Pressure dependent study of phase transition and elastic constant of KCl and KBr

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Abstract. A theoretical study of phase transition and various elastic constant using two body interaction model is carried out. The calculated values of phase transition pressure and the vast volume discontinuity in pressure–volume (PV) phase diagram indicate the structural phase transition from rock salt ($B1$) to zinc blend ($B2$) structure of potassium chloride (KCl) and Potassium Bromide (KBr). Fair agreement with lattice theoretical data calculated from an interaction potential model composed of Coulomb force, van der Walls force and first and second nearest neighbor repulsive forces is found. The present calculation have revealed good agreement with the available experimental data on the phase transition pressures (5 and 10 GPa). On the basis of Born's stability criteria the relations between the pressure dependence of the bulk modulus (B_T), shear moduli (C_{44}) and tetragonal moduli (C_S) to the $B1$-$B2$ transition are also investigated.

INTRODUCTION

Alkali halides known as ionic compounds are characterized by their highly crystalline nature, high melting points and strong miscibility in polar media [1, 2]. These materials can be considered as insulator materials with great technological importance [3]. As well known, when many alkali halides, for example NaCl, KCl or RbCI, 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 NaC1-type to the CsC1-type structure ($B1$ to $B2$). Because their transition pressures are comparatively moderate. This work is undertaken the effect of pressure on the crystal structure in particular alkali halides. We have chosen here to study the potassium halides KCl and KBr. Under normal conditions these substances have the NaC1- or $B1$-type crystal structure, but they transform under moderate pressures to the CsCl- or $B2$-type structure.

The transition pressures are about 5 GPa and 10 GPa for the potassium chloride and potassium bromide, respectively. In last few decades there are only known potassium chloride, KCl, has been extensively studied under pressure, both experimentally [4-6] and using ab initio simulations [7-9]. Two crystal structures are known for KCl: the rocksalt-type ($B1$) structure and cesium chloride-type ($B2$) structure, the latter becoming stable at ~5 GPa. Same behavior is also observed in Potassium Bromide (KBr). The phase transition mainly induced by pressure in KBr from the NaCI ($B1$) structure to the CsCI ($B2$) structure is of first order. The transformation at about 10 GPa is accompanied by a volume decrease. This was as observed by Bridgman in 1945 [10] and by Seipol in 1986 [11].

THEORY AND METHOD OF COMPUTATION

Effective interionic potential: For the description of cohesion in KCl and KBr, we have employed a two-body potential to express the crystal energy for a particular lattice separation (r) as:

$$U(r) = Uc(r) + U_R(r) + U_V(r) \qquad (1)$$

The first term is being the Coulomb energy, and follows

$$Uc(r) = -\sum_{ij} \frac{Z_i Z_j e^2}{r_{ij}} = -\frac{\alpha_m Z^2 e^2}{r} \qquad (2)$$

with α_m as the Madelung constant and r_{ij} denotes the separation distance between i and j ions. The second term

represents the short-range (SR) overlap repulsive energy,

$$U_S(r) = \sum_{ij} b\beta_{ij} \exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) \tag{3}$$

following Hafemeister and Flygare potential. β_{ij} are the Pauling coefficients. The symbols b and ρ are being the SR repulsive potential parameters. The ionic radii are r_i and r_j, respectively. The last term in Eqn. (1) is the van der Waals (vdW) energy, expressed as

$$U_V(r) = \sum_{ij} c_{ij} r_{ij}^{-6} + \sum_{ij} d_{ij} r_{ij}^{-8} = \frac{C}{r_{ij}^6} + \frac{D}{r_{ij}^8}. \tag{4}$$

The first and second terms are due to dipole-dipole (d-d) and dipole-quadrupole (d-q) interactions, respectively. The abbreviations C and D represent the overall vdW coefficients, due to interactions as mentioned in Eqn. (1). c_{ij} and d_{ij} being the vdW coefficients due to d-d and d-q interactions. We follow the variational method (Slater and Kirkwood) [12] to derive c_{ij} and d_{ij}.

It is evident from the above descriptions that the present effective interionic potential contains only two free parameters (b and ρ), which are determined from the equilibrium condition:

$$\left(\frac{dU}{dr}\right)_{r=r0} = 0 \tag{5}$$

The elastic stability plays a crucial role here, as we will use one of the free parameters to deduce the pressure-induced phase transition necessary to transform the rock salt structure to cesium chloride structure. In general, the bulk modulus in terms of effective interionic potential can be defined as:

$$B_T = \frac{1}{9kr0}\left(\frac{d^2U}{dr^2}\right) \tag{6}$$

Phase stability: It is known that 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. Obviously, the stability of a particular structure is decided by the minima of Gibb's free energy $G = U + PV - TS$, U being 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.

The Gibb's free energies $G_{B1}(r) = U_{B1}(r) + 2Pr^3$ for $B1$ phase and $G_{B2}(r') = U_{B2}(r') + 1.54Pr'^3$ for $B2$ phase become equal at the phase-transition pressure P and at zero temperature $T = 0$ K. Here the abbreviations U_B1 and U_B2 represent cohesive energies, as described earlier for $B1$ and $B2$ phases respectively.

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 KCl and KBr compound.

Compound	c_{11}	c_{12}	c_{22}	C	d_{11}	d_{12}	d_{22}	D
KCl	42.74	85.36	180.4	764.6	24.22	65.24	165.3	476.7
KBr	42.74	88.90	197.2	803.1	24.22	69.46	186.07	511.0

TABLE 2: Crystal data and model parameters for KCl and KBr.

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)
KCl	1.25	1.28	6.2 [12]	18.2 [13]	1.00	2.95	4.021
KBr	1.09	1.01	6.6 [12]	16.64[13]	1.00	3.42	8.84

Table 3 Calculated (reported) transition pressure and volume collapse in KCl and KBr. compoundS

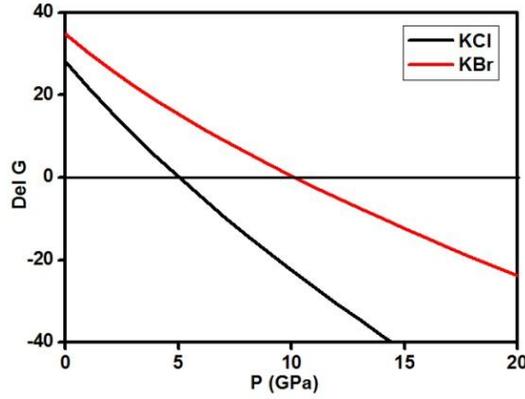| Compound	**Transition Pressure Pt (GPa)**			**Volume collapses %**
	Present	**Others**	**Experimental**	
KCl	5	7.4 [14], 1.1 [15], 1.7 [16]	1.74 [16], 3.6[17]	11
KBr	10	5.9 [14], 1.9 [15]	9.2 [17]	7.7

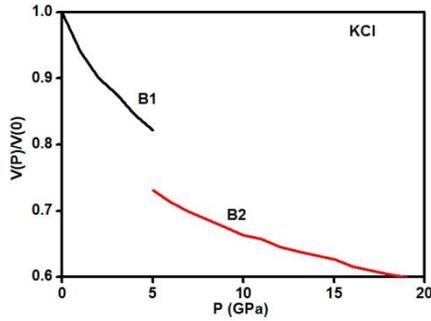Figure 1. Variation of Gibbs free energy difference (ΔG) with pressure (P).

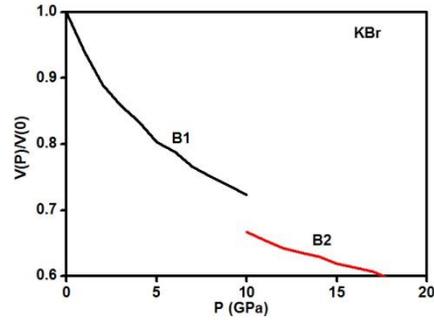Figure 2. Variation of $V(P)/V(0)$ as a function of pressure for KCl

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 two free parameters, namely the range and hardness parameters (b and ρ). While estimating the free parameters, we first deduce the vdW coefficients from the variation method [18], these are listed in table 1. The input data along with their relevant references and the model parameters for KCl and KBr 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 ΔG [= $G_{B2}(r)$ - $G_{B1}(r')$] have been plotted as functions of pressure (P) in Fig. 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 experimental data [5, 6] and other theoretical works [7 - 9] and are tabulated in table 3. The rather good agreement between the theoretically calculated and the experimental data confirms the validity of the used pair potentials of ion interactions.

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

$$\frac{V}{V_0} = \left(1 + \frac{B'}{B_0}P\right)^{-\frac{1}{B'}}$$
(7)

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 Figures 2 and 3 for KCl and KBr, respectively. 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 the present investigation, an effective interionic interaction potential with significant overlap repulsion only up to nearest second-neighbor ions is formulated in examining the high pressure structural behavior of KCl and KBr compounds. The model has two free parameters, *i.e.*, the range and hardness parameters (b and ρ) and is estimated by the proper utilization of the equilibrium distance and isothermal compressibility. The obtained values of free parameters allow us to predict phase transition pressure and associated volume collapse. Furthermore, the magnitude of the discontinuity in volume at the transition pressure as calculated from the phase diagram is consistent with the earlier results. It is believed that the vast volume discontinuity in pressure volume phase diagram identifies the structural phase transition from NaCl to CsCl crystal structure.

REFERENCES

1. J. E. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity, fourth ed.*, Prentice Hall, New York (1997).
2. P. Atkins, T. Overton, J. Rourke, M. Weller and F. Armstrong, *Inorganic Chemistry, fourth ed., Oxford University Press*, Oxford (2006).
3. Y. M. Gao, Y. F. Jiang and N. P. Wang, *Phys. B* **447**, 47 (2014).
4. A.J. Campbell, D.L. Heinz, *J. Phys. Chem. Solids* **52**, 495–499 (1991).
5. A.M. Homeister, *Phys. Rev. B* **56**, 5835–5855. (1997).
6. L.V. Al'tshuler, M.N. Pavlovskii, L.V. Kuleshova and G.V. Simakov, *Phys-Solid State* **5**, 203 (1963).
7. M. Durandurdu, *Comp. Mater. Sci.* **48**, 672–676 (2010).
8. J.M. Recio, A.M. Pendas, E. Francisco, M. Florez and V. Luana, *Phys. Rev. B* **48**, 5891–5901(1993).
9. C.E. Sims and G.D. Barrera, *Phys. Rev. B* **57**, 11164(1998).
10. P.W. Bridgnian, *Proc. Amcr. Acad. Arts Sci.* **76**, 1 (1945).
11. L.T. Seipol and H.A. Ullner, *Phys. stat. sol.* (a) **96**, 469 (1986).
12. J. C. Slater and J. G. Kirkwood, *Phys Rev* **37**, 682 (1931).
13. F. G. Fumi and M. P. Tosi, *J. Phye. Chem Solids* **25**, 31-43 (1964).
14. S.N. Vaidya and G.C. Kennedy, *J. Phys. Chem. Solids*, **32**, 951–964 (1971).
15. P. Wedephol, *Solid State Phys.* **10**, 1855 (1977).
16. M. Born and K. Huang, *Dynamic Theory of Crystal Lattices*, 162 (1954).
17. S. V. Karpenko, A. K. Kyarov, and A.I. Temrokov *High Temperature* **38**,722-727 (2000).
18. L. Keyan, D. Zhongsheng and X. Dongfeng, *Phys Status Solid B* **248** , 1227-1236 (2011).