Pressure induced structural phase transition of XC (X = Si, Ge, Sn)

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Abstract. An effective interionic interaction potential (EIOP) is developed to investigate the pressure induced phase transitions from ZnS-type (B3) to NaCl-type (B1) in XC [X = Si, Ge, and Sn] compounds. The long range Coulomb, van der Waals (vdW) interaction and the short-range repulsive interaction up to second-neighbor ions within the Hafemeister and Flygare approach with modified ionic charge are properly incorporated in the EIOP. The vdw coefficients are computed following the Slater-Kirkwood variational method, as both the ions are polarizable. The estimated value of the phase transition pressure (P_t) and the magnitude of the discontinuity in volume at the transition pressure are consistent as compared to the reported data. The vast volume discontinuity in pressure volume phase diagram identifies the structural phase transition from B3 to B1 structure.

1. Introduction
The pressure induced structural phase transition in binary SiC, GeC, and SnC compounds with the ZnS- type structure have received considerable attention in recent past [1 - 5]. The complexity of these exotic new materials poses a challenge to the physicist to investigate the fundamental properties of these compounds, such as, lattice constant and structural stability. Pressure is believed to be an attractive thermodynamical variable to reveal the mechanical properties of most of the solids and alloys. It has been shown that the pressure induced phase transition of SiC from B3 to B1 structure occurred at 100 GPa or higher [1]. Considerable theoretical studies of XC (X = Si, Ge, Sn) compounds have been published during the last few years [2 - 5]. In particular, Zhang et al. [2] have performed first-principles calculations to investigate the structural stability of XC compounds. The transition pressures at which these compounds undergo the structural phase transition from B3 to B1 phase are 62, 87, and 33 GPa for XC (X = Si, Ge, Sn), respectively.

The first principles density functional theory and microscopic tight binding models have been used successfully to address the electronic, magnetic and structural properties of binary compounds. On the hand, phenomenological lattice models [6, 7] have proved very successful in obtaining qualitative and quantitative understanding of binary compounds with proper parameterization. In the present paper, we have chosen two-body interaction potential because it includes vdw attractions, which are not well described by the standard methods currently used in first principle microscopic calculations.
2. Theory and method of computation
The understanding of thermodynamical properties for XC compounds needs the formulation of an effective interionic potential. The idea we have in mind follows: the change in force constants is small, the short range interactions are effective up to the second-neighbour ions, and the atoms are held together with harmonic elastic forces without any internal strains within the crystal. The effective interionic potential between pair of ions \( i \) and \( j \) is expressed as

\[
U(r) = \sum_q \frac{Z_q^2}{r_0^2} + \sum_q b_{ij} \exp\left(\frac{r_i + r_j - r_0}{\rho}\right) + \sum_q c_{ij} r_{ij}^{\rho} + \sum_q d_{ij} r_{ij}^8. \tag{1}
\]

Here, long-range Coulomb energy is represented by first term. Second term corresponds to Hafemeister and Flygare [8] kind of short-range overlap repulsive energy, van der Waals multipole energies are represented by third and fourth terms, respectively. Here, the Pauling coefficients \( \beta_{ij} \) are defined as: \( \beta_{ij} = [1+(z_i/n_i)/(z_j/n_j)] \) with \( z_i \) (\( z_j \)) and \( n_i \) (\( n_j \)) as the valencey and number of outermost electrons in the anions (cations), respectively. The symbols: \( c_{ij} \) and \( d_{ij} \) are representing the dipole-dipole (d-d) and dipole-quadrupole (d-q) van der Waals coefficients. \( Z_e \) is the modified ionic charge and parametrically includes the effect of Coulomb screening effects. \( b \) (hardness) and \( \rho \) (range) are short-range parameters. Thus, the effective interionic potential contains only three free parameters \( (Z_e, b \) and \( \rho) \) which can be determined from the crystal properties [2].

An isolated phase is stable only when its free energy is minimum for the specified thermodynamic conditions. As the temperature or pressure or any other variable acting on the systems is altered, the free energy changes smoothly and continuously. A phase transition is said to occur when the changes in structural details of the phase are caused by such variations of free energy. The test materials transform from their initial B3 to B1 structure under pressure. The stability of a particular structure is decided by the minima of Gibbs’s free energy, \( G = U +PV – TS \), \( U \) is internal energy, which at 0 K corresponds to the cohesive energy. \( S \) is the vibrational entropy at absolute temperature \( T \), pressure \( P \) and volume \( V \). The Gibbs’s free energies \( G_{B3}(r) = U_{B3}(r) + 3.08P r^3 \) for B3 phase and \( G_{B1}(r^\prime) = U_{B1}(r^\prime) + 2P r^3 \) for B1 phase become equal at the phase-transition pressure \( P \) and at zero temperature i. e., \( \Delta G (= G_{B1} – G_{B3}) \). Here, \( U_{B3} \) and \( U_{B1} \) represent cohesive energies for B3 and B1 phases, and are

\[
U_{B3}(r) = -1.6381 \frac{e^2 Z_i^2}{r} + 4V_{ij}(r) + 6V_{ji}(r) + 6V_{ij}(r), \tag{2}
\]
\[
U_{B1}(r^\prime) = -1.7475 \frac{e^2 Z_i^2}{r} + 6V_{ij}(r^\prime) + 6V_{ji}(r^\prime) + 6V_{ij}(r^\prime). \tag{3}
\]

\( r \) and \( r^\prime \) are nearest-neighbor (nn) separations corresponding to B3 and B1 phases, respectively. Here, \( V_{ij}(r) \) and \( V_{ij}(r^\prime) \) \( [V_{ij}(r)] \) are the overlap potentials between the nearest (anion - cation) and the next nearest neighbors (anion-anion or cation-cation), respectively, and defined as:

\[
V_{ij}(r) = b_{ij} \exp\left(\frac{r_i + r_j - r_0}{\rho}\right) - c_{ij} r_{ij}^{\rho} - d_{ij} r_{ij}^8; \quad i, j = 1, 2. \tag{4}
\]

Table 1 van der Waals coefficients of XC (X= Si, Ge, Sn) compounds.\( (c_{ij}) \) in units of \( 10^{60} \) erg cm\(^6\) and \( d_{ij} \) in unit of \( 10^{-26} \) erg cm\(^8\). \( C \) and \( D \) are the overall van der Waals coefficients.

| Compound | \( c_{ii} \) | \( c_{ij} \) | \( c_{ji} \) | \( C \) | \( d_{ii} \) | \( d_{ii} \) | \( d_{ij} \) | \( D \) |
|----------|----------------|----------------|----------------|----------|----------------|----------------|----------------|----------|
| SiC      | 28.76          | 0.64           | 0.023          | 13.77    | 14.28          | 0.25           | 0.003          | 2.82     |
| GeC      | 73.76          | 0.93           | 0.023          | 32.15    | 50.14          | 0.51           | 0.003          | 8.41     |
| SnC      | 168.73         | 1.27           | 0.023          | 69.83    | 151.14         | 0.94           | 0.003          | 22.97    |
3. Results and Discussion

Knowledge of the force constants is crucial to the understanding of the stability of the different structures at different volumes. Two different factors determine the response of any crystal structure to pressure. First, changes in nearest-neighbor distances, which affect the overlapping of adjacent ions and bandwidth of the conduction band. Second, changes in symmetry, which affect the hybridization and bond-repulsion. The formalism described above is applied to $XC$ compounds belonging to the cubic crystal system. For such purposes we have then three free parameters, namely, modified ionic charge, range and hardness parameters ($Z_m$, $\rho$ and $b$). To estimate the free parameters, we first deduce the vdw coefficients from the Slater-Kirkwood variational method [9] and are listed in table 1.

We consider that the $XC$ compound is to be partially ionic. It is perhaps worth to remark that we have deduced the values of free parameters, modified ionic charge ($Z_m$), range ($\rho$) and hardness ($b$), from the knowledge of equilibrium distance and the bulk modulus [1, 2] following the equilibrium conditions [7]. The deduced model parameters for $XC$ compounds are given in table 2. In an attempt to reveal the structural phase transition of the test materials, we minimise the Gibbs’s free energies $G_B(r)$ and $G_B(r')$ for the equilibrium interatomic spacing ($r$) and ($r'$). Fig. 1 shows the Gibbs’s free energy difference $\Delta G = G_B(r') - G_B(r)$ as functions of pressure ($P$) using the interionic potential discussed above for $XC$ compounds. Let us summarize the results of the plot. The pressure corresponding to $\Delta G$ approaching to zero is the phase transition pressure ($P_t$) [indicated by arrows in figure]. At zero pressure, the $B3$ crystal phase is thermodynamically and mechanically stable, while the $B1$ is not. As pressure increases, beyond the phase transition pressure ($P_t$), the $B1$ system becomes mechanically and thermodynamically stable.

Eventually, at a pressure higher than the theoretical thermodynamic transition pressure, the $B3$ crystal becomes thermodynamically unstable while the $B1$ phase remains stable up to the greatest pressure studied. In yttrium compounds, a crystallographic transition from $B3$ to $B1$ occurs. The phase-transition pressure ($P_t$) thus obtained are listed in table 2 and compared with available other experimental [1] and theoretical [2 - 5] results. It is inferred from the table that the calculated phase transition pressure of SiC is similar to the previous theoretical results. However, it is differing considerably from the experimental data [1]. Further, we found that the $P_t$ of GeC is higher than that of SiC. Such an observation could be due to existence of the d-core states in Ge as compare to Si, results in an extra repulsion, which leads to a higher transition pressure [3]. The consistency between band structure calculations data and the present lattice model calculation is attributed to the formulated effective interionic potential which considers the various interactions.

Let us now estimate the values of relative volumes associated with various compressions following Murnaghan equation of state [7] as

$$V/V_0 = \left(1 + \frac{B'}{B_0}P\right)^{-1/b'},$$

(5)

Here $V_0$ being the cell volume at ambient conditions. The estimated value of pressure dependent radius for both structures, the curve of volume collapse with pressure to depict the phase diagram is

| Compo-und | Model parameters | Calculated transition pressures ($P_t$) and volume collapse ($V_t$) |
|-----------|------------------|-------------------------------------------------------------|
|           | $Z_m^2$ | $b(10^{-12}$ erg) | $\rho (10^{-1}$ Å) | $P_t$ (GPa) | $V_t$ (%) |
| SiC       | 3.0    | 12.96           | 3.3             | 65 [2], 65.1 [3], 66.5 [4], 65.3 [5], 100 [1]) | 27 (18.2 [3]) |
| GeC       | 3.0    | 14.23           | 3.59            | 85 [2], 89.4 [3]) | 25 (13. 8 [3]) |
| SnC       | 2.2    | 7.46            | 3.37            | 34 [2], 32.5 [3]) | 28 (14.7 [3]) |

Table 2 Model parameters, calculated transition pressures and volume collapse at transition for $XC$ ($X$ = Si, Ge, Sn) compounds.
Figure 1. Variation of Gibbs free energy difference ($\Delta G$) with pressure ($P$) for $XC$.

Figure 2. Variation $V(P)/V(0)$ as a function of pressure for $XC$.

illustrated in Fig. 2 for $XC$ (X = Si Ge, Sn). It is noticed from the plot that our approach has predicted correctly the relative stability of competitive crystal structures, as the values of $\Delta G$ are positive. The magnitude of the discontinuity in volume at the transition pressure is obtained from the phase diagram and tabulated in table 2, which is in good agreement with those revealed from other theoretical [3] works for all the compounds.

4. Conclusion
An effective interionic interaction potential is formulated to analyzing the structural properties of $XC$ (X = Si Ge, Sn) compounds. The obtained values of free parameters allow us to predict phase transition pressure and associated volume collapse. We have found vast volume discontinuity in pressure volume phase diagram, identifies the structural phase transition from ZnS ($B3$) to NaCl ($B1$) structure. From our calculated results, it can be emphasized that the present approach reproduced the structural properties at high pressure consistently in terms of the screening of the effective Coulomb potential through modified ionic charge ($Z_m^+$).

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