High-pressure phase transitions in some alkali halides

High-pressure phase transitions in some alkali halides

N V K Prabhakar†‡, R K Singh†‡, N K Gaur†‡ and N N Sharma§

† Centre for Science and Technology Development Studies, MAPCOST, Bhopal-462016, India
‡ School of Physics, Barkatullah University, Bhopal-462026, India

Abstract. We have predicted the phase transition pressures in some alkali halides using a three-body potential (TBP) model. The phase transition pressures (29.0 and 2.2 GPa) obtained by us for two alkali halides (NaCl and KCl) are in closer agreement with their corresponding experimental data (29.0 and 2.0 GPa) compared with those obtained by earlier workers from the pseudopotential total energy method. This TBP model is promising with respect to prediction of the phase transition pressure of other alkali halides as well.

1. Introduction

The alkali halides are the simplest and ideal ionic solids on which much experimental and theoretical work has been done in the past (Singh 1982). They are model crystals for performing tests to validate new theories. They generally crystallise 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 (Singh 1982). These solids undergo structural phase transition (B1 → B2) at elevated pressures (Froyen and Cohen 1984, 1986, Basset *et al* 1968, Vaidya and Kennedy 1971). A survey of the literature reveals that, although a large amount of experimental work has been done on the phase transition in alkali halides (Vaidya and Kennedy 1971, Sato-Sorensen 1983, Heinz and Jeanloz 1984, Bridgman 1945), very scant attention has been paid to their theoretical understanding.

Recently, Froyen and Cohen (1984, 1986) have investigated the structural phase transition in NaCl and KCl using the pseudopotential total energy method within the local-density approximation. These workers have achieved successful predictions of the phase transition pressures and concluded that minor disagreements might be due to the exclusion of the effect of non-rigidity of ions in the model. The effects of such a non-rigidity of ions via three-body interactions (TBIs) (Singh 1982, Lowdin 1947, Lundqvist 1955) have been incorporated in the successful study of the phase transition and high-pressure elastic behaviour of II–VI and III–V compound semiconductors (Singh and Singh 1989a, b) and divalent metal oxides (Jog *et al* 1985, 1987). Motivated by these facts, we thought it pertinent to apply the three-body potential (TBP) model approach (Singh and Singh 1989a) for the prediction of the phase transition pressures in NaCl and KCl.

In this paper, the TBIs have been considered to arise from the effects of non-rigidity of ions (or charge-transfer mechanism (Singh 1982)) caused by the deformation of the

§ Present address: Department of Physics, Motilal Vigyan Model College, Bhopal-462011, India.

electron shells of the overlapping ions. We have adopted the graphical method for predicting the phase transition pressures by plotting the Gibbs free energy as a function of pressure.

The essentials of the present theory and method are given in section 2. The results are presented and discussed in section 3.

2. Essentials of the theory and method

The pressure causes a change in the volume of the crystals and consequently it alters the charge distribution of the electron shells. This mechanism leads to the deformation of overlapping electron shells and gives rise to the charge–transfer (or three-body) effects (Singh 1982). For thermodynamic stability of a crystal, the Gibbs free energy G at the pressure P and volume V can be written as

$$G = U + PV - TS \tag{1}$$

with U as the internal energy equal to the lattice energy at $T = 0$ K; S is the vibrational entropy whose effects can be ignored as our calculations refer to absolute temperature $T = 0$. Also, we have minimised the Gibbs free energy corresponding to the equilibrium interatomic spacings at $T = 0$ on the lines of Singh and Singh (1989a, b) and Singh and Gupta (1989).

At $T = 0$, the Gibbs free energy for NaCl (B1) and CsCl (B2) phases is expressed as (Jog *et al* 1987)

$$G_{B1}(r) = U_{B1}(r) + PV_1 \, (= 2.0r^3) \tag{2}$$

$$G_{B2}(r') = U_{B2}(r') + PV_2 \, (= 1.539r'^3). \tag{3}$$

Here, V_1 and V_2 are the unit-cell volumes expressed in terms of nearest-neighbour separations r and r' corresponding to NaCl and CsCl phases. Here, U_{B1} and U_{B2} are the cohesive energies of the NaCl and CsCl structures and considered to consist of the long-range Coulomb and TBIs (Singh 1982) and the short-range van der Waals and overlap repulsion (Singh and Singh 1989a, b) effective up to the second-neighbour ions. Their relevant expressions are (Jog *et al* 1987)

$$
\begin{aligned}
U_{B1} = & -(\alpha_M Z e^2/r)\,[Z + 12f(r)] + 6b\beta_{+-}\exp[(r_+ + r_- - r)/\varphi_{+-}] \\
& + 6b\beta_{--}\exp[(2r_- - \sqrt{2}r)/\varphi_{--}] + 6b\beta_{++}\exp[(2r_+ - \sqrt{2}r)/\varphi_{++}] \\
& - C/r^6 - D/r^8
\end{aligned} \tag{4}
$$

$$
\begin{aligned}
U_{B2} = & -(\alpha'_M e_Z^2/r')[Z + 16f(r')] + 8b\beta_{+-}\exp[(r_+ + r_- - r')/\varphi_{+-}] \\
& + 3b\beta_{--}\exp[(2r_- - 1.1547r')/\varphi_{--}] \\
& + 3b\beta_{++}\exp[(2r_+ - 1.1547r')/\varphi_{++}] - C'/r'^6 - D'/r'^8
\end{aligned} \tag{5}
$$

with α_M and α'_M the Madelung constants for the NaCl and CsCl structures, respectively, C and D the overall van der Waals coefficients corresponding to the B1 phase, and C' and D' those corresponding to the B2 phase. $f(r)$ and $f(r')$ are the three-body force parameters for NaCl and CsCl, respectively, expressed as (Cochran 1971)

$$f(r) = f_0 \exp(-r/\varphi)_{+-} \tag{6}$$

$$f(r') = f_0 \exp(-r'/\varphi)_{+-}. \tag{7}$$

Table 1. Model parameters of alkali halides.

Crystal	φ_{++} $(10^{-10}\,\text{m})$	φ_{--} $(10^{-10}\,\text{m})$	φ_{+-} $(10^{-10}\,\text{m})$	f_0	b $(10^{-19}\,\text{J})$
NaCl	0.159	0.492	0.345	8.738	0.348
KCl	0.325	0.325	0.325	32.547	0.319

Here, the values of f_0 are taken to be the same for both the structures (NaCl and CsCl). β_{ij} in the above equations are the Pauling coefficients defined as

$$\beta_{ij} = 1 + Z_i/n_i + Z_j/n_j$$

with Z_i and n_j the valency and number of electrons in the outermost orbit of i ions, Z_j and n_j the valency and number of electrons in the outermost orbit of j ions, b the strength parameter and φ the range parameter. r_i are the ionic radii.

The values of φ_{ij} appearing in the above equations are the same as reported by Hafemeister and Flygare (1965). The values of f_0 for NaCl and KCl were obtained from the overlap integrals. The only model parameter is b which was determined from the equilibrium condition using the value of the lattice constants (Hafemeister and Flygare 1965). The values of these parameters (b, f_0 and φ_{ij}) are listed in table 1 and used to compute the phase transition pressure and volume collapses in NaCl and KCl at 0 K. For this purpose, we have minimised the Gibbs free energies corresponding to the equilibrium interatomic separations r and r' for the NaCl and CsCl structures, respectively. The Gibbs free-energy differences $\Delta G(= G_{B2}(r') - G_{B1}(r))$ are plotted against the pressures in figures 1(a) and 2(a). The pressure at which ΔG becomes zero is called the phase transition pressure P_t; the values of P_t for NaCl and KCl are listed in table 2 and compared with experimental and other theoretical results.

Also, the equation of states were obtained by plotting $V(P)/V(0)$ (relative volume) against the pressure as shown in figures 1(b) and 2(b). The associated volume collapse $\Delta V(P_t)/V(0)$ and the phase transition pressure are listed in table 2 and compared with experimental data.

3. Results and discussion

The variations in ΔG and $V(P)/V(0)$ with pressure for NaCl and KCl presented in figures 1 and 2 show that ΔG tends to 0 at the phase transition pressures 29 GPa and 2.2 GPa for NaCl and KCl crystals, respectively. These values of the phase transition pressures are in much better agreement with the available experimental results (Basset *et al* 1968, Vaidya and Kennedy 1971, Sato-Sorensen 1983, Heinz and Jeanloz 1984, Bridgman 1945) than are those obtained by other theoretical workers (Froyen and Cohen 1986, Vaidya and Kennedy 1971, Jog 1988).

We have also calculated the percentage of relative volume changes using the compression curves and presented them in table 2. The values of these volume collapses $\Delta V(P_t)/V(0)$ have been obtained at the phase transition pressures and listed in table 2 along with their available experimental data (Basset *et al* 1968, Vaidya and Kennedy 1971, Sato-Sorensen 1983, Bridgman 1945).

A critical assessment of the results presented in figures 1 and 2 and table 2 reveals that the results obtained by us for the phase transition pressure and the associated
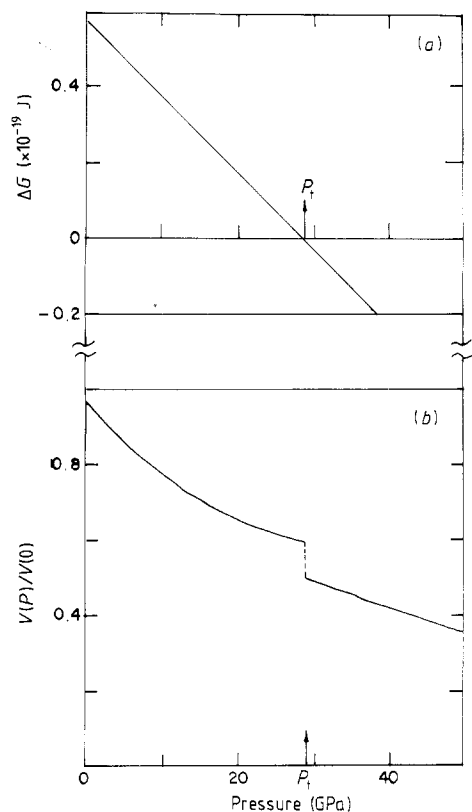
Figure 1. NaCl: (*a*) Variation in Gibbs free-energy difference ΔG with pressure P. (*b*) Variation in relative volume $V(P)/V(0)$ with pressure P.
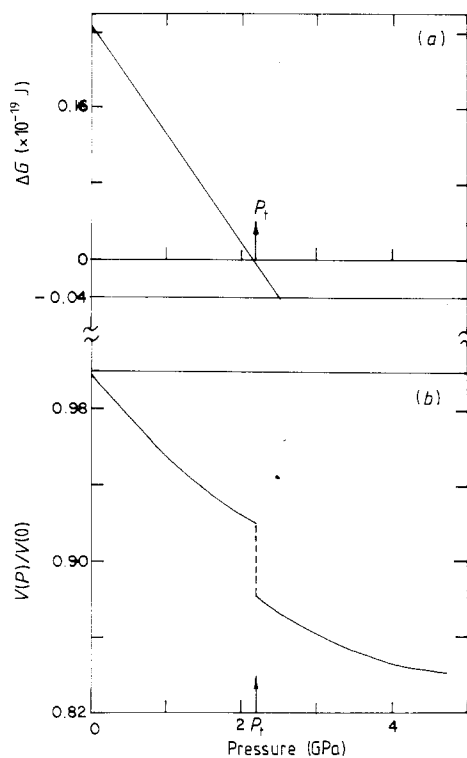

Figure 2. KCl: (*a*) Variation in Gibbs free-energy difference ΔG with pressure P. (*b*) Variation in relative volume $V(P)/V(0)$ with pressure P.

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

Crystal	Phase transition pressure (GPa)			Volume collapses $\Delta V(P_t)/V(0)$ (%)	
	Present	Experiment	Others	Present	Experiment
NaCl	29.0	29.0[a]	27.0[b]	−5.1	−5.8[f]
			27.4[c]		
			23.9[d]		
			4.5[e]		
KCl	2.2	2.0[g]	1.1[b]	−12.9	−12.3[a,g]
		1.9[h]			

[a] Vaidya and Kennedy (1971); Heinz and Jeanloz (1984).
[b] Froyen and Cohen (1986).
[c] Singh and Prabhakar (1987).
[d] Jog (1988).
[e] Singh and Nirwal (1979, 1981).
[f] Basset *et al* (1968); Sato-Sorensen (1983).
[g] Bridgman (1945).
[h] Vaidya and Kennedy (1971).

volume collapses are, generally, in good agreement with the available experimental results and better than those obtained by other theoretical workers. This relative success of TBP model approach is in keeping with the expectation by Froyen and Cohen (1986) as the present model includes the effect of non-rigidity of ions (or charge transfer) via TBIS.

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

Acknowledgments

References

Basset W A, Takahashi T, Mao H K and Weaver J S 1968 *J. Appl. Phys.* **39** 319
Bridgman P W 1945 *Proc. Am. Acad. Arts Sci.* **76** 1
Cochran W 1971 *Crit. Rev. Solid State Sci.* **2** 1
Froyen S and Cohen M L 1984 *Phys. Rev.* B **6** 3770
—— 1986 *J. Phys. C: Solid State Phys.* **19** 2623
Hafemeister D W and Flygare W H 1965 *J. Chem. Phys.* **43** 795
Heinz D L and Jeanloz R 1984 *Phys. Rev.* B **30** 6045
Jog K N 1988 *Ph.D. Thesis* Rani Durgawati University, Jabalpur
Jog K N, Singh R K and Sanyal S P 1985 *Phys. Rev.* B **31** 6047
—— 1987 *Phys. Rev.* B **35** 5235
Lowdin P O 1947 *Ark. Mater. Astr. Fys.* A **35** 30
Lundqvist S O 1955 *Ark. Fys.* **9** 435
Sato-Sorensen Y 1983 *J. Geophys. Res.* **88** 3543
Singh R K 1982 *Phys. Rep.* **85** 259
Singh R K and Gupta D C 1989 *Phys. Rev.* B **40**
Singh R K and Nirwal V V S 1979 *Phys. Rev.* B **20** 5379
—— 1981 *Physica* B **103** 87
Singh R K and Prabhakar N V K 1987 *Phys. Status Solidi* b **141** K29
Singh R K and Singh S 1989a *Phys. Rev.* B **39** 761
—— 1989b *Phase Transitions* **15** 127
Vaidya S N and Kennedy G C 1971 *J. Phys. Chem. Solids* **32** 951