

Thermoelastic Behavior of Orientationally Disordered Ammonium Iodide

Alpana Tiwari

Maharani Laxmibai Government Girls P.G.College, Bhopal-462002 .India.

Abstract We have investigated the second order elastic constants of orientationally disordered NH_4I using an Extended Three Body Force Shell Model (ETSM) in the temperature range $250\text{K} \leq T \leq 350\text{K}$. The second order elastic constants (C_{11} , C_{12} and C_{44}) obtained by us show an anomalous behaviour with the variation of temperature. The variation of the second order elastic constants with temperature is in good agreement with the measured data.

Introduction

The thorough studies of the lattice properties of ionic solids have long been the region of interest for experimental and theoretical workers. Their simple structures and versatile applications generate the ideas for the understanding of the complex systems. Pure ammonium halides have always been the systems of interest for the experimental and theoretical investigators due to their polymorphism and orientational disorder introduced by the fast reorienting ammonium ion. An enormous amount of experimental and theoretical efforts have been devoted to study the various aspects of lattice properties of these materials. Ammonium iodide undergoes order-disorder transition (λ -transition) at $T_\lambda=231\text{K}$. At room temperature NH_4I exhibits NaCl-type fcc structure with space group $\text{Fm}\bar{3}\text{m}$. This transforms to $\text{Pm}\bar{3}\text{m}$ structure at about 257K . It is interesting to note that its stability range of CsCl type structure is relatively small, narrowed down to 25K [1-11]. 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_4I . Although the average symmetry of these crystals is cubic, but the orientational disorder locally breaks the cubic symmetry and anomalous softening of shear elastic constant C_{44} is observed [12].

This is an attempt to investigate the lattice static and dynamic properties of ammonium iodide in their orientationally disordered phase by taking into account the effect of translation-rotation (TR) coupling, which has turned out to be responsible for important effects in orientationally disordered materials. Singh and Gaur [13] incorporated the effects of TR coupling in the framework of a realistic three body force shell model (TSM) [14] to develop ETSM. It has been applied successfully by Gaur *et.al.* and others 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 [15-23]. The present theoretical approach is motivated from the versatility and considerable success of the ETSM, we have thought it pertinent to apply this ETSM to investigate the temperature dependence of the second order elastic constants of NH_4I . 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.

Formulation of ETSM

The interionic interaction potential of ETSM has been expressed as [13]-

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

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) [14]. 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 [24]. The fifth term is the Hafemeister and Flygare (HF) type short-range (SR) overlap repulsion [25] 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 [26, 27]. The expressions for TR coupling coefficients are given a little later. Here, b and ρ are the hardness and range parameter.

The TR coupling effects have been introduced through the second order elastic constants (SOECs) derived from the Eq. (1) and expressed as [13]-

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

with C_{ij}^0 as their unrenormalized values and δC_{ij}^{TR} are the TR coupling contributions to the SOECs. For the calculation of δC_{ij}^{TR} , we have used the expressions as given in ref. [28].

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

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

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

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

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

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 [29] and Sahu and Mahanti [30] as-

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

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

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

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. [30]. 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 [30] and the method [21]. 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_4I are presented and discussed below.

Results and Discussion

The values of the vdW coefficients (c_{kk} and d_{kk}) and their overall coefficients (C , D) for NH_4I have been evaluated by us using their expressions reported elsewhere [24]. Their estimated values are listed in Table 1. The model parameters ($b, \rho, f(r)$) have been evaluated from the equilibrium condition and using the input data (r_0 , 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 [31].

$$f(r) = f_0 \exp(-r/\rho) \quad (10)$$

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. Experimentally determined values of r_0 have been used [32].

Table 1: The van der Waals coefficients [c_{kk} and d_{kk} in the units of 10^{-60} erg/cm⁶ and 10^{-76} erg/cm⁸, respectively] of NH_4I and TR coupling parameters of NH_4I at 300K.

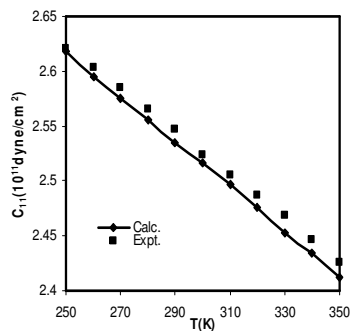
vdW coefficients	NH_4I	TR-coupling Parameters	Values
c_{kk}	101.07	$A_R [10^{-4}$ dyn]	-0.080
$c_{kk'}$	336.71	$B_R [10^{-4}$ dyn]	0.798
$c_{k'k'}$	1123.0		

d_{kk}	785.02	$A_Q [10^{-4} \text{dyn}]$	0.221
$d_{kk'}$	244.10	$B_Q [10^{-4} \text{dyn}]$	-0.187
$d_{k'k'}$	76.00		
C	5101		
D	2927		

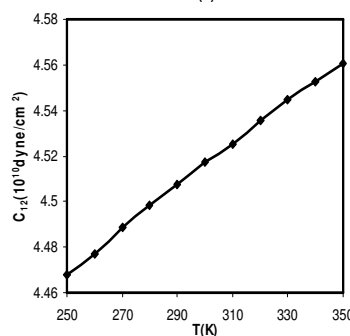
Using the expressions given in [21], we have computed the values of the second order elastic constants (C_{11} , C_{12} and C_{44}) as a function of temperature $250\text{K} \leq T \leq 350\text{K}$. While computing these elastic constants, the contributions from the translational-rotational coupling are taken into account. The values of the second order elastic constants obtained from ETSM have been plotted as a function of

Table 2: The input data [r_0 , B (10^{10}dyn.cm^2)] and the model parameters for NH_4I .temperature and concentration (x) as displayed in fig.1.

$r_0 [\text{\AA}]$	Model parameters		
	$b [10^{12} \text{erg}]$	$\rho [\text{\AA}]$	$f [r]$
3.620	4.227	4.997	-7.815

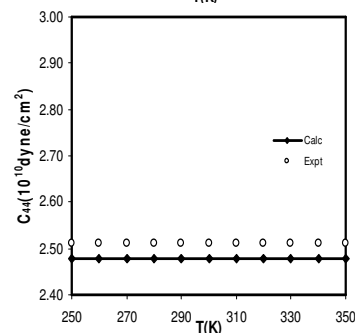


[a]



[b]

Fig 1: Variation of second order elastic constants of NH_4I as a function of temperature.



[c]

It can be seen in fig.1a that C_{11} shows decreasing trend with increase in temperature and in fig.1b that C_{12} shows increasing trend with increase in temperature this feature is usual behaviour of the rocksalt structure materials. Whereas C_{44} (fig.1c) becomes almost constant for the entire temperature range. It is totally softened. It has been observed that the agreement improve quite significantly in all the cases by the inclusion of TR coupling. An anomalous softening of the shear elastic constant C_{44} has is due to the TR coupling of the quadrupole moments of the NH_4^+ ions with the shear modes. Our results for C_{11} and C_{44} are fairly in agreement with Ultrasonic experiment data [33]. It is interesting to note that the observed anomalous softening occurring in C_{44} is reproduced well by the ETSM results. It is interesting to note that the Cauchy relation ($C_{12}=C_{44}$) which are believed to be fulfilled by the alkali halides are violated by all the ammonium halides.

Conclusion

The present ETSM has been applied, probably for the first time, to explore the elastic properties of the orientationally disordered ammonium iodide. 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 polarizabilities (dielectric properties) and the TR coupling effects for the present system of orientationally disordered materials. A detailed description of the theoretical investigation of the second order elastic constants of the orientationally disordered ammonium iodide crystals has been presented in this paper.

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