Thermoelastic properties of mixed \((\text{NaCN})_x(\text{NaCl})_{1-x}\)

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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 \(0<x<1\) in the temperature range \(60K\leq T\leq 300K\). The anomalous elastic behaviour observed in \(C_{44}\) in Brillouin scattering measurements for the composition \(x=0.20, 0.30\) and \(0.59\) has been predicted well by ETSM results in the orientationally disordered \((\text{NaCN})_x(\text{NaCl})_{1-x}\) mixed crystals. Besides, the results on cohesive and thermal properties are also discussed.

1. Introduction

An enormous amount of research has been devoted in the recent past to investigate the static and dynamic behaviour of the mixed molecular crystals. Most of the experimental and theoretical studies are focused on the orientational disorder and glassy behaviours 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]. When a dumb-bell shaped CN\(^-\) replaces Cl\(^-\) in NaCl system a mixed system \((\text{NaCN})_x(\text{NaCl})_{1-x}\) is obtained. The mixed systems containing molecular groups of this type show glassy behaviour at low temperature and over a wide range of concentration [3]. This feature is brought about by the dumb-bell shaped CN\(^-\) ions forming elastic quadrupoles, which determine the anomalous static and dynamic properties. The most prominent examples which have been thoroughly investigated by various experimental methods are the quadrupolar glasses of the type \((\text{MCN})_x(\text{X})_{1-x}\) where M and X stand for an alkali ion mostly Na\(^+\), K\(^+\), and Rb\(^+\) etc and halide ion mostly Br\(^-\) and Cl\(^-\). These systems generally show the cubic structure of the alkali halide crystal mostly fcc, where the sites of the anions are statistically occupied by halide ions and the dumbbells shaped CN\(^-\) ions performing fast reorientational motion. At higher CN\(^-\) concentrations the system performs structural ferroelastic phase transition. At lower CN\(^-\) concentrations there exists a range where the system stays cubic down to lowest temperatures. Although the average symmetry of these crystals is cubic, but the orientational disorder locally breaks the cubic symmetry and the anomalous behavior of shear elastic constant \(C_{44}\) is observed [4]. 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-rotation (TR) coupling [5]. It gives rise to lattice-mediated CN\(^-\)CN\(^-\) coupling which, upon cooling triggers a weakly first order phase transition in the pure materials. Earlier experimental work reveals that the mixed alkali cyanide halide systems exhibit glass like properties at intermediate CN\(^-\) concentration \((x = 0.5)\) [6].

Motivated from the Brillouin Scattering measurements[4] and the softening of the second order elastic constant \(C_{44}\) due to translation-rotation (TR) coupling, we thought it pertinent to investigate the
temperature dependence of second order elastic constants of \((\text{NaCN})_x(\text{NaCl})_{1-x}\) using the Extended three body force shell model (ETSM), which is developed by Singh and Gaur [7] by incorporating the translational rotational (TR) coupling effects in the framework of Three body force shell model (TSM). It has been applied successfully by Gaur et al. [8-11] 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.

The essentials of present theory and method of computations are described in section 2. The results obtained by us are presented and discussed in the subsequent sections.

2. Formulation of ETSM

The interionic interaction potential of ETSM has been expressed as [7]

\[
\phi = -\frac{e^2}{2}\sum_{k} Z_{k} Z'_{k} e^{r_{kk}^{-1}} \left[ 1 + \sum_{k} f'_{k} (r_{kk}) \right] - \sum_{k} C_{kk} r_{kk}^{-6} - \sum_{k} D_{kk} r_{kk}^{-8} - b \sum_{k} \delta_{kk} r_{kk} \exp \left( \frac{r_{kk}^{+} r_{kk}^{-} r_{kk}^{0}}{\rho} \right) + \phi^{TR} 
\]

(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). 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. The fifth term is the Hafemeister and Flygare (HF) type short-range (SR) overlap repulsion, extended up to the second neighbour ions. \(\beta_{kk'}\) are the Pauling coefficients [7]. Here, \(b\) and \(\rho\) are the hardness and range parameters, whose values are obtained by using the equilibrium condition

\[
[d\phi/dr]_{r=r_0} = 0 
\]

(2)

and the expression for the bulk modulus

\[
B = (9k_{r_0}^2) [(d^2\phi/dr^2)]_{r=r_0} 
\]

(3)

where \(r\) is the nearest neighbour (nn) separation and \(r_0\) is the equilibrium nn separation. \(K\) is the crystal structure constant. The last term, \(\phi^{TR}\) is the new contribution due to the translation-rotational (TR) coupling. The TR coupling parameters are obtained on the lines of Sahu and Mahanti [13,14]. The TR coupling effects have been introduced through the second order elastic constants (SOECs) derived from the Eq. (1) and expressed as

\[
c^{TR}_{ij} (T) = c^{0}_{ij} + \Delta c^{TR}_{ij} (T) 
\]

(4)

with \(c^{0}_{ij}\) as their unrenormalized values and \(\Delta c^{TR}_{ij} (T)\) are the TR coupling contributions to the SOECs. For the calculation of \(\Delta c^{TR}_{ij} (T)\), we have used the expressions as given in ref. [15-17].

The calculated results of the second order elastic constants \((C_{11}, C_{12}, C_{44})\) of \((\text{NaCN})_x(\text{NaCl})_{1-x}\) are presented and discussed below.

3. Results & Discussion

The model parameters \((b, \rho, f(r))\) have been evaluated by applying equilibrium condition [2] and the input data \((r_0, B)\), vdW coefficients and TR-coupling parameters. We have obtained the mixed values of \(r_0\) and \(B\) for given compositions and temperature by applying the well known Vegard’s law [18] and thermodynamics, from the data available for pure NaCN\([r_0(Å)=2.95, B(10^{11} \text{dyne/cm}^2)=1.80)\] and NaCl\([r_0(Å)=2.82, B(10^{11} \text{dyne/cm}^2)=2.37)]\) [21,22]. The model parameters thus obtained are depicted in Table I. The first and second order space derivatives of \(f(r)\) have been evaluated from the relation [23]

\[
f(r) = f_0 \exp (-r/\rho) 
\]

(5)
Using the expressions given in our earlier paper [8], we have calculated the SOECs of (NaCN)$_x$(NaCl)$_{1-x}$ as the function of temperature. While computing these elastic constants, the contributions from the translation-rotation coupling are taken into account. The $C_{11}$, $C_{12}$ and $C_{44}$ obtained from ETSM are plotted as a function of temperature and displayed in figures 1-3. Figure 1 reveals that $C_{11}$ shows quasilinear behaviour for all the compositions while figure 2 shows the decrease in $C_{12}$ with increasing temperature.

**Figure 1.** Variation of $C_{11}$ with temperature

**Figure 2.** Variation of $C_{12}$ with temperature

**Figure 3.** Variation of $C_{44}$ with temperature. Black dots show the experimental data [4].

| Properties | 0.20 | 0.30 | 0.59 |
|------------|------|------|------|
| $\phi$ (KJ/Mol) | -750.68 | -748.05 | -740.93 |
| $\beta$ ($10^{11}$dyne.cm$^{-2}$) | 6.4619 | 6.5403 | 6.5013 |
| $\nu_0$ (THz) | 4.8608 | 4.8402 | 4.8820 |
| $b$ ($10^{12}$erg) | 0.477 | 0.481 | 0.485 |
| $\theta_D$ (K) | 232.36 | 230.28 | 234.34 |
| $\rho$ (Å) | 0.303 | 0.308 | 0.313 |
| $\alpha_c/(10^3 J)$ | 4.8728 | 4.9729 | 5.1801 |
| $\theta_D$ (K) | 232.36 | 230.28 | 234.34 |
| $f (r)$ | -0.016 | -0.017 | -0.019 |
| $\gamma$ | 2.2218 | 2.1773 | 2.1089 |
In orientationally disordered mixed crystals sheer elastic constant $C_{44}$ plays a significant role in explaining the behaviour of the crystal at particular temperature and concentration. Figure 3 clearly demonstrates that there is a considerable elastic softening seen in the system with the low concentration of CN$^-$ ions. This deviation can be attributed to the difference in ionic radii of CN$^-$ and Cl$^-$. It is interesting to note that softening exhibited by $C_{44}$ might be due to the strength of the coupling of the CN$^-$ ions. The temperature dependence of $C_{44}$ reflects the collective behaviour of the coupled impurity. For all the concentrations it softens down to a critical temperature, on further cooling hardening is observed. The critical temperatures for $x=0.20$, 0.30 and 0.59 are 120K, 140K and 150K respectively. This subsequent hardening of $C_{44}$ followed by softening is indicative of forming the glass state. The trend shown in the figure 3 matches very well with their Brillouin scattering measured data [4]. These results are interpreted on the basis of Landau theory of the phase transition with a linear coupling between the strain and the order parameter.

We have computed the cohesive energy given by equation (1) to test the validity of our model. It has been noticed from the values of the cohesive energy that the contribution of short range (SR) interaction is less than 10% of the total cohesive energy. This feature is indicative of the fact that the major contribution to the cohesion is due to the Coulomb interaction along with the supplementary contribution from TR-coupling. Here, it is noteworthy that the negative values of cohesive energies show the stability of this compound. We have also computed the compressibility ($\beta$), molecular force constant (f), Reststrahlen frequency ($\nu_0$), Debye temperature($\theta_D$), Gruneisen parameter ($\gamma$) and the ratio of volume expansion coefficient to volume specific heat ($\alpha_v/c_v$) at 300K, using their expressions given in our earlier paper [10] and listed the values in Table 1. These calculated values could not be compared due to lack of experimental data on them.

4. Conclusion

It can be concluded from the above discussion that the agreement between the experimental [4] and our theoretical results for elastic properties are reasonably good. This is not unexpected as ETSM framework is capable to account for the effects of the Cauchy violations (elastic properties), the polarizibilities (dielectric properties) and the TR coupling for the present system of orientationally disordered materials. Here, some of the results are at present of only academic interest but they will certainly work as a guide to the experimental workers in future.

Acknowledgement One of us Alpana Tiwari is thankful to University Grants Commission, New Delhi for the award of teacher research fellowship.

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