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High Pressure Structural Phase Transition and Elastic Properties of CuX (X = Cl, Br and I) Compounds

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Abstract: ***We have evolved an effective interionic interaction potential to investigate the pressure-induced phase transitions from zinc blende (B3) to rock salt (B1) structure in I-VII [CuCl, CuBr and CuI] semiconducting compound by using the Slater-Kirkwood variational method to estimate the vdW coefficients. We report a phenomenological model based calculation of pressure-induced structural phase transition and elastic properties of CuX (X= Cl, Br and I) compound. Gibb's free energy is obtained as a function of pressure by applying an effective inter ionic interaction potential, which includes the long range Coulomb, van der Waals (vdW) interaction and the short-range repulsive interaction upto second-neighbor ions within the Hafemeister and Flygare approach. From the present study, we predict a structural phase transition from ZnS structure (B3) to NaCl structure (B1) at 9.5 GPa for CuCl, 8.0 GPa for CuBr and 8.3 GPa for CuI. The estimated value of the phase transition pressure (Pt) and the magnitude of the discontinuity in volume at the transition pressure are consistent as compared to the reported data. The variations of elastic constants with pressure follow a systematic trend identical to that observed in others compounds of ZnS type structure family and the Born relative stability criteria is valid in CuX (X= Cl, Br and I) compounds.***

Keywords: Structural phase transition, high pressure, elastic constants

1. Introduction

There is a continuous interest in the study of the structural and electronic properties of high-pressure modification of I-VII CuCl , CuBr and CuI copper halides, due to their unusual properties compared to IV-IV, III-V and II-VI binaries [1-8]. The copper halides (CuX: X=Cl, Br, I) crystallize under normal conditions in the zinc-blend structure and form the end of the class of tetrahedrally coordinated semiconductors. The application of pressure to the copper halides often results in a transformation from the zinc-blend (B3) to the rock salt (B1) structure with the corresponding increase in cation–anion coordination from tetrahedral to octahedral. The strong p–d hybridization separates the copper halides from the other compounds. The high-pressure structural and optoelectronic properties of the copper halides have been the subject of extensive theoretical study to predict the high pressure behavior of the tetrahedrally coordinated compounds [1-5,9]. Further, experimental studies [5,10-12] suggest that CuCl, CuBr and CuI adopt the rock salt structure at a pressure in the region of 10 GPa, though the zinc blende- rock salt transition occurs via several intermediate structures of lower symmetry.

Among the lattice models, to discuss the mechanical properties of several solids and alloys, charge transfer approach [13], following Hafemeister and Flygare [14] type overlap repulsion extended up to second neighbor ions besides short-range interactions. We refer to the pioneering work of Tosi [15], who properly incorporated van der Waals interaction along with dipole-dipole (d-d) and dipole-quadrupole (d-q) interactions to reveal the cohesion in several ionic solids. In trying to understand the structural aspects, we admit that the vdW attractions are the corner stone of lattice phenomenological models that is ignored in the first principle microscopic calculations. Motivated from above theoretical and experimental studies and the charge transfer effect approach [13] for the successful description of the phase transition and high- pressure behavior of binary compounds, 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. It is worth noting that vdW interaction appears to be effective in revealing the elastic and structural properties of binary compounds. Therefore, it is necessary to study fundamental properties, such as structural stability, lattice constants and elastic properties of CuX (X = Cl, Br and I) compounds.

2. Theory and Method of Computation

The understanding of thermo dynamical properties for CuX (X = Cl, Br and I) compound requires the formulation of an effective inter ionic potential. To begin with, we made the following assumptions: 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 inter ionic potential between pair of ions (i and j^{th}) is expressed as

$$U(r) = \sum_{ij} \frac{Z_m e^2}{r_{ij}} + \sum_{ij} b\beta_{ij} \exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) + \sum_{ij} c_{ij} r_{ij}^{-6} + \sum_{ij} d_{ij} r_{ij}^{-8}. \quad (1)$$

Where, long-range Coulomb is represented by first term, second term correspond to Hafemeister and Flygare form of short-range repulsive energies [14] and vander Waals multipole are represented by third and fourth terms, respectively. The Pauling coefficients β_{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*) vander Waals coefficients. $Z_m e$ is the modified ionic charge and parametrically includes the effect of Coulomb screening effects. *b* (hardness) and ρ (range) are short-range parameters. Thus, the effective inter ionic potential contains only three free parameters (Z_m, *b* and ρ) which can be determined from the crystal properties [16].

2.1 Phase transition

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 *B*3 to *B*1 structure under pressure. The structural stability of a particular structure is decided by the minima of Gibbs free energy:

$$G = U + PV - TS \quad (2)$$

U is the 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*.

We have estimated the Gibbs free energy for both the *B*3 and *B*1 phases. The Gibbs free energies $GB3(r) = UB3(r) + 3.08Pr3$ for the zinc blende (*B*3) [real] phase and $GB1(r') = UB1(r') + 2Pr'^3$ for the NaCl (*B*1) [hypothetical] phase become equal at the phase-transition pressure *P* and at zero temperature *i. e.*, ΔG (= $G_{B3} - G_{B1}$). Here, U_{B3} and U_{B1} represent cohesive energies for *B*3 and *B*1 phases, and are

$$UB3(r) = -1.6381\frac{e^2 Z_m^2}{r} + 4V_{ij}(r) + 6V_{ii}(r) + 6V_{jj}(r), \quad (3)$$

and

$$U_{B1}(r') = -1.7475\frac{e^2 Z_m^2}{r'} + 6V_{ij}(r') + 6V_{ii}(r') + 6V_{jj}(r'). \quad (4)$$

Here, *r* and *r'* are nearest-neighbor (*nn*) separations corresponding to ZnS and NaCl phases, respectively. The short-range potentials (V_{ij}) (in equations 3 and 4) for both the phases between the ions follow

$$V_{ij}(r) = b\beta_{ij} \exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) - c_{ij} r_{ij}^{-6} - d_{ij} r_{ij}^{-8}; \quad i, j = 1,2. \quad (5)$$

Here, *b* and *ρ* being the short-range parameters. The effective interionic interaction potential can then have three material parameters: modified ionic charge (Z_m), range (*b*) and hardness parameters (ρ), which can be determined from the known crystal properties.

2.2 Elastic constants

The study of the second-order elastic constants (SOEC) (C_{11}, C_{12} and C_{44}) and their pressure derivatives at 0 K is quite important for understanding the nature of the inter atomic forces in them. Since these elastic constants are functions of the first- and second-order derivatives of the short-range potentials, their calculations will provide a further check on the accuracy of short-range forces in these materials. We use the following second-order elastic constants (SOEC) for *B*3 phase:

$$C_{11} = \frac{e^2}{4a^4}\left[0.2477Z^2 + \frac{1}{3}(A_1 + 2B_1) + \frac{1}{2}(A_2 + B_2)\right], \quad (6)$$

$$C_{12} = \frac{e^2}{4a^4}\left[-2.6458Z^2 + \frac{1}{3}(A_1 - 4B_1) + \frac{1}{4}(A_2 - 5B_2)\right], \quad (7)$$

$$C_{44} = \frac{e^2}{4a^4}\begin{bmatrix} -0.123Z^2 + \frac{1}{3}(A_1 + 2B_1) + \frac{1}{4}(A_2 + 3B_2) \\ -\frac{1}{3}\left(-7.53912Z^2 + A_1 - B_1\right) \end{bmatrix}. \quad (8)$$

Eqs. (6)–(8) are the SOECs (C11, C12 and C44) for *B*3 phase.

Similarly, the SOECs for B1 phase follows:

$$C_{11} = \frac{e^2}{4r_0^4}\left[-5.112Z_m^2 + A_1 + \frac{(A_2 + B_2)}{2}\right], \quad (9)$$

$$C_{12} = \frac{e^2}{4r_0^4}\left[0.226 Z_m^2 - B_1 + \frac{(A_2 - 5B_2)}{4}\right], \quad (10)$$

$$C_{44} = \frac{e^2}{4r_0^4}\left[2.556 Z_m^2 + B_1 + \frac{(A_2 + 3B_2)}{4}\right], \quad (11)$$

where (A_1, B_1) and (A_2, B_2) are the short-range parameters for the nearest and the next nearest neighbors, respectively. These parameters are defined as

$$A_1 = \frac{4r_0^3}{e^2}\left[\frac{d^2}{dr^2}V_{ij}(r)\right]_{r=r_0}, \quad (12)$$

$$A_2 = \frac{4(r_0\sqrt{2})^3}{e^2}\left[\frac{d^2}{dr^2}V_{ii}(r) + \frac{d^2}{dr^2}V_{jj}(r)\right]_{r=r_0\sqrt{2}}, \quad (13)$$

$$B_1 = \frac{4r_0^2}{e^2}\left[\frac{d}{dr}V_{ij}(r)\right]_{r=r_0}, \quad (14)$$

$$B_2 = \frac{4(r_0\sqrt{2})^2}{e^2}\left[\frac{d}{dr}V_{ii}(r) + \frac{d}{dr}V_{jj}(r)\right]_{r=r_0\sqrt{2}}, \quad (15)$$

where $V_{ij}(r)$ and $V_{ii}(r)$ [$V_{jj}(r)$] are the overlap potentials between the nearest and the next nearest neighbors, respectively. Where, $r_0\sqrt{2}$ denotes the next nearest neighbor distance in $B1$ phase. We shall now compute numerically the high pressure phase transition and elastic properties for $B1$ phase in the next section.

Table 1: The values of van der Waals coefficients c_{ij} (i, j = 1,2) [in units of 10^{-60} erg cm^6], d_{ij} (i, j = 1,2) [in units of 10^{-76} erg cm^8] and overall van der Waals coefficients (C, D) for CuX (X = Cl, Br and I) compounds

	vdW coefficients							
Solids	c_{11}	c_{12}	c_{22}	C	d_{11}	d_{12}	d_{22}	D
CuCl	520	229	107	1237	679	246	83	1102
CuBr	520	313	193	1636	679	356	181	1562
CuI	520	460	408	2360	679	577	490	2506

Table 2: Crystal data and model parameters for CuX (X = Cl, Br and I).

	Material Parameters				Model Parameters		
	r_i (Å)	r_j (Å)	a (Å)	B_T (GPa)	Z_m^2	ρ (10^{-1} Å)	b(10^{12} erg)
CuCl	1.35	1.81	5.424 [17]	39.8 [18]	3.68	4.39	7.296
CuBr	1.35	1.95	5.695 [17]	36.6 [17]	3.68	4.53	6.753
CuI	1.35	2.16	6.054[17]	36.6[17]	3.84	4.63	5.76

Table 3: Calculated (reported) transition pressure and volume collapse in CuX compounds

Compounds	Transition pressure P_t (GPa)	Volume collapses (%)
CuCl	9.5 ([10a], 10.5[b], 8.8[c] ,9[d])	8.60%
CuBr	8 (8[a] ,9[b],7.4[d])	7.80%
CuI	8.3 (8[a] ,7.5[b] , 9[d])	14%

[a]Ref. [10], [b]Ref. [11], [c]Ref. [12], [d]Ref. [5]

3. Results and Discussion

The effective inter ionic potential described in section (2) for the zinc blende ($B3$) and rock salt ($B1$) phases. We have undertaken such structural and elastic properties in an ordered way. For such purposes we have then three free parameters, namely, modified ionic charge, range and hardness parameters (Z_m, ρ and b). To estimate the free parameters, we first deduce the vdW coefficients from the Slater-Kirkwood variational method [19] and are listed in table 1. We consider that the CuX compounds to be partially ionic.

It is perhaps worth to remark that we have deduced the values free papameters modified ionic charge (Z_m), range (ρ) and hardness (b) from the knowledge of equilibrium distance and the bulk modulus following the equlibrium conditions [16]. The input data along with their relevant references and the model parameters for CuX 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 $G_{B1}(r)$ and $G_{B3}(r')$ for the equilibrium inter atomic spacing (r) and (r'). The Gibbs's free energy difference ΔG [= $G_{B3}(r)$ - $G_{B1}(r')$] have been plotted as functions of pressure (P) in Fig. 1 by using the inter ionic potential discussed above. Let us summarize the results of the plots. The pressure corresponding to ΔG 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 (its ΔG function value is negative than that of $B3$ crystal). Eventually, and 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 CuX (X = Cl, Br and I) compound a crystallographic transition from $B3$ to $B1$ occurs at around 9.5 GPa for CuCl, 8.0 GPa for CuBr and 8.3 GPa for CuI respectively. These results are tabulated in Table 3.

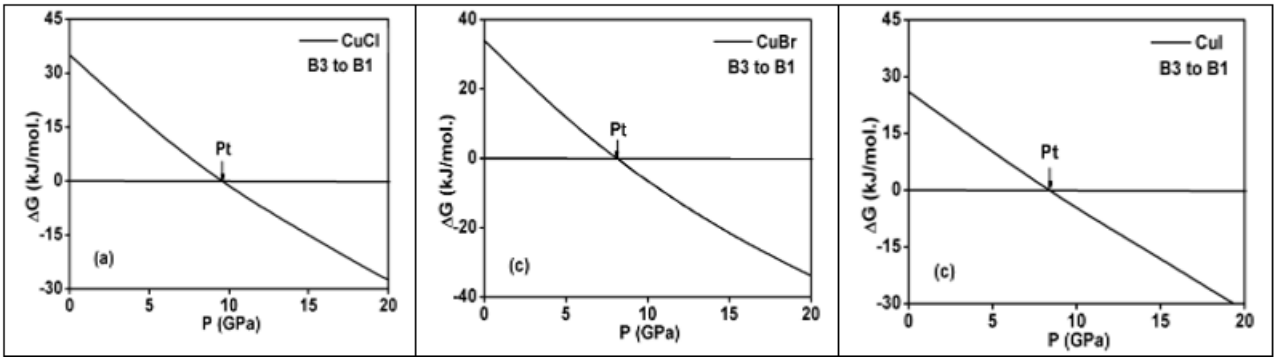

Figure 1: Variation of Gibbs free energy difference (ΔG) with pressure (*P*) for CuCl , CuBr and CuI compounds

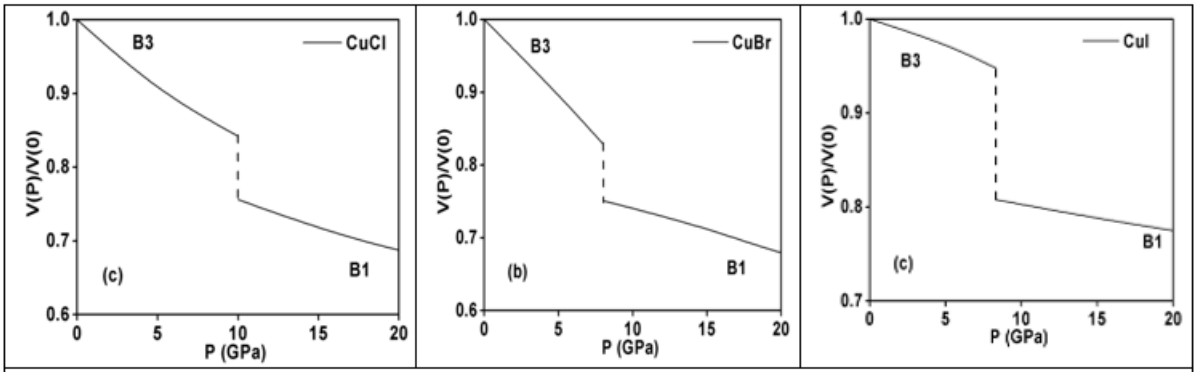

Figure 2: *V*(*P*)/*V*(0) as a function of pressure (*P*) for CuCl, CuBr and CuI compounds

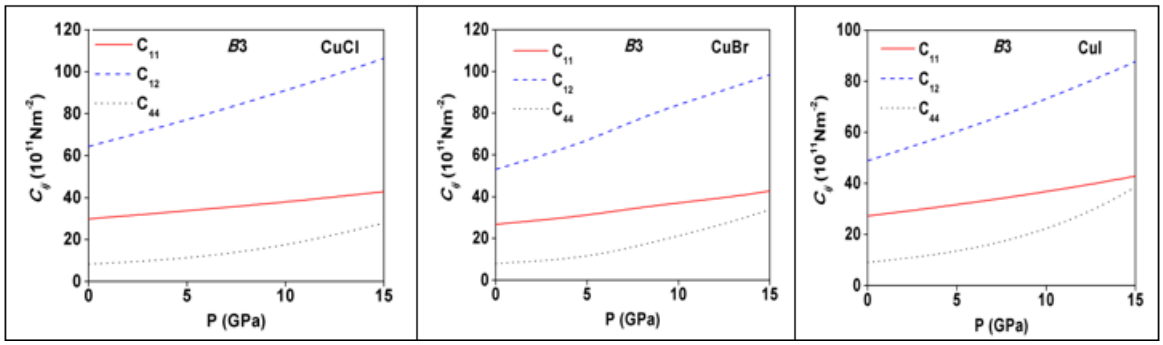

Figure 3: Variation of second order elastic constants with pressure (*P*) for CuCl, CuBr and CuI compounds

Let us now estimate the values of relative volumes associated with various compressions following Murnaghan equation of state [20]

$$\frac{V}{V_0} = \left(1 + \frac{B'}{B_0} P\right)^{-1/B'}, \qquad (16)$$

Where 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 represented in Fig. 2. It is noticed from the plot that our approach has predicted correctly the relative stability of competitive crystal structures, as the values of ΔG are positive. The magnitude of the discontinuity in volume at the transition pressure is obtained from the phase diagram and its value is tabulated in Table.

In order to study the high-pressure elastic behaviour of these compounds, we have computed the second-order elastic constants (SOEC) and their variation with pressure as shown in Fig. 3. We note that C_{44} has very marginal pressure dependence and does not tend to zero at the phase transition pressure, which is in accordance with the first order character of the transition. On the contrary, the values of C_{11} and C_{12} increase linearly with pressure. The variations of elastic constants with pressure follow a systematic trend identical to that observed in others compounds [16].

4. Conclusion

In this study, we have investigated the structural, elastic properties and their pressure dependence of CuCl,CuBr and CuI using developed model potential. The structural phase transformation at which these compounds undergo

the structural transition from *B*3 to *B*1 is predicted at 9.5 GPa for CuCl, 8.0 GPa for CuBr and 8.3 GPa for CuI, which is consistent with reported data. The variations of elastic constants with pressure follow a systematic trend in both the phases.

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