

High Pressure Phase Transition of Copper Halides

Deoshree BAGHMAR¹, Neeraj Kumar GAUR¹, Sadhna SINGH¹,
Dinesh Chandra GUPTA²

¹*Department of Physics, Barkatullah University, Bhopal - 462 026, INDIA*
e-mail: deoshreebaghmar@gmail.com

²*School of Studies in Physics, Jiwaji University, Gwalior - 474 011, INDIA*

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Abstract

The structural changes within copper halides induced by pressure from zinc-blend to rock-salt passing through an intermediate tetragonal structure have been investigated using an effective interionic interaction potential. The values of the phase transition pressures obtained by us for the copper halides are in good agreement with their available experimental data. We have also investigated the equation of state, which shows an appreciable volume collapses at the phase transition pressures.

Key Words: High Pressure, Structural Phase Transition, Gibbs free energy, Volume Collapses, Cohesive Energy.

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1. Introduction

Investigation on the structural phase transformations and behaviour of binary AB compounds under hydrostatic pressure has been a popular topic in Condensed matter research over the past few decades [1, 2]. Numerous II-VI and III-V semiconductors crystallize in the four coordinate zinc-blende or wurtzite crystal structures and exhibit phase transitions to six coordinate structures, particularly rock-salt [3] at high pressure. The same transitions also notably occur in copper and silver halides. The copper halides (CuX: X = I, Br, Cl) are the most ionic crystals with a zinc-blende (ZB) lattice structure [4, 5] under ambient conditions. A basic feature, however, separates the copper halides from the other members of the mentioned family: The 3d electrons of copper hybridize very heavily with the p-like valence electron of halogen and thus the number of valence electrons per formula unit instead of 8 becomes 18. Their ionicities approach the critical threshold at which the ZB structure becomes unstable with respect to the more closely packed NaCl or CsCl structure, due to the electrostatic interactions [6]. As a result of this near structural instability, a large number of pressure-induced polymorphs are possible.

Copper halides behave as superionic conductors at elevated temperatures [7, 8] and exhibit an ionic conductive phase at high temperatures [9]. Also, they become nonconductive at extremely low temperatures [10]. Due to lack of inversion symmetry their properties are somewhat peculiar as compared with those of the alkali halides. A survey of the literature reveals that in recent year most of the theoretical [11-13] and experimental [14-16] investigators have paid attention to the study of dynamical, thermal and anharmonic properties of these materials and their mixed compounds. Static compression favors transitions to more densely packed structures, so copper halides quite generally at a particular pressure are known to undergo

a first order phase transitions from zinc-blende (B_3) space group ($F\bar{4}3m$) to rock-salt (B_1) space group ($Fm\bar{3}m$) through an intermediate tetragonal (B_T) space group ($P4/nmm$) structure [17, 18].

Dynamics stabilites are often responsible for phase transitions under pressure [19]. Lattice dynamics plays an important role in understanding the different mechanics of phase transition in the compounds. Previous attempts have been made by Chelikowsky [20] to predict the zinc-blende to rock-salt phase transition pressures by means of an ab-initio Pseudo potential Total Energy (PTE) method. Also, by means of the Diamond Anvil Cell (DAC) [21] and x-ray [22] techniques and found to transform zinc-blende to rock salt structure at ~ 10.5 , 9.0 and >10 GPa. for CuCl CuBr and CuI respectively. It is known that upon application of pressure ZB structure of CuCL, CuBr and CuI first transforms to intermediate tetragonal phase [23] at about 5 , 5 and 4.6 GPa. And further to the rock-salt structure [18] for pressure above ~ 10 GPa.

Many experimental results on phase transition has been reported for the copper halides, for both the tetragonal and rock-salt structure and some theoretical attempts have been made to explain the structural properties of copper halides [24, 25] from zinc-blende to rock salt structure, but no one has attempted for the intermediate tetragonal phase. Motivated from it, we have investigated the effect of high pressure, structural stability of the compounds CuX (X= Cl, Br, I) using an interionic interaction potential for all the phases. The major part of cohesion in these potential is contributed by Long-range Coulomb interactions, which is counter balanced, by the Short-range overlap repulsion. We have also incorporated van der Waals dipole-dipole (d-d) interaction to reveal the cohesion in copper halides.

The structural properties, phase transition pressure (P_t) and relative volume collapse $[\Delta V(P_t)/V(O)]$ of copper halides are being calculated for parent structure zinc-blende (ZnS) to intermediate (tetragonal) structure and finally to sodium chloride (NaCl) structure by using an effective interionic potential described in section II. Results and discussion along with conclusion are given in section III.

Computational Method

It is well known that pressure causes change in the volume of the crystal and consequently it alters the charge distribution of the electron shells. Therefore, a proper account of phenomenon has to be taken in a theoretical analysis of the crystal under compression. The stability of a lattice is attained at the minimum Gibbs free energy for a particular lattice spacing r , given as:

$$G = U + PV - TS \quad (1)$$

Here, U is the internal energy, which at $0K$ corresponds to the cohesive energy, S is the vibrational entropy at absolute temperature T and V is the volume at pressure P . At sufficient low temperature near zero [22, 26] ($T = 0K$) one can ignore the entropy term (TS) and thus Gibbs free energy for zinc-blende (B_3), tetragonal (B_T) and rock salt (B_1) structures are expressed as:

$$G_{B_3}(r) = U_{B_3}(r) + PV_{B_3}(r) \quad (2)$$

$$G_{B_T}(r') = U_{B_T}(r') + PV_{B_T}(r') \quad (3)$$

$$G_{B_1}(r'') = U_{B_1}(r'') + PV_{B_1}(r'') \quad (4)$$

with lattice energies (U) [27] defined as:

$$U_{B_3}(r) = -\frac{\alpha_M e^2 Z^2}{r} - \left(\frac{C}{r^6}\right) + b \sum_{ij} \beta_{ij} \exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) \quad (5)$$

$$U_{B_T}(r) = -\frac{\alpha'_M e^2 Z^2}{r'} - \left(\frac{C'}{r'^6}\right) + b \sum_{ij} \beta_{ij} \exp\left(\frac{r_i + r_j - r'_{ij}}{\rho}\right) \quad (6)$$

$$U_{B_1}(r) = -\frac{\alpha_M'' e^2 Z^2}{r''} - \left(\frac{C''}{r''^6}\right) + b \sum_{ij} \beta_{ij} \exp\left(\frac{r_i + r_j - r''_{ij}}{\rho}\right) \quad (7)$$

Here, the first term represents the Coulomb attraction corresponding to the nearest neighbor separations $r(r'/r'')$ and Madelung constant $\alpha_M(\alpha'_M/\alpha''_M)$ for ZB (Tetragonal/RS) structure and Ze is the ionic charge [28]. The second term is the van der Waals (vdW) interaction due to dipole-dipole (d-d) interactions with $C(C'/C'')$ as their overall coefficients [29], obtained using the Slater Kirwood variation (SKV) method. The last term is the Hafemeister-Flgyare (HF) type [30] repulsive interaction operative upto the second neighbor ions. β_{ij} is the Pauling coefficients with r_i (r_j) as the ionic radii of the cations (anions); ρ and b are the range and hardness model parameters determined by the equilibrium condition

$$\left|\frac{d\phi(r)}{dr}\right|_{r=r_o} = 0 \quad (8)$$

and the bulk modulus

$$B_o = \frac{1}{9Kr_o} \left[\frac{d^2\phi(r)}{dr^2}\right]_{r=r_o} \quad (9)$$

where, r is the nearest interionic separation; r_o is the equilibrium separation i.e. $r = r_o$ and K as the crystal structure constant.

2. Results and Discussion

The model parameters ρ and b have been calculated using the input data [24, 31, 32] listed in Table 1. The values of model parameters alongwith the vdW coefficients are also depicted in Table 1.

Table 1. Input data and Model Parameters of Copper halides.

Compounds	Input Data		Model Parameters		vdW Coefficients
	r_o (Å)	B_o (GPa)	ρ (Å)	b (10^{-12} ergs)	C(10^{-60}) ergcm ⁶
CuBr	2.46 ^a	38.87 ^a	0.485	0.5201	105.24 ^b
CuCl	2.34 ^a	39.30 ^a	0.275	0.3362	455.66 ^b
CuI	2.62 ^a	35.50 ^a	0.313	0.3663	1017.01 ^b

^aref. [24, 31]; ^bref. [32]

We have followed the technique of minimization of $U_{B_3}(r)$, $U_{B_T}(r')$ and $U_{B_1}(r'')$ at different pressures in order to obtain the interionic separation r , r' and r'' for B_3 , B_T and B_1 phases, respectively, associated with minimum energies, we have evaluated the corresponding Gibbs free energy $G_{B_3}(r)$, $G_{B_T}(r')$ and $G_{B_1}(r'')$ and their differences ΔG . At ambient pressure, these materials crystallize in zinc-blende (B_3) structure and undergo transition to tetragonal (B_T) and NaCl (B_1) structure upon compression.

Table 2 and 3 shows that the present computed cohesive energies and phase transition from B_3 to B_T and finally B_1 structure are closer to the experimental data [21, 23]. Here, it is interesting to note that the contribution of short-range interaction in cohesive energy is less than 10% of the total cohesive energy (Table 2). This feature is indicative of the fact that the major contribution to the cohesion is due to the coulomb attraction.

In order to explain the phase transition pressure we have computed the Gibbs free energy difference ΔG [$= G_{B_3}(r) - G_{B_T}(r')$; $G_{B_T}(r') - G_{B_1}(r'')$] from zinc-blende to tetragonal and from tetragonal to rock salt structure on the lines of earlier papers [26, 29, 34]. As the pressure is increased, ΔG for respective phases decreases and approaches zero at the phase transition pressure. Beyond this pressure, where, other phase is more stable, ΔG becomes negative. The Gibbs free energy difference ΔG has been plotted as a function of pressure (P) in Figure 1. The pressure corresponding to ΔG approaching zero is the phase transition

pressure (P_t) marked by arrows in respective figures. At these transition pressure (P_t) a crystallographic transition from B_3 (zinc-blende) to B_T (tetragonal) to B_1 (rock salt) occurs in copper halides. A comparison of the present results with available experimental data [18, 21, 33, 35-37] are shown in Table 3 and are found to be in good agreement between them.

Table 2. Cohesive energies for B_3 , B_T and B_1 phases of Copper halides (in Kcal/mol).

Compounds	U_{B_3}		U_{B_T}		U_{B_1}	
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
CuBr	-270.13	-279.17 ^a	-228.28	-261.16 ^a	-215.26	-247.66 ^a
		-262.97 ^b		-225.14 ^b		-234.15 ^b
CuCl	-279.85	-283.68 ^a	-261.96	-270.17 ^a	-243.48	-258.46 ^a
		-287.28 ^b		-262.06 ^b		-256.66 ^b
CuI	-285.96	-333.21 ^a	-257.87	-292.68 ^a	-236.04	-261.16 ^a
		-266.58 ^b		-260.26 ^b		-243.15 ^b

^aref. [21]; ^bref. [33].

Table 3. Structural properties of the Copper Halides.

Compounds		P_t (GPa)		$[\Delta(P_t)/V(O)]$ (%)	
		Cal.	Exp.	Cal.	Exp.
CuBr	ZnS-Tetragonal	6.5	5.0 ^{a,b} 4.85 ^c	5.74	-
	Tetragonal-NaCl	10.5	> 7.5 ^a ≥ 10 ^b 9.28 ^c 7.4 - 9.3 ^{d,e}	4.15	-
CuCl	ZnS-Tetragonal	5.5	5.0 ^{a,b} 5.12 ^c	5.60	-
	Tetragonal-NaCl	14.25	9.0 ^a ≥ 10.0 ^b 10.6 ^{c,d}	9.41	-
CuI	ZnS-Tetragonal	7.5	4.6 ^a > 4 - 10 ^b 5.5 ^c 4.0 - 5.0 ^f	2.88	-
	Tetragonal-NaCl	10.0	9.0 ^a > 10.0 ^{b,e,f}	2.37	2.3 ^d

^aref. [21]; ^bref. [33]; ^cref. [18]; ^dref. [35]; ^eref. [36]; ^fref. [37].

We have calculated the percent $[\Delta V(P_t)/V(O)]\%$ of relative volume changes using the compression curves are displayed in Figure 2. There is an abrupt change in figure (2a), (2b) and (2c) of volume discontinuity at the phase transition pressures for both the phases, showing compression of the lattice due to which the zinc blende structures becomes unstable at high pressure and transforms to an intermediate tetragonal structure, which on further increment of pressure transforms to a denser phase i.e. six fold coordinated structure. CuX ($X = Cl, Br, I$) are the covalent-ionic materials in the semiconductor family and hence eventually reach the rock salt (RS) structure. The values of volume collapse reported in the table are within the criterion of Philips [6] ($19 \pm 2\%$ for covalent-ionic transition). These calculated values could not be compared due to the lack of the experimental data and our comments on the reliability of percentage of volume collapses are

restricted until the report of experimental data on them. Here, it is to be noted that the volume change of copper halides follows the same trend as obtained experimentally for other compounds of the family.

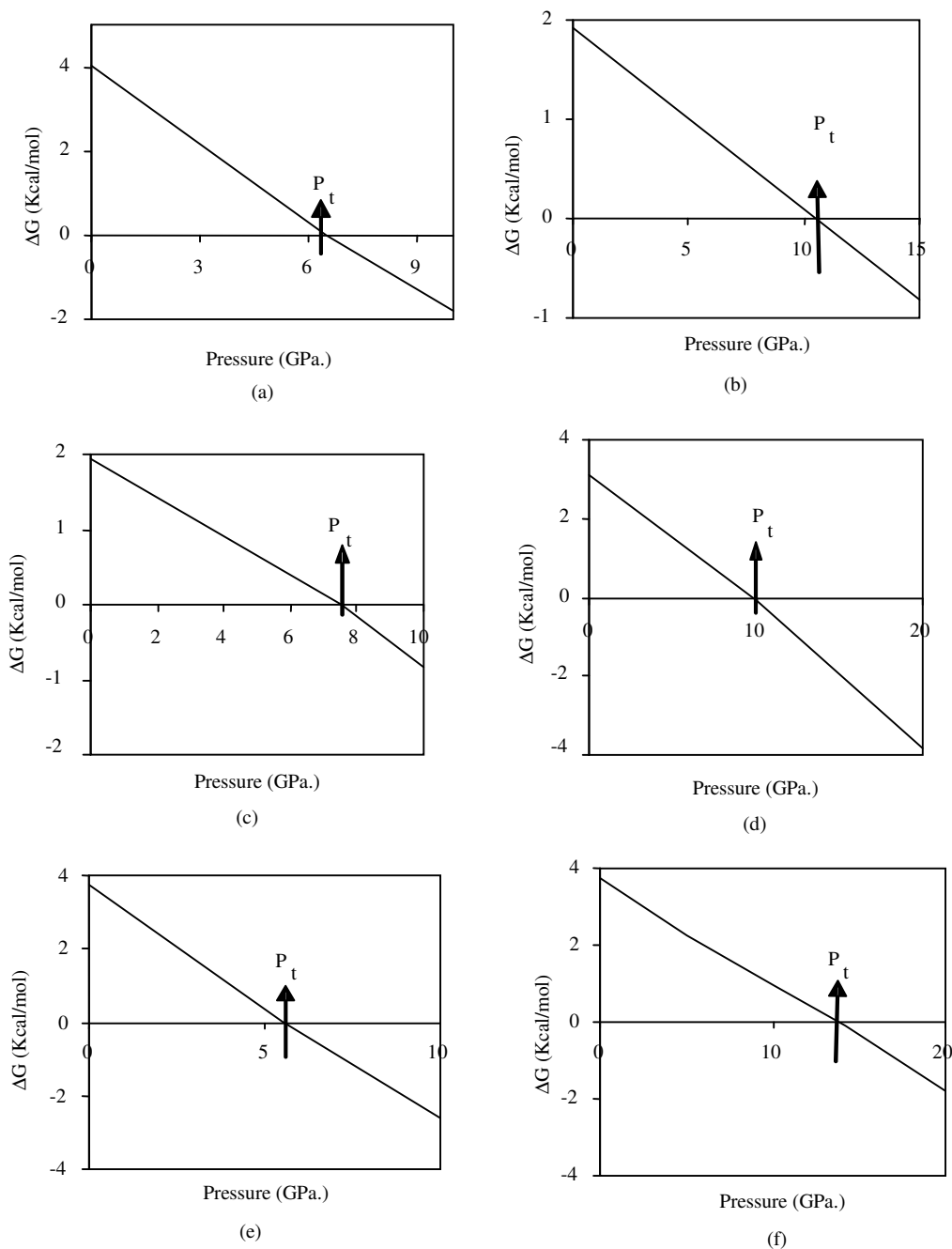
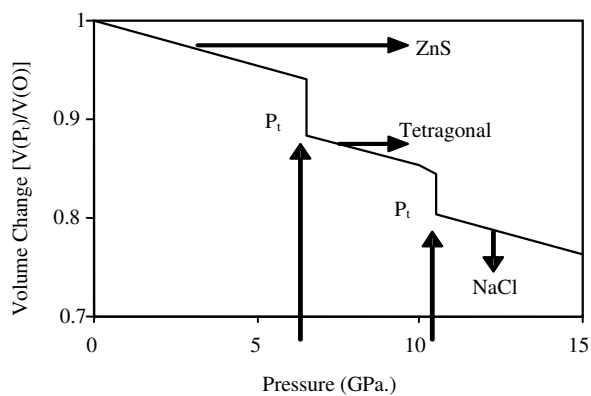
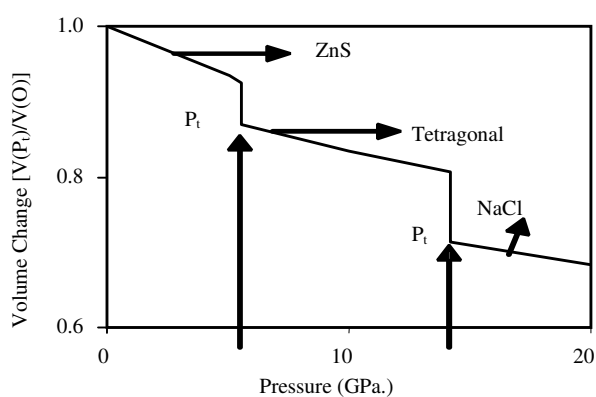


Figure 1. Gibbs free energy as a function of Pressure (P) for CuBr in (a, b); for CuCl in (c,d) and for CuI in (e,f); (a,c,e) from Zinc Blende to Tetragonal (b,d,f) from Tetragonal to Rock Salt.

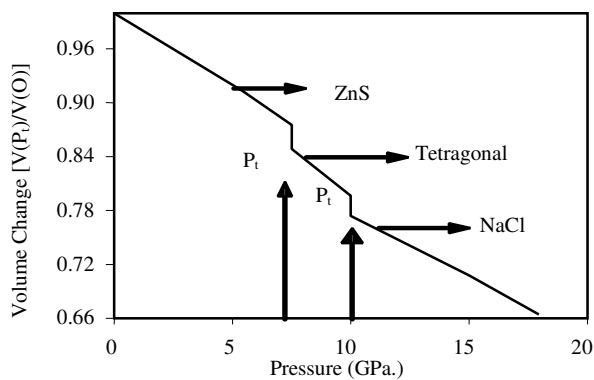
In view of the overall achievements, it may be concluded that the present effective interionic potential is adequately suitable for the description of the phase transition phenomenon of copper halides. This approach, being relatively simpler, has promise to reveal the high pressure phase transformation and other properties of compounds in their parental (ZnS), intermediate (Tetragonal) and adopted (NaCl) structure.



(a)



(b)



(c)

Figure 2. Volume Collapse as a function of Pressure (P) for CuBr , CuCl and CuI in a,b and c: from zinc blende to tetragonal and from tetragonal to rock salt structure.

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