

Theoretical analysis of static properties of mixed ionic crystal: $\text{NH}_4\text{Cl}_{1-x}\text{Br}_x$

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Abstract. In the present paper, we have investigated the static properties of the mixed ionic crystal $\text{NH}_4\text{Cl}_{1-x}\text{Br}_x$ 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 for the end point members ($x = 0$ and 1) are in good agreement with the experimental data. The results on compressibility, molecular force constant, infrared absorption frequencies and Debye temperature are presented probably for the first time for these mixed crystal counterparts.

Keywords. Compressibility; molecular force constant; infrared absorption frequencies; Debye temperature.

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1. Introduction

Alkali metal halides are dimorphic, crystallizing in the CsCl-type crystal structure at low temperatures and in the NaCl-type crystal structure at high temperatures with the exception of NH_4F , which crystallizes in the ZnS-type lattice [1]. These alkali halides have electrostatic attraction between the ions and possess high melting and boiling points due to which their electrical conductivity is high. They are hard, brittle, and usually soluble in polar liquids. Ionic solids formed between atoms widely differ in ionization potentials. The predominantly ionic character of binding in ammonium halides motivated the researchers to concentrate on their static and dynamical properties [2,3].

Bleick [1] computed the cohesive energies of ammonium halides using the Born–Mayer (BM) equation taking into account the dispersion terms and generalized Huggins–Mayer (GHM) form of the repulsion energy. The van der Waals terms (vdW) were computed using London–Mayer (LM) formulas [4], following the isoelectronic sequence procedure. Many methods [5–9] for 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 and Murthy [2] using the extended-BM form; by Thakur and Sinha [12] using the logarithmic form; and by Shukla *et al* [13] using the charge-transfer model with varying degrees of success. The static properties of ammonium halides are determined in the BM model of ionic crystals using the modified form of repulsion energy [14]. In some recent studies, transport phenomenon and phase transition have been analysed [15,16].

This paper compiles the cohesive energies of ammonium mixed halides, using the three-body potential model (TBPM) [17] for the cohesive energy. From X-ray structure analysis it has been observed that the mixed ionic crystals are a 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 $\text{NH}_4\text{Cl}_{1-x}\text{Br}_x$ successfully using TBPM. The importance of three-body interactions in potential model to improve results has also been emphasized by others like Sims *et al* [18] and Froyen and Cohen [19]. We have utilized the three-body interaction effects in the case of semiconductors [19] and more recently in the case of rare-earth monotellurides [20]. We have also calculated successfully the thermophysical 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 assess the capabilities of the present interionic potential. Thus, the potential which includes all the interactions given by the expression below is expected to give better results.

$$\begin{aligned}
 \Phi &= \Phi_c + \phi_{\text{TBI}} + \phi_{\text{vdW}} + \phi_{\text{SR}} \\
 &= -\frac{1}{2N} \sum_{\ell k} \sum_{\ell' k'} \frac{Z_k Z_{k'} e^2}{|\vec{r}(\ell k, \ell' k')|} \\
 &\quad + e^2 \sum_{\ell k} \sum_{\ell' k'} \sum_{\ell'' k''} \frac{Z_k Z_{k'}}{|\vec{r}(\ell k, \ell' k')|} f\vec{r}(\ell k, \ell'' k'') \\
 &\quad + \sum_{kk'} C_{kk'} r_{kk'}^{-6} + \sum_{kk'} D_{kk'} r_{kk'}^{-8} + nb\beta_{kk'} \exp\left(\frac{r_k + r_{k'} - r_{kk'}}{\rho}\right) \\
 &\quad + \frac{n}{2} b \left[\beta_{kk} \exp\left(\frac{2r_k - r_{kk'}}{\rho}\right) + \beta_{k'k'} \exp\left(\frac{2r_{k'} - r_{k'k'}}{\rho}\right) \right], \tag{1}
 \end{aligned}$$

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 which are taken from Slater and Kirkwood [10], $r_{kk'}$ is the separation between k th and k' th ions, β_{ij} ($i = k$ and $j = k'$) 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 parameters. In the second term $f\bar{r}(\ell k, \ell'' k'')$ is the three-body interaction parameter expressed as

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

Here the first term is the Coulombic energy, second term is the TBI, third and fourth terms are the 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 (ij) and the next-nearest neighbours (ii and jj) [22–26].

As reported in an earlier paper [22], according to virtual crystal approximation (VCA) [23] the mixed crystals are regarded as an array of average ions whose masses, force constants and effective charges are considered to scale linearly with concentration (x). The measured data on lattice constants in $\text{NH}_4\text{Cl}_{1-x}\text{Br}_x$ [14] and $\text{NH}_4\text{Cl}_x\text{Br}_{1-x}$ [14] have shown that they vary linearly with concentration (x) and hence they follow the Vegard's law

$$a(A_{1-x}B_xC) = (1-x)a(\text{AC}) + xa(\text{BC}). \quad (3)$$

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

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

$$D_{\text{mix}}(A_{1-x}B_xC) = (1-x)D_{\text{AC}} + xD_{\text{BC}}. \quad (5)$$

Using the values of the vdW coefficients for mixed crystals, the values of model parameters (b , ρ and f) have been evaluated knowing the lattice constants and the second-order elastic constants (SOECs) and the equilibrium condition:

$$\left[\frac{dU}{dr} \right]_{r=r_0} = 0 \quad \text{and} \quad \left[\frac{d^2U}{dr^2} \right]_{r=r_0} = 9kr_0B_T. \quad (6)$$

The values of these model parameters are the same for end point members (AC – NH_4Cl) and (BC – NH_4Br) as reported earlier. The values of these parameters for their mixed crystal components have been determined by the application of Vegard's law to the corresponding measured data for AC and BC.

The model parameters (b , ρ and f) and input data are listed in table 1.

3. Discussion and conclusion

Table 1 represents the values of the input data and model parameters for NH_4Cl – NH_4Br mixed ionic solids. Table 2 represents values of van der Waals coefficients of

Table 1. Values of the input data and model parameters for $\text{NH}_4\text{Cl}-\text{NH}_4\text{Br}$ mixed ionic solids.

	Input data					
	NH_4Cl	$\text{NH}_4\text{Cl}_{80}\text{Br}_{20}$	$\text{NH}_4\text{Cl}_{60}\text{Br}_{40}$	$\text{NH}_4\text{Cl}_{40}\text{Br}_{60}$	$\text{NH}_4\text{Cl}_{20}\text{Br}_{80}$	NH_4Br
r_0 (Å)	3.34 [1]	3.38	3.41	3.44	3.47	3.51 [1]
C_{11} (10^{11} dyne cm^{-2})	4.74 [2]	4.63*	4.56*	4.18*	3.85*	3.42 [3]
C_{12} (10^{11} dyne cm^{-2})	1.64 [2]	1.45*	1.42*	0.74*	0.72*	0.77 [3]
C_{44} (10^{11} dyne cm^{-2})	1.43 [2]	1.32*	1.28*	0.74*	0.73*	0.76 [3]
Model parameters						
b (10^{-12} erg)	0.29	0.31	0.32	0.34	0.36	0.38
ρ (Å)	0.32	0.35	0.36	0.38	0.40	0.41
$f(r)$	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01

*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 NH_4Cl-NH_4Br mixed ionic solids ($c_{kk'}$ and $d_{kk'}$) are in 10^{-60} erg cm^6 and 10^{-76} erg cm^8 respectively.

Properties	NH_4Cl	$NH_4Cl_{80}Br_{20}$	$NH_4Cl_{60}Br_{40}$	$NH_4Cl_{40}Br_{60}$	$NH_4Cl_{20}Br_{80}$	NH_4Br
$c_{kk'}$	179.45	206.11	233.87	262.71	292.66	323.71
c_{kk}	135.52	144.29	153.25	162.38	171.69	181.16
$c_{k'k'}$	239.78	297.46	360.90	430.02	504.87	585.40
$d_{kk'}$	100.50	118.79	138.21	158.76	180.44	203.24
d_{kk}	68.37	74.33	80.55	87.01	93.72	100.68
$d_{k'k'}$	146.31	87.73	234.33	286.06	342.96	405.02
C	2228.03	2577.99	2948.00	3337.88	3747.85	4177.80
D	1055.78	1257.01	1473.50	1705.05	1951.79	2213.64

Table 3. Cohesive Energy $\Phi(r)$ (kcal/mole) of the NH_4Cl-NH_4Br mixed ionic solid.

Properties	NH_4Cl	$NH_4Cl_{80}Br_{20}$	$NH_4Cl_{60}Br_{40}$	$NH_4Cl_{40}Br_{60}$	$NH_4Cl_{20}Br_{80}$	NH_4Br
$\Phi_c(r)$	-178.39	-176.21	-174.26	-172.25	-170.56	-169.45
$\Phi_v(r)$	-23.45	-23.69	-25.14	-27.42	-29.21	-31.45
$\Phi_T(r)$	23.45	22.96	21.33	20.12	19.46	18.21
$\Phi_R(r)$	27.59	29.20	31.45	33.06	35.40	37.24
$\Phi_{Total}(r)$	-148.80	-148.04	-147.4	-146.78	-146.1	-145.45
$\Phi_{exp}(r)$	-150.20 [14]	-148.76*	-147.32*	-145.88*	-144.44*	-143.00 [1]
$\Phi_{others}(r)$	-146.92 [25]	-146.67*	-146.42*	-146.18*	-145.93*	145.69 [18]

*The pseudo-experimental values which can be obtained from the formula AB_xC_{1-x} .

Table 4. Thermodynamic properties of NH₄Cl–NH₄Br mixed ionic solids. Bulk modulus, molecular force constant and restrahlen frequencies with and without Lorentz field effect are also given.

Properties	NH ₄ Cl	NH ₄ Cl ₈₀ Br ₂₀	NH ₄ Cl ₆₀ Br ₄₀	NH ₄ Cl ₄₀ Br ₆₀	NH ₄ Cl ₂₀ Br ₈₀	NH ₄ Br
$B_T(10^{12}$ dyne cm ²)	0.23 0.24* 0.26 [12]	0.22 0.23* 0.23*	0.20 0.21* 0.21*	0.18 0.20* 0.19*	0.15 0.18* 0.17*	0.14 0.16* 0.15 [12]
$\Theta_D(0\text{ K})$	348.45 351.81** 346.74 [21]	344.67 330.90* 390.05*	340.66 313.32** 313.36*	336.22 298.28** 296.68*	332.01 285.21** 279.99*	328.66 273.72** 263.31 [21]
$f'(10^3$ dyne cm ⁻¹)	20.69	20.21	19.45	18.66	17.23	14.65
$\nu'_0(10^{12}\text{ Hz})$	5.22 5.33 [24]	4.76 5.13*	4.92 4.94*	4.55 4.75*	4.33 4.56*	3.99 4.37 [24]

From the relation $B_T^ = (C_{11} + 2C_{12})/3$.

**From the Karlson formula.

NH₄Cl–NH₄Br mixed ionic solids. We have obtained these coefficients from SKV (Slater–Kirkwood variation) approach which is more suitable than other methods. It is also inferred that the values of C and D increase with the increase in concentration of x .

Table 3 represents the cohesive energy $\Phi(r)$ of the NH₄Cl–NH₄Br mixed ionic solid. It is clear from table 3 that the cohesive energies of NH₄Cl _{x} Br _{$1-x$} increase with the increase in concentration x of bromine due to change in active masses. We obtained these trends for NH₄Cl 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. NH₄Cl and NH₄Br. Overall agreement between the calculated and available experimental values could not be compared with experimental values due to the unavailability of cohesive energy data for intermediate concentration. So we have calculated them from the experimental values of pure end crystals using eq. (3). The starred (*) values in table 3, which are the pseudo-experimental values, show that our results are in good agreement with the other [14] values. The various contributions of energy to the total energy are given in table 3. It is also notable that the TBI holds good contribution to the total energy and because of this our cohesive energy is more suitable than values from other work [14]. We have also plotted the cohesive energy $\Phi(r)$ vs. concentration x in figure 1. It is clear from figure 1 that the present value of $\Phi(r)$ shown by the solid line increases with concentration x . The experimental and the other work represented by the solid rectangle and triangle are also shown in figure 1. Our calculated bulk modulus (B_T) from the TBPM model for the extreme ends, i.e. NH₄Cl and NH₄Br, are also best suited with experimental values as shown in table 4. In figure 2, we have also shown the variation of B_T with the concentration. It is inferred from figure 2 that the value of B_T decreases from NH₄Cl to NH₄Br.

Moreover, we have calculated various thermodynamic properties such as molecular force constant f and restrahlen frequencies ν_0 with and without Lorentz field

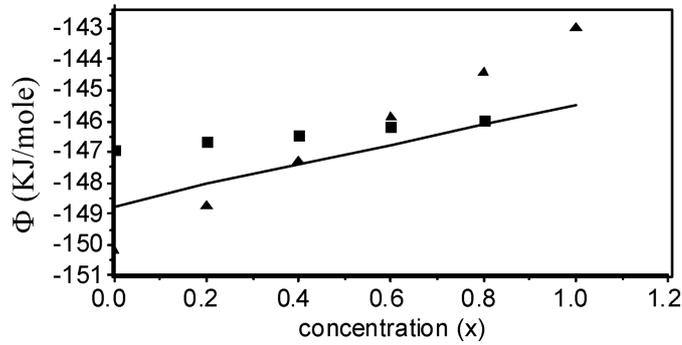


Figure 1. Variation of cohesive energy with concentration. The solid rectangles and triangles indicate the experimental and other theoretical works [24–26].

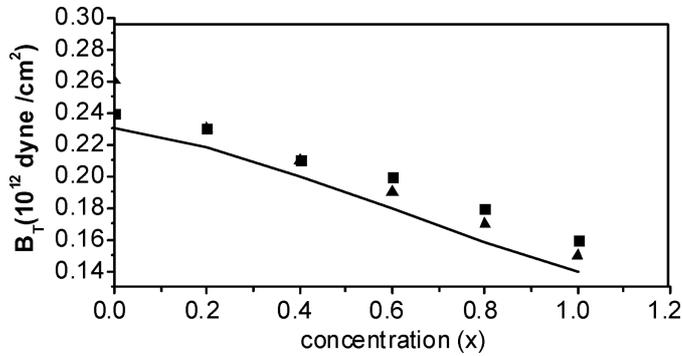


Figure 2. Variation of bulk modulus with concentration. The solid rectangles and triangles indicate the experimental and other theoretical works [24–26].

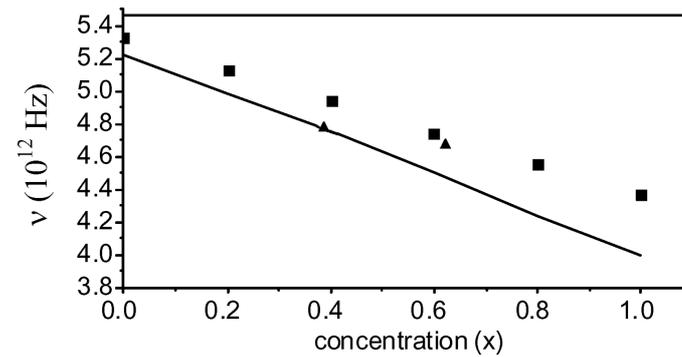


Figure 3. Variation of restrahlen frequencies with concentration. The solid rectangles and triangles indicate the experimental and other theoretical works [24–26].

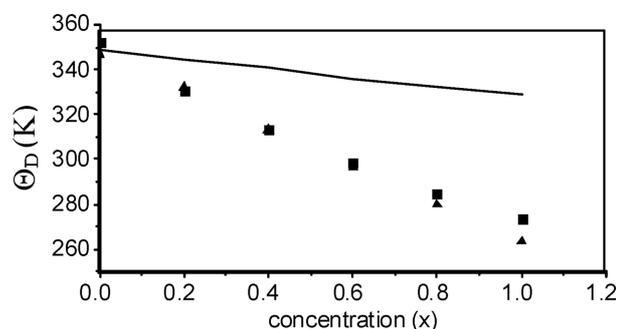


Figure 4. Variation of Debye temperature with concentration. The solid rectangles and triangles indicate the experimental and other theoretical works [24–26].

effect of $\text{NH}_4\text{Cl}_x\text{Br}_{1-x}$ which are given 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 for the extreme ends. Table 4 also gives the molecular force constant f' and restrahlen frequencies ν_0 with and without Lorentz field effect for $\text{NH}_4\text{Cl}_x\text{Br}_{1-x}$ mixed ionic solids. It is clear from figure 3 that its values decrease linearly with concentration showing the highly electronegative nature of halide ions. The values we get for their extreme ends are close to the experimental results. Finally, we have calculated the Debye temperature Θ_D for their extreme end as well as for the intermediate mixed ions. Our results vary slightly from the experimental values as shown in figure 4 and from table 4 as we have ignored the zero point effect and the temperature effects.

Thus, it is concluded that the calculated values for extreme ends using TBPM for the mixed crystal $\text{NH}_4\text{Cl}_x\text{Br}_{1-x}$ are in good agreement with the experimental results but for intermediate concentrations are of only academic interest at present. But they may be useful for experimentalists to work on these systems.

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