International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:8, No:8, 2014

Lattice Dynamics of $(ND_4Br)_x(KBr)_{1-x}$ Mixed Crystals

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Abstract**—**We have incorporated the translational rotational (TR) coupling effects in the framework of three body force shell model (TSM) to develop an extended TSM (ETSM). The dynamical matrix of ETSM has been applied to compute the phonon frequencies of orientationally disordered mixed crystal $(ND_4Br)_x(KBr)_{1-x}$ in (q00), (qq0) and (qqq) symmetry directions for compositions $0.10 \leq x \leq 0.50$ at T=300K.These frequencies are plotted as a function of wave vector k. An unusual acoustic mode softening is found along symmetry directions (q00) and (qq0) as a result of translation-rotation coupling.

Keywords**—**Orientational glass, phonons, TR-coupling.

I. Introduction

ENORMOUS efforts have been done in the recent past to investigate the static and dynamic behavior of the mixed molecular crystals. Most of the experimental and theoretical studies are focused on the orientational disorder and glassy behaviour of these materials. They represent a new class of disordered materials which serve as a conceptual link for an understanding of the dynamic processes in glasses [1], [2]. ND_4Br is the deuterated isomorphs of NH_4Br. $(ND_4Br)_x(KBr)_{1-x}$ is miscible over the entire concentration range and dilution with a sufficient amount of KB**r**, the mixed system stabilizes in NaCl structure down to low temperatures. When tetrahedral ND_4^+ molecules in deutero ammonium bromide are statistically diluted by spherical K^+ions, the mixed crystals $(ND_4Br)_x(KBr)_{1-x}$ are formed which exhibit an orientational glass state at low temperatures for intermediate concentration range. Changing of protons to deuteron neither affects the crystal structure nor the dynamics of reorienting molecules. The phase diagrams for the protonated and deuterated isomorphs are similar. Only the phase transition temperatures are significantly reduced in the deuterated isomorphs. The rotational behavior of tetrahedral ammonium molecules in ammonium alkali halide mixed systems has been investigated by the number of experiments [3]-[13]. The inelastic neutron scattering studies [4] have indicated that the motion of ND_4^+ ion is consistent with a model of energy states for a tetrahedron in an octahedral field [3].

The NaCl phase of $(ND_4Br)_x(KBr)_{1-x}$ is characterized by a dynamical disorder of the ND_4 molecules. Below the critical concentration x_c=0.50, the cubic order of the center of mass lattice is preserved for all the temperatures and a freezing transition of orientational degrees of freedom is found [9]. In the dynamically disordered phase, distortions are introduced due to non-equivalence of N-D bonds, which induce elastic quadrupolar moments of ND_4^+ in $(ND_4Br)_x(KBr)_{1-x}$ mixed systems [14]. Although the average symmetry of these crystals is cubic, but the orientational disorder locally breaks the cubic symmetry and the anomalous softening of TA phonons is observed. The reason for the same has been attributed to the coupling of rotator function to the long wavelength acoustic displacements, popularly known as the translation-rotational (TR) coupling.

This theoretical approach is motivated from the *k*-dependent anomalous softening found in TA phonons frequencies along (q00) and (qq0) symmetry directions at T=300K due to the translational rotational coupling. In order to depict the variation of TA phonon frequencies with wave vector *k* for orientationally disordered $(ND_4Br)_x(KBr)_{1-x}$ mixed crystals, we have applied the Extended Three Body force Shell Model (ETSM) [15]. Earlier it has been applied successfully to explain the elastic, thermal and phonon properties of the orientationally disordered ammonium halides [16] and their alkali halide mixed crystals [17]-[20].

The essential formulation of the present model is given in the next section and the results obtained by us are presented and discussed in the subsequent section.

II. Formulation of ETSM

The interionic interaction potential of ETSM has been expressed as [21]:

$$\phi = -\frac{e^2}{2}\sum Z_k Z_{k'}\, r_{kk'}^{-1}\left[1+\sum_{kk'} f_k\,(r_{kk'})\right] - \sum_{kk'} c_{kk'}\, r_{kk'}^{-6}$$

$$-\sum_{kk'} d_{kk'}\, r_{kk'}^{-8} + b\sum_{kk'} \beta_{kk'} \exp\left\{\frac{r_k+r_{k'}-r_{kk'}}{\rho}\right\} + \Phi^{TR} \qquad (1)$$

here, k(k') denote the positive (negative) ions and sum is taken over all the (kk') ions. In the above expression, the first two terms represent the long-range Coulomb and three body interactions (TBI) [22]. The third and fourth terms are the additional van der Waals (vdW) attraction terms due to the dipole–dipole (d-d) and dipole–quadrupole (d–q) interactions [23]. The fifth term is the Hafemeister and Flygare (HF) type short-range (SR) overlap repulsion [24] extended upto the second neighbour ions. $\beta_{kk'}$ are the Pauling coefficients expressed as:

$$\beta_{kk'} = 1 + \frac{Z_k}{n_k} + \frac{Z_{k'}}{n_{k'}} \qquad (2)$$

with $Z_K(Z_{K'})$ and $n_k(n_{k'})$as the valency and the number of effective electrons in the outermost orbit of the cations (anions) [25]. The last term, Φ^{TR} is the new contribution due to the translation-rotational (TR) coupling. The TR coupling

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coefficients are obtained on the lines of Sahu and Mahanti [26], [27]. The expressions for TR coupling coefficients are given in [17]. Here, *b* and *ρ* are the hardness and range parameters, whose values are obtained by using the equilibrium condition:

$$[d\Phi/dr]_{r=ro} = 0 \tag{3}$$

and the expression for the bulk modulus:

$$B= (9Kr_o)^{-1} [d^2\Phi/dr^2]r=r_o \tag{4}$$

where r is the nearest neighbour (nn) separation and r_0 is the equilibrium nn separation. *K* as the crystal structure constant.

Phonon frequencies have been calculated by means of dynamical matrix corresponding to ETSM [20].

$$\begin{aligned} D(\vec{q}) &= \underline{R}(\vec{q}) + \underline{Z}_m C'(\vec{q})\underline{Z}_m) - \underline{R}(q) + \underline{Z}_m C'(\vec{q})\underline{Y}_m) \\ &\times \underline{R}'(\vec{q}) + Y_m C'(\vec{q})\underline{Y}_m)^{-1}(K_m + R^T(\vec{q}) + Y_m C'(\vec{q})\underline{Z}_m) + \underline{D}^{TR}(\vec{q}) \end{aligned} \tag{5}$$

where R, Z_m, Y_m and K_m are (6x6) diagonal matrices formed by the short- range interaction, modified ionic charge and shell charge and C' is the modified LR coulomb matrix. The last term in the above expression is the TR contribution and has non-zero elements in the alkali ion sub matrix D^{TR}(q) given in [20].

The last term in equation (5) is the TR contribution and has non-zero elements in the alkali ion sub matrix $\underline{D}^{TR}$ (q), the approximate expression is given as-

$$D^{TR}(\vec{q}) = \begin{pmatrix} \underline{D}^{TR}(\vec{q}) & 0 \\ 0 & 0 \end{pmatrix} \tag{6}$$

with

$$D_{+}^{TR}(\vec{q}) = -V(\vec{q}) \times V^{+}(\vec{q}) \tag{7}$$

where *V(q)* is the rotational-vibrational coupling matrix and X is the rotation–rotation response matrix as discussed in the earlier section. *V (q)* is given as defined by Strauch et al. [28]:

$$\vec{V(q)} = \frac{2}{\sqrt{m_+}} \begin{pmatrix} A_R S_X & -A_R S_X & B_R S_Y & 0 & B_R S_Z \\ A_R S_Y & A_R S_Y & B_R S_X & B_R S_z & 0 \\ -2A_R S_z & 0 & 0 & B_R S_Y & B_R S_X \end{pmatrix} \tag{8}$$

where S_i=sinq_i r_0, (i=x, y, z) with $q_{I=}$ (q_x, q_y, q_z) as the phonon vectors and m_+ is an alkali ion mass. The potential energy of the present ETSM has now been applied to derive phonon frequencies.

III. Results & Discussion

The model parameters (b, ρ, f(r)) have been evaluated from (3) and (4) and using the input data and the values of vdW and TR-coupling coefficients, listed in Table I. The values of the model parameters thus obtained have also been depicted in Table I. The values of the first and second order space derivatives of f(r) have been evaluated from the relation [29]:

$$f(r) = f_o \exp(-r/\rho) \tag{9}$$

In order to obtain input data at different temperatures, we have used the thermal expansion relation. Also, we have obtained the values of the counterparts mixed crystal at different concentrations (x) by applying the well-known Vegard's law [30].

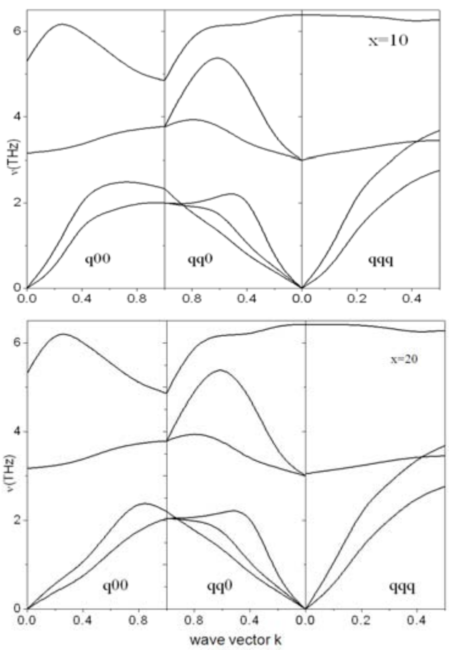
TABLE I
INPUT DATA AND MODEL PARAMETERS FOR $(ND_4Br)_x(KBr)_{1-x}$ AT 300K

Properties	**Values**	
	ND_4Br	KBr
r_0(Å)	3.513	3.293
ν_{TO}(THz)	4.380	6.380
α_+(Å^3)	2.302	1.301
α_-(Å^3)	4.617	4.130
ε_0	7.300	4.520
ε_∞	2.927	2.390

Model parameters

Concentration x	**ρ(10^{-09} cm)**	**b(10^{-13}ergs)**	**f(r)(10^{-3})**
0.10	3.835	2.966	-0.218
0.20	3.848	3.041	-0.136
0.30	3.862	3.104	-0.050
0.40	3.870	3.120	0.040
0.50	3.880	3.128	0.130

Employing (5), we have computed phonon frequencies in q00, qq0 and qqq symmetry directions for compositions 0.10≤x≤0.50 at T=300K. These frequencies are plotted as a function of wave vector *k* to obtain phonon dispersion curves. These curves are displayed in Fig. 1. It can be seen in Fig. 1 that for all the concentrations TA phonon frequencies show considerable softening near zone boundary in q00 and qq0 directions.



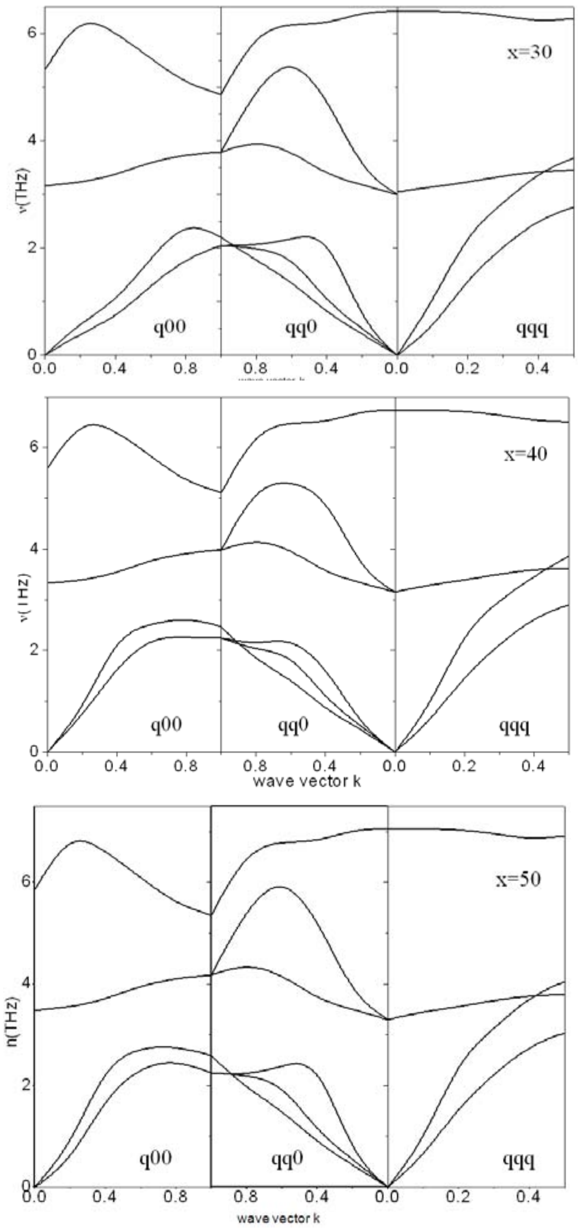


Fig. 1 Phonon dispersion curves of $(NH_4Br)_x(KBr)_{1-x}$ at 300K for $0 \leq x \leq 0.50$

This behavior is same as observed experimentally for ammonium-potassium iodide mixed crystals of the same class [31]. *k*-dependant anomalous phonon softening occurs due to the translation-rotation coupling of the quadrupole moments of ND_4^+ ions with the acoustic modes. This behavior is same as shown by the cyanide halide mixed crystals but weak as compared to those obtained in cyanide halide mixed crystals [32]. It is clear from the PDCs that there is no crossover between LO and TO branches which is found in other orientationally disordered materials. This suggests that the magnitude of quadrupole moment of ammonium molecular ion is small and the effect of TR-coupling is weak.

It is interesting to note that the anomalous softening occurring in the phonon frequencies as a function of wave vector *k* is reproduced well by the ETSM results. This implies that ETSM formalism properly incorporates the TR coupling effects in $(ND_4Br)_x(KBr)_{1-x}$ mixed crystals which is responsible for the anomalous behavior of TA phonons.

IV. Conclusion

The present ETSM has been applied, to explore the lattice dynamics of the orientationally disordered deuterated ammonium alkali iodide mixed crystals. ETSM framework is capable to account for the effects of the Cauchy violations (elastic properties), realistic interaction potential, polarizibilities (dielectric properties) and the TR coupling effects for the present system of orientationally disordered mixed materials. A detailed study of phonon frequencies and phonon dispersion curves of the orientationally disordered deuterated ammonium bromide mixed crystals has been presented in this paper. Here the results are of academic interest at present but they may serve as a guide to the experimental workers in future.

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