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Lattice dynamics of calcium fluoride by an angular force model

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Abstract. The lattice dynamics of CaF_2 has been studied on the basis of a non-central model using CGW type angular forces. The experimental data agree with the data obtained for the dispersion curves. The model has also been used to calculate lattice specific heat and Debye-Waller factors.

Keywords. CGW angular forces; fluorite lattice; phonon dispersion; coulomb coupling coefficients; elastic constants.

1. Introduction

In recent years a number of workers have used the Clark-Gazis-Wallis (CGW) type of angular forces in their lattice dynamical studies. Clark *et al* (1964) applied them to the bcc metals, Yuen and Varshini (1967) to fcc metals and Pandey and Dayal (1972, 1973) to diamond type solids. Arunsingh and Dayal (1970) have used them in the study of the fluorite lattice and have calculated the elastic constants of Mg_2Sn and Mg_2Si. The same technique has been adopted by Anasthasakis and Hawranek (1972) to calculate the elastic constants of Mg_2X type compounds, where X stands for Si, Ge, Sn and Pb. They found that the agreement showed improvement with the increase in the degree of covalency of the compound. To further test this point they also calculated the elastic constants of CaF_2, which is more ionic in character and obtained a poorer fit with the experimental data.

In addition to the fact that both the above groups of workers had a very limited objective, they resorted to several approximations. In particular, out of the four angular force constants, two were arbitrarily assumed to be zero. Further the overlap forces were considered to be significant only between the nearest neighbours.

Essentially the same technique has been adopted in the present work to study the lattice dynamics of calcium fluoride. However the approximations used by the above authors have been avoided. All the four angular force constants have been retained and are found to have quite significant values. The overlap interaction between the next neighbours has also been included. Whereas Anasthasakis and

Hawranek (1972) confined themselves to a study of its elastic constants with a view to interpret the large Cauchy discrepancy, we have used the model to calculate the phonon dispersion curves, specific heat and Debye–Waller factor. A good agreement with the available experimental data has been obtained.

2. Dynamics of the calcium fluoride lattice

CaF_2 is an ionic solid crystallising according to the fluorite lattice with three atoms per unit cell. The fluorite lattice has been adequately described by Whitten *et al* (1965). It consists of three interpenetrating face-centered cubic sublattices. For CaF_2 these are occupied by one calcium and two non-equivalent fluorine atoms F_1 and F_2.

The lattices of F_1 and F_2 are displaced along the body diagonal of the calcium lattice by $2a$ $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $2a$ $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ respectively where $2a$ is the lattice constant (figure 1). Each calcium atom is surrounded by four flourine atoms F_1 and four fluorine atoms F_2, the eight atoms lying at the corners of a cube with Ca at the centre. Each fluorine atom is surrounded by four calcium atoms arranged in a tetrahedral fashion around it.

The vibration frequencies are determined from the secular equation:

$$\left| \omega^2 m_k \delta_{kk'} \delta_{\alpha\beta} - \begin{bmatrix} K K' \\ \alpha \beta \end{bmatrix} \right| = 0 \tag{1}$$

where m_k is the mass of the k-th atom and $\begin{bmatrix} K K' \\ \alpha \beta \end{bmatrix}$ are the coupling coefficients. Here α and β represent the Cartesian directions x, y and z.

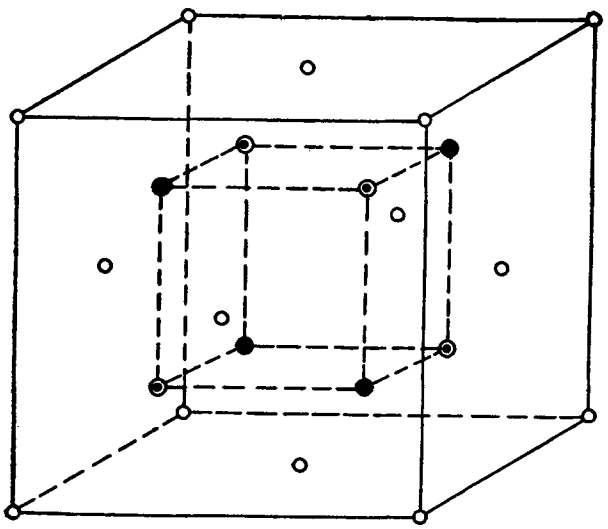

Figure 1. Conventional cubic unit cell of a fluorite (RX_2) crystal lattice.

The coupling coefficients can be split into a Coulomb part and a non-Coulomb part.

$$\begin{bmatrix} K & K' \\ \alpha & \beta \end{bmatrix} = {}^{c}\begin{bmatrix} K & K' \\ \alpha & \beta \end{bmatrix} + {}^{n}\begin{bmatrix} K & K' \\ \alpha & \beta \end{bmatrix} \tag{2}$$

(*a*) *Coulomb part*: The Coulomb coupling coefficients have been used for the 47 irreducible lattice vector points in 1/48 of the first Brillouin zone of the reciprocal space to which a mesh of 1000 wave vector points reduces by symmetry considerations. Kellerman (1940) has calculated the coefficients ${}^{c}\begin{bmatrix} K & K \\ \alpha & \beta \end{bmatrix}$ and ${}^{c}\begin{bmatrix} 24 \\ \alpha\beta \end{bmatrix}$ for those 47 points, while Whitten *et al* (1965) have computed ${}^{c}\begin{bmatrix} 12 \\ \alpha\beta \end{bmatrix}$ at the same points. We have used these values in the present work after multiplying them with $Z_2^2\, e^2/V$. Here Z_2 is the effective positive charge of the Ca-ions (in units of e) and V is the volume of the unit cell.

(*b*) *Non-Coulomb part*: The non-Coulomb part of the coupling coefficients can be expressed as a linear combination of terms involving short range and angular forces. The short range coupling coefficients have been calculated in terms of the central force constants a_1, a_2 and a_3 using the method discussed by de Launay (1956). The constants a_1, a_2, and a_3 indicate respectively the Ca–F, Ca–Ca and F–F interactions.

The CGW type angular forces have been calculated following the method described by Gazis *et al* (1960) and as used by Arunsingh and Dayal (1970). The angular force constants σ_1, σ_2, σ_3 and σ_4 are associated with the four bond angles of the two types of triangles considered by them. In this paper of Arunsingh and Dayal, the coupling coefficient $\begin{bmatrix} 22 \\ xy \end{bmatrix}$ was printed as all real. The symbol i was not appended to the imaginary part. This has been duly corrected in the present text.

The typical expressions obtained for the coupling coefficients are the following:

$${}^{n}\begin{bmatrix} 11 \\ \alpha\alpha \end{bmatrix} = 8a_1 + 8a_2 + 32\sigma_1 + 48\sigma_2 + 28\sigma_3 + 28\sigma_4 - 2\,(2a_2 + \sigma_3)\, C_{2\alpha}\,(C_{2\beta} + C_{2\gamma}) + (8\sigma_3 + 4\sigma_4)\, C_{2\beta}\, C_{2\gamma}$$

$${}^{n}\begin{bmatrix} 11 \\ \alpha\beta \end{bmatrix} = (4a_2 + 2\sigma_3)\, S_{2\alpha} S_{2\beta}$$

$${}^{n}\begin{bmatrix} 12 \\ \alpha\alpha \end{bmatrix} = (-4a_1 - 16\sigma_1 - 24\sigma_2 - 16\sigma_3 - 16\sigma_4)\,(C_\alpha C_\beta C_\gamma - iS_\alpha S_\beta S_\gamma)$$

$${}^{n}\begin{bmatrix} 12 \\ \alpha\beta \end{bmatrix} = (4a_1 - 8\sigma_1 - 12\sigma_2 - 8\sigma_3)\,(S_\alpha S_\beta C_\gamma - iC_\alpha C_\beta S_\gamma)$$

$${}^{n}\begin{bmatrix} 22 \\ \alpha\alpha \end{bmatrix} = 4a_1 + 2a_3 + 24\sigma_1 + 36\sigma_2 + 14\sigma_3 + 14\sigma_4 + (4\sigma_3 + 2\sigma_4)\, C_{2\beta} C_{2\gamma} - \sigma_3\, C_{2\alpha}\,(C_{2\beta} + C_{2\gamma})$$

$${}^{n}\begin{bmatrix} 22 \\ \alpha\beta \end{bmatrix} = \sigma_3 S_{3\alpha} S_{2\beta} + i2\,(\sigma_3 + \sigma_4)\, S_{2\gamma}\,(C_{2\alpha} - C_{2\beta})$$

$$^{n}\begin{bmatrix}24\\ \alpha\alpha\end{bmatrix} = (-2a_3 - 16\sigma_1)\, C_{2\alpha} + (4\sigma_1 - 6\sigma_2)\,(C_{2\beta} + C_{2\gamma})$$

$$^{n}\begin{bmatrix}24\\ \alpha\beta\end{bmatrix} = -i\,(4\sigma_1 + 6\sigma_2)\, S_{2\gamma}.$$

The other coefficients can be derived by a cyclic interchange of α, β and γ and by using the fact that the dynamical matrix is Hermetian. The following relations hold between the coupling coefficients:

$$\begin{bmatrix}k\,k'\\ \alpha\,\beta\end{bmatrix} = \begin{bmatrix}k'\,k\\ \beta\,\alpha\end{bmatrix}^{*} \quad \begin{bmatrix}1\,4\\ \alpha\,\beta\end{bmatrix} = \begin{bmatrix}1\,2\\ \alpha\,\beta\end{bmatrix}^{*} \quad \begin{bmatrix}2\,2\\ \alpha\,\beta\end{bmatrix} = \begin{bmatrix}4\,4\\ \alpha\,\beta\end{bmatrix}.$$

In the above expressions

$$C_\alpha = \cos\left(\frac{\pi}{2}q'_\alpha\right); \quad S_\alpha = \sin\left(\frac{\pi}{2}q'_\alpha\right)$$

$$C_{2\alpha} = \cos(\pi\, q'_\alpha); \quad S_{2\alpha} = \sin(\pi q'_\alpha)$$

q'_α, q'_β and q'_γ are the reduced wave-vector components defined by

$$q = \frac{2\pi}{2a}(q'_\alpha,\ q'_\beta,\ q'_\gamma) \tag{3}$$

where $2a$ is the lattice constant.

3. Evaluation of force constants

The elastic constants, the optic frequencies at $q = 0$, and some zone boundary frequencies can be expressed in terms of interatomic force constants and an effective ion charge. These relations can be used for the evaluation of force constants. The following expressions for the elastic constants have been derived by the method of long waves as discussed by Verma (1971) and using the numerical values of Rajgopal (1962) for the Coulomb contributions to the elastic constants.

$$aC_{11} = a_1 + 2a_2 + a_3 + 12\sigma_1 + 6\sigma_2 + 6\sigma_3 + 4\sigma_4 + 3{\cdot}276\, z_2^2\, \frac{e^2}{V} \tag{4}$$

$$aC_{12} = a_1 + a_2 - 6\sigma_1 - 15\sigma_2 - 3\sigma_3 - 2\sigma_4 - 5{\cdot}395\, z_2^2\, \frac{e^2}{V} \tag{5}$$

$$aC_{44} = a_1 + a_2 + 2\sigma_1 + 9\sigma_2 + \sigma_3 + 2\sigma_4 - 1{\cdot}527\, z_2^2\, \frac{e^2}{V} - \frac{\left(-a_1 + 2\sigma_1 + 3\sigma_2 + 2\sigma_3 + 5{\cdot}038\, z_2^2\, \frac{e^2}{V}\right)^2}{a_1 + a_3 + 8\sigma_1 + 12\sigma_2 + 4\sigma_3 + 4\sigma_4}. \tag{6}$$

In the limit of long wavelength, the dynamical matrix can be solved for the zone centre. This yields the following expressions for the optic frequencies at $q = 0$:

$$\omega^2(\Gamma\triangle_1 0) = \left(\frac{2}{m_1} + \frac{1}{m_2}\right)\left(4a_1 + 16\sigma_1 + 24\sigma_3 + 16\sigma_3 + 16\sigma_4\right.$$

$$+ \frac{16\pi}{3} z_2^2 \frac{e^2}{V}\Big) \tag{7}$$

$$\omega^2 (\Gamma\triangle_5 0_2) = \Big(\frac{2}{m_1} + \frac{1}{m_2}\Big)\Big(4a_1 + 16\sigma_1 + 24\sigma_2 + 16\sigma_3 + 16\sigma_4 - \frac{8\pi}{3} z_2^2 \frac{e^2}{V}\Big) \tag{8}$$

$$\omega^2 (\Gamma\triangle'_2) = \Big(\frac{1}{m_2}\Big)\ (4a_1 + 4a_3 + 32\sigma_1 + 48\sigma_2 + 16\sigma_3 + 16\sigma_4). \tag{9}$$

We have used the group-theoretical notation of Kearney *et al* (1970). They have described the block diagonalisation of the dynamical matrix in symmetry directions. At the point (001) the block matrices for $\triangle_1$, ane $\triangle'_2$ give directly the following expressions for the frequencies at the zone boundary:

$$\omega^2 (X\triangle_1 A) = \Big(\frac{1}{m_1}\Big)\Big(8a_1 + 16a_2 + 32\sigma_1 + 48\sigma_2 + 40\sigma_3 + 32\sigma_4 + 17{\cdot}334\ z_2^2 \frac{e^2}{V}\Big) \tag{10}$$

$$\omega^2 (X\triangle_1 0) = \Big(\frac{1}{m_2}\Big)\Big(4a_1 + 4a_3 + 48\sigma_1 + 24\sigma_2 + 20\sigma_3 + 16\sigma_4 + 19{\cdot}375\ z_2^2 \frac{e^2}{V}\Big) \tag{11}$$

$$\omega^2 (X\triangle'_2) = \Big(\frac{1}{m_2}\Big)\Big(4a_1 + 48\sigma_2 + 20\sigma_3 + 16\sigma_4 - 10{\cdot}707\ z_2^2 \frac{e^2}{V}\Big). \tag{12}$$

These equations were solved to evaluate the seven force constants and the charge parameter z_2^2 (e^2/V). The input data and the calculated force constants are given in table 1.

4. Results and discussion

The vibration frequencies of calcium fluoride calculated on the basis of the present model for various reduced wave vectors q's along the principal symmetry directions have been shown in figure 2. The experimental points of Elcombe and Pryor (1970) have also been shown for comparison. It is readily observed that the agreement in all the three directions is very good. The characteristic features, namely, the crossing over of optical and acoustical branches in (001) direction are well reproduced. There is a minor discrepancy at the point $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ for the A_1O_2 branch and also another near the zone boundary for the $\triangle_5 A$ branch. Such discrepancies are usually observed when phonon frequencies are computed from force models containing only a small number of parameters. This is due to the fact that some of the quantities from which parameters are calculated have large uncertain errors. In addition to this there are approximations which are inherent in the model itself. In the present model one such approximation is the assumption of rigid ions. It is pertinent to remark that Ganesan and Srinivasan (1962) explained some of the discrepancies between the theoretical results on CaF_2 and

Table 1. Input data and calculated force constants of CaF_2

Input Data				Force constants	
Property		Value	Ref.	Force Constant	Value
Elastic constants (10^{11} dyn/cm^2)	C_{11}	16·484	Ho and	a_1	12634·8
	C_{12}	4·458	Ruoff	a_2	3725·7
	C_{44}	3·377	(1967)	a_3	22151·3
Optical frequencies (T Hz)	$\Gamma\Delta_1 0$	14·00	Elcombe	σ_1	−1208·5
	$\Gamma\Delta_5 0_2$	7·74	and Pryor	σ_2	− 850·3
	$\Gamma\Delta'_2$	9·66	(1970)	σ_3	−1523·5
Zone boundary frequencies (T Hz)	$X\Delta_1 A$	9·60	Elcombe	σ_4	5049·9
	$X\Delta_1 0$	11·75	and Pryor	$Z_2^2 e^2/V$	3459·2
	$X\Delta'_2$	4·30	(1970)		
Lattice Constant $2a$ (10^{-8} cm)		5·463	Wyckoff (1963)		
Masses of ions Ca: m_1		40·08	Kittel		
(a.m.u) F: m_2		19·00	(1963)		

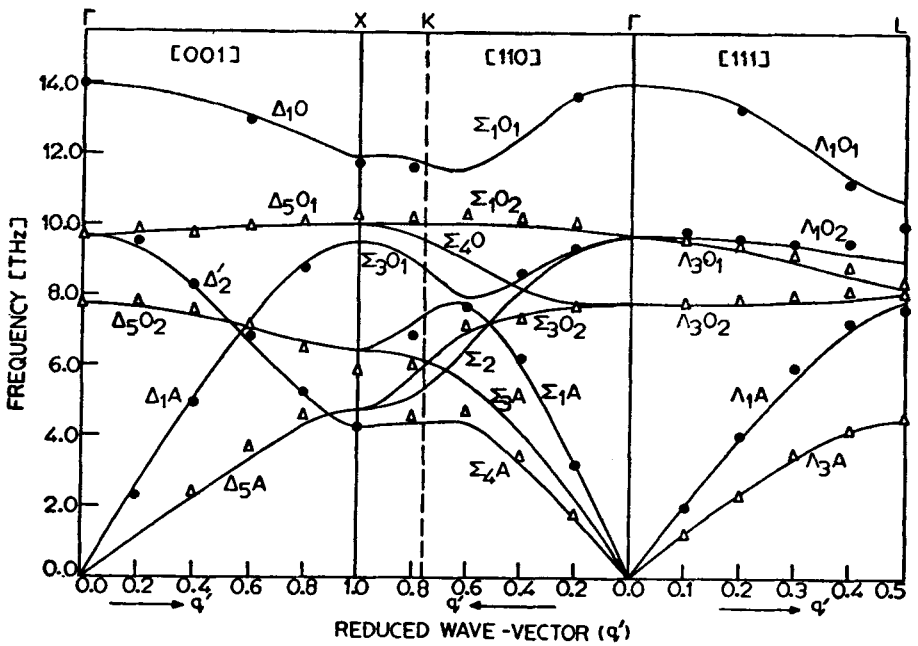

Figure 2. Phonon dispersion curves of CaF_2 for the symmetry directions. Experimental points of Elcombe *et al* are shown by ● for longitudinal and by △ for transverse branches.

experimental data by assuming that one of the force constants is a function of the wave vector.

Early lattice dynamical studies on CaF_2 were mostly concerned with derivation of expressions for the long-wavelength eigenfrequencies. The main aim was to study the elastic constants and the dielectric properties. Srinivasan (1958), Reitz *et al* (1961) and Rajgopal (1962) used a central force scheme proposing a Born-Mayer type repulsive interaction. These models do not account for the difference between C_{12} and C_{44}. Ganesan and Srinivasan (1962) used a general non-central short range interaction for extensive calculations of both lattice dynamics and derived quantities. This was further extended through Srinivasan's (1968) work on the lattice theory of an elastic dielectric. Denham *et al* (1970) used a simple rigid-ion model in which the parameters of the model were chosen to fit the long-wavelength data. Axe (1965) based his simple dipole shell model on the long-wavelength data and successfully explained the Cauchy discrepancy. Catlow and Norgett (1973) used more general forms of second-neighbour interaction in their shell model calculations which were also based on long-wavelength data. Since the main aim of the present work is to calculate the phonon dispersion curves, it is not possible to compare our results with those of the above workers.

The first computation of dispersion curves of CaF_2 was made by Ganesan and Srinivasan (1962) but they did not compare their results with experimental data which were probably not available at that time. Elcombe and Pryor (1970) used the neutron scattering technique to obtain the phonon dispersion curves of CaF_2 in the symmetry directions. For interpreting their measurements they used rigid ion and fourteen parameter shell models, whose parameters were determined by least squares fit to the measured phonon frequencies. The results of our present investigation give a better fit than their rigid-ion model calculations and compare well with their shell model results. We have thus been able to produce good results with a simpler technique and a model having lesser number of parameters. Further improvement is expected if the parameters of our model are adjusted by least squares fit.

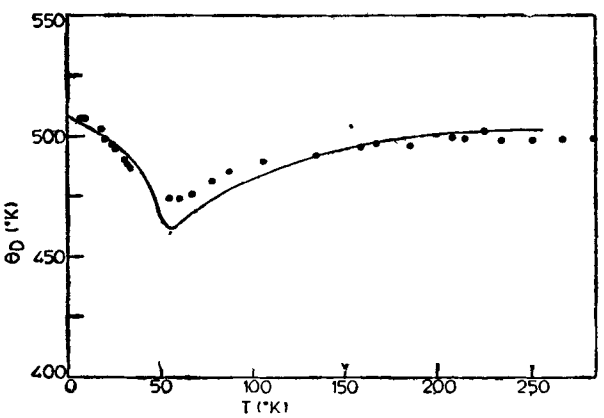

Figure 3. Calculated Debye temperature of CaF_2 as a function of temperature. Closed circles show the experimental points of Todd above 50° K and of Huffmann *et al* below 50° K.

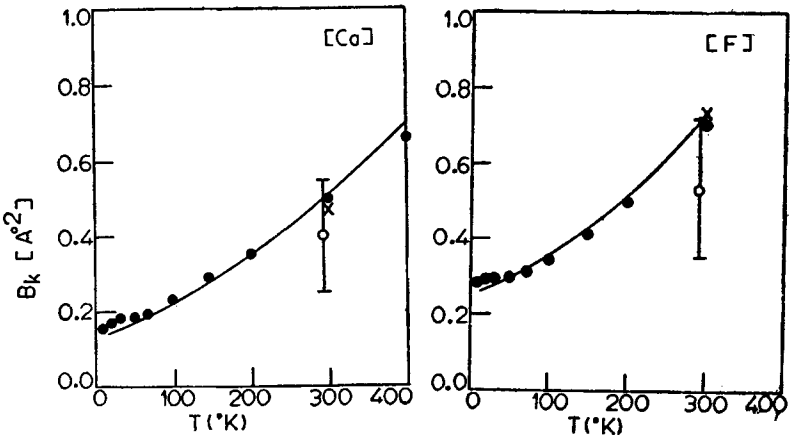

Figure 4. Debye-Waller factors of CaF_2. Full curve shows the results of present calculations. Closed circles are the calculated values of Elcombe *et al* while the open circles refer to the experimental measurements of Willis. The X represents the measurement of Togawa.

As a test of the accuracy of the phonon frequencies for general directions also vibrational properties like specific heat and Debye-Waller factor have been calculated. The specific heat results are displayed in figure 3 in the customary manner in terms of the Debye-curve as a function of temperature together with the experimental measurements of Huffmann and Norwood (1960) and Todd (1949). Accurate calculations could not be made below 20° K, and the curve has been smoothly joined to the value at 0° K taken from the paper of Elcombe and Pryor (1970).

The conventional Debye-Waller B_k-values have also been computed as a function of temperature following the method discussed in the paper of Dolling *et al* (1965). The results are given in figure 4 along with the calculated values of Elcombe and Pryor (1970) and the experimental results of Willis (1965) and Togawa (1964). The agreement is satisfactory.

The present calculations thus bring out the success of CGW type angular forces for a fluorite lattice. No effect of anharmonicity has been considered in the calculations, which may account for the deviations at high temperatures.

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