High-Pressure Phase Transition in Some Alkali Halides Using Interatomic Potential Model

Harun Reşit YAZAR
Department of Physics, Kırıkkale University,
71450, Yahşihan, Kırıkkale-TURKEY
e-mail: hzyazar@hotmail.com

Abstract

We have predicted the phase transition pressure in some alkali halides NaCl and KCl using an interatomic potential approach based on a rigid ion model. We have obtained phase transition pressures 28.69 and 2.4 GPa, respectively, and are in close agreement with their corresponding experimental transition pressures 29.0 and 2.0 GPa. This approach is promising with respect to the prediction of the phase transition pressures of other alkali halides.

Key Words: Alkali halide, phase transition, interatomic potential.

1. Introduction

The alkali halides are the simplest ionic solids on which much experimental and theoretical work has been done [1] to validate new theories. They generally crystallize in either the NaCl (B1) or the CsCl (B2) structure. Their elastic, dynamic and thermodynamic properties have been extensively investigated by various experimental and theoretical workers [2, 3]. These solids undergo structural phase transition B1 → B2 at elevated pressures [4]. A survey of the literature reveals that, although a large amount of experimental work has been done on the phase transition in alkali halides [5], very scant attention has been paid to their theoretical understanding.

The effects of such a non-rigidity of ions via three-body interaction have been incorporated in the successful study of the phase transition and high-pressure elastic behaviors of II-VI and III-V compound semiconductors [6] and divalent metal oxides [7]. Motivated by these facts, we thought it pertinent to apply the Woodcock potential for the prediction of the phase transition pressures in NaCl and KCl [8].

In this paper, the three-body interaction has been considered to arise from the effects of non-rigidity of ions caused by the deformation of the electron shells of the overlapping ions. We have adopted the graphical method for predicting the phase transition pressure by plotting the Gibbs free energy as a function of pressure.

2. Theory and Method of Calculation

The lattice energy for an ionic crystal in terms of an effective pair potential is written as [9]

$$\varphi(r_{ij}) = -\frac{\alpha_M e^2}{r_{ij}} + \frac{b}{r_{ij}^n} \exp\left(-\frac{r_{ij}^m}{\rho}\right) - \frac{C}{r_{ij}^6} - \frac{D}{r_{ij}^8} \tag{1}$$

where r_{ij} is the interionic distance. The first term on the right hand side of Eq. (1) is the long-range electrostatic Madelung energy term, the second term represents the short-range overlap repulsive interaction; and the last two terms represent the Van Der Waals dipole-dipole and dipole-quadrupole interactions, respectively. Following Michielsen et al. [10], we take n=4 and m=1 so that

$$\varphi(r) = -\frac{\alpha_M e^2}{r_{ij}} + \frac{V_{ij}}{r_{ij}^4} - \frac{C}{r_{ij}^6} - \frac{D}{r_{ij}^8}, \tag{2}$$

where $V_{ij} = \beta_{ij} b \exp(-r_{ij}/\rho_{ij})$ is a short range potential. The equilibrium condition is [1].

$$b/r_0 \Big\{ \beta_{ij} \exp[r_i + r_j - r_0)/\rho_{ij}] + 2\beta_{ij} \exp[(2r_i - \sqrt{2}r_0)/\rho_{ij}]$$

$$+ 2\beta_{ij} \exp[2r_j - \sqrt{2}r_0)/\rho_{ij}] \Big\} = (2\alpha_M/3)z^2 e^2/2\nu, \tag{3}$$

where $\beta_{ij}(i,j=1,2)$ are the Pauling coefficients, b and ρ are the range parameters, ν is the unit cell volume. For simplicity we denote ρ instead of the ρ_{ij}.

This potential has only two parameters b and ρ and can be determined from the equilibrium condition using the value of the lattice constants [11]. The calculated values of these parameters (b, ρ) and input parameters, such as r_0, r_+, r_- and B_0 were taken from the literature [11] and are listed in Table 1 and are used to compute the phase transition pressure and volume collapses in NaCl and KCl at 0 K.

Table 1. Input data and model parameters for NaCl and KCI.

	r_0	r_+	r_-	B_0	f_0	Model parameters	
						$b(10^{-12}$ erg)	$\rho(A^0)$
NaCl	2.82	1.54	1.99	240	8.78	0.341	0.353
KCl	3.14	1.51	1.63	173	32.547	0.313	0.315

r_0, r_+, r_- are in Å units and B_0 (Bulk Modulus is $\times 10^8$ Pa) [10].

Thermodynamically, a phase transition is said to occur when the changes in structural parameters of the phase are caused by variation of free the energy. The compound then transforms from its initial B1 (NaCl) state to the B2 (CsCl) structure. The difference between the free energy of the two phases becomes zero at the phase transition pressure. The stability of a particular structure is decided by the minimum of the Gibbs energy

$$G = \varphi + PV - TS, \tag{4}$$

where φ is the internal energy, which at 0 K corresponds to the cohesive energy; S is the vibrational entropy at absolute T, pressure P and volume V.

The Gibbs free energies $G_{B1}(r) = U_{B1}(r) + 2\,\mathrm{Pr}^3$ for the NaCl B1 phase and $G_{B2}(r') = U_{B2}(r') + 8\sqrt{3}/3\,\mathrm{Pr}'^3$ for the CsCl B2 phase become equal at the phase transition pressure P and temperature 0 K, i.e. the point where $\Delta G = G_{B1} - G_{B2}$ becomes zero. The U_{B1} and U_{B2} phases are given by [1]

$$U_{B1}(r) = -1.7475 e^2 Z(Z + 6f(r)/r + 6V_{ij}(r) + 6V_{ii}(r) + 6V_{jj}(r),$$

and

$$U_{B2}(r') = -1.7627 e^2 Z(Z + 8f(r')/r' + 8V_{ij}(r') + 8V_{ii}(r') + 8V_{jj}(r'), \tag{5}$$

respectively. Here, r and r' are nearest neighbor separations corresponding to NaCl and CsCl phases, respectively. $f(r)$ and $f(r')$ are the three-body force parameters for NaCl and CsCl, respectively, and are expressed as [12]

$$
\begin{aligned}
f(r) &= f_0 \exp(-r/\rho_{ij}) \\
f(r') &= f_0 \exp(-r'/\rho_{ij}).
\end{aligned}
\tag{6}
$$

Here, the input values of f_0 are taken to be the same for both structures (NaCl and CsCl) [13].

For predicting transition pressure, we have minimized the Gibbs free energies with respect to interatomic separations and calculated $\Delta G = G_{B1} - G_{B2}$ for various pressures. The pressure at which ΔG approaches zero corresponds to the phase transition.

3.   Results and Discussion

Figures 1a and 2a show that ΔG tends to 0 at the phase transition pressure 28.69 Gpa for NaCl and 2.4 Gpa for KCl crystals. These values of the phase transition pressures are in good agreement with the available experimental results [2, 5, 14].

We have also calculated the percentage of relative volume changes using the compression curve and showed the data in Figures 1b and 2b. The values of these volume collapses $\Delta V(P)/V(0)$ have been obtained at the phase transition pressures and are listed in Table 2 along with their available experimental data [2, 15].
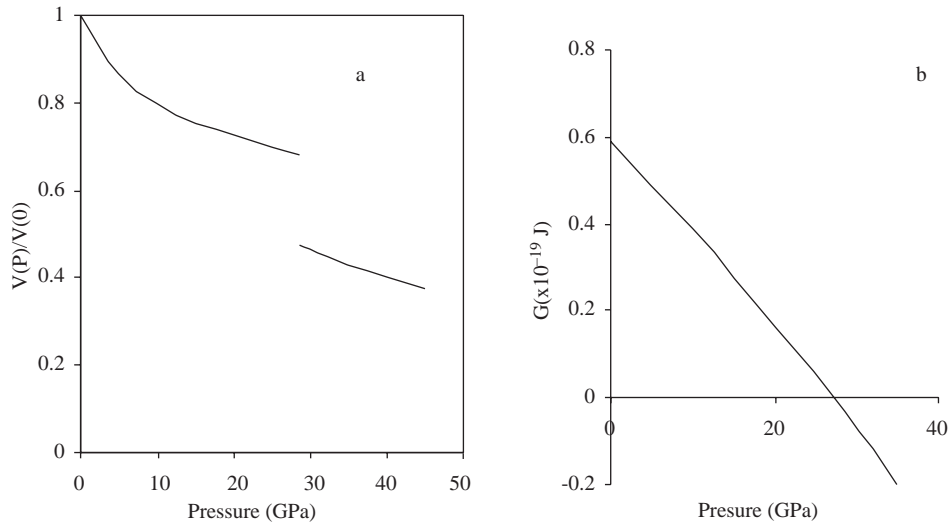

Figure 1a) NaCl : Variation in relative volume $V(P)/V(0)$ with pressure P.

Figure 1b) NaCl : Variation in Gibbs free- energy difference ΔG with Pressure P.
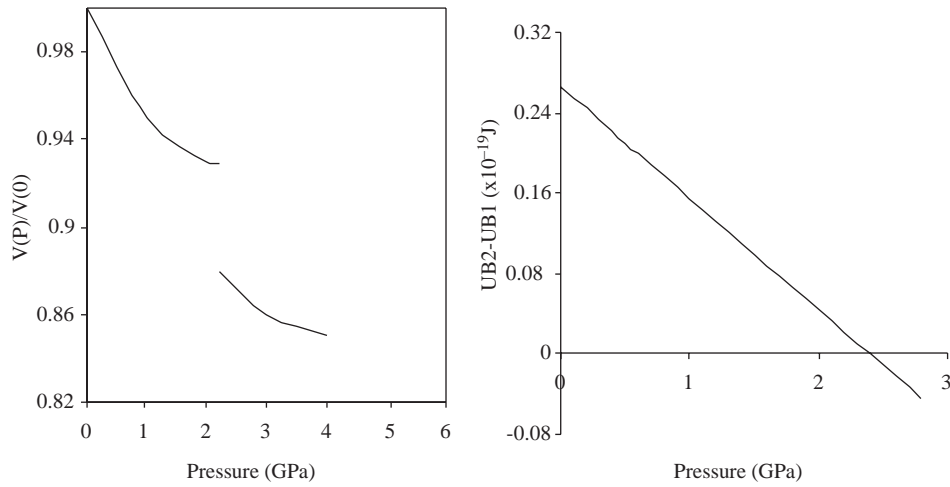
Figure 2a) KCl: Variation in relative volume $V(P)/V(0)$ with pressure P.

Figure 2b) Variation in Gibbs free- energy difference ΔG with Pressure P.

Table 2. Phase transition pressures and volume collapses of alkali halides.

	Phase transition pressure(Gpa)			Volume collapses $\Delta V(P)/V(0)(\%)$	
Crystal	Present	Experiment	Others	Present	Experiment
NaCl	28.6	29.0^a	27.0^b	-4.5	-5.8^e
			27.4^c		
			23.9^d		
KCl	2.4	2.0^f	1.1^b	-14.3	-12.3^f
		1.9^g			

$^{[a]}$ Ref. [14], $^{[b]}$ Ref. [16], $^{[c]}$ Ref. [17], $^{[d]}$ Ref. [18], $^{[e]}$ Ref. [15], $^{[f]}$ Ref. [2], $^{[g]}$ Ref. [5]

The results shown in Table 2 reveal that the phase transition pressure and the associated volume collapses are, in general, in good agreement with the available experimental results and better than those obtained by other theoretical workers.

On the basis of overall achievements, it may be concluded that effective pair potential model approach adopted by us is capable of providing a better understanding of the high pressure phase transition behavior of alkali halides.

References

[1] R.K. Singh. Phys. Rep., **85,** (1982), 259.

[2] P.W. Bridgman, *Proc. Am. Acad. Arts. Sci.,* **76**, (1945).

[3] H.R. Yazar, S. Ağan and K. Çolakoğlu, *Turk J Phys.,* **25**, (2001), 345-353.

[4] M.L. Cohen and S. Froyen, *Phys. Rev.,* **B6,** (1984), 3770.

[5] G.C. Kennedy and S.N. Vaidya, *J. Phys. Chem. Solids*, **32,** (1971), 951.

[6] V.V.S. Nirwal and R.K. Singh. *Phys. Rev.,* **B20,** (1979), 5379.

[7] K.N. Jog, R.K. Singh and S.P.Sanyal, *Phys. Rev.,* **B31,** (1985), 6047.

[8] H.R. Yazar, MSc., Thesis Gazi University, (1997).

[9] D.B. Sirdeshmukh, K.G. Subhadra, *Phys. Stat, Sol.,* **B150,** (1988), K11.

[10] J. Michielson, P. Woerlee, F.V.D. Graff and A.A. Ketelaar, *J. Chem. Soc. Faraday Trans. II*, **71,** (1975), 1730.

[11] D.W. Hafemeister and W.H. Flygare, *J. Chem. Phys.,* **43**, (1965), 795.

[12] W. Cochran, *Crit. Rev. Solid State Sci.,* **21**, (1971).

[13] C.S. Smith and L.S. Chain, *J. Phys. Chem. Solids*, **36**, (1975),205-209.

[14] D.L. Heinz and R. Jeanloz, *Phys. Rev.,* **B30**, (1984), 6045.

[15] W.A. Basset, T. Takahashi, H.K. Mao and J.S. Weaver, *J. Appl. Phys.,* **39**, (1968), 319.

[16] M.L. Cohen and S. Froyen, *J. Phys. C: Solid State Phys.,* **19**, (1986), 2623.

[17] R.K. Singh and N.V.K. *Phys. Stat. Sol., B,* **141**, (1987), K29.

[18] K.N. Jog, PhD. Thesis Rani Durgawati University, Jabalpur, (1988).