

PHASE TRANSITION STUDY OF SODIUM HALIDE CRYSTALS

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ABSTRACT

The phase transition and relative stability of sodium halide crystals have been studied using an interionic potential which consists of long-range Coulombian, three-body, van der Waals (vdW) dipole-dipole and dipole-quadrupole and short-range overlap repulsive interactions. The vdW coefficients used in the present investigation have been evaluated from Slater-Kirkwood variational method. Hafemeister-Flygare type short-range overlap repulsive potential effective up to second neighbour has been considered. Results obtained show good agreement with experimental data.

INTRODUCTION

THE first detailed theoretical studies on phase transition were those of Jacobs¹, who employed a crude semi-empirical Born-Mayer energy expansion with nearest neighbour (nn) short-range interactions. His calculated values of transition pressure did not agree well with the experimental results but certain trends such as the importance of volume change at the transition were recognized. Cohen and Gorden² employed a more detailed approach described by Born and Haung³ and Tosi⁴ to calculate the transition pressure and cohesive energy in NaCl phases (P_1 and P_2), respectively. Their results of transition pressure did not agree well with the experimental data but were successful to illustrate qualitative trends in the series of alkali halides. Their results specially in fluorides showed large departure from the experimental ones. This departure might be due to the non-inclusion of three-body interaction and the short-range potential effective up to the nearest neighbour only. Recently the transition pressure of some alkali halides has been computed⁵. This potential includes three-body interaction and short-range potential effective up to the next nearest neighbour but their results failed to predict the relative stability of some alkali halides. The reason for this seems to be the non-inclusion of vdW interaction potential which is an important part of crystal energy, as its contribution to the total energy is about 15%.

In the present paper, our main object is to investigate the phase transition properties of sodium halides using an interionic potential which consists of all long-range and short-range interactions, namely long-range Coulombian, three-body, vdW dipole-dipole and dipole-quadrupole (d-q) in-

teractions and Hafemeister-Flygare (HF) type short-range overlap repulsive potential effective up to next nearest neighbours. To estimate the vdW energy, vdW coefficients due to dipole-dipole (d-d) and dipole-quadrupole (d-q) have been evaluated by Slater Kirkwood variational (SKV) method which is superior to that based on perturbation theory.

The potential proposed here has been used to perform calculations of phase transition properties of sodium halides. Results obtained show a closer agreement with experimental values than those achieved so far. The essential formulation required for the present calculations has been described in the next section. The computed results and discussion are presented in the last section.

THEORY

In order to achieve the above goal, we have employed an interionic potential, which has been adequately successful in describing the cohesive⁶, anharmonic⁷ and dynamic⁸ properties of both NaCl and CsCl structures of ionic solids. The essential framework of this potential energy per unit cell for NaCl (real) structure P_1 phase is written as,

$$\begin{aligned} \Phi_1(r) = & -\frac{\alpha_M e^2 Z^2}{r} - \left(\frac{C}{r^6} + \frac{D}{r^8} \right) - \frac{n\alpha_M e^2 Z}{r} f(r) \\ & + 6b\beta_{kk'} \exp\left(\frac{r_k + r_{k'} - r}{\rho}\right) \\ & + 6b \left[\beta_{kk} \exp\left(\frac{2r_k - r_{kk}}{\rho}\right) \right. \\ & \left. + \beta_{k'k'} \exp\left(\frac{2r_{k'} - r_{k'k'}}{\rho}\right) \right] \end{aligned} \quad (1)$$

Here, the first term represents the Coulombian energy α_M being the Madelung constant. The second term represents the van der Waals energy due to d-d and d-q interactions. The third term is three-body interaction (TBI) energy, which owes its origin from charge transfer mechanism between neighbouring ions with $f(r)$ a parameter dependent on overlap integrals; n is the nn number and having values of 6 for NaCl structure. The remaining terms represent the repulsive energy of HF type. The details regarding the model used for the present calculation have already been reported in our earlier papers^{6,9}. When the crystal undergoes a polymorphic phase transition to the P_2 phase at pressure P , the potential energy corresponding to the hypothetical (CsCl) phase becomes,

$$\begin{aligned} \Phi_2(\bar{r}) = & -\frac{\alpha_M e^2 Z^2}{\bar{r}} - \left(\frac{C'}{\bar{r}^6} + \frac{D'}{\bar{r}^8} \right) - \frac{n' \alpha_M e^2 Z}{\bar{r}} f(r) \\ & + 8b\beta_{kk'} \exp\left(\frac{r_k + r_{k'} - \bar{r}}{\rho}\right) \\ & + 3b \left[\beta_{kk} \exp\left(\frac{2r_k - \bar{r}_{kk}}{\rho}\right) \right. \\ & \left. + \beta_{kk'} \exp\left(\frac{2r_{k'} - \bar{r}_{k'k}}{\rho}\right) \right]. \end{aligned} \quad (2)$$

Here, α_M is the Madelung constant, \bar{r} is interionic separation, C' and D' are appropriate vdW coefficients belonging to the hypothetical (CsCl) structure. The parameters b , ρ and $f(r)$ in the above equation have been assumed to be structure-independent. The equilibrium nn separation (\bar{r}_0) for CsCl phase is determined from the condition

$$\left. \frac{d\Phi_2(\bar{r})}{d\bar{r}} \right|_{\bar{r}=\bar{r}_0} = 0, \quad (3)$$

which holds at $T = 0^\circ\text{K}$. The Gibbs free energy at this temperature (T) and pressure (P) maintains thermodynamical equilibrium between the two structures such that³

$$\Phi_1(r) + PV_1 = \Phi_2(\bar{r}) + PV_2. \quad (4)$$

Consequently, the phase transition pressure (P) is obtained as,

$$P = \frac{\Phi_2(\bar{r}) - \Phi_1(r)}{V_1 - V_2} \quad (5)$$

with $V_1 - V_2$ as the corresponding phase transition volume.

The model parameters b , ρ and $f(r)$ have been calculated using the equilibrium condition and bulk modulus expressions as illustrated in our earlier papers^{6,9}

$$\left. \frac{d\Phi_1(r)}{dr} \right|_{r=r_0} = 0, \quad (6)$$

$$B_T = \Phi_1''(r_0) [9Kr_0]^{-1}, \quad (7)$$

where $K (= 2$ for NaCl structure) is a constant and $r = r_0$ is interionic separation.

The TBI parameter $f(r)$ and its derivatives have been evaluated from the knowledge of second order elastic constants and from the relation¹⁰

$$f(r) = f_0 \exp(-r/\rho). \quad (8)$$

The cohesive energies $\Phi_1(r)$ and $\Phi_2(\bar{r})$ have been estimated as the function of nearest neighbour separation (r , \bar{r}) in the two phases using the input data and model parameters given in tables 1 and 2 respectively. The phase transition pressure has been evaluated using (5) and shown in table 3 with their experimental and theoretical results.

RESULTS AND DISCUSSION

Table 3 reveals that our model is quite successful to explain the phase transition properties of sodium halides. According to Sangster and Atwood¹¹ a model predicts the relative stability of crystal structure correctly if the difference remains always positive.

$$d\Phi = \Phi_{\text{hypo}}(\bar{r}) - \Phi_{\text{real}}(r) = \Phi_2(\bar{r}) - \Phi_1(r). \quad (9)$$

Table 3 also shows that our model is quite successful to explain the relative stability of sodium halides having all the values of $d\Phi$ positive. Nirwal and Singh's study of phase transition reveals negative values of $d\Phi$ in case of RbCl for which they did not assign any reason. Our investigations of phase

transition properties of rubidium halides¹² yield a positive value of $d\Phi$. It seems that the negative results of Singh and Nirwal are due to non-inclusion of vdW interaction in their potential.

Transition pressures calculated by us show a close agreement with their experimental values in com-

Table 1 Input data for sodium halide crystals

Solids	NaF		NaCl		NaBr		NaI	
	Values	Ref.	Values	Ref.	Values	Ref.	Values	Ref.
$r(10^{-8} \text{ cm})$	2.317	[15]	2.820	[15]	2.989	[15]	3.236	[15]
$\bar{r}(10^{-8} \text{ cm})$	2.236	[*]	2.720	[*]	2.887	[*]	3.154	[*]
$r_k(10^{-8} \text{ cm})$	1.181	[16]	1.181	[16]	1.181	[16]	1.181	[16]
$r_k'(10^{-8} \text{ cm})$	1.36	[17]	1.81	[17]	1.95	[17]	2.16	[17]
$c_{12}(10^{11} \text{ dyn/cm}^2)$	2.29	[18]	1.27	[19]	0.98	[18]	0.59	[20]
$c_{44}(10^{11} \text{ dyn/cm}^2)$	2.90	[18]	1.40	[19]	1.09	[18]	0.80	[20]

* \bar{r} is interionic separation for hypothetical state (CsCl structure)

Table 2 Model parameters for sodium halide crystals

Solids	NaF	NaCl	NaBr	NaI
$b(10^{-12} \text{ ergs})$	0.443	0.348	0.345	0.340
$\rho(10^{-8} \text{ cm})$	0.301	0.345	0.357	0.382
f_o	3.400	8.738	11.042	12.422
$f_{\text{real}}(r)$	0.00154	0.00263	0.00277	0.00283
$f_{\text{hypo}}(r)$	0.00102	0.00160	0.00163	0.00152
$C(10^{-60} \text{ ergs cm}^6)$	136.0945	525.8974	812.5761	1447.4188
$D(10^{-76} \text{ ergs cm}^8)$	46.7289	207.9914	322.0072	577.5724

Table 3 Transition energies (in 10^{12} ergs), transition volumes (in 10^{-24} cm^3) and phase transition pressure (in kbar) for sodium halide crystals

Solids		NaF	NaCl	NaBr	NaI
Cohesive energy	Φ_{Real}	-15.274	-12.864	-12.243	-11.412
	Φ_{Hypo}	-14.527	-11.985	-11.202	-10.229
	Φ_{Expt}	-15.236 [21]	-12.987 [21]	-12.390 [21]	-11.591 [21]
Transition energy	$d\Phi$	0.747	0.969	1.041	1.183
Volume	V_{Real}	24.878	44.852	53.408	67.773
	V_{Hypo}	22.362	40.262	48.107	62.758
Transition volume	dV	2.516	4.59	5.301	5.015
Phase transition	Present study	296.90	211.11	196.378	235.892
	Expt	>200	300	>100	>100
	Others	200 [3]	74 [3]	53 [3]	39 [3]
		15.6 [13]	-	-	-
		326 [2]	107 [2]	79 [2]	23 [2]
		106.8 [14]	44.6 [14]	39.2 [14]	32 [14]

parison to the values evaluated earlier^{2,13,14}. This seems to be due to the complete potential considered as suggested by Tosi⁴.

The overall description of phase transition properties of sodium halides shows that three-body and vdW interactions play an important role in phase transition properties of alkali halides as they do in the case of their lattice dynamical, dielectric and elastic properties.

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ANNOUNCEMENT

XIV INTERNATIONAL UNION OF CRYSTALLOGRAPHY CONGRESS (IUCr)

The XIV International Union of Crystallography Congress will be held during 12-20 August 1987, at Perth, Australia. The organizing chairman is Dr E.

W. Maslen, Director, Crystallography Centre, University of Western Australia, Perth 6009, Australia.
