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Study of Cohesive and Harmonic Properties of NH_4Cl– NH_4Br Mixed Crystal

ALVIN DAUD
Department of Physics, Lucknow Christian College, Lucknow, India
E-mail: *alvindaud11@gmail.com*

Abstract

A three–body interaction potential has been employed for the study of cohesive, harmonic and anharmonic elastic properties of NH_4Cl–NH_4Br mixed crystals. This interaction potential consists of the long–range Coulomb interactions, van der Waals (vdW) dipole–dipole and dipole–quadrupole interactions and overlap of Born Mayer repulsive potential. This model potential has succeeded in predicting the cohesive energy, thermal properties and the second order elastic (SOE) constants of the NH_4Cl–NH_4Br mixed crystals.

I. Introduction

In recent past several useful phenomenological models [1-5] have been developed and explored to study the dynamical, statical, thermodynamical, photo elastic and other different properties of ionic crystals. Recently Rana et. al. [6-7] have investigated the dynamical, statical and other crystal properties of Ammonium halides using three body shell model (TSM). All these studies were able to predict that three body interaction (TBI), play an important role in describing the crystal properties. Later Singh et. al [8-10] have also calculated the dynamical, statical, thermodynamical, photo elastic and other different crystal properties using the three-body shell model (TSM) for Caesium and Thallous halides.

Three body interaction (TBI)also has significant influence on lattice, static, dynamic and dielectric properties of Ionic crystals and semiconductors of rock salt [12], caesium chloride [13] and Fluorite [14] structures. These third body interaction (TBI), arise from the electron shell deformation effect, also occur in halides compounds and give rise to long [15] and short range [16], three body interaction (TBI) energy in them. The effect of long range three body interaction (TBI) has been investigated thoroughly on their cohesive, harmonic and second order elastic constant [17], while the short–range three body interaction (TBI) has been employed for statical, thermal and elastic properties [17, 18] of rock salt crystals.

In the present study the influence of three body interaction (TBI) has been investigated, on mixed halide crystals (NH_4 Cl $_x$–Br $_{1-x}$), which are important subject as they provide a useful testing ground for theories to represent the interaction mechanism and describes various properties (statical, elastic, dielectric and anharmonic) of their host crystals and mixed crystals.

NH_4 Cl and NH_4 Br are interesting crystals of CsCl structure as they exhibit polymorphism and internal rotation of NH_4^+ ion. Pertinent differences in terms of colour centres, ionic mobilities, elastic anisotropy do exist of solids crystallising in two lattices. There is a clear zest still exist to explore the various statical properties of disordered ionic crystals of CsCl structure.

Mixed crystals are the materials with large concentration of substitutional impurity. They are an important example of randomly disordered matter, whose investigations have received much less attention by the physicist then did pure crystalline materials. The mixed crystal according to virtual crystal approximation (VCA) are regarded as an array of “average ions “whose masses, force constants and effective charges are assumed to vary linearly with the concentration.

Recently many studies have been performed to explore various crystal properties of mixed ionic crystal.

Massa et. al. [11] have explored the dynamical properties of mixed alkali halides, while Rana et al [17, 18] have investigated the statical properties of KCl-KBr, KBr-KI and KI- KCl mixed ionic crystals using an interaction system mostly consists of the long–range Coulomb, three – body interaction (TBI), van der Waals (vdW) and short-range overlap repulsion.

The interionic model proposed by Rana et. al. [17, 18] was able to successfully explored the cohesive energy, second order elastic constants (SOE), Third Order elastic constants (TOE), isothermal bulk modulus (B_T) and its pressure derivatives, Debye temperature (θ_D), Poisson’s ratio and its volume dependence, of KCL-KBr, KBr-KI and KI-KCl crystals. The results so obtained by Rana et.al. [17, 18] agree fairly well with the available experimental data of the mixed and host KCL-KBr, KBr-KI and KI-KCl ionic crystals.

In the present study, our aim is to investigate the interionic potential developed by Rana et. al. [17, 18] on NH_4Cl–NH_4Br mixed crystals. A detailed technique of evaluation of model parameter has already given in our earlier papers [17, 18].

Results and Discussion

In the present study, Slater and Kirkwood variational (SKV) [20] approach, which has been proved better than other methods, has been employed to evaluate (vdW)van der Waals energy term. In table III the cohesive energy of NH_4Cl–NH_4Br mixed crystals has been represented. The increase in cohesive energy of NH_4Cl–NH_4Br mixed crystals also been exhibited graphically in Figure 2.

The increase in cohesive of NH_4Cl–NH_4Br mixed crystals, as is evident from the Figure 2 predicts that cohesive energy increases with increase of molar percentages of NH_4Br crystal. This is expected to be due the variation of interionic separation (Table 1 and Figure1), because cohesive energy depends on interionic separation. This linear variation of cohesive energy with molar concentration is identical with the results, already reported by Rana et. al. [17, 18] for KCl-KBr, KBr-KI and KI-KCl mixed ionic crystals. Cohesive energies, in the present case also do fairly comparable with available experimental data for the host crystals and with the results obtained from Francher and Barsch relation [21], for mixed crystals.

Table 1. Values of the input data and model parameters for NH_4Cl–NH_4Br mixed crystals (interionic separation in A^0 and elastic constants are in 10^{11} dyn cm^{-2})

% Crystal	**r_0**	**C_{11}**	**C_{12}**	**C_{44}**	**f(r)**	**Z_m^2**
$NH_4\ Cl_{100}\ Br_0$	3.348[24]	4.740[25]	1.64000 [25]	1.43000 [25]	-0.0180	0.713
$NH_4\ Cl_{80}\ Br_{20}$	3.380*	-	-	-	-0.0176*	0.694
$NH_4\ Cl_{60}\ Br_{40}$	3.413*	-	-	-	-0.0172*	0.674
$NH_4\ Cl_{40}\ Br_{60}$	3.445*	-	-	-	-0.0168*	0.674
$NH_4\ Cl_{20}\ Br_{80}$	3.478*	-	-	-	-0.0164*	0.635
$NH_4\ Cl_{100}\ Br_0$	3.510 [24]	3.429 [26]	0.772 [26]	0.761[26]	-0.0160	0.635

*From linearity relation $\beta x_1 + (1 - \beta)\ x_2$

where β is the concentration of mixed crystal and x_1 and x_2 are the value of host crystals

Table 2. Cohesive Energy [K. Cal/mole] of NH_4Cl–NH_4Br

Crystal %	U_C	U_R	U_V	U_T	U_{total}	U_{exp} .
NH_4 Cl_{100} Br_0	–179.42	28.86	-22.40	23.46	–149.50	-150.20[27]
NH_4 Cl_{80} Br_{20}	–177.64	30.81	-24.10	22.03	–148.90	
NH_4 Cl_{60} Br_{40}	–175.80	32.73	-25.60	20.37	–148.30	
ND_4 Cl_{40} Br_{60}	–174.10	34.68	-27.34	19.04	–147.72	
ND_4 Cl_{20} Br_{80}	–172.34	36.60	-29.04	17.66	–147.12	
ND_4 Cl_0 Br_{100}	–170.55	38.52	-30.55	16.03	–146.55	–143.00 [28]

Table 3. Elastic and Thermal Properties of Mixed NH_4Cl– NH_4Br Crystals

% Crystal	**Br [10^{12}dyn cm^{-2}]**			**Debye temperature θ_D [K]**		
	Present Study	**Expt.**	**Ref.**	**Present Study**	**Expt.**	**Ref.**
NH_4 Cl_{100} Br_0	0.230	0.260	[29]	349.40	346.74	[30]
NH_4 Cl_{80} Br_{20}	0.124	0.238*		345.48	33.05**	
NH_4 Cl_{60} Br_{40}	0.196	0.216*		341.54	313.37**	
NH_4 Cl_{40} Br_{60}	0.178	0.194*		337.60	296.68**	
NH_4 Cl_{20} Br_{80}	0.160	0.172*		333.68	280.00**	
NH_4 Cl_{100} Br_0	0.14 0	0.150	[29]	329.68	263.31	[30]

*Calculated from Varotsos relation [22]
**Calculated from Karlson formula [23]

Table 4. Second-order elastic constants of Mixed NH_4Cl–NH_4Br Crystals [10^{11} dyn cm^{-2}]

% Crystal	**C_{11}**	**C_{12}**	**C_{44}**
NH_4 Cl_{100} Br_0	4.7400	1.6400	1.4300
NH_4 Cl_{80} Br_{20}	4.4778	1.4664	1.2962
NH_4 Cl_{60} Br_{40}	4.2156	1.2928	1.1624
NH_4 Cl_{40} Br_{60}	3.9534	1.1192	1.0286
NH_4 Cl_{20} Br_{80}	3.6912	0.9456	0.8948
NH_4 Cl_{100} Br_0	3.4290	0.7720	0.7610

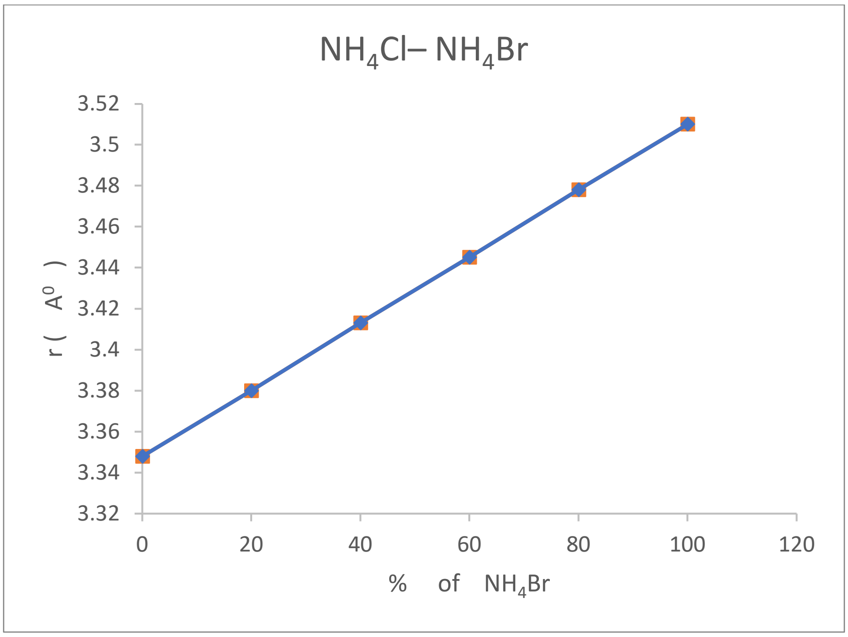

Figure1. Variation of lattice constant (r) with mole percentage concentration of Br^- in NH_4Cl crystal

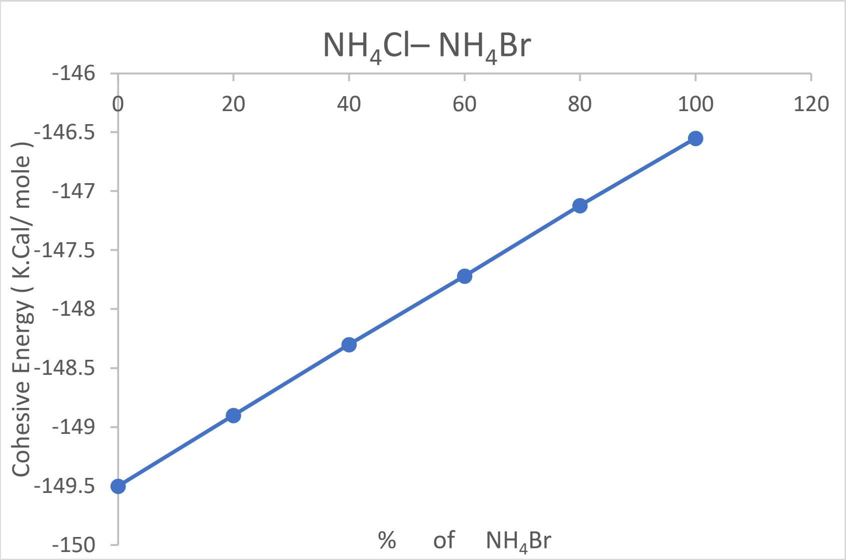

Figure 2. Variation of cohesive energy with mole percentage concentration of Br^- in NH_4Cl crystal

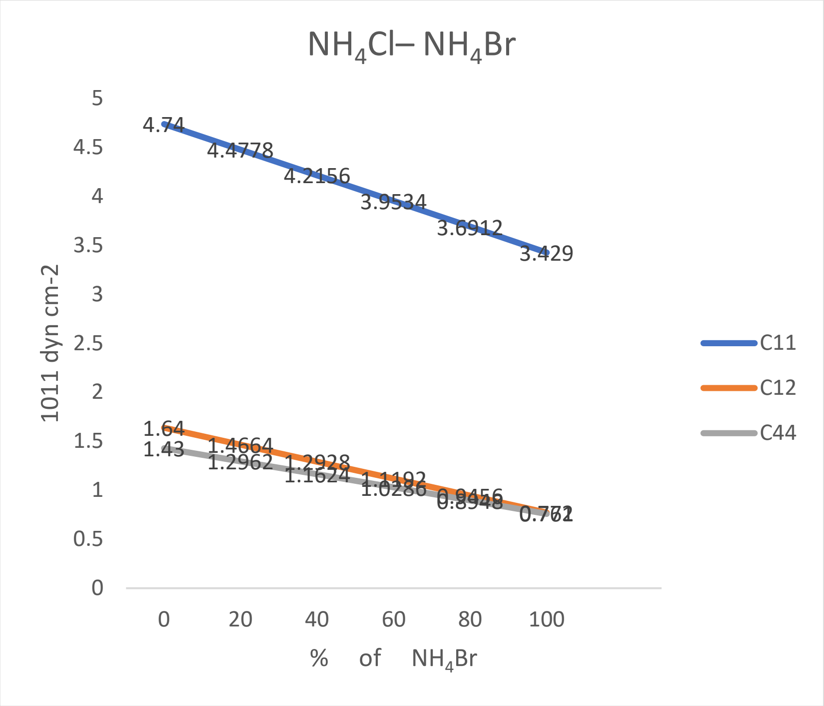

Figure 3. Variation of SOE constant with mole percentage concentration of Br^- in NH_4Cl crystal

The calculated values of Bulk Modulus (B_T) and Debye temperature (θ_D) has been presented in Table3. Our calculated values of Bulk Modulus from the present interionic model fairly comparable with available experimental data for pure component crystals. The percentage dependence of Bulk Modulus for mixed crystals predicted by Varotsos formula [22] is in good agreement with our evaluated results.

The Table 3 exhibits the evaluated values of Debye Temperature (θ_D) for $NH_4Cl–NH_4Br$ mixed crystals. The evaluated results of Debye temperature (θ_D) for the host crystal of $NH_4Cl–NH_4Br$ mixed crystals, though have little departure from the experimental results. However, they follow the same trend of variation obtained from the Karlson formula [23] for the $NH_4Cl–NH_4Br$ mixed crystals. Results obtained from present study for Debye Temperature (θ_D) for $NH_4Cl– NH_4Br$ mixed crystals are also consistent with our earlier studies of KCl-KBr, KBr-KI and KI-KCl mixed ionic crystals.

The second order elastic constants (SOE) evaluated from present interaction potential are evaluated and presented in Table 4. The second order elastic constants (SOE) are also exhibited graphically in Figure 3. A look at Table 4 and Figure 3 makes it evident that our results of second order elastic constants (SOE) for $NH_4Cl–NH_4Br$ mixed crystals follow a schematic trend, which is consistent with results [17-18]. Results of SOE for mixed positions of crystals could not be compare due to lack of experimental data on them and will always attract the attention of future explorer.

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