LATTICE DYNAMICS AND SPECIFIC HEAT OF CAESIUM CHLORIDE

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ABSTRACT

Lattice dynamics of caesium chloride has been worked out employing the shell model of Cowley et al[3]., taking into account the polarisabilities of both the ions. With the phonon branches at the fifty six representative points in the Brillouin zone, the frequency distributions and the specific heats are calculated and a fair agreement is found between the infrared maxima predicted by the model and also the specific heats obtained from calorimetric data. However it is shown that the modified shell model put forward by Deo and Dayal are not consistent with the symmetry of the normal modes on the zone boundary and also the agreement between the calculated and observed specific heats are not satisfactory in this model.

INTRODUCTION

In recent years, there has been considerable success in the application of shell model to describe the lattice vibrations in ionic (NaF, KI, KBr, NaI)[1, 5, 8, 14] and covalent (Ge, C)[2, 12] crystals. Phonon dispersion in caesium halides have not been measured so far, probably due to the large neutron absorption cross section of caesium and therefore there has not been much progress on the dynamics of these crystals. However the validity of the lattice dynamical models for these crystals could be tested from their ability to explain the thermal properties and the second order Raman and Infrared spectra of these crystals. It was with this view that one of us[8], worked out the dynamics of caesium iodide to enumerate the distribution of intensities in the second order Raman spectrum of caesium iodide. This was followed by a detailed investigation of the dynamics[15] of caesium halides and Rubidium chloride employing the shell models to interpret the two phonon Raman and Infrared spectra using the combined density of states of Johnson and Cochran[6]. Recently, a modified shell model for potassium iodide has been put forward by Deo and Dayal[4] to include many body forces and to explain the Cauchy discrepancy. It was therefore felt necessary to study the utility of their model for caesium chloride structures and to compare the results of simple and modified shell models and the results of such an investigation are presented in this note.

THE SHELL MODEL

The equations of motion for the cores and shells of the ions in the unit cell in the harmonic – adiabatic – electrostratic approximations are given by

$$W^2 M_d U_c = (R + Z_d CZ_d)\, U_c + (T + Z_d CY_d)\, W_c \qquad [1]$$

$$0 = (\tilde{T}^* + Y_d CZ_d)\, U_c + (s + Y_d CY_d)\, W_c \qquad [2]$$

On eliminating W_c in [1] using [2] we obtain the dynamical matrix

$$[(R + Z_d CZ_d) - (T + Z_d CY_d)\,(s + Y_d CY_d)^{-1}\,(\tilde{T}^* + Y_d CZ_d) - w^2 M_d]U_c = 0 \qquad [3]$$

giving the frequencies of the normal modes and their polarisation vectors. In these equations, R, T, S are the matrices specifying the short range interactions while C is the matrix of Coulomb coefficients. M_d, Y_d and Z_d are diagonal matrices representing the mass, charge on the shell and the ionic charge. U_c is a column vector specifying the amplitude of the displacement of the ion $Y_d W_c$ is the electronic dipole moment of the ions. The long range and short range matrices are defined as

$$^{c}\begin{bmatrix} kk' \\ xy \end{bmatrix} = -\sum_{l'} \phi^{c}_{xy} \begin{pmatrix} 1 1' \\ kk' \end{pmatrix} \exp.\,(-i\,\mathbf{q}.\mathbf{r}) \begin{pmatrix} 1 1' \\ kk' \end{pmatrix} \qquad [4]$$

and $$^{R}\begin{bmatrix} kk' \\ xy \end{bmatrix} = -\sum_{ll'} \phi^{R}_{xy} \begin{pmatrix} 1 1' \\ kk' \end{pmatrix} \exp.\,(-i\,\mathbf{q}\,\mathbf{r}) \begin{pmatrix} 1 1' \\ kk' \end{pmatrix} \qquad [5]$$

The expressions for T and S are similar to those for R.

The matrix

$$S_{xy'} = S_{xy} + Y_k^2/\alpha_k\, \delta_{xy}\, \delta_{RR'} \qquad [6]$$

where α_k is the polarisability of the kth ion. Following Woods et al.[14] we assume $R = T = S$ which implies that the short range interaction acts through the shells.

In order to work out the short range coupling coefficients, we define the parameters A, B, A_1, B_1 and A_2, B_2 for the nearest and next nearest neighbour anion-anion and cation-cation interactions respectively,

$$\left[\frac{1}{r}\,\frac{d\phi}{dr}\right]_{r=\sqrt{(3r_0)}} = (e^2/2\,v\,B) \qquad [7]$$

$$\left[\frac{d^2\phi^{R}}{dr^2}\right]_{r=\sqrt{(3\,r_0)}} = (e^2/2\,v)\,A \qquad [8]$$

$$\left[\frac{1}{r}\frac{d\phi^{R}}{dr}\right]_{r=2r_0} = (e^2/2v)\, B_1 \qquad [9]$$

$$\left[\frac{d^2\phi^{R}}{dr^2}\right]_{r=2r_0} = (e^2/2v)\, A_1 \qquad [10]$$

$$\left[\frac{1}{r}\frac{d\phi^{R}}{dr}\right]_{r=2r_0} = (e^2/2v)\, B_2 \qquad [11]$$

$$\left[\frac{d^2\phi^{R}}{dr^2}\right]_{r=2r_0} = (e^2/2v)\, A_2 \qquad [12]$$

with these parameters, the short range matrix elements turn out to be

$$\left[\frac{11}{xx}\right] = \frac{e^2}{v}\left[\tfrac{4}{3}(A+2B) + A_1 + 2B_1 - A_1\cos 2\pi q_x - B_1(\cos 2\pi q_y + \cos 2\pi q_z)\right]$$

$$\left[\frac{11}{xy}\right] = 0$$

$$\left[\frac{12}{xx}\right] = \frac{-e^2}{v}\,\tfrac{4}{3}(A+2B)\cos\pi q_x \cos\pi q_y \cos\pi q_z$$

$$\left[\frac{12}{xy}\right] = \frac{e^2}{v}\,\tfrac{4}{3}(A-B)\cos\pi q_z \sin\pi q_x \sin\pi q_y$$

$$\left[\frac{22}{xx}\right] = \frac{e^2}{v}\left[\tfrac{4}{3}(A+2B) + A_2 + B_2 - A_2\cos 2\pi q_x - B_2(\cos 2\pi q_y + \cos 2\pi q_z)\right]$$

$$\left[\frac{22}{xy}\right] = 0 \qquad [13]$$

All the other elements can be obtained by a cyclic interchange of x, y and z.

The expression for the elastic constants and the equilibrium conditions are

$$C_{11} = (e^2/vr_0)\left[(A+2B)/6 + (A_1+A_2)/4 + 1.40179\, z^2\right] \qquad [14]$$

$$C_{12} = (e^2/vr_0)\left[\tfrac{1}{6}(A-4B) - \tfrac{1}{4}(B_1+B_2) - 1.37935\, z^2\right] \qquad [15]$$

$$C_{44} = (e^2/vr_0)\left[\tfrac{1}{6}(A+2B) + \tfrac{1}{4}(B_1+B_2) - 0.70089\, z^2\right] \qquad [16]$$

The expressions for ω_{L_0} and ω_{T_0} are obtained by solving the dynamical matrix for $q \to 0$.

$$\mu\,\omega_{T0}^2 = R_0' - \frac{4\pi\, e^2\,(z + d_1 - d_2)^2\,(\epsilon_\infty + 2)}{9v} \qquad [17]$$

$$\mu\,\omega_{LO}^2 = R_0' + \frac{8\pi\, e^2\,(z+d_1-d_2)^2\,(\epsilon_\infty+2)}{9\,v\,\epsilon_\infty} \qquad [18]$$

where $R_0' = R_0 - e^2\left(\frac{d_1^2}{\alpha_1} + \frac{d_2^2}{\alpha_2}\right)$ and $R_0 = \frac{4}{3}\,\frac{e^2}{v}(A+2B)$ [19]

It can also be shown that

$$R_0' = \mu\, w_{To}^2\left(\frac{\epsilon_0+2}{\epsilon_\infty+2}\right) \qquad [20]$$

Therefore, from these equations, one can obtain $d_1 - d_2$, R_0' and hence the parameters A, B and d_1, d_2 the distortion polarisabilities of the ions, assuming $z = 1$ and using the relation (d/R_0) is a constant for each iono.

For the computations on a simple shell model it was assumed that the short range interaction extends upto the nearest neighbours only and the following set of parameters were obtained from the compressibility and the infrared maxima.

$A = 9.34716$
$B = -0.67847$
$(\alpha_1/v) = 0.04105$
$(\alpha_2/v) = 0.04206$
$d_1 = 0.05471$
$d_2 = 0.18094$

The parameters of the model being known, a program was written for the CDC-3600 computer at Tata Institute Fundamental Research Bombay, to generate the dynamical matrix and to diagonalise it by a modified Jacobi method. The eigen values of the dynamical matrix at properly weighted fifty-six nonequivalent points, were used to construct the frequency distribution shown in Fig. 1. The peak corresponding to transverse optical branches agrees well with the infrared maximum[7].

Using the frequency distribution, the specific heat of the crystal was computed over a range of temperatures, by numerical integration of

$$C_v = 3kn \int_0^\infty g(\omega)\, E(h\omega/kT)\, d\omega$$

where n is the atomicity of the crystal and $E(h\omega/kT)$ is the Einstein function and $\int_0^\infty g(w)\, d\omega = 1$. The experimental and calculated values agree well as shown in Table 1.

From the specific heat values, the Debye temperatures (θ_D) are calculated and the temperature variation of θ_D is shown in Fig. 2 and exhibits the characteristic dip at low temperatures.

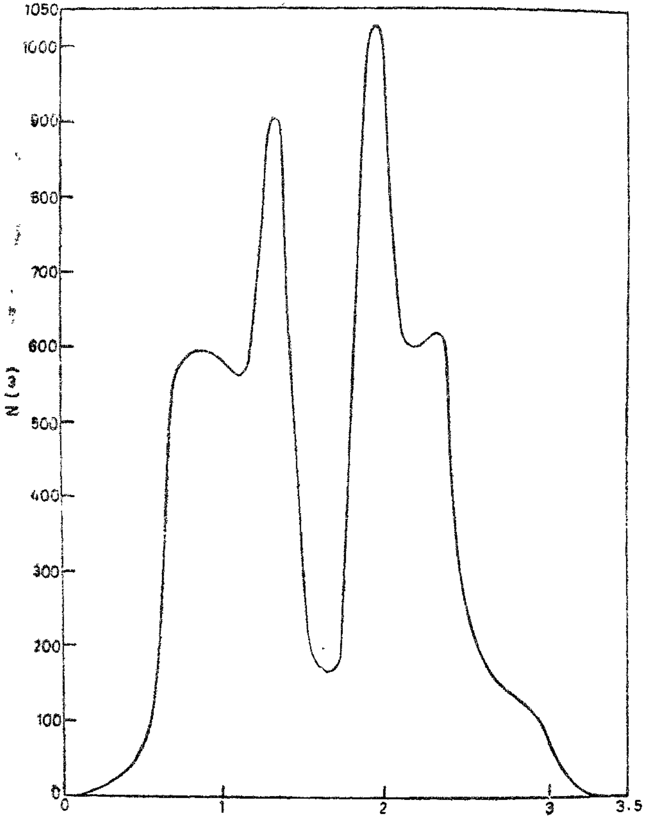

FIG. 1
Frequency Distribution of Cs Cl

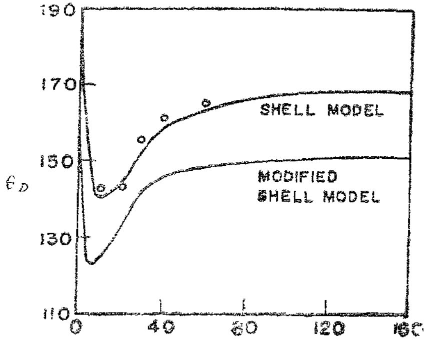

FIG. 2

Variation of θ_D with temperature for Cs Cl
O—experimental values
— — Calculated values

TABLE I

Specific Heat of CsCl, experimental and calculated, at different temperatures.

Temp. $K°$	C_v (calc.)	C_v (Expt.)
10	0.317	0.335
20	2.114	2.141
30	4.213	4.158
40	6.050	5.912
60	8.432	8.244
80	9.701	9.549
100	10.408	10 282

THE MODIFIED SHELL MODEL

Even though the shell model accounts for the dielectric properties of crystals, the expressions for the elastic constants remain the same as in the rigid ion model and hence it fails to explain the Cauchy discrepancy in alkali halides. Löwdin[9] was the first to show that the Cauchy discrepancy can be explained by including manybody forces. Following Lundquist[4], Verma and Dayal[12] worked out the Fuch's relations for rocksalt structures by including volume dependent forces to represent approximately the three body interactions. In their rigid ion model containing these volume forces, the dynamical matrix is given by

$$[(R + V + Z_d C Z_d) - M_d \omega^2] U_c = 0 \qquad [21]$$

where the elements of the matrix 'V' are given by

$$V\begin{bmatrix} kk' \\ xy \end{bmatrix} = -\sum \phi^V_{xy}\begin{pmatrix} ll' \\ kk' \end{pmatrix} e^{-i\vec{q}.\vec{r}}\begin{pmatrix} ll' \\ kk' \end{pmatrix} \qquad [22]$$

and

$$\phi^V_{xy}(kk') = \frac{e^2}{2v}\,\sigma\,\frac{q_x q_y}{q^2} \qquad [23]$$

σ is a volume dependent force constant and the introduction of this potential affects only the longitudinal vibrations. Deo and Dayal[4] incorporate these forces in the shell models by assuming that the volume dependent forces operate only between the cores of the ions to arrive at the dynamical matrix

$$[\{(R + V + Z_d C Z_d) - (T + Z_d C Y_d)(s + Y_d C Y_d)^{-1} \times (\tilde{T}^* + Y_d C Z_d)\} - M_x \omega^2] U_c = 0 \qquad [24]$$

Employing the definition of the volume dependent coupling coefficients, we get

$$V\begin{bmatrix} 1\,1 \\ x\,y \end{bmatrix} = [-(4\sigma_{12} + 3\sigma_{11}) + \sigma_{11}(\cos 2\pi q_x + \cos 2\pi q_y + \cos 2\pi q_z)]\frac{q_x q_y}{q^2}$$

$$V\begin{bmatrix} 2\,2 \\ x\,y \end{bmatrix} = [-(4\sigma_{12} + 3\sigma_{22}) + \sigma_{22}(\cos 2\pi q_x + \cos 2\pi q_y + \cos 2\pi q_z)]\frac{q_x q_y}{q^2}$$

$$V\begin{bmatrix} 1\,2 \\ x\,y \end{bmatrix} = 4\sigma_{12}\cos\pi q_x \cos\pi q_y \cos\pi q_z\,\frac{q_x q_y}{q^2} \qquad [25]$$

where σ_{12} is a force constant for unlike neighbours and σ_{11} and σ_{22} are those for like neighbours. Employing the method of long waves the contribution of these volume forces to the elastic constants is found to be

$$C^V_{11} = \frac{e^2}{2vr_0}\left(\frac{\sigma_{11} + \sigma_{22} + 2\sigma_{12}}{2}\right) \qquad [26]$$

$$C^V_{12} = \frac{e^2}{2vr_0}\left(\frac{\sigma_{11} + \sigma_{22} + 2\sigma_{12}}{2}\right) \qquad [27]$$

$$C^V_{44} = 0 \qquad [28]$$

Thus the inclusion of the many body forces contribute to the elastic constant C_{12} and not to the shear constant C_{44} and also from symmetry considerations, the contributions to C_{12} and C_{11} are equal. With these contributions included in equations 14 to 16 and assuming that the equilibrium condition remains unaltered and restricting to nearest neighbour interactions alone, the parameter Z and B can be obtained from the equilibrium condition and C_{44}. A can be obtained from

$$(C_{11})_{\text{expt.}} = \frac{e^2}{v r_0} \left(\frac{A + 2B}{6} + 1.40179\, Z^2 \right) + (C_{12} - C_{44})_{\text{expt.}}$$

while the parameter $\sigma_{11} = \sigma_{22}$, is obtained from $(C_{12} - C_{44})$ expt. assuming $\sigma_{12} = 0$.

Thus in the modified shell model the expression for B is the same as in the simple shell model except that Z is not necessarily equal to one. Also the value of A is identical with that obtained with shell model with an adjusted value of C_{11} which is obtained after subtracting the Cauchy discrepancy $(C_{12} - C_{44})$ from the experimental C_{11}. The longitudinal optical mode at $k \rightarrow 0$ is given by

$$\mu \omega_{L0}^2 = R_0 - e^2 \left(\frac{d_1^2}{\alpha_1} + \frac{d_2^2}{\alpha_2} \right) + 4\sigma_{12} \frac{e^2}{v} + \frac{8\, \pi e^2 (Z + d_1 - d_2)^2}{9 v\, \epsilon_\infty} (\epsilon_\infty + 2)$$

while the transverse optical branch remain unaffected by the introduction of the volume forces.

An attempt was made to compute the phonon dispersion in thallium bromide in addition to the computation of the specific heats of caesium chloride. The parameters of this model taking into account second-neighbour interactions also, were calculated from the elastic constants, infrared frequencies ω_{T0} and ω_{L0} and the equilibrium condition, assuming $\sigma_{11} = \sigma_{22}$ and $\sigma_{12} = 0$ and that the second neighbour interactions between the anion-anion and cation-cation are identical. The volume dependent forces σ_{11} increase with the increasing $(C_{12} - C_{44})$ expt. For example $\sigma_{11} = -0.0954$ for potassium iodide with $C_{12} = 0.22$ and $C_{44} = 0.368$ while σ_{12} is -0.821 for lithium flouride with $C_{12} = 4.24$ and $C_{44} = 6.49$. Nevertheless in the case of TlBr and CsCl, $C_{12} > C_{44}$, and $(C_{12} - C_{44})$ is fairly high in the former and the constant σ_{11} is positive for both the crystals and have values $\sigma_{11} = 0.60446$ in TlBr and $\sigma_{11} = 0.09648$ in CsCl. The effective charge on the ions was also found to be very nearly equal to unity when the second neighbour forces were taken into account.

With these parameters, the dynamical matrix was solved for the fifty six non-equivalent points in the reduced zone. On account of the high symmetry of the CsCl structure it is found[8] that there is a pair of threefold degenerate modes at the zone corner $R\,(0.5, 0.5, 0.5)$ and a pair of doubly degenerate modes for all points on the surface of the zone with $q_x = q_y = 0.5$, in our earlier rigid ion model calculations. The shell model computation also give us similar type of normal modes consistent with the symmetry of the lattice. However, with the volume forces included, we obtain for example at R(0.5, 0.5, 0.5) non vanishing

$$V\begin{bmatrix}11\\xy\end{bmatrix} \text{ and } V\begin{bmatrix}22\\xy\end{bmatrix}$$

terms which split up the degeneracy of the modes This is also found to be in case for all points with $q_x = q_y = 0.5$ where instead of a pair of doubly degenerate roots, we obtain four non degenerate roots, the reason for this discrepancy being the choice of this particular form of the $\phi^1_{xy}\,(kk')$ involving $q_x q_y / q^2$. Thus in the modified shell model, the expression for the frequencies are not exactly periodic in reciprocal space and also the zone boundary phonons are highly influenced by the choice of the volume dependent potential. Since the volume forces are small, one can assume a wave vector dependence of these forces and assume that they are zero at the zone boundaries, thereby satisfying the symmetry requirements. A plot of θ-T for CsCl in the modified shell model is given in Fig. 2, and the agreement between theory and experiment is not satisfactory. It is felt that a better way of introducing volume forces involving reciprocal lattice vectors will help to solve the dynamics of alkali halides explaining the dielectric and elastic properties in addition to phonon dispersion and thermal properties.

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