

CENTRE FOR THEORETICAL PHYSICS
5894/85

IC/85/167
INTERNAL REPORT
(Limited distribution)

REFERENCE

ABSTRACT

International Atomic Energy Agency
and
United Nations Educational Scientific and Cultural Organization
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

SS

A COMPARATIVE STUDY OF SEMI-EMPIRICAL INTERIONIC POTENTIALS
FOR ALKALI HALIDES - II *

CM

F.A. Khwaja **
International Centre for Theoretical Physics, Trieste, Italy

and

S.H. Naqvi ***
Department of Physics, Quaid-i-Azam University, Islamabad, Pakistan.

MIRAMARE - TRIESTE
August 1985

A comprehensive study of some semi-empirical interionic potentials is carried out through the calculation of the cohesive energy, relative stability and pressure induced solid-solid phase transformations in alkali halides. The theoretical values of these properties of the alkali halides are obtained using a new set of van der Waals coefficients and zero-point energy in the expression for interionic potential. From the comparison of the present calculations with some previous sophisticated ab-initio quantum-mechanical calculations and other semi-empirical approaches, it is concluded that the present calculations in the simplest central pairwise interaction description with the new values of the van der Waals coefficients and zero-point energy are in better agreement with the experimental data than the previous calculations. It is also concluded that in some cases the better choice of the interionic potential alone in the simplest semi-empirical picture of interaction gives an agreement of the theoretical predictions with the experimental data much superior to the ab-initio quantum mechanical approaches.

* To be submitted for publication.

** Permanent address: Department of Physics, Quaid-i-Azam University, Islamabad, Pakistan.

*** On study leave from the Punjab Education Department. Presently working in the Department of Physics, Government College H-9, Islamabad, Pakistan.

INTRODUCTION

In a previous paper by us [1], we reviewed at length some five representative forms of interionic potentials used in the calculations of thermodynamical and structural properties of alkali halides and other ionic crystals. The adequacy and plausibility of these semi-empirical potentials to describe the interionic interactions was analysed through a comparative study which was carried out by calculating some anharmonic properties of the alkali halides only. The unknown parameters in the potentials were redetermined through Hildebrand conditions by including some new values of the van der Waals interaction coefficients [2] and zero-point energy in the expression for binding energy. The calculations were performed in the simplest model of the ionic crystals i.e., by assuming that (i) the crystals were an assembly of positive and negative ions with no direct chemical bonds between them and (ii) the interactions of the ions were central pairwise. The second and third nearest-neighbour contributions were neglected because the anharmonic properties are a measure of second and third derivative of the potential with respect to distances which depend on the nearest-neighbour distances of short-range potential only. Moreover, since the three-body interaction potentials decay very sharply with the distance, the contributions from the higher-order derivatives of these potentials were assumed to be insignificant in our calculations. It was concluded that the predicting power of all these potentials forms was greatly enhanced due to the inclusion of the van der Waals interaction coefficients, which are three to four times larger [2] than the traditional values of these coefficients obtained by Mayer [3], and zero-point energies. It was also concluded that as far as the short-range behaviour of the potential forms is concerned, it satisfactorily describe the ion-ion interactions at short-separations for all the properties calculated for alkali halide with the new values of the van der Waals interaction coefficients and zero-point energy.

In order to have a some comprehensive study of these potential forms with the new set of the van der Waals coefficients and zero-point energy, it was thought worthwhile to analyze their behaviour by calculating cohesive energy, relative stability and polymorphic phase transition pressures and volumes of alkali halide. To the best of our knowledge these potential forms with the new set of the values of van der Waals interaction coefficients and zero point energy have not been used to calculate the polymorphic phase transformation in alkali halides.

Most of the theoretical investigations of polymorphic transformations in ionic crystals are related to the calculation of phase transition pressures and usually in alkali halides. It is well known that these materials undergo a polymorphic phase transition from their Na Cl structure to a more compact Cs Cl structure under high pressure even at room temperature. These pressures and corresponding volumes for ionic crystals have been measured by dynamic shockwave [4-6] and diamond-anvil higher pressure cell methods [7-9]. The theoretical predictions of the polymorphic phase transition pressures have been made by several authors using semi-empirical [10-19] and quantum mechanical [20-29] approaches. Recently, the pseudopotential approximation, which is most suited to metallic systems where the electron density is slowly varying, has been used within the framework of local density theory of Kohn et al. [30] to evaluate pressure induced solid-solid phase transition in alkali halides. Because of their simplicity, the semi-empirical approaches to the study of ionic crystals are more popular than the quantum mechanical one to many real advances in the understanding of these materials. However, in all these approaches, the cohesive energy is considered to be a measure of binding and is obtained as the sum of potential energy contributions coming from Coulomb's attractive potential Φ_C , the two and three-body overlap repulsive potential Φ_R , the attractive van der Waals potential Φ_{vdW} and zero-point oscillation potential Φ_{zp} . Thus one writes the expression for cohesive energy $\Phi(r)$ as follows:

$$\Phi(r) = -\Phi_C(r) - \Phi_{vdW}(r) + \Phi_R(r) + \Phi_{zp} \quad (1)$$

where these potentials are functions of distance r . The minus sign indicates that the potential is attractive, whereas the plus sign stands for repulsive interaction between the ions. The short-range repulsive potential forms used in our calculations here have been explained in [1] and are given below:

$$(i) \quad \Phi_R^{BM}(r) = Q_{ij} e^{-|r|/a} - P r^2$$

$$(ii) \quad \Phi_R^{VS}(r) = P e^{-k r^{3/2}}$$

$$(iii) \quad \Phi_C^{AF}(r) = k e^{-r}$$

The symbols EM, VS and GP stand for Born-Mayer, Varshni-Shukla and Gohel-Patel. The values of the constants in these potentials were recalculated for the new set of ^{the} Van der Waals interaction coefficients and zero-point energy in the expression for the cohesive energy and were reported in [1]. The same values of these constants have been used in the present calculations of the polymorphic phase transition pressures.

1. Relative Stability

The relative stability of a crystal is described by calculating cohesive energy for both the real (Na Cl) and hypothetical (Cs Cl) structures using Eq.(1) at $T = 0$ and $P = 0$. Using the equilibrium condition

$$\left[\frac{d\Phi(r)}{dr} \right]_{r=r_0} = 0 \quad (2)$$

where $\Phi(r)$ is calculated from Eq.(1) corresponding to real and hypothetical phases, the equilibrium separations r_0 and \tilde{r}_0 can be found corresponding to the two phases, respectively. (It may be mentioned here that the equilibrium separation \tilde{r}_0 for the hypothetical phase is calculated assuming that the repulsive parameters of the short-range overlap potential are structure independent.) On substituting the equilibrium separation values of r_0 and \tilde{r}_0 in Eq.(1), one gets the values of cohesive energy $\Phi_{\text{real}}(r)$ and $\Phi_{\text{hyp}}(r)$ of the real and hypothetical structures, respectively, at $T = 0$ and $P = 0$. The quantity Δ can then be obtained as

$$\Delta = \Phi_{\text{hyp}}(\tilde{r}_0) - \Phi_{\text{real}}(r_0) \quad (3)$$

and its sign determines the relative stability. Obviously the value of Δ should always be positive for the correct prediction of the relative stability of the alkali halide crystals under investigation. The calculated values of Δ in our scheme using different forms of the repulsive potentials $\phi_R(r)$ are given in Table I along with some previous results taken from [17,28] for comparison.

2. Phase Transition Pressure

At the transition pressures the two phases of the crystal stand in equilibrium and hence the transition pressure P_t can be obtained from the condition that the Gibbs free energy for the two phases of the crystal is the same at P_t . Thus one writes

$$U_1 + PV_1 - TS_1 = U_2 + PV_2 - TS_2 \quad (4)$$

where U_i and S_i are the internal energy and entropy of the system corresponding to two phases ($i = 1,2$). Since the phase transition in alkali halides are known to exhibit very little temperature dependence [31], the internal energy U at $T \approx 0$ may be taken as the cohesive energy and hence P_t in this approximation becomes

$$P_t = \frac{\Phi_2(\tilde{r}_p) - \Phi_1(r_p)}{(v_1 - v_2)} \quad (5)$$

where $(v_1 - v_2)$ is the corresponding phase transition volume of the unit cell and can be calculated from the values of nearest-neighbour separations r_p and \tilde{r}_p corresponding to Na Cl and Cs Cl structures, respectively. The values of r_p and \tilde{r}_p are calculated from the equation of state

$$P_t = - \frac{1}{3\eta r^2} \left. \frac{d\Phi(r)}{dr} \right|_{r=r_p} \quad (6)$$

$$P_t = - \frac{1}{3\eta' r'^2} \left. \frac{d\Phi(r')}{dr'} \right|_{r'=r'_p} \quad (7)$$

where $\eta = v/r^3$. Similarly for η' . Eqs.(4),(6) and (7) are solved to get values of P_t , r_0 and \tilde{r}_0 and are given in Tables II and III, along with the results of some previous calculations and the experimental data about the extrapolated values of high temperature phase transition pressures [7-9, 32-34].

DISCUSSION OF THE RESULTS

The calculated values of Δ in our scheme of calculation show that all the semi-empirical forms of the interionic potentials are fairly successful in correctly predicting the observed structure of all the system studied even in the simplest pairwise nearest-neighbour interaction description of these crystals with the new values of van der Waals interaction coefficients and zero-point energy. Thus our calculations contradict the criticism by Narayan [35] of the semi-empirical theories that all of these approaches are so far unable to predict the observed structure of these crystals. They pointed out that some of the well-studied lithium and sodium halides turned out to be more stable in ZnS structure as compared to NaCl in the semi-empirical theories of Tosi-Fumi [11] and Huggin-Mayer [35]. One may also note that much more sophisticated quantum mechanical approach in [28], in which the interionic potentials energies are calculated through Hartree-Fock wave function with all the manipulations of exchange and correlation calculations in calculating the local electron density, failed to correctly predict the observed structure in iodides of potassium and rubidium. However, the authors [28] attributed this discrepancy to the imperfect description of the dispersion forces in the nearest-neighbour interaction in their approach and the non-availability of some correct values of van der Waals interaction coefficients.

One may note also that both the Varshni-Shukla and Gohel-Patel interionic potentials in our scheme of calculations give the same trend in the variation of Δ for LiF to RbI as predicted previously by Cohen-Gordon and Sangester-Atwood. The predicted values of Δ by these two potentials are, too, in close agreement with the quantum-mechanical calculations of Cohen-Gordon and semi-empirical evaluations of Sangester-Atwood. On the other hand, although the Born-Mayer potential predicts the correct, observed structure for all the alkali halides, it probably overestimates the values of Δ for potassium and rubidium halides as compared to other potentials.

The results of polymorphic transformation pressures P_t summarized in Table III for all the interatomic potentials seem to be satisfactory since these correspond well to the structural trends in the alkali halides and the energy difference trends established for these crystals in Table I. As one goes from LiF to RbI, one sees that these potentials predict the same trend in the variation of P_t as predicted by some previous quantum mechanical calculations (see column 5) [28]. The overall features of the prediction by Varshni-Shukla and Gohel-Patel potentials are the same as that of Cohen-Gordon.

However, in some cases, for example RbI and KI, the predictions of the VS and GP potentials are better than those of Cohen-Gordon results. On the other hand, the Born-Mayer potential overestimates the values of P_t for the alkali halides like KCl, KBr, KI, RbCl, RbBr and RbI as compared to the results of other potentials. It may be noted that very accurate experimental values of polymorphic phase transition pressures of KCl, KBr, KI, RbCl, RbBr and RbI are now known generally using diamond-anvil high pressure cells [7,8]. Recently, Sorensen [9] has measured the phase changes in NaF, NaCl, NaBr and NaI using diamond-anvil high pressure cells method and reported the transformation of NaF and NaCl from the rocksalt to the CsCl phase at ~ 230 Kbar and ~ 290 Kbar, respectively. NaBr and NaI, however, are reported to transform from rocksalt phase to an unidentified phase with a lower symmetry than the CsCl phase at ~ 330 Kbar and ~ 320 Kbar, respectively. The shock wave data by Carter [6] also suggested a NaCl \rightarrow CsCl transition in NaF around 240 Kbar, whereas, no static experiments have ever confirmed this transition. Thus one notices from Table III that Born-Mayer and Gohel-Patel potentials give an excellent agreement with the experimental data about P_t in the case of NaF. Similarly, the calculated results of these two potentials in the case of NaCl are better, too, than that of Jacob, Cohen-Gordon and Lombardi et al. It may be mentioned here that in another recent ab-initio calculation [29] involving pseudopotentials and density-functional theory [30] the predicted pressure for transformation in NaCl is 270 Kbar, which is in excellent agreement with the experimental data and much superior to all the present and previous predictions. Since this theory has been used only in the case of NaCl, it is difficult to judge the overall predictive power of this approach for all the alkali halides as compared to the present calculations or some previous quantum-mechanical or semi-empirical theories. In the light of ^{the} above described latest experimental observations of phase changes for NaBr and NaI one finds all the present and past theoretical predictions to be wrong in these two cases.

IV. CONCLUSIONS

From the above discussion of the results the following conclusions can be drawn:

- 1) The simplest central pairwise interaction description in the semi-empirical theories with new values of the van der Waals interaction and zero-point energy gives the correct prediction of the observed structure in all the alkali halides.

- ii) The Varshni-Shukla interionic potential, which was initially used to calculate the thermodynamic properties of alkali halide molecules only, successfully reproduces the polymorphic phase transition pressure in almost all the alkali halides.
- iii) The P_t predictions of Varshni-Shukla and Gohel-Patel interionic potentials in our scheme of calculations are much superior to some previous sophisticated quantum-mechanical calculations in the case of potassium and rubidium halides.
- iv) In the light of the most recent experimental investigations of P_t in sodium halides using the diamond-anvil high pressure cells technique by Sorensen, all the hitherto theoretical predictions, quantum mechanical as well as semi-empirical, are found to be wrong in the case of Na Br and Na I.

ACKNOWLEDGMENTS

The authors are very grateful to Professor M.P. Tosi for some helpful comments he made in the presentation of the manuscript. One of us (F.A.K.) is also thankful to Professor Abdus Salam, the International Atomic Energy Agency and UNESCO for hospitality at the International Centre for Theoretical Physics, Trieste.

- [1] Farid A. Khwaja, S.H. Naqvi and M.S.K. Razmi, Phys. Stat. Sol. (b) in press (1985).
- [2] J. Shankar and G.G. Agrawal, Phys. Stat. Sol. (b) 123, 11 (1984).
- [3] J.E. Mayer, J. Chem. Phys. 1, 270 (1933).
- [4] M.H. Rice, R.G. McQueen and J.M. Walesh, Solid State Physics 6, 1 (1958).
- [5] J.N. Fritz, S.P. Marsh and R.G. McQueen, Nat'L Bur. Stand. Publ. N326 (US).
- [6] W.J. Carter, High Temperatures, High Pressures 5, 313 (1973).
- [7] W.A. Bassett, T. Takahashi and J.K. Campbell, Trans. Am. Cryst. Assoc., 5, 93 (1969).
- [8] W.A. Bassett, T. Takahashi, H.K. Mao and J.S. Weaver, J. Appl. Phys., 39, 319 (1968).
- [9] Yosiko Sato-Sorensen, J. Geophys. Res. 88, 3543 (1983).
- [10] R.B. Jacobs, Phys. Rev. 54, 468 (1938).
- [11] M.P. Tosi and F.G. Fumi, J. Phys. Chem. Solids 23, 359 (1962).
- [12] A.K. Sarkar and S. Sengupta, Phys. Stat. Sol. 36, 359 (1969); Solid State Commun. 7, 367 (1968).
- [13] E. Lombardi, L. Jansen and R. Ritter, Phys. Rev. 185, 1150 (1969).
- [14] A. Gosh, A.N. Basu and S. Sengupta, Proc. Roy. Soc. (Lond.) A340, 199 (1974).
- [15] J.K. Jain, J. Shanker and D.P. Khandeswal, Phys. Rev. B13, 2692 (1976).
- [16] C.R.A. Catlow, K.M. Diller and M.J. Norgett, J. Phys. C10, 1395 (1977).
- [17] M.J.L. Sangster, U. Schroder and R.M. Atwood, J. Phys. C11, 1523 (1978); M.J.L. Sangster and R.M. Atwood, J. Phys. C11, 1541 (1978).
- [18] V.K. Crag, D.S. Puri and M.P. Verma, Phys. Stat. Sol. (b) 87, 401 (1978).
- [19] V.V.S. Nirwal and R.K. Singh, Physica 103B, 187 (1981); R.K. Singh and V.V.S. Nirwal, Nuovo Cimento 22, 559 (1978).
- [20] E.A. Hylleraas, Z. Phys. 63, 771 (1930).
- [21] R. Landshoff, Z. Phys. 102, 201 (1936); Phys. Rev. 52, 246 (1937).
- [22] P.O. Löwdin, A Theoretical Investigation into Some Properties of Ionic Crystals (Almqvist and Wiksell, Uppsala, 1948); Advance Phys. 5, 1 (1956).

- [23] L.P. Howland, Phys. Rev. 109, 1927 (1958).
- [24] A. Froman and P.O. Löwdin, J. Phys. Chem. Solids 23, 75 (1962).
- [25] K. Mansikka and F. Bystrand, J. Phys. Chem. Solids 27, 1073 (1966).
- [26] J. Vallin, G. Petterson, J.L. Calais and K. Mansikka, Ark. Fys., 37, 267 (1968).
- [27] Y.S. Kim and R.G. Gordon, Phys. Rev. B9, 3548 (1974).
- [28] M.L. Cohen and R.G. Gordon, Phys. Rev. B12, 3228 (1975).
- [29] S. Froyen and M.L. Cohen, Phys. Rev. B29, 3770 (1984).
- [30] W. Kohn and L.J. Sham, Phys. Rev. 140, A113 (1965).
- [31] C.W.F. Pistorius, J. Chem. Phys. 43, 1557 (1955).
- [32] S.N. Vaidya and G.C. Kenedy, J. Phys. Chem. Solids 32, 951 (1971).
- [33] A.L. Ruoff and L.C. Chhabildas, J. Appl. Phys. 47, 4867 (1976).
- [34] M. Born and K. Huang, Dynamical Theory of Crystal Lattices (Clarendon, Oxford, 1954).
- [35] Ramesh Narayan and S. Ramaseshan, Phys. Rev. Lett. 42, 992 (1979).

TABLE I

The values of relative stability factor Δ for alkali halides

Crystal	Born-Mayer	Varshni-Shukla	Gohel-Patel	Sangster-Atwood [17]	Cohen-Gordon [28]
Li F	10.2	8.4	3.0	25.5	16.6
Li Cl	8.5	24.4	7.8	17.5	11.6
Li Br	16.7	18.9	7.6	16.0	10.5
Li I	8.5	3.2	2.1	15.3	6.4
Na F	8.5	7.1	7.8	8.5	8.8
Na Cl	7.4	6.3	6.9	8.9	6.0
Na Br	7.3	6.2	4.5	8.6	5.2
Na I	7.2	6.1	4.5	8.6	2.4
K F	7.7	4.9	4.9	2.1	4.9
K Cl	8.2	2.4	3.0	3.0	3.4
K Br	7.1	2.4	2.6	2.9	2.6
K I	6.9	2.2	2.4	3.2	0.5
Rb F	10.4	2.6	2.8	0.9	4.3
Rb Cl	6.8	1.8	2.0	1.1	2.3
Rb Br	6.9	0.8	0.9	1.1	1.5
Rb I	5.7	0.6	0.7	1.3	-0.3

TABLE II

The calculated values of nearest-neighbours distances r_p (a.u.)

Crystal	Born-Mayer		Varshni-Shukla		Gohel-Patel	
	Na Cl	Cs Cl	Na Cl	Cs Cl	Na Cl	Cs Cl
Li F	3.661	3.925	3.551	3.710	3.410	3.943
Li Cl	4.232	4.561	4.564	4.871	4.652	4.851
Li Br	5.892	6.232	5.280	5.520	4.963	5.215
Li I	6.128	6.401	5.898	6.201	5.632	5.874
Na F	4.127	4.521	4.277	4.408	4.352	4.501
Na Cl	5.210	5.422	5.421	5.628	5.231	5.441
Na Br	5.550	5.742	5.642	5.830	5.560	5.669
Na I	5.921	6.200	5.837	6.107	6.105	6.289
K F	4.524	4.829	4.982	5.325	4.976	5.108
K Cl	4.907	5.116	5.692	5.951	5.730	5.952
K Br	5.008	5.284	5.947	6.248	6.182	6.321
K I	5.184	5.492	6.318	6.718	6.462	6.765
Rb F	5.421	5.659	5.093	5.318	6.460	6.621
Rb Cl	5.894	6.024	6.061	6.253	6.312	6.510
Rb Br	6.103	6.214	6.348	6.563	6.554	6.934
Rb I	6.327	6.489	6.784	7.042	6.834	7.289

TABLE III

The calculated values of transition pressures p_t (kbar)
in static lattice approximation at $T=0$

Crystal	Born-Mayer	Varshni-Shukla	Gohel-Patel	Jacob [6]	Cohen-Gordon[26]	Lombardi et al.[10]	Experiment [4,30-32,53,54]
Li F	550.0	402.1	71.7	300.0	2900.0	517.0	> 100.0
Li Cl	209.2	158.8	170.3	140.0	980.0	231.0	> 100.0
Li Br	486.0	128.2	143.3	105.0	924.0	189.0	> 100.0
Li I	150.3	148.6	128.7	68.0	184.0	127.0	> 100.0
Na F	248.9	194.4	219.3	200.0	326.0	109.0	~ 230.0
Na Cl	117.4	92.8	108.6	74.0	107.0	68.0	300.0 (257)* (290)
Na Br	96.4	82.0	65.1	53.0	79.0	86.0	~ 330.0
Na I	77.9	71.4	69.1	44.0	23.0	78.0	~ 320.0
K F	137.9	98.0	98.0	88.0	85.0	14.1	> 100.0
K Cl	80.7	23.1	20.8	74.0	34.0	16.9	20.0
K Br	70.8	22.2	24.0	59.0	23.0	18.6	19.0
K I	56.4	22.8	24.9	49.0	3.6	16.6	17.8
Rb F	113.9	34.2	36.8	68.0	65.0	10.3	> 100.0
Rb Cl	63.6	5.2	5.5	39.0	17.1	4.3	5.5
Rb Br	59.2	4.8	5.4	30.0	9.7	5.4	5.0
Rb I	35.0	3.4	3.9	22.0	< 0	4.8	3.4

