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Van-der Waal three body force shell effect on SOEC-TOEC and cauchy discrepancy of CsI

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ABSTRACT

Expression for second order, third order elastic constant, pressure derivative and Cauchy discrepancy of CsI crystallizing in CsCl structure are presented with the help of (VTSM) model. It includes the effect of van der Waals interactions and three body interactions in the framework rigid shell model. The short-range overlap repulsion is operative to the second neighbor ions. The theoretical results are compared with experimental one by calculating pressure derivative of second order elastic constant SOEC, third order elastic constant TOEC and Cauchy discrepancy. It is concluded that the VTSM is adequately essential for description of Elastic constants and complete lattice dynamics of Cesium Iodide.

Keywords: Second order, Third order elastic constants, pressure derivative and Cauchy discrepancy

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INTRODUCTION

The studies of crystal dynamics of cesium chloride structure have been the matter of great interest in solid state physics. The materials in this group are CsCl, CsBr and CsI. The detail of this progression for the study of phonon behavior and lattice dynamical properties of CsI at room temperature has been traced by several experimental [1-4] and theoretical workers [5-8].The availability of measured data on second order, third order elastic constants, pressure derivatives, cauchy discrepancy, dielectric constants, for all of them with moderate success, has motivated the present author for the need of a lattice dynamical model for the description of these properties.

The rigid ion model (RIM) of Kellerman [9] is the first important model for the ionic crystals, which considers the ion of the crystals to be rigid, undeformable and unpolarizable spherical particles. The RIM was an uttar failure as it could not interpret well the dynamical, optical and elastic properties of ionic crystals. It could not give the adequate interpretation of the experimental phonon dispersion curves. The next is the deformation dipole model (DDM) of Karo and Hardy [10] and rigid shell model (RSM) of Dick and Overhauser [11] and Woods et.al. [12] by the two different groups at the same time. The DDM allows only the redistribution of charges in deformed electron cloud while the shell model consider the relevant displacement. So both effects (deformation and displacement) are present in ionic crystals. These models have failed to explain successfully the phonon dispersion curves and their Cauchy violation $C_{12} \neq C_{44,}$ which is large for CsI as well as ionic crystals. A general way to remove this deficiency is to include the deformation of electron shell in the framework of RSM. . The agreement between model frequencies and those obtained in their experiments is good at low value of q for acoustic branches, but there is discrepancy between the elastic constant derived from model parameters and those obtained from neutron scattering measurements.

Later on Singh et al. [7] used extended three body force shell model (ETSM) which are essentially an amalgamation of two most commonly used and realistic phenomenological models namely the RSM and deformation dipole model (DDM).ETSM contains the two-body long-range coulomb interaction and short range repulsion effective up to second-neighbour ions, three body long range interaction, and dipole character of constituent ions. Despite of these successes ETSM has revealed some features which do not have much physical significance.

A formal description of VWI and TBI in the framework of RSM has been described in next section. The present model VTSM as mentioned above has been applied to describe the complete lattice dynamics of cesium halides (CsCl, CsBr, CsI). The motivation for present solids lies in the fact that they have high energy gap, some discrepancies in PDCs and Cauchy violations. Also we have tasted the VTSM model by determining a set of 12-parameter and calculating the properties like two phonon Raman spectra, Debye temperature and combined density of states in our earlier paper [38].Now we have reported the adequacy of VTSM model by calculating the elastic constants etc.

2. THEORY

The general formulation of VTSM can be derived from the crystal potential whose relevant expression per unit cell is given by

$\Phi = \Phi_{COL} + \Phi_{TBI} + \Phi_{SR} + \Phi_{vWI}$ ----------(1)

Where the first two terms represent, respectively, long range Coulomb and three body interactions (TBI) energies. The next term is the Hafemeister and Flygare [19] form of SR overlap repulsive energy extended to the next nearest neighbor ions. The last term is the short range vWI interaction due to dipole-dipole and dipole-quaderpole interactions.

The introduction of vWI and TBI in the frame work of RSM [10, 14] yields secular determinant

$|D(q) - \omega^2 MI|$ ----------(2)

Where D (q) is written as

$D(q) = (R + Zm\ C'\ Zm) - (T + Zm\ C'Ym)\ (S + Ym\ C'\ Ym)^{-1}\ (T^T + Ym\ C'Zm)$ ---- ---------(3)

The expression for the elastic constants derived from the dynamical matrix corresponding to our model is

$C_{11} = e^2/4a^4\ \{0.7010\ Z^2m + (A_{12}+2B_{12})/6 + (A_{11}+A_{22})/4 + 5.4283\ Z\ r_0 f'_0\}$ --------(4)

$C_{12} = e^2/4a^4\ \{-0.6898\ Z^2m + (A_{12}+4B_{12})/6 + (B_{11}+B_{22})/4 + 5.283\ Zrof'_0\}$ --------(5)

$C_{44} = e^2/4a^4\ \{-0.3505\ Z^2m + (A_{12}+2B_{12})/6 + (B_{11}+B_{22})/4\}$ --------(6)

And r0 = (a√3) is interionic sepration
In view of well known equilibrium condition
$B_{11} + 2B_{12} + B_{22} = -0.6786\ Z^2m$ ----------(7)

EXPRESSIONS FOR TOEC FOR CESIUM CHLORIDE STRUCTURE:

$$C_{111} = P\left[-4.5656\,Z_m^{\ 2} + \frac{C_1 - 3A_1 - 24B_1}{18} + \frac{C_2 - 3A_2}{2} + 2.7138\ r_0^{\ 2} f_0^{''} + 13.1567\ r_0 f_0^{'}\right] \text{-------(8)}$$

$$C_{112} = P\left[0.7001\,Z_m^{\ 2} + \frac{C_1 - 3A_1 - 3B_1}{18} + 2.7138\ r_0^{\ 2} f_0^{''} - 6.2677\ r_0 f_0^{'}\right] \text{-------- (9)}$$

$$C_{166} = P\left[0.3609\,Z_m^{\ 2} + \frac{C_1 - 3A_1 - 3B_1}{18} - (B_1 + B_2) + 0.9046\ r_0^2 f_0^{''} - 5.3266\ r_0 f_0^{'}\right] \text{(10)}$$

$$C_{123} = P\left[1.2000\ Z_m^{\ 2} + \frac{C_1 - 3A_1 - 3B_1}{18} + 2.7138\ \ r_0^2\ f_0^{''} - 15.9799\ \ r_0\ f_0^{'}\right] \quad \text{---------- (11)}$$

$$C_{144} = P\left[1.2000\ Z_m^{\ 2} + \frac{C_1 - 3A_1 - 3B_1}{18} + 0.9046\ \ r_0^2\ f_0^{''} - 5.3266\ \ r_0\ f_0^{'}\right] \quad \text{----------(12)}$$

$$C_{456} = P\left[1.2000\ Z_m^{\ 2} + \frac{C_1 - 3A_1 - 3B_1}{18}\right] \quad \text{---------- (13)}$$

where $P = \frac{e^2}{4a^4}$, $C_1 = \frac{A_1^2}{B_1^2}$, $C_2 = \frac{A_2^2}{B_2^2}$

PRESSURE DERIVATIVES FOR CESIUM CHLORIDE STRUCTURE:

$$\frac{dK'}{dP} = -(3\Omega)^{-1}\left[2.0350 Z_m^{\ 2} + \frac{C_1 - 3A_1 + C_2 - 3A_2}{2} + 24.4242 r_0^2\ f_0'' - 56.4091 r_0\ f_0^{'}\right] \quad \text{---------- (14)}$$

$$\frac{dS'}{dP} = -(2\Omega)^{-1}\left[-5.229 Z_m^{\ 2} + \frac{A_1 - B_1 + C_2}{2} + 47.9383\, r_0\ f_0^{'}\right] \quad \text{-------- (15)}$$

$$\frac{dC'_{44}}{dP} = -(\Omega)^{-1}\left[1.2321 Z_m^{\ 2} + \frac{A_1 - 7B_1 + C_1 + 3A_2 - 9B_2}{6} + 2.7138\, r_0^2\ f_0'' - 6.5791\, r_0\ f_0^{'}\right] \quad \text{-----(16)}$$

where $\Omega = -0.3392\ Z_m^2 + \frac{A_1 + A_2}{2} + 9.4008\ r_0\ f_0'$

$K' = \frac{C'_{11} + 2C'_{12}}{3}$ and $S' = \frac{C'_{11} - C'_{12}}{2}$ ------- (17)

THE CAUCHY DISCREPANCIES AMONG THE TOE CONSTANTS OF CsCl STRUCTURE ARE GIVEN BY

$C_{12} - C_{44} = e^2/4a^4\ (5.4283\ \ Zr_0f'_0)$ ---------(18)

$$C_{112} - C_{166} = \frac{e^2}{4a^4}\left[1.8092\ \ r_0^2\ \ f_0'' - 0.9411\ \ r_0\ \ f_0'\right] \quad \text{---------(19)}$$

$$C_{123} - C_{456} = \frac{e^2}{4a^4}\left[2.7138\ \ r_0^2\ \ f_0'' - 15.9799\ \ r_0\ \ f_0'\right] \quad \text{----------(20)}$$

$$C_{144} - C_{456} = \frac{e^2}{4a^4}\left[0.9046\ \ r_0^2\ \ f_0'' - 5.3266\ \ r_0\ \ f_0'\right] \quad \text{----------(21)}$$

$$C_{123} - C_{144} = \frac{e^2}{4a^4}\left[1.8092\ \ r_0^2\ \ f_0'' - 10.6533\ \ r_0\ \ f_0'\right] \quad \text{----------(22)}$$

These expressions have been taken from Ref. [20]

3. COMPUTATIONS

Table -1: Input data and model parameter for CsI
[C_{ij} (in 10^{12} dyne/cm^2), ν (in 10^{12} Hz), r_0 (in 10^{-8} cm), α_i (in 10^{-24} cm^3), 2a (in 10^{-8} cm)]

Input Data		Ref.	Model Parameter	
Properties	Value		Parameter	Values
C_{11}	2.434	2	Z^2m	0.8062
C_{12}	0.636	2	$r_0f'_0$	-.0026
C_{44}	0.666	2	A_{11}	-0.9536
$\nu_{TO}^{(\Gamma)}$	1.918	4	B_{11}	0.06825
$\nu_{LO}^{(R)}$	1.815	4	A_{12}	7.105
$\nu_{LA}^{(R)}$	1.719	4	B_{12}	0.4030
$\nu_{TO}^{(X)}$	1.214	4	A_{22}	2.969
$\nu_{TA}^{(X)}$	1.266	4	B_{22}	1.6805
α_1	3.131	7	d_1	0.3094
α_2	6.191	7	d_2	0.5053
ε_0	5.65	2	Y_1	-1.7843
ε_∞	3.020	7	Y_2	-2.1601
2a	4.567	7		

Table: 2 TOEC (in units 10^{12} dyn / Cm^2) for Cesium Iodide

Property	Present Study (VTSM)
C_{111}	–0.5317
C_{112}	–0.1806
C_{123}	–0.1697
C_{144}	–0.1704
C_{166}	–0.1863
C_{456}	-0.1707

Table: 3 Pressure derivatives of SOEC and TOEC (dimensionless) of Cesium Iodide

Property	Present Study (VTSM)	Expt.[37]
dC'_{44}/dP	4.251	3.72
dS'/Dp	–1.252	0.84
dK'/Dp	9.051	

Table: 4 The values of Cauchy discrepancy (in 10^{12} dyn /cm^2) for lattice dynamics of Cesium Iodide

Property	values
C_{112}– C_{166}	0.000033
C_{123}– C_{456}	0.000945
C_{144}– C_{456}	0.000315
C_{123}– C_{144}	0.000630

RESULTS AND DISCUSSION

The input data with calculated model parameters are presented in table (1).It is interesting to note that our results on TOEC, pressure derivatives of SOEC and value of Cauchy discrepancy are generally better than those of other theoretical workers. However, the results are closer to their experimental values [5,6]. It can be seen from table (4) that the Cauchy discrepancy is smaller for TOE constant than for SOE 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 and TOE constants calculated by us have been given in table (3) and table (2) and found to be generally in good agreement with their observed data.

CONCLUSION

In view of the overall achievements described above, it may be concluded that the modification introduced by TBI and VWI in the frame work of RSM is very much importance in the crystals under considerations. In fact, the present model VTSM has revealed much better descriptions of dynamical properties as well as pressure derivative of second order elastic constant SOEC, third order elastic constant TOEC and Cauchy discrepancy of cesium iodide than those obtained by rigid shell model [30], deformation shell model [15], breathing shell model [31], extended three-body force shell model [7].

It is concluded that the modifications introduced by VWI and TBI in the framework of RSM with second neighbour repulsive interactions is important in cesium iodide (CsI). In fact the present model VTSM has revealed better descriptions of dynamical properties of the solids under consideration. At last, we can say that the inclusion of VWI and TBI are essential for the description of lattice dynamics of these compounds.

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