Advances in Physics Theories and Applications
ISSN 2224-719X (Paper) ISSN 2225-0638 (Online)
Vol.19, 2013 - Selected from International Conference on Recent Trends in Applied Sciences with Engineering Applications
www.iiste.org

Thermoelastic Behaviour of Orientationally Disordered $(NH_4Br)_x (KBr)_{1-x}$

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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). This ETSM has been applied to reveal the second order elastic constants (C_{11},C_{12} and C_{44}) in the dilute regimes $0 \leq x \leq 0.50$ as a function of temperature for $0K \leq T \leq 320K$. The anomalous elastic behaviour in C_{44} has been depicted well by ETSM results in the orientationally disordered $(NH_4Br)_x(KBr)_{1-x}$ mixed crystals. In order to present a visual comparison of the TR-coupling effect on second order elastic constants, we have evaluated the SOECs with and without TR coupling term in ETSM.

Keywords: Orientational glass, TR-coupling, Elastic constants.

1. Introduction

In the past few years, an enormous amount of research has been devoted to investigate the static and dynamic behavior of the mixed molecular crystals. These mixed crystals exhibit an orientational glass state at low temperatures. They represent a new class of disordered solids which serve as a conceptual link for an understanding of dynamic processes in glasses [1, 2]. When the tetrahedral NH_4^+ molecules in ammonium bromide are statistically diluted by spherical K^+ ions, the mixed crystals $(NH_4Br)_x(KBr)_{1-x}$ exhibit an orientational glass state at low temperatures[3]. It is well known that mixed crystals $(NH_4Br)_x(KBr)_{1-x}$ possess rocksalt (NaCl) structures at room temperature and over certain concentration (x) range. This NaCl phase is characterized by a dynamical disorder of the NH_4 molecules. Below the critical concentration x_c=0.55, 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. The neutron scattering experiments and infrared spectroscopy revealed a quasielastic line width indicating the existence of orientational glass (OG) state in $(NH_4Br)_x(KBr)_{1-x}$ mixed crystals. In the dynamically disordered phase, distortions are introduced due to non-equivalence of N-H bonds, which induce elastic quadrupolar moments of NH_4^+ions in $(NH_4Br)_x(KBr)_{1-x}$ mixed systems. Although the average symmetry of these crystals is cubic, but the orientational disorder locally breaks the cubic symmetry and anomalous softening of sheer elastic constant C_{44} is observed. The reason for the same has been attributed to the coupling of rotator function to long wavelength acoustic displacements, popularly known as the translational-rotational (TR) coupling [3-7].

Singh and Gaur [8] incorporated the effects of TR coupling in the framework of a realistic three body force shell model (TSM) [9] to develop ETSM. It has been applied successfully by Gaur *et.al.* to explain the elastic, thermal and dynamical properties of the orientationally disordered alkali cyanides, their mixed crystal counterparts, sodium superoxide, ammonium halides and ammonium-alkali halide mixed crystals [10-16]. The present theoretical approach is motivated from the versatility and considerable success of the ETSM. We have applied this ETSM to investigate the temperature dependence of the second order elastic constants of $(NH_4Br)_x(KBr)_{1-x}$. 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.

1.1 Formulation of ETSM

The interionic interaction potential of ETSM has been expressed as [8]

$$\phi = -\frac{e^2}{2}\sum Z_k Z_{k'} r_{kk'}^{-1}\left[1+\sum_{kk'} f_k\left(r_{kk'}\right)\right] - \sum_{kk'} c_{kk'} r_{kk'}^{-6} - \sum_{kk'} d_{kk'} r_{kk'}^{-8} + b\sum_{kk'} \beta_{kk'} \exp\left\{\frac{r_k + r_{k'} - r_{kk'}}{\rho}\right\} + \phi^{TR} \qquad (1)$$

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) [9]. 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 [17]. The fifth term is the Hafemeister and Flygare (HF) type short-range (SR) overlap repulsion [18] extended upto the second neighbour ions. $\beta_{kk'}$ are the Pauling coefficients. The last term, Φ^{TR} is the new contribution due to the translation-rotational (TR) coupling. The TR coupling coefficients are obtained on the lines of Sahu and Mahanti (19, 20). The expressions for TR coupling coefficients are given a little later. Here, *b* and *ρ* are the hardness and range parameters.

The TR coupling effects have been introduced through the second order elastic constants (SOECs) derived from the Eq. (1) and expressed as [8]:

$$C_{ij} = C_{ij}^{0} + \delta C_{ij}^{TR} \qquad (2)$$

with C_{ij}^{0} as their unrenormalized values and C_{ij}^{TR} are the TR coupling contributions to the SOECs. For the calculation of C_{ij}^{TR}, we have used the expressions as given in ref.[21].

$$\delta C_{11}^{TR} = -\frac{8}{a} A_{eff}^{2} \chi_{11}(T) \qquad (3)$$

$$\delta C_{12}^{TR} = \frac{4}{a} A_{eff}^{2} \chi_{11}(T) \qquad (4)$$

$$\delta C_{44}^{TR} = -\frac{2}{a} B_{eff}^{2} \chi_{44}(T) \qquad (5)$$

Here, *a* is the lattice constant. The effective coupling constants A_{eff} and B_{eff} are given by

$$A_{eff} = A_R + A_Q \quad \text{and} \quad B_{eff} = B_R + B_Q \qquad (6)$$

with A_R and B_R as the parameters associated with the short-range repulsive interactions and A_Q and B_Q are associated with the quadrupole electric field gradient interaction given by Michel and Naudts [22] and Sahu and Mahanti [23] as

$$A_R = \sqrt{5}\pi\,(b/\rho)\,(d^2+a^2)^{-1/2}\,[a(3f_2-f_0) + d(f_1-3f_3)] \qquad (7)$$

$$B_R = -\sqrt{30}\pi\,(b/\rho)\,(d^2+a^2)^{-1/2}\,[d\,(f_1-3f_3)] \qquad (8)$$

With

$$f_0 = -g^{(n+1)} \int_{\sqrt{1-g}}^{\sqrt{1+g}} (1-y^2)^n e^{-yh}\, dy \qquad (9)$$

Where, $h = (1/\rho)\,(d^2+a^2)^{1/2}$ and $g = 2da/(d^2+a^2)$

The various symbols appearing in the above eqns. (3) to (9) are explained in ref. [23]. The quadrupole electric field gradient interaction A_Q and B_Q and the SR repulsive interaction parameters A_R and B_R are calculated using their expressions from [23] and the method [10]. The calculated values of these parameters and the vdW coefficients are listed in Table 1. The susceptibility χ_{11} is related to C_{11} and C_{12} through A_{eff}, while χ_{44} is related to C_{44} through B_{eff}. The computed results on the elastic constants (C_{11}, C_{12}, C_{44}) of $(NH_4Br)_x(KBr)_{1-x}$.are presented and discussed below.

1.1.1 Results and Discussions

The values of the vdW coefficients ($C_{kk'}$ and $d_{kk'}$) and their overall coefficients (C, D) for NH_4Br and KBr have been evaluated by us using their expressions reported elsewhere [17]. Their estimated values are listed in Table 1 and used to compute their values for the mixed crystals $(NH_4Br)_x(KBr)_{1-x}$ applying the Vegard's law [24]. The model parameters (b, f(r)) have been evaluated from the equilibrium condition and using the input data (r_o, B) from Table 2 and the values of vdW and TR-coupling coefficients listed in Table 1. The values of the model parameters thus obtained have also been depicted in Table 2. The values of the first and second order space derivatives of f(r) have been evaluated from the relation [25]

$$f(r) = f_o \exp(-r/\ ) \qquad (10)$$

The novelty in our calculations lies in the fact that we have not used those properties as the input data which are intended for the prediction. In order to obtain such 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 [24]. Experimentally determined values of r_0 at various concentrations have been used [5]. Using the expressions given in [12], we have computed the values of the second order elastic constants (C_{11}, C_{12} and C_{44}) as a function of temperature $0K \leq T \leq 320K$ for dilute regimes $0 \leq x \leq 0.50$. while computing these elastic constants, the contributions from the translational-rotational coupling are taken into account. This TR coupling has played a significant role in explaining the anomalous behaviour of the sheer elastic constant (C_{44}) of the mixed crystals below the temperature, T=60K and x = 0.30, 0.40 and 0.50. The values of the second order elastic constants obtained from ETSM have been plotted as a function of temperature and concentration (x) as displayed in fig.1. For all the concentrations (x=0.10 to 0.50), the values of

C_{11} (fig.1a) are decreasing with temperature, while on the contrary values of C_{12} (fig.1b) are increasing with the increase of temperature and this feature is usual behaviour of the rocksalt structure materials. Also, there is no remarkable change in the values of C_{11} and C_{12} for different concentrations (x=0.10 to 0.50). The reason for this decrease of C_{11} for all the concentrations has been ascribed by Berret et.al. [26] to anharmonic three phonon interaction process. Though experimental observations are not available for these mixed crystals but a similar trend of variation is revealed from the experimentally observed data [26] for ammonium iodide mixed crystals of same class [15].However, the effects of the concentration (x=0.10 to 0.50) on the shear elastic constant (C_{44}) are more pronounced (see fig1c), but weak as compared to those obtained in cyanide halide mixed crystals [27].This suggests that the magnitude of the quadrupole moment of ammonium molecular ion (NH_4^+) is small and the effect of TR-coupling is weak in $(NH_4Br)_x(KBr)_{1-x}$. At lower ammonium concentration (x=0.10, 0.20), the values of C_{44} remain nearly constant in the temperature range 0K<T<320K. However, an anomalous softening of the shear elastic constant (C_{44}) is noticed (fig. 1c) to occur below 60K for higher concentrations (x = 0.30, 0.40 and 0.50). This anomaly can be attributed to the TR coupling [19, 22, 26] of the quadrupole moments of the NH_4^+ ions with the sheer modes [26]. It has been observed that the agreement improve quite significantly in all the cases of inclusion of TR coupling denoted by ‘x’.It is noticed in fig.1c when we evaluate C_{44} with TR coupling, softening is observed at lower temperatures, which is not found in the absence of TR coupling term. Hence it may be concluded that the softening can be seen only by incorporating the TR coupling in the formulation of TSM. This implies that ETSM formalism properly incorporates the TR coupling effects in $(NH_4Br)_x(KBr)_{1-x}$. Values of C_{11}, C_{12} and C_{44} for which the comparison could not be made due to the lack of experimental data shall work as a guide to the experimental workers in future. It is interesting to note that the anomalous softening occurring in C_{44} below the intermediate temperature range is similar to the observed variations in mixed crystals of the same class [26].

1.1.2 Conclusion

The present ETSM has been applied to explore the elastic properties of the orientationally disordered ammonium alkali bromide. It can be concluded on the basis of the above discussions that our theoretical results for elastic properties show the similar behaviour as experimentally observed for the orientationally disordered mixed crystals of same category and are reasonably good. This is not unexpected as the ETSM framework is capable to account for the effects of the Cauchy violations (elastic properties), the realistic interaction potential, the polarizibilities (dielectric properties) and the TR coupling effects for the present system of orientationally disordered mixed materials. A detailed description of the theoretical investigation of the second order elastic constants of the orientationally disordered ammonium bromide mixed crystals has been presented in this paper. Here the results on elastic constants are of academic interest at present but it may serve as a guide to the experimental workers in future.

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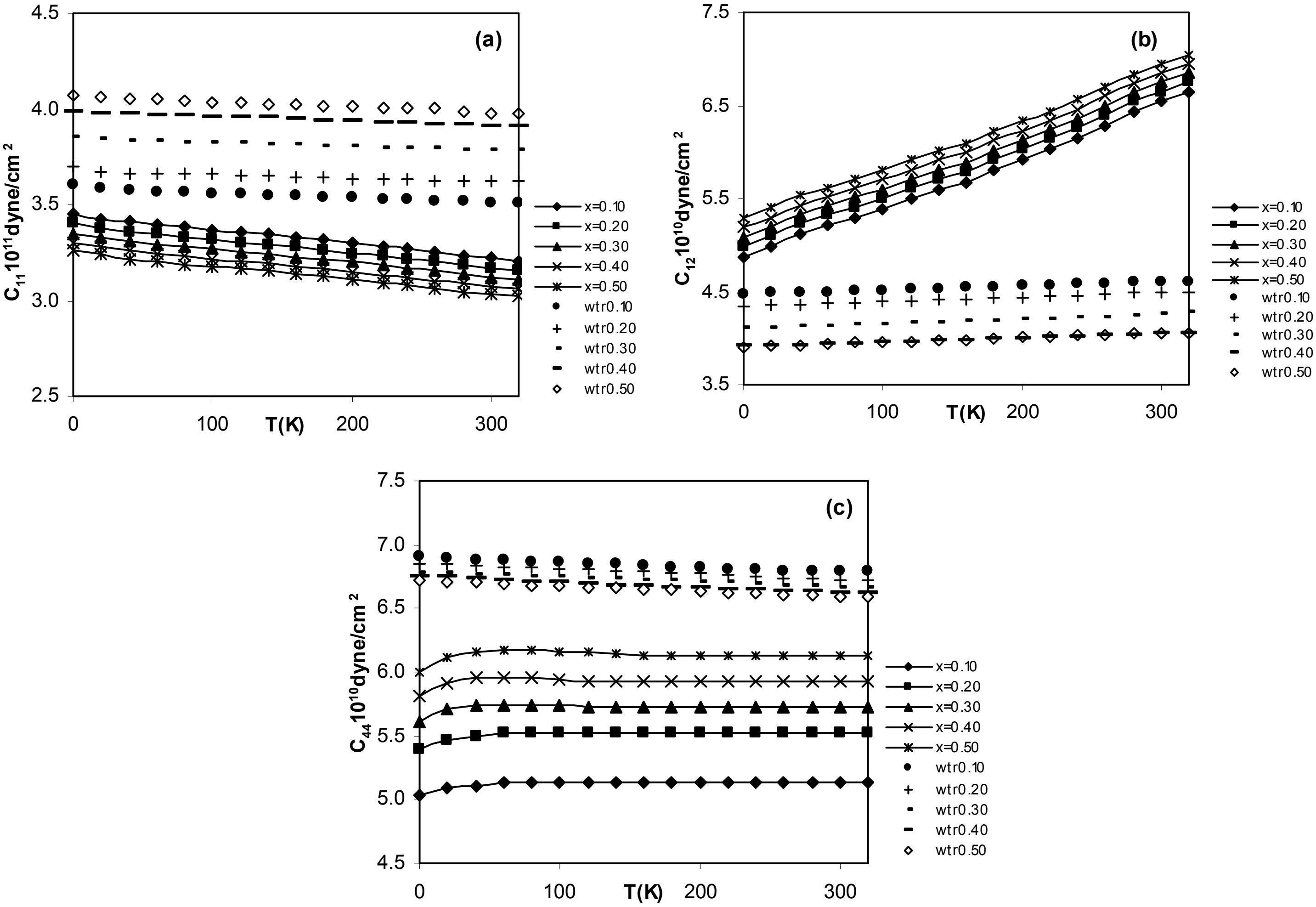
Table 1. The van der Waals coefficients (c_{kk} and d_{kk} in the units of 10^{-60}erg/ cm^6 and 10^{-76}erg/ cm^8, respectively) of NH_4Br & KBr and TR coupling parameters for NH_4Br at 300K.

vdW coefficients	Values		TR-coupling Parameters	Values
	NH_4Br	KBr		
c_{kk}	181.07	36.40	A_R (10^{-4}dyn)	-0.080
$c_{kk'}$	323.71	94.90	B_R (10^{-4}dyn)	0.798
$c_{k'k'}$	585.40	266.90	A_Q (10^{-4}dyn)	0.221
d_{kk}	100.68	54.40	B_Q (10^{-4}dyn)	-0.187
$d_{kk'}$	203.24	197.30		
$d_{k'k'}$	405.02	715.70		
C	4177	898		
D	2213	1520		

Table 2. Model parameters for $(NH_4Br)_x(KBr)_{1-x}$ at 300K.

Concentration x	Model Parameters		
	b (10^{12}erg)	ρ (Å)	f (r)
0.10	2.966	3.535	-0.218
0.20	3.041	3.675	-0.136
0.30	3.093	3.871	-0.050
0.40	3.120	3.880	0.040
0.50	3.128	3.892	0.135

Figure 1. SOECs C_{11} (a), C_{12}(b) and C_{44}(c) for $(NH_4Br)_x$ $(KBr)_{1-x}$for $0 \leq x \leq 0.50$ and $0 \leq T \leq 320$K. 'wtr' represents the curves without TR coupling.


(a)
$C_{11}10^{11}$dyne/cm^2
4.5
4.0
3.5
3.0
2.5
0
100
T(K)
200
300
x=0.10
x=0.20
x=0.30
x=0.40
x=0.50
wtr0.10
wtr0.20
wtr0.30
wtr0.40
wtr0.50
(b)
$C_{12}10^{10}$dyne/cm^2
7.5
6.5
5.5
4.5
3.5
0
100
T(K)
200
300
x=0.10
x=0.20
x=0.30
x=0.40
x=0.50
wtr0.10
wtr0.20
wtr0.30
wtr0.40
wtr0.50
(c)
$C_{44}10^{10}$dyne/cm^2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
0
100
T(K)
200
300
x=0.10
x=0.20
x=0.30
x=0.40
x=0.50
wtr0.10
wtr0.20
wtr0.30
wtr0.40
wtr0.50

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