Ultra Scientist Vol. 24(1)B, 125-132 (2012).

$ND_4Cl_{1-x}Br_x$ Studies on static properties of mixed ionic crystal

D. RAWAT

Deptt. of Physics
Saifia P. G. College of Science and Education, Bhopal, 462001 (INDIA)

(Acceptance Date 17th January, 2012)

Abstract

In the present paper, we have investigated the static properties of mixed ionic crystal $ND_4Cl_{1-x}Br_x$ using three-body potential model (TBPM) by the application of Vegard's law. The results for the mixed crystal counterparts are also in fair agreement with the pseudo-experimental data generated from the application of Vegard's law. The results are in good agreement with the experimental data. The results on compressibility, molecular force constant, infrared absorption frequencies and Debye temperature are probably presented for the first time for these mixed crystal counterparts.

Key words: compressibility, molecular force constant, infrared absorption frequencies, Debye temperature.

1 Introduction

Ionic crystals are the simplest solids and crystallize in the CsCl- type structure at low- temperatures and in the NaCl-type crystal structure at high temperatures[1]. These ionic solids have electrostatic attraction between the ions and possess high melting and boiling point due to which their electrical conductivity is high. They are hard, brittle, and usually soluble in polar liquids. Ionic solids formed between atoms widely differing in ionization potentials[2]. A predominantly ionic character of binding in ammonium halides motivated the recent researchers to concentrate on the studies of their static and dynamical properties[3].

Bleick[1] computed the cohesive energies of ammonium halides using the Born-Mayer (BM) equation taking the account of the dispersion terms and generalized Huggins-Mayer (GHM) form of the repulsion energy. The van der Waals terms (vdW) were computed by using Mayer formulas[4], following the isoelectronic sequence procedure. Many methods[5-9] of determining vdW coefficients for a number of ionic crystals were reported. After the development of London's theory, an entirely different attempt was made to evaluate the van der Waals energy by Slater and Kirkwood[10] employing the variational method. Attempts to compute the cohesive energies have been made by Ladd and Lee[11] using the BM form; by Murthy *et al*.,[2] with the extended- BM form; by Thakur *et al*.[12] using the logarithmic form; Shukla *et al*.[13] using the charge- transfer model with varying degrees of success. The static properties of ammonium halides are determined by the BM model of ionic crystals using the modified form for repulsion energy[14].

This paper compiles the cohesive energies of ammonium mixed halides, using a Three-body potential model (TBPM)[15-17] for the cohesive energy. From X-ray structure analysis it has been observed that the mixed ionic crystals are formed by the mixture of pure components and are truly crystalline and their lattice constants change linearly with concentration from one pure member to another. So, pseudo-experimental data for mixed compounds can be generated by applying Vegard's law to experimental values available for end point members. We have studied mixed system of $ND_4Cl_{1-x}Br_x$ successfully using TBPM. The importance of three body interactions in potential model to improve results has also been emphasized by other like Sims *et al*.[18] and Froyen and Cohen[19]. We have also utilized the three-body interaction effects in case of semiconductors[20] and more recently in case of rare-earth mono-tellurides[21]. We have also explored successfully our efforts to calculate the thermo-physical properties viz bulk modulus molecular force constant, reststrahlen frequency and Debye temperature using TBPM.

2 *Theory and method :*

We have calculated the cohesive energy of ionic ammonium mixed solids to test the capabilities of the present interionic potential. Thus, the potential which includes all the interactions is given below.

$$\phi = \phi_c + \phi_{TBI} + \phi_{vdw} + \phi_{SR}$$

$$= -\frac{1}{2N}\sum_{\ell k}\sum_{\ell' k'}\frac{Z_k Z_{k'} e^2}{\left|\vec{r}(\ell k, \ell' k')\right|} + e^2\sum_{\ell k}\sum_{\ell' k'}\sum_{\ell'' k''}\frac{Z_k Z_{k'}}{\left|\vec{r}(\ell k, \ell' k')\right|} f\vec{r}(\ell k, \ell'' k'')$$

$$+\sum_{kk'} C_{kk'} r_{kk'}^{-6} + \sum_{kk'} D_{kk'} r_{kk'}^{-8} +$$

$$nb\beta_{kk'}\exp\left(\frac{r_k + r_{k'} - r_{kk'}}{\rho}\right) + \frac{n}{2}b\left[\beta_{kk}\exp\left(\frac{2r_k - r_{kk'}}{\rho}\right) + \beta_{k'k'}\exp\left(\frac{2r_{k'} - r_{k'k'}}{\rho}\right)\right] \quad (1)$$

Where n is the number of molecules per unit cell in the first term, $C_{kk'}$ and $D_{kk'}$ are the vdW coefficients due to dipole-dipole (d-d) and dipole- quadrupole (d-q) interactions are taken from Slater-Kirkwood-variation (SKV) method[10], $r_{kk'}$ is the separation between kth and k'th ions, β_{ij} are the Pauling coefficients r_i (r_j) are the ionic radii of the ions i(j), b and ρ are the hardness and range parameter. In the second term $f\vec{r}(\ell k, \ell'' k'')$ is the three-body interaction parameter expressed as

$$f(r) = f_0 \exp(-r/\rho) \qquad (2)$$

Here first term is the columbic energy, second term is the Three body interaction TBI, third and fourth terms are vdW energy due to dipole-dipole (d-d) and dipole- quadrupole (d-q) interactions, the fifth and sixth terms are the short range repulsive energy terms due to the overlap repulsion between the nearest and the next nearest neighbours ions.

Table 1. Values of the input data for ND_4Cl - ND_4Br mixed ionic solids

Input datas

	ND_4Cl	$ND_4Cl_{0.80}$ $Br_{0.20}$	$ND4Cl_{0.60}$ $Br_{0.40}$	$ND4Cl_{0.40}$ $Br_{0.60}$	$ND4Cl_{0.20}$ $Br_{0.80}$	ND_4Br
r_0 A°	3.30[2]	3.34	3.38	3.42	3.46	3.51[1]
$C_{11}(10^{11}$ dynes -cm-2)	4.79[2]	4.78*	4.40*	4.00*	3.81*	3.42[3]
$C_{12}(10^{11}$ dynes -cm^{-2})	1.64[2]	1.60*	1.55*	1.32*	1.04*	0.77[3]
$C_{44}(10^{11}$ dynes -cm-^{2})	1.43[2]	1.40*	1.25*	1.18*	1.11*	0.76[2]
N_k'	17	18*	19*	20*	21*	22
s_{ii}	1.12[13]	1.35*	1.59*	1.82*	2.06*	2.30[13]
s_{ij}	3.68	3.87*	4.05*	4.24*	4.42*	4.61
Model Parameters of ND_4Cl - ND_4Br mixed ionic solids						
b (10^{-12} ergs)	0.25	0.27	0.30	0.33	0.35	0.38
ρ (A°)	0.32	0.34	0.36	0.38	0.40	0.41
f(r)	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01
Zm^2	0.68	0.70	0.70	0.71	0.73	0.73
$\in_{\oe}$	2.69[2]	2.74*	2.78*	2.83*	2.88*	2.92
$\in_0$	6.964	7.02*	7.09*	7.16	7.23*	7.30
w_T (r) 10^{13} rad./ sec	3.232	3.18	3.09	2.96	2.84	2.606

* From the linearity relation $\lambda_1 X_1 + \lambda_2 X_2$, where λ_1 and λ_2 are the respective proportions of the values X_1 and X_2 of the host crystals.

Table 2. Values of van der Waals coefficients of ND_4Cl - ND_4Br mixed ionic solids ($c_{kk'}$ and $d_{kk'}$ are in the units 10^{-60} ergs.-cms^6 and 10^{-76}ergs.-cms^8 respectively

Properties	ND_4Cl	$ND_4Cl_{0.80}Br_{0.20}$	$ND_4Cl_{0.60}Br_{0.40}$	$ND_4Cl_{0.40}Br_{0.60}$	$ND_4Cl_{0.20}Br_{0.80}$	ND_4Br
$c_{kk'}$	143.88	171.11	211.67	247.59	284.86	323.46
c_{kk}	61.56	82.01	104.33	128.36	154.01	181.16
$c_{k'k'}$	366.92	406.41	447.91	491.41	536.92	584.45
$d_{kk'}$	82.18	103.07	125.89	149.70	175.51	203.01
d_{kk}	23.876	34.99	48.23	63.60	81.08	100.68
$d_{k'k'}$	258.00	284.62	312.54	341.77	372.30	404.14
C	2012.48	2408.06	2822.19	3254.70	3705.36	4173.91
D	982.64	1192.05	1423.46	1666.69	1929.96	2210.82

Table 3. Values of Cohesive Energy $\Phi(r)$ [k cals. / Mole] of ND_4Cl- ND_4Br mixed ionic solids.

Properties	ND_4 Cl	$ND_4Cl_{0.80}Br_{0.20}$	$ND_4Cl_{0.60}Br_{0.40}$	$ND_4Cl_{0.40}Br_{0.60}$	$ND_4Cl_{0.20}Br_{0.80}$	ND_4Br
$\Phi_{c\ (r)}$	-176.13	-165.11	-163.91	-161.23	-159.47	- 160.20
$\Phi_{v\ (r)}$	-25.12	-25.61	-26.15	-28.11	-29.89	-37.55
$\Phi_{T(r)}$	24.92	24.17	23.11	21.92	20.81	19.81
$\Phi_{R(r)}$	27.59	29.11	31.28	33.47	39.21	40.23
$\Phi_{Total(r)}$	-148.74	-137.44	-135.67	-132.99	-130.34	-131.70
$\Phi_{EXP(r)}$	-150.0 [ref.14] [a]	-148.60#	-147.20#	-145.80#	-144.40#	-143.0 [ref.14] [a]
$\Phi_{others\ (r)}$	-145.51 [ref.12] [b]	-142.53#	-139.56#	-136.59#	-129.34#	-130.65 [ref.12] [b]

[a] Experimental[14]

[b] Others[12]

Hash # symbols represent the pseudo experimental values which can be obtained from the formula $AB_x C_{1-x}$ Where A, B and C are different ions and x be the concentration of the ions.

Table 4. Thermodynamic properties of ND_4Cl- ND_4Br mixed ionic solids. Molecular Force Constant and Restrahlen frequencies with and without Lorentz field effect.

Properties	ND_4Cl	$ND_4Cl_{0.80}$ $Br_{0.20}$	$ND_4Cl_{0.60}$ $Br_{0.40}$	$ND_4Cl_{0.40}$ $Br_{0.60}$	$ND_4Cl_{0.20}$ $Br_{0.80}$	ND_4Br
$B_T(10^{12}$ dynes-cms$^{-2})$	0.26 0.24[ref.12]^a	0.24 0.23$^\#$	0.21 0.22$^\#$	0.19 0.21$^\#$	0.18 0.20$^\#$	0.16 0.19[ref.12]^a
(dB_T/dP)	5.30 1.90 [ref.21]^b	5.10 1.87$^\#$	5.01 1.84$^\#$	4.82 1.82$^\#$	4.70 1.79$^\#$	4.70 1.77[ref.21]^b
α_V $(10^{1o}$ C.G.S units)	20.16 29.76[ref.21]^b	22.22 30.88$^\#$	23.79 32.00$^\#$	25.26 33.12$^\#$	26.62 34.24$^\#$	28.86 35.37[ref.21]^b
$d(\log B_T/dT$	74.26 56.68[ref.21]^b	80.21 57.90$^\#$	86.25 59.12$^\#$	95.68 60.34$^\#$	99.13 61.56$^\#$	105.76 62.78[ref.21]^b
Γ	2.15 2.34[ref.21]^b	2.05 2.28$^\#$	2.00 2.20$^\#$	1.92 2.14$^\#$	1.87 2.07$^\#$	1.82 2.01[ref.21]^b
$\theta_D(0\,^oK)$	332.20 338.77** 338.68[ref.21]	302.11 310.75* 319.52$^\#$	290.23 288.70** 300.36$^\#$	269.20 270.76** 281.21$^\#$	268.01 255.80** 262.05$^\#$	258.15 243.07** 242.90[ref.21]
C_1	4.53	5.16	5.01	4.85	4.70	4.70
$f(10^3$ dynes - cms$^{-1})$	4.03	3.66	3.34	3.05	2.96	2.53
ν_0 $(10^{12}$ Hz .)	2.13	1.96	1.83	1.71	1.68	1.49

**From the Karlson Formula

$^{a,\,b}$ Experimental^{12,21} Hash $^\#$ symbols represent the pseudo experimental values which can be obtained from the formula AB_xC_{1-x} Where A, B and C are different ions and x be the concentration of the ions.

As reported in earlier paper[21], according to virtual crystal approximation (VCA)[22] mixed crystals are regarded as array of average ions whose masses, force constants and effective charges are considered to vary linearly with concentration (x). The measured data on lattice constants of $ND_4Cl_{1-x}Br_x$ [14] and $ND_4Cl_xBr_{1-x}$ [14] have shown that they vary linearly with concentration (x) and hence follow Vegard's law

$$a(A_{1-x}B_xC) = (1-x)a\,(AC) + xa\,(BC) \tag{3}$$

In this expression A, B and C are the different ions, x be the concentration, a be the number of different ions in the mixed halides. Following, Vegard's law, the value of the overall vdW coefficients for these mixed ammonium halides can be obtained from the vdW coefficients for the end or host crystal

$$C_{mix}(A_{1-x}B_xC) = (1-x)C_{AC} + x\,C_{BC} \tag{4}$$

$$D_{mix}(A_{1-x}B_xC) = (1-x)D_{AC} + x\,D_{BC} \tag{5}$$

Using the values of the vdW coefficients for mixed crystals, the values of model parameters [b, ρ and f(r)] have been evaluated with the knowledge of the lattice constants and the second order elastic constants (SOEC's) by using the equilibrium condition given below

$$\left[\frac{dU}{dr}\right]_{r=r0} = 0 \text{ and } \left[\frac{d^2U}{dr^2}\right]_{r=r0} = 9kr_0B_T \tag{6}$$

The values of these model parameters are the same for end point members *i.e.* (AC- ND_4Cl) and (BC- ND_4Br) as reported earlier[21]. The values of these parameters for their mixed crystal components have been determined from the application of Vegard's law to the corresponding measured data for AC and BC.

The model parameters [b, ρ and f(r)] and input data are listed in Table 1.

3. **Results and Conclusion**

Table 1 represents the values of input data and model parameters for ND_4Cl-ND_4Br mixed ionic solids. Table 2 represents values of van der Waals coefficients of ND_4Cl - ND_4Br mixed ionic solids. We have obtained these coefficients from SKV approach[10] which is suitable method than others. It is also inferred that the value of C and D increases with the increase in concentration (x).

Table 3 represents the Cohesive Energy ϕ(r) of the ND_4Cl- ND_4 Br mixed ionic solid. It is clear from Table 3 that the cohesive energies of ND_4Cl_x Br_{1-x} increase with the increase in concentration(x) of bromine due to change in active masses. These trends we obtained for ND_4Cl due to change in the value of hardness parameter b, range parameter ρ and three-body interaction parameter f(r). Experimental values of cohesive energies are not available except for two pure end crystals *i.e.* for ND_4Cl and ND_4Br. Overall agreement between calculated and available experimental values could not be compared with experimental values due to their unavailability of cohesive energies data for intermediate concentration, so we have calculated them from the experimental values of end pure crystals by using eqn. (3). The Hash # values in the Table 3 are the pseudo-experimental values calculated from the formula stated before, which are in good agreement with the other theoretical[21] values. The Table 3 indicates the various contribution of energy to the total energy. It is also informative to say that the TBI holds good contribution to the total energy and because of this our cohesive energy is more suitable than present work[21]. Our calculated bulk modulus (B_T) from the TBPM model for the extreme ends *i.e.* ND_4Cl and ND_4Br are also best suited with experimental values ends as shown in Table 4.

Moreover, we have calculated various thermodynamic properties such as molecular force constant f and restrahlen frequencies ν_0 with and without effect of Lorentz field for $ND_4Cl_x Br_{1-x}$ which are well illustrated in Table 4. Experimental values available for extreme ends have also been listed for comparison and we found that the values which we obtained are in closer agreement with the experimental results. It is inferred from Table 4 that these values show variation with concentration *i.e.* decreases linearly with concentration. Finally, we have calculated the Debye temperature Θ_D for their extreme end as well as for the intermediate mixed ions, our results[21] varies slightly from the experimental values and in this Table 4 as we have ignored the zero point effect and the temperature effects.

Thus, it is concluded that the values calculated for extreme ends from TBPM for mixed crystal $ND_4Cl_x Br_{1-x}$ are better suited with the experimental results and also for the intermediate concentrations are of only academic interest at present but they may be useful for experimentalists to work on these mixed systems.

References

1. W. E Bleick, *J. Chem. Phys. 2,* 160 (1934).
2. C. S. N. Murthy and Y.V.G.S. Murthy, J. Phys. C3, L22 (1970).
3. R. K. Singh and J.P.S. Rana, Nuovo Cimento 57B, 177 (1980).
4. J. E. Mayer, *J. Chem. Phys. 1,* 270 (1933)
5. M.L Huggins and Y. Sakamoto, *J. Phys. Soc. Jpn. 12,* 241 (1957).
6. J. Shanker, G. G. Agarwal and R. P. Singh *J. Chem. Phys. 69,* 670 (1978).
7. D. Rawat, N.K. Gaur, S. Singh, A. Gour Pramana- *J. Phys.* Vol. *73,* No. 6 (2009).
8. H. Margenau and N.Kestner, An Introduction to the theory of Intermolecular forces (Pergamon, New York) (1971).
9. R. Narayan, *J. Phys. Chem. Solids 38,* 1097 (1977).
10. J. C. Slater and J. G. Kirkwood, Phys. Rev. 37, 682 (1931).
11. M.F.C. Ladd and W.H. Lee, *J. Inorg. Nucl. Chem. 13,* 218 (1960).
12. L. Thakur and S. K. Sinha, *Ind. J. Phys. 52A,* 521 (1978).
13. D. D. Shukla, D. C. Gupta and M. N. Sharma, *Proc. Ind. Natl. Sci. Acad. 46A,* 525 (1980).

14. Ch. Satyanarayana, *Phys. Rev. B 30,* 1004 (1984).
15. R. K. Singh, *Phys. Rev. 85,* 259 (1982).
16. D. Rawat, N.K Gaur, S. Singh, *Ultra Scientist* Vol. *22(2),* 461-463 (2010).
17. D. Rawat, N.K. Gaur *Ultra Scientist* Vol. *23(2),* 305-312 (2011).
18. C. E. Sims, G. D. Barrera and N. L. Allan *Phys. Rev. B 57,* 11164 (1998).
19. S. Froyen and M. L. Cohen, *J. Phys. C 19,* 2623 (1983).
20. R. K. Singh and S. Singh, *Phys. Rev. B 38,* 76 (1989).
21. A. Gour, S. Singh and R.K. Singh, *J. Phys. Chem. Solids 69,* 1669 (2008).
22. R.K. Singh and S. Singh, *Phase transitions,* 54, 61 (1995).