



Lattice Dynamics of ND₄Cl and TlCl using Vander Walls and Three Body Interactions

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ABSTRACT

Complete lattice dynamical behaviour of ND₄Cl as well TlCl have been studied with the help of new phenomenological model, van der Waals three-body force shell model (VTSM), incorporating the effect of van der Waals interactions (vWI) along with long-range screened Coulomb and three-body interactions (TBI) in the frame work of rigid shell model where short range interactions are operative up to the second neighbour in these halides. This new model presents an excellent agreement with available experimental data and a vast improvement for the theoretical available data for phonon dispersion curve (PDCs) for [q00], [qq0] and [qqq] directions in case, variation of Debye Temperature Curve and combined density state (CDS) curve and anharmonic properties such as third and fourth order elastic constants and pressure derivative of second order elastic constants. It is observed this new model presents an excellent agreement with available experimental data and a vast improvement for the theoretical available data for phonon dispersion curve (PDC), variation of Debye Temperature Curve and combined density state (CDS) curve and anharmonic properties such as third and fourth order elastic constants and pressure derivative of second order elastic constants. It is believed that incorporation of van der Waals interaction enables us to produce a vast study of lattice dynamical and other derivable properties. A good agreement has been obtained between experimental and VTSM values for dependant properties.

Keywords: Lattice Dynamics, Phonon Dispersion Curves, Debye Temperature, Two Phonon IR and Raman Spectra, Anharmonic Elastic Constants, Combined Density of States.

1. INTRODUCTION

The lattice dynamical study of monovalent heavier metal halides (such as thallium and ammonium halides especially ND₄Cl at 85K & TlCl at 100K) crystallizing into CsCl-type structured solids having physical, thermal and anharmonic properties with application of various physical conditions and using several techniques, both theoretically and experimentally, have received considerable interest in recent years. At ambient condition, these halides of heavy metals (as thallium and ammonium halides especially ND₄Cl at 85K & TlCl at 100K) crystallizes eight-fold coordinated CsCl-type structure with space group symmetry Pm3m (221) whose Brillion zone is simple cubic. (Here TlCl is called indirect band-gap ionic crystal). The survey of the phonon dynamical behaviour of these halides on elastic constants¹⁻⁴, dielectric constants^{4,5,6,7,8,9}, phonon dispersion curves^{10,11,12,13}, Debye temperature variations¹⁴, two phonon IR and Raman spectra [15], third and fourth order elastic constants and their pressure derivatives¹⁶ and their interpretations by means of theoretical models^{12,18,19,20,21,22} with moderate success, has motivated the present author to the basic need for a lattice dynamical model for the satisfactory description of their interesting properties. Kellermann²³ using rigid ion model (RIM) by considering the ions of the crystal to be rigid, undeformable and unpolarizable spherical particles, fails to interpret the dynamical, optical and elastic properties of these crystals. At the next stage in progress of lattice dynamics, deformation dipole model (DDM) of Karo and Hardy²⁴, rigid shell model (RSM) of Dick and Overhauser²⁵ and Woods et. al.²⁶ by two different groups of workers. The DDM allows only the redistribution of charges in deformed electron cloud while the shell model considers the relative displacement. So both effects (deformation and displacement) are present in ionic crystals. A general way to remove this deficiency is to include the deformation of electron shells in the framework of RSM. The most prominent amongst them are breathing shell model (BSM) of Schroder²⁷, the deformable shell model [DSM] of Basu and Sengupta²⁸ and three-body force shell model (TSM) of Verma and Singh²⁹.

Further, Singh et al. used extended three-body-force shell model (ETSM) which is an amalgamation of RSM and DDM. ETSM contains (i) the two-body long-range coulomb interaction and short-range repulsion effective up to the second-neighbour ions, (ii) The long-range three-body forces and (iii) the dipole character of the constituent ions. Despite of these successes, ETSM has revealed some features which do not have much physical significance. In our earlier papers³⁰⁻³⁵ we investigated the phonon dynamical behaviour of CsCl at various temperature with the application of our most realistic model, van der Waals three body force shell model (VTSM) for the lattice dynamics of various CsCl-structured crystals (as TlCl & ND₄Cl at 85K) developed by us introducing the effect of van der Waals interactions (VWI) and three body interactions (TBI) in the framework of RSM, where the short-range interactions have been considered up to the second neighbours.

Furthermore, here in this paper, we are extending our study for the crystals such as TlCl & ND₄Cl of the same group (CsCl structured solids) to check the applicability to produce complete lattice dynamics and other derivable properties of CsCl crystals by application of various physical parameters with the help of our new developed model van der Waals Three body force shell model (VTSM).

2. THEORY AND METHOD OF COMPUTATION

Inclusion of the effects of van der Waals interactions and three-body interactions in the frame work of both ions Polarizable rigid shell model (RSM), the general formalism of present model (VTSM) can be derived from the crystal potential whose relevant expression per unit cell is given by

$$\Phi(\mathbf{r}) = \Phi_{LR}(\mathbf{r}) + \Phi_{SR}(\mathbf{r}) \quad (1)$$

Where the first term $\Phi_{LR}(\mathbf{r})$ represents the long-range Coulomb and three body interaction (TBI) energies expressed by

$$\Phi_{LR}(\mathbf{r}) = \sum_{ij} \frac{Z_i Z_j e^2}{r_{ij}} \left\{ 1 + \sum_{ijk} f(r_{ik}) \right\} = \frac{\alpha_M Z^2 e^2}{r} \left\{ 1 + \frac{16}{Z} f(r) \right\} \quad (2)$$

where Z is the ionic charge parameter of i^{th} ion, r_{ij} separation between i^{th} and j^{th} ion, $f(r_{ik})$ is the three body force parameter dependent on nearest-neighbour separation r_{ik} and is a measure of ion size difference³⁶ and α_M is Madelung constant (-1.762670). The second term in (1) is short-range energy contributions from overlap repulsion and van der Waals interactions (vdWI) expressed as³⁷

$$\Phi_{SR}(\mathbf{r}) = Nb \sum_{i,j=1}^2 \beta_{ij} \exp \left[\frac{r_i + r_j - r_{ij}}{\rho} \right] + \sum_{ij} \frac{c_{ij}}{r_{ij}^6} + \sum_{ij} \frac{d_{ij}}{r_{ij}^8} \quad (3)$$

Where the first term is the Hafemeister and Flygare (HF) potential³⁸. The second term and third term represent the energy due to vdW dipole-dipole (d-d) and dipole-quadrupole (d-q) interactions, respectively. By using the crystal energy expression given in equation (1), the equations of motion of two cores and two shells can be written as:

$$\omega^2 \underline{M} \underline{U} = (\underline{R} + \underline{Z}_m \underline{C}' \underline{Z}_m) \underline{U} + (\underline{T} + \underline{Z}_m \underline{C}' \underline{Y}_m) \underline{W} \quad (4)$$

$$0 = (\underline{T}^T + \underline{Y}_m \underline{C}' \underline{Z}_m) \underline{U} + (\underline{S} + \underline{K} + \underline{Y}_m \underline{C}' \underline{Y}_m) \underline{W} \quad (5)$$

Here \underline{U} and \underline{W} are vectors describing the ionic displacements and deformations, respectively. \underline{Z}_m and \underline{Y}_m are diagonal matrices of modified ionic charges and shell charges, respectively. The elements of matrix \underline{Z}_m consists of the parameter Z_m thereby giving the modified ionic charge.

$$Z_m = Z\xi = \pm Z \sqrt{1 + (12/Z) f_0} \quad (6)$$

The elimination of \underline{W} from eqns. (6) and (7) leads to the secular determinant:

$$\left| \underline{D}(\vec{q}) - \omega^2 \underline{M} \underline{I} \right| = 0 \quad (7)$$

For the frequency determination. Here $\underline{D}(\vec{q})$ is the (6×6) dynamical matrix given by

$$\underline{D}(\vec{q}) = (\underline{R}^l + \underline{Z}_m \underline{C}' \underline{Z}_m) + (\underline{T} + \underline{Z}_m \underline{C}' \underline{Y}_m) \times (\underline{S} + \underline{K} + \underline{Y}_m \underline{C}' \underline{Y}_m)^{-1} (\underline{T}^T + \underline{Y}_m \underline{C}' \underline{Z}_m) \quad (8)$$

The numbers of adjustable parameters have been largely reduced by considering all the short-range interactions to act only through the shells. The expressions derived for elastic constants from eqn. (7) corresponding to VTSM are obtained as

$$C_{11} = \frac{e^2}{4a^4} \left[0.7010Z_m^2 + \frac{A_{12} + 2B_{12}}{6} + \frac{A_{11} + A_{22}}{4} + 5.4283 \xi'^2 \right] \quad (9)$$

$$C_{12} = \frac{e^2}{4a^4} \left[-0.6898Z_m^2 + \frac{A_{12} - 4B_{12}}{6} - \frac{B_{11} + B_{22}}{4} + 5.4283 \xi'^2 \right] \quad (10)$$

$$C_{44} = \frac{e^2}{4a^4} \left[-0.3505Z_m^2 + \frac{A_{12} + 2B_{12}}{6} + \frac{B_{11} + B_{22}}{4} \right] \quad (11)$$

In view of the equilibrium condition $[(d\Phi/dr)_0=0]$ we obtain

$$B_{11} + 2B_{12} + B_{22} = -0.6786Z_m^2 \quad (12)$$

Where $Z_m^2 = Z^2 \left(1 + \frac{16}{Z} Z_0\right)$ and $\xi^2 = Zr_0 f_0'$ (13)

$$f_0' = (df/dr)_{r=r_0}, \quad r_0 = a\sqrt{3} \text{ is the inter-ionic se}$$

The term f_0 is a function dependent on the overlap integrals of the electron wave functions and the subscript zero indicates the equilibrium value.

By solving the secular eqn. (7) along $[q, 0, 0]$ direction and subjecting the short and long-range coupling coefficients to the long-wavelength limit $q \rightarrow 0$, two distinct optical vibration frequencies are obtained as

$$(\mu\omega_L^2)_{q=0} = R_0' + \frac{(z/e)^2}{\nu f_L} \cdot \frac{8\pi}{3} (1 + 12Z_m^{-2} Zr_0 f_0') \quad (14)$$

$$(\mu\omega_T^2)_{q=0} = R_0' - \frac{(z/e)^2}{\nu f_T} \cdot \frac{4\pi}{3} \quad (15)$$

Where the abbreviations stand for

$$R_0' = R_0 - e^2 \left(\frac{d_1^2}{\alpha_1} + \frac{d_2^2}{\alpha_2} \right); \quad Z' = Z_m + d_1 - d_2 \quad (16)$$

$$f_L = 1 + \frac{8\pi\alpha}{3\nu} (1 + 12Z_m^{-2} Zr_0 f_0') \quad (17)$$

$$f_T = 1 - \frac{4\pi\alpha}{3\nu} \quad (18)$$

and $\alpha = \alpha_1 + \alpha_2$ (19)

Thus by using basic model parameters which have been determined by making use of the expressions for the three second order

elastic constants (C_{11}, C_{12}, C_{44}), on the line of our previous paper³²⁻³⁵ and the equilibrium condition, $\left(\frac{d\Phi(\mathbf{r})}{dr}\right)_{r=a\sqrt{3}} = 0$ with

inclusion of van der Waals interactions (VWI), the values of the input data (s) and model parameters of TlCl & ND₄Cl have been listed in table 1 & 2. The values of $A_{11}, A_{12}, A_{22}, B_{11}, B_{12}, B_{22}, C_{11}, C_{12}$ & C_{44} thus calculated from the knowledge of the values of various order of derivatives of $f(r_0)$ like $[f'(r_0), f''(r_0), f'''(r_0)]$ are also obtained by using functional form $(r_0) = f_0 e^{-\frac{r}{\rho}}$. Further, these twelve (12) model parameters and vdW coefficients calculated through *SKV Approach as suggested by Singh and Singh*, have been used to compute $[Z_m, r_0 f'(r_0), A_{11}, A_{12}, A_{22}, B_{11}, B_{12}, B_{22}, d_1, d_2, Y_1 \& Y_2]$ of the VTSM with knowledge of experimental values of the equilibrium inter-atomic separation (r_0), the vibration frequencies $\nu_{LO}(\Gamma), \nu_{TO}(\Gamma), \nu_{LO}(R), \nu_{LA}(R), \nu_{TO}(X)$ & $\nu_{TA}(X)$ and also with the values of $\alpha_1, \alpha_2, \epsilon_0, \epsilon_\infty$ for these halides. The model parameters of VTSM have been used to compute the phonon spectra for these halides (TlCl & ND₄Cl) for the allowed 56 non-equivalent wave vectors in the first Brillion zone at Computer Centre, Banaras Hindu University, and Varanasi. The frequencies along the symmetry directions have been plotted against the wave vector to obtain the phonon dispersion curves (PDCs) from present used model. These curves have been compared with those measured by means of the coherent inelastic neutron scattering technique.

Since the neutron scattering experiments provide us only very little data for the symmetry directions, we have studied the combined density of states (CDS) for the complete description of the frequencies for the Brillion zone.

The complete phonon spectra have been used to calculate the combined density of states (CDS), $N(v_j + v'_j)$ corresponding to the sum modes $(v_j + v'_j)$, following the procedure of Smart et al.¹⁵. A histogram between $N(v_j + v'_j)$ and $(v_j + v'_j)$ has been plotted and smoothed out to obtain the CDS curves. These curves show well defined peaks which correspond to two-phonon Raman scattering peaks. Since no observed data on two-phonon IR/Raman spectra are available, these CDS peaks have been compared with the assignments calculated by using our present theoretical data and neutron data. Furthermore, the division of the Brillion 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.³⁸. Besides above properties, the third order elastic constants (TOECs) and pressure derivatives of second order elastic constants (SOEC) and Cauchy discrepancy of third order elastic constant (TOEC) have also been calculated using the VTSM.

3. RESULTS

The input data and twelve (12) model parameters of our present model VTSM which have been calculated using above formalism are shown in Tables 1 & 2 along with available model parameters. These twelve model parameters have been used to compute the phonon dispersion curves of TlCl and ND₄Cl. The calculated phonon dispersion curves of TlCl and ND₄Cl have been traced with available experimental^{41, 13} and other theoretical data^{40, 42} in figure 1 and 2 respectively. The phonon dispersion curves (PDCs) for TlCl and ND₄Cl are almost similar but there are certain features which deserve special attention. Three-body interactions have influenced both LO and TO branches much more than the acoustic branches (LA and TA) in these halides. Another striking feature of the present model is noteworthy from the excellent reproduction of almost all the acoustic branches. The agreement achieved from the present model is also excellent for the longitudinal acoustic (LA) branch along [q q q] direction. This may be particularly because the zone centre vibration frequencies have been used as input data in the calculation of model parameters. A quantitative interpretation of the general features of PDC is also obvious from the present model when it predicts the gap between the acoustical and optical branches similar to the forbidden gap between the valence and the conduction band. The agreement between our computed phonon spectra and experimental data is excellent in Tables 3 and 4 for TlCl and ND₄Cl. Our model VTSM has successfully explained the phonon anomalies even along (q, 0, 0), (q, q, 0) and (q, q, q) directions.

Table. 1
Input Data and Model Parameters for TlCl [C_{ij} (in 10^{12} dyne / cm²),
 ν (in THz), r_0 (in 10^{-8} cm), α_i (in 10^{-24} cm³)

Input Data			Model Parameters	
Properties	Values	Ref.	Parameters	Values
C_{11}	4.690	8	Z_m	0.5552
C_{12}	1.740	8	$r_0 f'_0$	0.02406
C_{44}	1.080	8	A_{12}	11.5052
$\nu_{TO}(\Gamma)$	2.08	4	B_{12}	-0.5650
$\nu_{LO}(\Gamma)$	5.07	4	A_{11}	-0.4235
$\nu_{LO}(R)$	2.34	4	B_{11}	-2.2393
$\nu_{LA}(R)$	1.14	4	A_{22}	2.7131
$\nu_{TO}(X)$	1.69	4	B_{22}	-2.4696
$\nu_{TA}(X)$	1.04	4	d_1	0.8623
A_1	4.800	9	d_2	0.9716
A_2	2.927	9	Y_1	-3.1004
ϵ_0	37.600	4	Y_2	-1.6779
ϵ_∞	5.000	4		
2a	3.678	10		

Table 2.
Input Data and Model Parameters for ND₄Cl [C_{ij} (in 10^{12} dyne / cm²),
 ν (in THz), r_0 (in 10^{-8} cm), α_i (in 10^{-24} cm³), a (in Å⁰)]

Input Data			Model Parameters	
Properties	Values	Ref.	Parameters	Values
C_{11}	4.69	3	Z_m	0.8275
C_{12}	1.57	3	$r_0 f'_0$	0.0119
C_{44}	1.29	3	A_{12}	5.9946
r_0	3.3074	13	B_{12}	-0.3324
$\nu_{LO}(\Gamma)$	7.7	13	A_{11}	-0.9063
$\nu_{TO}(\Gamma)$	5.25	13	B_{11}	-0.3998
$\nu_{TO}(X)$	4.07	13	A_{22}	2.9981
$\nu_{TA}(X)$	3.14	13	B_{22}	-0.2040
$\nu_{LO}(R)$	5.32	13	d_1	0.2731
$\nu_{LA}(R)$	3.92	13	d_2	0.3872
α_1	2.0592	15	Y_1	-1.9240
α_2	2.9470	15	Y_2	-1.9421
ϵ_∞	2.81			
$2a$	3.8190			

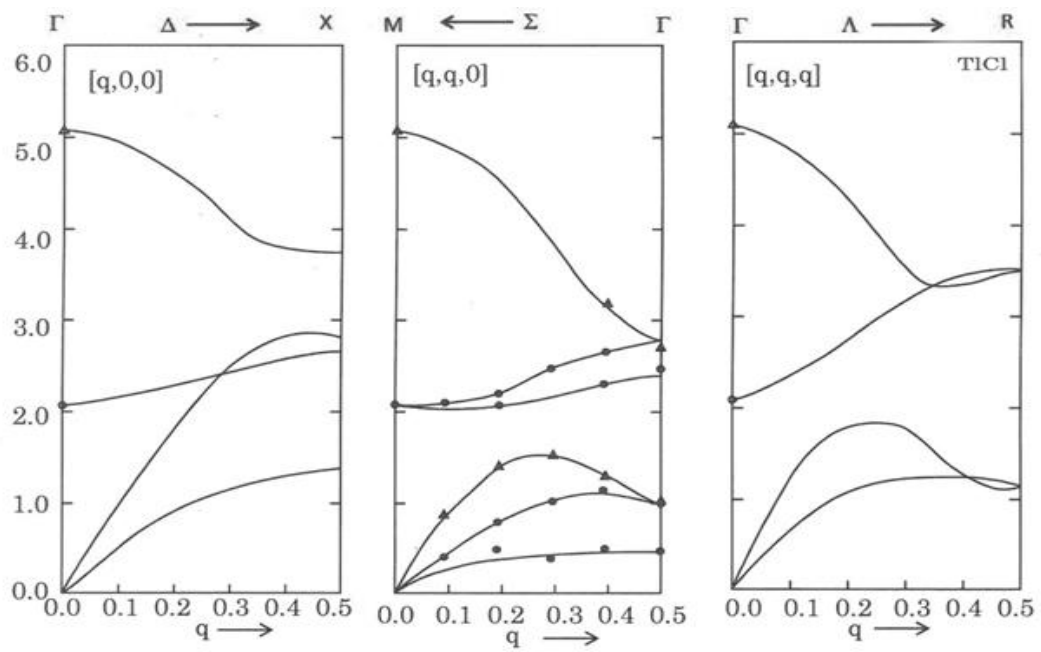


Figure 1:: Phonon Dispersion Curve for TlCl

Transverse
 Longitudinal
 } Experimental Points [7]
—— Present Study

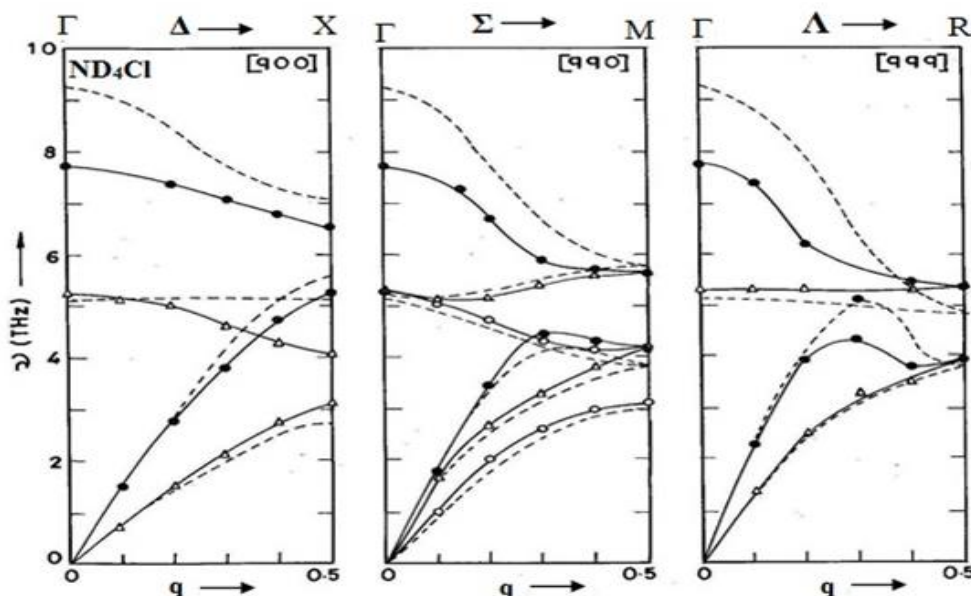


Fig. 2 Phonon dispersion curves for ND₄Cl at 85 K

— Present Study
 - - - Teh & Brockhouse
 Experimental Points
 • Longitudinal
 Δ, ○ Transverse

4. DISCUSSION

From Fig-1, it is observed that for TlCl, the percentage deviation of frequencies for VTSM from the experimental values, are maximum 2.83% along TO (M) branch and for 2.56% along LO (M) whereas no deviation is observed no deviation along both acoustic branches (LA and TA) M-symmetry direction. Also due to non-availability of experimental values for X- and R- symmetry directions, no deviation couldn't be ascertained between theoretical and calculated values through VTSM model. That is why the total percentage of theoretical and calculated values TlCl through VTSM model, along with all the directions, is within 2.83%. shown in Table-8. And from Fig. 2 with Table-2, it is evident that as VTSM has successfully explained the phonon frequencies along [q, 0, 0], [q, q, 0] & [q, q, q] symmetry directions that is why it is observed that the overall deviation between theoretical and experimental results due to VTSM (present model), is maximum 0.73% along TO (X) which describe reasonably in realistic manner the phonon dispersion curves (PDCs), combined density states curves (CDS curves), two phonon IR & Raman spectra providing a complete set for the validity of the present model for entire range of phonon spectra. This shows that the VTSM model (modification introduced by *three body interaction TBI* with *van der Waals interaction VWI* in the framework of *rigid shell model RSM*) is revealed a better description of lattice dynamical properties of TlCl and ND₄Cl during experimental workers^{41, 13} than the theoretical workers^{40, 42}.

Further, the present model VTSM have been applied to solve the elements of the secular equations for all the 56-representative non-equivalent wave vectors corresponding to a division in 1000 equal parts of the first Brillouin zone. The frequencies along symmetry directions are plotted against corresponding values of reduced wave vectors together with the neutron scattering results. As due to lack of the measured neutron data for the off symmetry directions, the complete phonon spectra cannot be tested as such, the test of the complete spectra is possible only through the physical properties derivable from it as the two-phonon density of states, sensitive to higher frequencies region. In continuation it after the study of the combined density state curves (CDS Curves) for TlCl and ND₄Cl presented in figures 3 & 4 respectively and the comparison of CDS peaks with neutron data peaks and their assignments from two-phonon Raman and IR peaks for TlCl & ND₄Cl, with the help of present model VTSM, have been shown in Tables 3 & 4, given below:

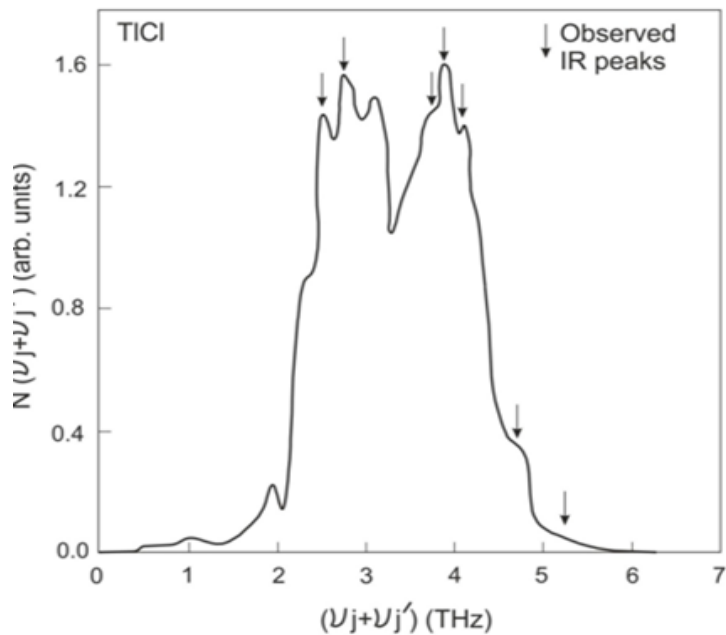


Figure 3 Combined (two phonon) density of states curve for TlCl

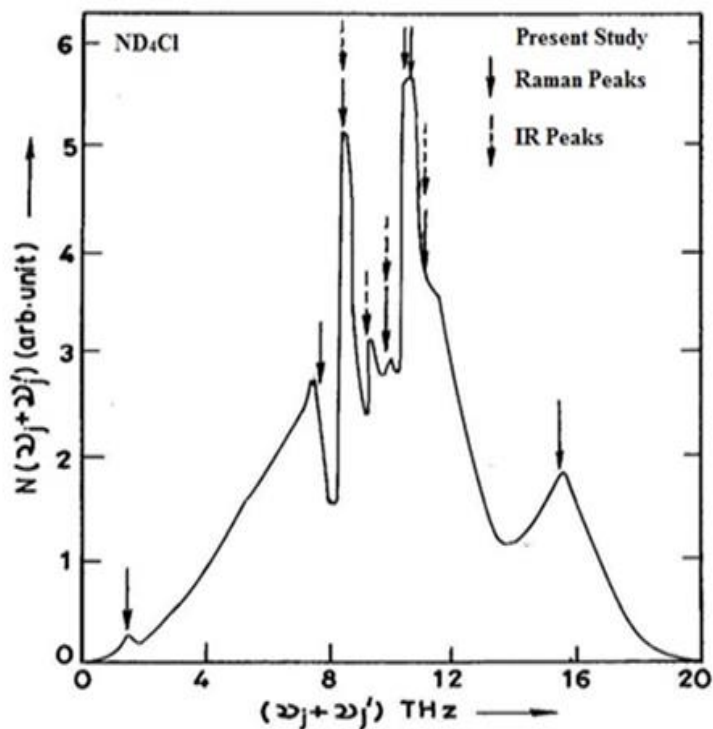


Figure 4 Combined (two phonon) density of states curve for ND₄Cl

7, 9, 11 Comparison of CDS peaks with neutron data peaks and their assignments from two-phonon Raman and IR peaks for TlCl & ND₄Cl

Table-3
Assignments of Two- Phonon Infra-Red peaks for TICl

CDS Peaks (Cm ⁻¹)	Infra – Red Active		
	Observed [16] Peaks (Cm ⁻¹)	Present Study	
		Assignment	Values (cm ⁻¹)
35	---	2TA(M)	34
69	---	2LA(M)	70
128	---	LO + LA(M)	128
155	---	LO + LA(R), LO + TA(R) TO + LA(R), TO + TA(R)	155
167	168	---	---
183	184	2LO(M)	186
207	---	---	---
247	249	---	---
257	255	---	---
273	272	---	---
313	315	---	---
---	350	---	---

Table-4
Comparison of our CDS peaks with neutron data peaks and their assignments from two phonons Raman and IR assignment peaks for ND₄Cl

Our CDS Peaks (cm ⁻¹)	Raman Peaks			IR Peaks		
	Neutron data Peaks* (cm ⁻¹)	Present Study		Neutron data Peaks* (cm ⁻¹)	Present Study	
		Assignments	Values (cm ⁻¹)		Assignments	Values (cm ⁻¹)
50	47	LO-LA(M)	48	---	---	---
250	262	2LA(R)	260	---	---	---
280	280	2LA(M)	280	280	2LA(M)	280
307	---	---	---	308	LO+LA(R)	308
327	327	LO+LA(M)	327	327	LO+LA(M)	327
350	350	2TO(Γ) = 2LA(X)	350	---	---	---
				---	---	---

	354	2LO(R)	357	---	---	---
				---	---	---
373	374	2LO(M)	373	374	2LO(M)	373
---	392	LO+LA(X)	392	---	---	---
---	434	2LO(X)	434	---	---	---
513	514	2LO(Γ)	513	---	---	---

* Calculated by us

After that third order elastic constants (TOECs), pressure derivatives of second order elastic constants (SOEC) and Cauchy discrepancy of TlCl and ND₄Cl have been presented in Tables 5, 6 & 7. Since no experimental data are available so far, we have not compared our results with those of measured data.

Table -5
TOECs' (in unit's 10¹² dyne/cm²) for TlCl & ND₄Cl

Property	VTSM (values) for TlCl	VTSM (values) for ND ₄ Cl
C_{111}	-1.1217	0.5595
C_{112}	-0.3163	-0.8271
C_{123}	-0.3053	-0.8274
C_{144}	-0.2987	-0.8124
C_{456}	-0.2953	-0.8062
C_{166}	-0.3201	-0.8491

Table-6
Pressure Derivatives of SOECs' (dimensionless) for TlCl & ND₄Cl

Property	VTSM (values) for TlCl	VTSM (values) for ND ₄ Cl
dC_{44}/dP	16.3425	7.0103
dS'/dP	-4.6612	-1.0418
dK'/dP	14.8985	7.8098

Table-7
Values of Cauchy discrepancy of TOECs' (in unit's 10¹² dyne/cm²) for TlCl & ND₄Cl

Property	VTSM (values) for TlCl	VTSM (values) for ND ₄ Cl
$C_{112} - C_{166}$	-0.0038	-0.0022
$C_{123} - C_{456}$	-0.0149	-0.021
$C_{144} - C_{456}$	-0.0034	-0.0062
$C_{123} - C_{144}$	-0.0176	-0.0152

The results on third order elastic constants (TOECs) of TlCl and ND₄Cl shown in Table 5 is probably the first report and as such it is not possible to comment on their reliability in the absence of experimental data. However, it is interesting that they show a close resemblance in signs with those obtained from CsCl structures crystals. A similar comment holds true for pressure derivatives of SOECs given in Table 6 and calculated Cauchy discrepancy in Table 7 for these crystals namely TlCl and ND₄Cl. These results in anharmonic elastic properties are, however, of only academic importance.

5. CONCLUSION

Present work is a systematic theoretical investigation of lattice dynamics of TlCl and ND₄Cl. The VTSM model proposed for this purpose has been developed by incorporating the effects of van der Waals interactions (VWI) and three body interactions (TBI) in the framework of rigid shell model (RSM) originated by Cochran and his collaborators⁴³. The theoretical and experimental results thus established make an evident that out of the presently available models, VTSM is reasonably better for describing the phonon dispersion curves, two-phonon infra-red and Raman spectra of TlCl and ND₄Cl. The overall success achieved by VTSM reveals that the physical effects underlying in these crystals are almost the same as those occurring in the interaction system of the present model VTSM. The definite improvements achieved by the VTSM over other models clearly indicate that the interaction mechanism beyond the dipolar approximation is mainly the van der Waals interactions, which manifests the many body interactions with most significant contribution from their three - body component. In view of its adequacies, the VTSM may be recognized as a powerful but simple approach for a comprehensive study of harmonic as well as other properties of the crystals under consideration. The only limitation of the model is the requirement of the knowledge of certain experimental information to use as input data.

Further, as the two-phonon Raman and infra-red (IR) spectra are sensitive to the higher frequency side of the phonon spectra and the specific heat is sensitive to its lower side, it seems, therefore, essential to investigate the extent to which the present model is capable to interpret the Raman and IR spectra, providing a complete test for the validity of the present models for entire range of the spectra. The results of these investigations from CDS approach for TlCl & ND₄Cl depicted in Fig. 3 and 4 show that the agreement between experimental^{41, 13} and our theoretical peaks is generally good for both Raman and IR spectra of monovalent behaviour metal halides (TlCl & ND₄Cl). The assignments made by the present study listed in Tables 3 and 4 show reasonably good agreement with the neutron data peaks corresponding to Raman and IR spectra for TlCl & ND₄Cl. The interpretation of Raman and IR spectra achieved from both CDS approach and critical points analysis may be considered satisfactory in all cases. These predictions can be improved further using a sophisticated programme for generating the combined density of states.

It is interesting to note that our results on TOEC, pressure derivatives of SOEC and Cauchy discrepancy for TlCl and ND₄Cl, are generally better than those of others as is evident from the Tables 5, 6 & 7. However, the results are similar to the experimental values for similar crystals having CsCl structured solids with no experimental values of TOEC, pressure derivatives of SOEC and the Cauchy discrepancy is available for these crystals. It can be seen from Table-7 that the Cauchy discrepancy is smaller for third order elastic constants than for second order elastic constants. A possible explanation for this fact seems to be that many-body and/or thermal effects are more pronounced for SOEC than for TOEC. The pressure derivatives of the effective SOE constants calculated by us have been given in Table-6 and the same could not be compared with the experimental data due to non availability of the same.

In view of the overall achievements described above, it may be concluded that the modification introduced by TBI & VWI in the framework of RSM, known as VTSM, are very much important in the crystals (TlCl and ND₄Cl) under considerations. In fact, the present model VTSM for TlCl and ND₄Cl have revealed much better descriptions of harmonic and anharmonic dynamical behaviour of TlCl and ND₄Cl.

To sum up, overall achievements given in this paper, it is concluded that VTSM model is important for the study of these properties of TlCl & ND₄Cl. At last, we can say that the inclusion of TBI and VWI are essential for the study of harmonic as well as the anharmonic dynamical study of CsCl structure ionic solids.

Table-8
Comparison of frequencies for TlCl at X-points, M-points and R-points

Points	Frequencies In THz	Experimental values [39]	VTSM (present study)		
			Values	± Deviation	% Deviation
X point [.5, 0, 0]	LO (X)	...	3.75
	TO (X)	...	2.70
	LA (X)	...	2.85
	TA (X)	...	1.40
M point [.5, .5, 0]	LO (M)	2.73	2.80	0.07	2.56 %
	TO (M)	2.47	2.40	0.07	2.83 %
	LA (M)	1.04	1.04	0.00	0.00 %
	TA (M)	0.52	0.52	0.00	0.00 %
R point [.5, .5, .5]	LO (R)	...	3.50
	TO (R)	...	3.50
	LA (R)	...	1.15
	TA (R)	...	1.15

Table-9
Comparison of frequencies for ND₄Cl at X-points, M-points and R-points

Points	Frequencies In THz	Experimental values [13]	VTSM (present study)		
			Values	± Deviation	% Deviation
X point	LO (X)	6.50	6.51	0.01	0.15
	TO (X)	4.07	4.10	0.03	0.73
	LA (X)	5.25	5.25
	TA (X)	3.14	3.15	0.01	0.31
M point	LO (M)	5.60	5.60
	TO (M)	5.60	5.60
	LA (M)	4.20	4.20
	TA (M)	4.20	4.20
R point	LO (R)	5.32	5.35	0.03	0.56
	TO (R)	5.32	5.35	0.03	0.56
	LA (R)	3.92	3.90	0.02	0.51
	TA (R)	3.92	3.90	0.02	0.51

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