ORIGINAL PAPER

UNIFIED STUDY OF ND_4I BY LATTICE DYNAMICAL APPROACH

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Abstract. *The unique features and physical properties of the ND_4I has given an increased interest in the study of their lattice dynamics by using the present model modified three-body force shell model (MTSM), which includes van der Waals interactions, three-body interactions and second neighbour repulsive interactions into the framework of rigid shell model (RSM). Due to availability of experimental results on dispersion relations, combined density of states (CDS), Debye temperature and elastic property of ND_4I has motivated to the author for the theoretical lattice dynamical study of ND_4I.A Dispersion curve for translational phonons propagating in the high-symmetry directions of ND_4I was determined by the elastic neutron scattering from single crystals. The discrepancies like observed phonon energies with general repulsive short-range forces, second-neighbors discrepancies in the PDC and some other anomalies, we have successfully explained through the present model. The merits of these models have performed with a critical comparison of theoretical and experimental results.*

Keyword*: Lattice vibrational properties, dispersion relation, CDS curve, Raman spectra & elastic properties.*

1. INTRODUCTION

In recent years several workers [I-6] have been thoroughly investigated the dynamical properties of ammonium halide crystals. Ammonium ions are orientationally disordered in the phases which exhibit cubic NaCl and CsC1-type structures, respectively. ND_4I has the NaCl-structure at the room temperature in which the ND_4^+ ions are oriented at random in sites with six fold coordination shown in fig.1.Crystal neutron diffraction study of ND_4I indicates that the average ammonium-ion orientations are such that the proton density has broad maxima in the [100] directions [7].The partial investigations are possible in sodium chloride phases because the structural and dynamical disorder make the studies more difficult. However, deuterated ammonium iodide with the sodium chloride structure in terms of a rigid shell model (RSM) and a breathing shell model (BSM).has been studied neutron-spectroscopically by Vegelatos et al. [7]. A deformation dipole model (DDM) has also been used to account for these curves by Goel et a1.[8]. Scrutiny of these studies reveals that the success achieved with the RSM and DDM is only moderately successful.

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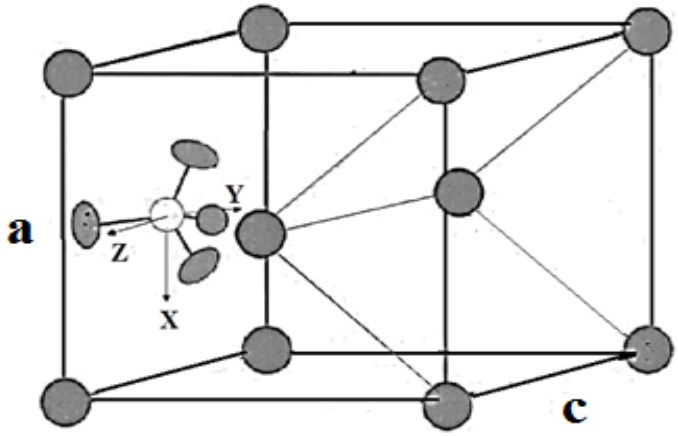

Figure 1. ND_4I crystal structure.

The agreement with the BSM is, however, excellent but the model parameters are many in number and their values are fitted. In order to obtain improved agreement but without applying any fitting procedure, the present author has applied the extended three-body force shell model (ETSM) developed by Singh and Gupta [9] and successfully applied to many ionic crystals of rock salt [l0] structures. The potential of present model has been also used to compute several other properties of ND_4I in order to give a more complete description of its behavior.

2. THEORY

The aim of this section is, therefore, to give a detailed account of the essential formalism of the present lattice dynamical model. Thus, the inclusion of VWI, TBI effects in RSM will employ the Hietler-London and the free-electron approximations. The interaction system of the present model thus consists of the long-range Coulomb and three-body interactions and the overlap repulsion operative upto the second neighbour ions. Looking to the adequacy of this interaction system, the present model (MTSM) may hopefully be regarded as successful model for the dynamical and dielectric descriptions of the ND_4I. The general formalism of MTSM can be derived from the crystal potential whose relevant expression per unit cell is given by

$$\Phi = \Phi^{C} + \Phi^{R} + \Phi^{TBI} + \Phi^{VWI} \tag{1}$$

where Φ^{C} is long-range Coulomb interaction potentia1.The analytical expressions by the inverse and exponential power laws for the repulsive energy are given as

$$\Phi^{R}(r_{ij}) = a r_{ij}^{\,n} \text{ (Born Potential)} \quad , \quad \Phi^{R}(r_{ij}) = b \exp.(-r_{ij}/\rho) \quad \text{(B-M) Potential)}$$

where, a (or b) and η(orρ) are the Born exponents called the strength and hardness parameters, respectively. Φ^{R} is short-range overlap repulsion potential. Third term Φ^{TBI} long-range TBI interaction potential expressed as

$$\Phi^{TBI} = \alpha_m \frac{Z^2 e^2}{r_0}\left[\frac{2n}{Z} f(r)_0\right]$$

where, α_m and r_0 are Madelung constant and equilibrium nearest neighbors distance the term $f(r)_0$ is the equilibrium electron wave-functions. Since we consider only one ion to be polarizable and deformable, the basic equations of Singh and Verma's [11] model are modified. The secular determinant equation is given by

$$\left|\underline{D}(\vec{q}) - \omega^2 \underline{M I}\right| = 0 \tag{2}$$

Here $\underline{\vec{D}}$ *(q)* is the (6 x 6) dynamical matrix for Rigid Shell model expressed as: The dipole-dipole (VWI) energy up to second neighbour is expressed as:

$$\Phi_{dd}^{VWI}(r) = -S_V \left| \frac{C_{++} + C_{--}}{6r^6} \right| = \Phi^V(r) \tag{3}$$

where, S_v is lattice sum and the constants C_{++} and C_{--} are the positive-positive and negative-negative ion pairs, respectively. By use of the secular equation (2) the expressions for elastic constants can derived and given as:

$$C_{11} = \frac{e^2}{4r_0^4}\left[-5.112 Z_m^{\ 2} + A_{12} + \frac{1}{2}(A_{11} + A_{22}) + \frac{1}{2}(B_{11} + B_{22}) + 9.3204\ \xi'^2\right] \tag{4}$$

$$C_{12} = \frac{e^2}{4r_0^4}\left[0.226 Z_m^{\ 2} - B_{12} + \frac{1}{4}(A_{11} + A_{22}) - \frac{5}{4}(B_{11} + B_{22}) + 9.3204\ \xi'^2\right] \tag{5}$$

$$C_{44} = \frac{e^2}{4r_0^4}\left[2.556 Z_m^{\ 2} + B_{12} + \frac{1}{4}(A_{11} + A_{22}) + \frac{3}{4}(B_{11} + B_{22})\right] \tag{6}$$

at equilibrium condition $[(d\Phi/dr)_0 = 0]$ we obtain

$$B_{11} + B_{22} + 2B_{12} = -0.6786\ Z_m^{\ 2} \tag{7}$$

where

$$Z_m^2 = Z^2\left(1 + \frac{16}{Z} f_0\right) \qquad \text{and} \qquad \xi'^2 = Z r_0 f_0' \tag{8}$$

By solving the secular equation (2) along [q00] direction and subjecting the short and long-range coupling coefficients to the long-wavelength limit ($\vec{q} \to 0$), two distinct optical vibration frequencies are obtained as

$$\left(\mu\omega_L^2\right)_{q=0} = R_0 + \frac{(Z'e)^2}{v f_L} \cdot \frac{8\pi}{3}(\xi^2 + 6\xi^2) \tag{9}$$

$$\left(\mu\omega_T^2\right)_{q=0} = R_0 - \frac{(Z'e)^2}{v f_T} \cdot \frac{4\pi}{3}(\xi^2) \tag{10}$$

By solving the dynamical matrix along [.5, .5, .5] directions at L-point modified expression for $\omega_{LO}(L)$, $\omega_{TO}(L)$, $\omega_{LA}(L)$ and $\omega_{TA}(L)$ are as follows:

$$m_1\omega_{LA}^2(L) = R_0 + \frac{Z^2e^2}{V}(2A_{11} + B_{11}) - \frac{Z^2e^2d_1^2}{\alpha_1} + \frac{Z^2e^2}{V}\,C'_{1L}(Z_m + d_1)^2\,[1 + \frac{\alpha_1}{V}\,C'_{1L}]^{-1} \tag{11}$$

$$m_2\omega_{LO}^2(L) = R_0 + \frac{Z^2e^2}{V}(2A_{22} + B_{22}) - \frac{Z^2e^2d_2^2}{\alpha_2} + \frac{Z^2e^2}{V}\,C'_{1L}(Z_m - d_2)^2\,[1 + \frac{\alpha_2}{V}\,C'_{1L}]^{-1} \tag{12}$$

$$m_1\omega_{TA}^2(L) = R_0 + \frac{Z^2e^2}{2V}(A_{11} + 5B_{11}) - \frac{Z^2e^2d_1^2}{\alpha_1} + \left(\frac{Z^2e^2}{V}\right)C'_{1T}(Z_m + d_1)^2\,[1 + \frac{\alpha_1}{V}\,C'_{1T}]^{-1} \tag{13}$$

$$m_2\omega_{TO}^2(L) = R_0 + \frac{Z^2e^2}{2V}(A_{22} + B_{22}) - \frac{Z^2e^2d_2^2}{\alpha_2} + \left(\frac{Z^2e^2}{V}\right)C'_{1T}(Z_m - d_2)^2\,[1 + \frac{\alpha_2}{V}\,C'_{1T}]^{-1} \tag{14}$$

To determine the phonon density of states for each polarization is given by

$$g(\omega)=dN/d\omega= N\int_{BZ}\sum_j \delta[\omega-\omega_j(q)]dq =(VK^2/2\pi^2).dK/d\omega \tag{15}$$

and

$$N = (L/2\pi)^3\,(4\pi K^3/3)$$

where N as a normalization, K is wave vector and L^3=V. The value of $g(\omega)d\omega$ is the ratio of the number of eigen states in the frequency interval $(\omega, \omega+d\omega)$ to the total number of eigen states $\omega_j(q)$ is phonon frequency of the jth normal mode of the phonon wave vector q such that $\int g(\omega)d\omega = 1$.

3. COMPUTATIONS

The calculations on the ND_4I have been performed with our model MTSM described using the 12-parameters [Z_m, r_of_o', A_{11}, A_{22}, A_{12}, B_{11}, B_{22}, B_{12}, d_1, d_2, Y_1 and Y_2] of the model have been determined from the knowledge of experimental values of the equilibrium interatomic separation (r_o), the elastic constants (C_{11}, C_{12} and C_{44}), the vibrational frequencies [$\nu_{LO}(\Gamma)$, $\nu_{TO}(\Gamma)$, $\nu_{LO}(L)$, $\nu_{TO}(L)$, $\nu_{LA}(L)$ and $\nu_{TA}(L)$], the electronic polarizabilities (α_1, α_2) parameters are given in table -1. These model parameters are used to compute the complete phonon spectra for the allowed 48-nonequivalent wave vectors in the first Brillouin zone.

Table 1. Input data and Model parameters for ND_4I.

Input data	ND_4I	Parameters	ND_4I
	Values		Values
C_{11} (10^{11} dyn cm^{-2})	3.460[7]	Z_m	0.6545
C_{12} (10^{11} dyn cm^{-2})	0.428[8]	$r_o f_o'$	0.14014
C_{44} (10^{11} dyn cm^{-2})	0.240[8]	A_{12}	11.462
$\nu_{LO}(\Gamma)$ (THz)	4.900[7]	B_{12}	1.4859
$\nu_{TO}(\Gamma)$(THz)	3.800[7]	A_{11}	–5.6246
$\nu_{LO}(L)$ (THz)	3.950[#]	B_{11}	–2.9862
$\nu_{TO}(L)$ (THz)	4.450[#]	A_{22}	22.7541
$\nu_{LA}(L)$ (THz)	1.870[7]	B_{22}	9.74661
$\nu_{TA}(L)$ (THz)	1.480[8]	d_1	0.10457
r_0 (10^{-8} cm)	3.620[7]	d_2	0.24389
α_1 (10^{-24} cm^3)	2.485[8]	Y_1	–2.73960
α_2 (10^{-24} cm^3)	6.294[8]	Y_2	–4.98719

 # extrapolated values

The frequencies along the symmetry directions have been plotted against the reduced wave-vector to obtain the phonon dispersion curves (PDC) in Figs 2-4. These curves have been compared with those measured by means of the coherent inelastic neutron scattering technique. For this purpose, the specific heat C_v has been computed at different temperatures using Blackmann's [12] sampling technique. A Dispersion curve for translational phonons propagating in the high-symmetry directions of ND_4I was determined by the elastic neutron scattering from single crystals. The observed phonon energies were fitted to RSM and BSM (breathing shell model) with general repulsive short-range forces by Vagelatos et al**. [7]**. Thereafter S.C.Goel [13] used the DDM (deformation dipole model) incorporating general short range forces out to second-neighbours and tried to explain various discrepancies in the PDC of ND_4I.

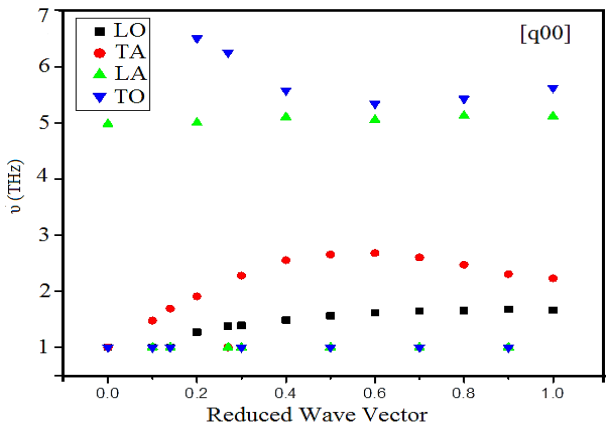

Figure 2. Phonon dispersion curve for ND_4I in [q00] direction.

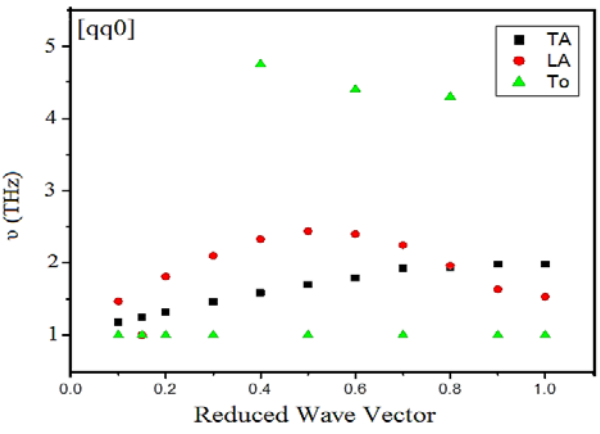

Figure 3. Phonon dispersion curve for ND_4I in [qq0] direction.

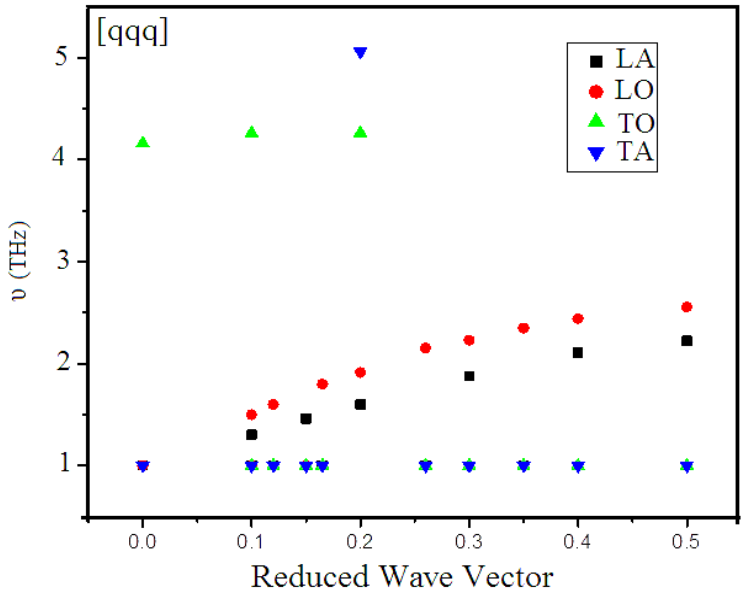

Figure 4. Phonon dispersion curve for ND_4I in [qqq] direction.

It should also be noted that the ND_4I dispersion curves are qualitatively similar to the dispersion curves of the alkali halides with the NaCl structure [14, 15] or one can say very similar to KI [15] and the effective radii of the two ions are quite comparable for K^+ and for ND_4^+. Perry and Lowndes [16] calculated the energy for the LO mode at q = 0 .The phonon spectra have been used to calculate the combined density of states (CDS), $N(\nu_j + \nu_{j'})$ corresponding to the sum modes $(\nu_j + \nu_{j'})$ and energy in mev, following the procedure of *Smart et al.* [17]. A histogram between $N(\nu_j + \nu_{j'})$ or g(υ) and $(\nu_j + \nu_{j'})$ or energy in mev has been plotted and smoothed out to obtain the CDS curves in fig.-4. These curves show well defined peaks which correspond to two phonon infrared absorption and Raman scattering peaks.

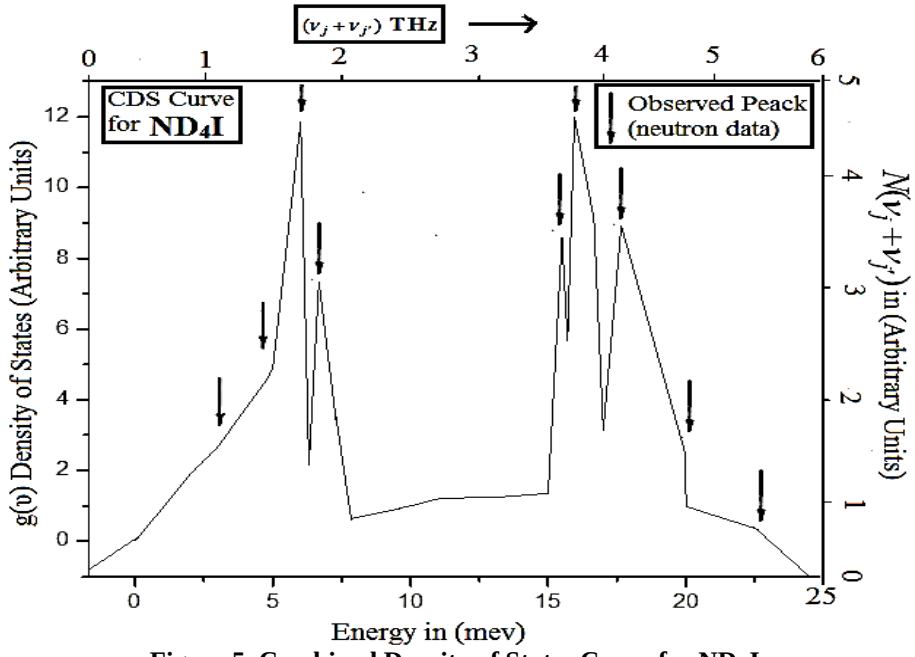

Figure 5. Combined Density of States Curve for ND_4I.

These CDS peaks have been compared with the available observed peaks. Since the division of the Brillouin zone in the present case is somewhat coarse, therefore, the fine structure of the infra-red and Raman shifts may not be reproduced completely. In order to interpret them, the critical point analysis has been used following the method prescribed by Burstein et al. [18]. A successful interpretation of these spectra has provided the next best test of any model for higher range of frequency spectra.

4. RESULTS

By solving the secular equation for the six-vibration frequencies corresponding to each phonon wave vector (q) along the principal symmetry directions [q,o,o], [q,q,o] and [q,q,q] phonon dispersion relations are obtained. The (PDC) have been obtained by plotting these vibrational frequencies (ω) against the reduced wave vector (q) and displayed in fig.- 2,3 and 4 for ND_4I respectively. Three-body interactions (TBI) influence longitudinal branches more than the transverse branches. However, the inclusion of VWI with three-body interactions (TBI) have influenced both LO and TO branches much more in crystal, which has also improved the agreement between theoretical and experimental results, significantly. Due to absence of the measured data on two phonon Raman spectra for ND_4I, we have used the peaks assigned from the observed neutron data on phonon frequencies [7] for critical points. As the Raman spectra are sensitive to the higher frequency side of the phonon spectra and the specific heats are sensitive to its lower side. The results of these investigations from combined density of states (CDS) approach depicted in fig.-5.It is hoped that more detailed investigations will provide a better understanding of the dynamics of such highly disordered crystals, which include broad groups of complex inorganic solids and organic plastic crystals.

5. CONCLUSION

In view of the overall achievements described above, it may be concluded that the modifications introduced by the TBI and VWI in the framework of RSM is very much important for the crystal under considerations. In the (PDC) of ND_4I, our results are in good agreement with the experimental points measured by Vagelatos et al. **[7]**. However, some discrepancies are present in the [q00] direction near the zone boundary particularly, for LO and LA modes. But as compared to the breathing shell model (BSM), our results are more close to the experimental data. This is the great achievement of our model. In view of the overall successes, it may be concluded that our MTSM provides a good agreement which is certainly better than rigid shell model. In the case of ND_4I it is better than RSM and BSM by Vagelatos et al. [7] and deformation dipole model used by Goel et al. [8].The present model has been already successfully applied for calculating the elastic constant, dispersion relation, two phonon Raman/IR spectra and Debye temperatures variation by different researchers [19-31] for alkali halides and semiconducting materials.

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