_t \) is consistent with that revealed from experiment, 13 [14.5, 9] GPa (Smith and Martin 1985; Nelmes and Mccmohan 1998). The consistency is attributed to the properly formulated effective interionic potential as well as use of free parameters. It is worth to point out that the uncertainties in the transition pressures can be as large as 10% or more. Quite generally, the experimental high-pressure measurements can suffer from several problems including calibration, inhomogeneous pressure, and metastability. Van Vechten (1973) briefly discussed these aspects, e.g. the role of metastability in pressure experiments.

In order to study the high-pressure elastic behaviour of ZnX, we have computed the second-order elastic constants (SOEC) and their variation with pressure is shown in figures 4.3(a). We note that \( C_{44} \) decreases linearly with the increase of pressure away from zero at the phase transition pressures. This feature is in accordance with the first-order character of the transition for all the compounds and is similar to that earlier reported in the cases of HgTe (Se) (Miller et al 1981; Ford et al 1982). On the contrary, values of \( C_{11} \) and \( C_{12} \) increase linearly with pressure and resemble that observed in HgTe (Se).

It is instructive to mention that the Born criterion for a lattice to be mechanically stable is that the elastic energy density must be a positive definite quadratic function of strain. This requires that the principal minors (alternatively the eigen values) of the elastic constant matrix should all be positive. The stability of a cubic crystal is expressed in terms of elastic constants as follows: \( BT = [C_{44} - 2C_{11}] / 3 > 0 \), \( C_{11} > 0 \) and \( s = [C_{11} - C_{12}] / 2 > 0 \). Here, \( C_{ij} \) are the conventional elastic constants and \( BT \) the bulk modulus. The quantities, \( C_{44} \) and \( s \), are shear. Phase diagram of ZnX \( [X = S, Se, Te] \), tetragonal moduli of a cubic crystal. Estimated values of bulk modulus of ZnSe (ZnS, ZnTe) are \( BT = 0.95 (1.1, 0.75) \times 10^{11} \text{ Nm}^{-2} \) and shear moduli, \( C_{44} = 0.72 (0.85, 0.55) \times 10^{11} \text{ Nm}^{-2} \) and tetragonal moduli, \( s = 0.20 (0.23, 0.15) \times 10^{11} \text{ Nm}^{-2} \) well satisfied the above elastic stability criteria. In addition, Vukcevich (1972) proposed a high-pressure stability criterion for ionic crystals, combining mechanical stability with minimum energy conditions. In accordance, the stable phase of a crystal is one in which the shear elastic constant, \( C_{44} \), is nonzero (for mechanical stability) and which has the lowest potential energy among the mechanically stable lattices.
In continuation, the variations of TOEC with pressure are shown in figures 4.4(a). These points reveal that the values of $C_{111}$, $C_{122}$, $C_{113}$, $C_{166}$, $C_{456}$ are negative, while that of $C_{444}$ is positive as obtained from the effective interionic potential at zero pressure. Furthermore, $C_{111}$ and $C_{112}$ increase, on the other hand, remaining TOEC decreases with pressure and follows a systematic trend. Experimental studies on the TOEC of the system of solids under consideration are relatively difficult and the only measurements available up to date are on the pressure derivatives of the SOE constants.

4. Conclusions

In the present investigation, an effective interaction potential is formulated in analysing the mechanical properties as well as anharmonicity in II–VI semiconductors. It is to predict phase transition pressure and associated volume collapse. It is believed that vast volume discontinuity in pressure volume phase diagram identifies the structural phase transition from ZnS to NaCl structure. In continuation we explore our efforts to check the validity of Born criterion by computing the second order elastic constants that support high-pressure structural stability of binary ZnX semiconductors. It is noticed that $C_{44}$ decreases linearly with increase of pressure and does not tend to be zero at the phase transition pressures. This feature is in accordance with the first order character of the transition. The above analysis reveals that the deviation from the experimental values of pressure derivative of elastic constant, $C_{44}$, is attributed to the fact that we have neglected the thermal effects and assuming the overlap repulsion significant only up to nearest neighbour.

We note that the variation of third order elastic constants with pressure points to the fact that the values of $C_{111}$, $C_{122}$, $C_{133}$, $C_{456}$, $C_{666}$ are negative while that of $C_{144}$ is positive as obtained from the effective interionic potential at zero pressure. The present study also presents a quantitative description of the physical thermodynamical parameters of the chosen semiconductor compound, ZnX, and tests the appropriateness of the effective interionic potential.

REFERENCES