

Structural Phase Transition in Lithium Bromide: Effect of Pressure and Temperature

Aayushi Jain^{a)} and R.C. Dixit^{b)}

Department of Physics, Government Holkar Science College, A. B. Road, Indore 452001, MP, India
^{a,b)} Corresponding author: *aayushijain2810@gmail.com, dixitrc@rediffmail.com*

Abstract. As well known, when many alkali halides, for example NaCl, KCl or RbCl, are subjected to high pressure, phase transformation take place in them with a marked decrease in specific volume and reconstruction of the crystal lattice from the NaCl-type to the CsCl-type structure ($B1$ to $B2$). This work is undertaken the effect of pressure on the crystal structure with incorporating effect of temperature for the first time. An effective interionic interaction potential (EIOP) includes long range Coulomb, van der Waals (vdW) interaction and the short-range repulsive interaction upto second-neighbor ions within the Hafemeister and Flygare approach with modified ionic charge. In this paper effect of temperature on phase transition make the EIOP model more suitable for calculating $B1$ to $B2$ phase transition.

INTRODUCTION

The $B1$ (rocksalt)- $B2$ (cesium chloride) phase transformation dependent on pressure in alkali-metal halides and has been studied both experimentally and theoretically by a number of investigators [1-5]. The transformation has been found to be first order and reversible. Among the IA–VIIIB compounds the Lithium Bromide LiBr is found to undergo a pressure induced first order phase transformation from the six fold coordinated NaCl-type ($B1$) (Fm3m) to eight fold coordinated CsCl-type ($B2$) (Pm3m) structure. The $B1$ -structure is face centered cubic structure having six atoms of opposite type, while the $B2$ structure is body centered structure having eight atoms of opposite type. Hence, in $B1$ – $B2$ phase transition the coordination number changes from 6 to 8 [6]. In the present paper, we have used the effective interionic potential model to get structural phase transition in LiBr with including the effect of pressure and temperature. The main aim of this paper is a critical assessment of the performance of this potential in predicting the phase transition and high pressure behavior of LiBr including the role of temperature.

THEORY AND METHOD OF COMPUTATION

The many body interaction effect [7] was due to the deformation of solids by the overlapping electron shells of the adjacent ions in solids. The effective interionic potential (EIOP) is utilized in the evaluation of Gibbs free energy ($G=U+PV-TS$), in order to obtain the stability condition for a crystal structure. Here U is the internal energy, which at $T=0K$ is equivalent to the lattice energy, S is the vibrational entropy at absolute temperature T . To obtain temperature dependency in pressure induced phase transition in theoretical calculations, we have used range of temperature instead 0 K. The Gibbs free energies for rock salt ($B1$, real) and CsCl ($B2$, hypothetical) structures at temperature T is given by:

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

Here the abbreviations U represent cohesive energy, V represent volume and S represent entropy of the system. The Gibbs Free Energy for NaCl crystal structure:

$$GB_1(r1) = UB_1(r1) + 2P(r1)^3 - TS(B1) \quad (2)$$

and for CsCl

$$GB_2(r2) = UB_2(r2) + \frac{8}{3\sqrt{3}}P(r2)^3 - TS(B2) \quad (3)$$

The notations $UB_1(r1)$ and $UB_2(r2)$ denotes cohesive energies for $B1$ and $B2$ phases, respectively, and are expressed as

$$U_{B1} = (-\alpha_M Zm^2 e^2/r) - \sum_{ij} c_{ij} r^{-6} - \sum_{ij} d_{ij} r^{-8} + nb\beta_{ij} \exp[(r_i + r_j - r_{ij})/\rho] + (n'b/2) \left[\beta_{ii} \exp\left(\frac{2r_i - k_1 r_{ij}}{\rho}\right) + \beta_{jj} \exp\left(\frac{2r_j - k_1 r_{ij}}{\rho}\right) \right]$$

$$U_{B2} = (-\alpha'_M Zm^2 e^2/r) - \sum_{ij} c_{ij} r'^{-6} - \sum_{ij} d_{ij} r'^{-8} + mb\beta_{ij} \exp[(r_i + r_j - r'_{ij})/\rho] + (m'b/2) \left[\beta_{ii} \exp\left(\frac{2r_i - k_1 r'_{ij}}{\rho}\right) + \beta_{jj} \exp\left(\frac{2r_j - k_1 r'_{ij}}{\rho}\right) \right]$$

Here the first term is the potential energy due to long range Coulomb force. The second and third terms are the short-range (SR) vdW attraction energies due to dipole-dipole and dipole-quadrupole interaction. Last term is SR repulsive energy due to the overlap repulsion between ij , ii and jj ions. c_{ij} and d_{ij} are the vdW coefficients. β_{ij} are the Pauling coefficient and $k1$ ($k2$) being the structure factor for ($B1$) phase. This potential has three parameter Zm , b and ρ known as effective charge, hardness and range parameters, respectively.

Now the entropy differences in the last term of Eqs. (2) and (3) can be calculated from the relation

$$S1 - S2 = \Delta S = \int_{T1}^{T2} \frac{Cv dt}{T} \quad (4)$$

here, $S1$ and $S2$ stands for the entropy for $B1$ and $B2$ phases, Cv is the specific heat in the respective phase and can be calculated by

$$C_v = 12\pi^4 \frac{NK_b}{5} (T/\theta)^3 \quad (5)$$

Here, N is Avogadro's number, k_b is Boltzmann constant, T is the temperature at which we calculated phase transition and θ is the Debye temperature.

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 Vander Waals coefficients (C, D) for LiBr compound.

Compound	c_{11}	c_{12}	c_{22}	C	d_{11}	d_{12}	d_{22}	D
LiBr	23.29	83.18	297.46	838.38	27.17	93.60	321.89	714.8

TABLE 2: Crystal data and model parameters for LiBr compound.

Compound	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)
LiBr	0.88	1.03	5.8 [8]	29 [9]	1.00	3.39	6.32

TABLE 3: Calculated (reported) transition pressure and volume collapse in LiBr compound

Compound	Temperature (K)	Transition pressure P_t (GPa)		Volume collapses (%)
		Present	Others	
LiBr	0	19.2	11,20,18.9[10-12]	8% [13]
	5	19.07		
	10	19.03		
	15	18.84		
	20	18.41		

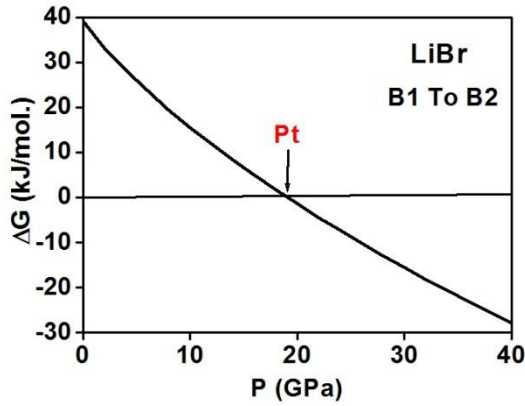


Figure 1. Variation of Gibbs free energy difference (ΔG) with pressure (P).

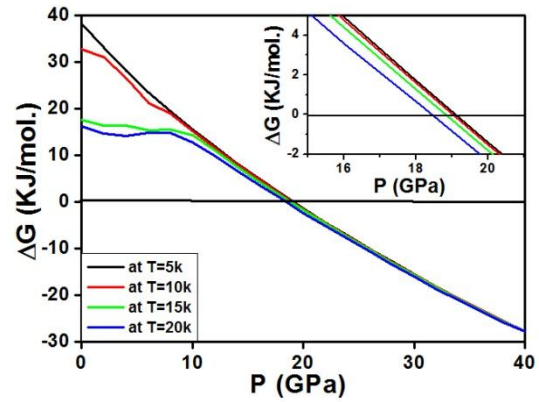


Figure 2. Variation of Gibbs free energy difference (ΔG) with pressure (P) at different temperatures (T).

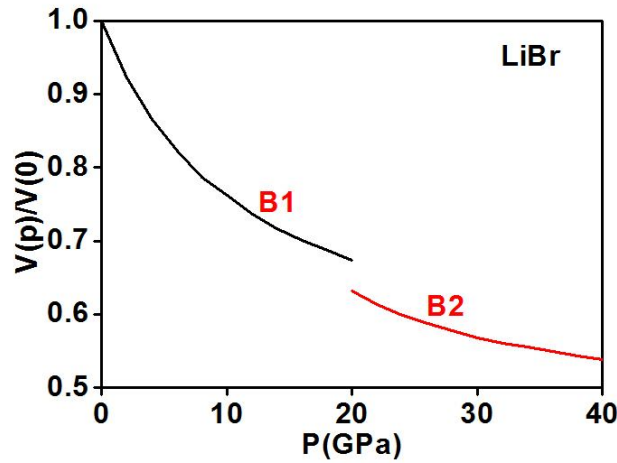


Figure 3. Variation of $V(P)/V(0)$ as a function of pressure for KBr.

RESULTS AND DISCUSSION

The effective interionic potential described in the earlier section for rock salt ($B1$) and cesium chloride ($B2$) phases contains three free parameters, namely, the effective charge, range and hardness parameters (Zm , b and ρ). While estimating the free parameters, we first deduce the vdW coefficients from the variation method [14], these are listed in Table 1. The input data along with their relevant references and the model parameters for LiBr are given in table 2. In an attempt to reveal the structural phase transition of the test materials, we minimize the Gibbs's free energies $\Delta G [= GB2(r1) - GB1(r2)]$ have been plotted as functions of pressure (P) in Figure 1. The pressure corresponding to ΔG approaching to zero is the phase transition pressure (Pt). As pressure increases, beyond the phase transition pressure (Pt), the $B2$ system becomes mechanically and thermodynamically stable. These results may be successfully compared with those available data [10-12] and are tabulated in Table 3. Further, following equations (4) and (5), the effect of temperature is also estimated by same method as done for 0K. Fig. 2 shows the effect of temperature on the Gibb's free energy differences in $B1$ and $B2$ phases. The values of transition pressures are tabulated in table 3.

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

$$\frac{V}{V_0} = \left(1 + \frac{B'}{B_0} P\right)^{-\frac{1}{B'}} \quad (6)$$

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 illustrated in Figure 3 for LiBr compound. The magnitude of the discontinuity in volume at the transition pressure is obtained from the phase diagram and their values are tabulated in table 3.

CONCLUSIONS

In this paper we have studied possible mechanisms for the $B1$ - $B2$ phase transition in Lithium Bromide crystal, using both potential-based and vdW calculations, including short range interaction calculations. The results of this study strongly suggest the inclusion of the higher coordination spheres when studying the structural phase transitions in LiBr. On the basis of above work, it is concluded that the EIOP approach prove to be more realistic at room temperature instead of 0 K.

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