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The Deformable Shell Model Calculation of Infrared Absorption Frequencies of Ionic Crystals

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The deformable shell model which includes many-body effects and accounts for the breakdown of Cauchy relation is extended to the case of the CsCl structure. The TO mode frequencies for $q = 0$ are calculated for eight ionic crystals of both NaCl and CsCl structures. For comparison, the shell model values are also calculated. The results are compared with the infrared absorption frequencies. It is found that the deformable shell model gives better agreement than the shell model. The result is particularly striking for crystals showing a large Cauchy relation breakdown.

Das deformierbare Schalenmodell, das Vielteilcheneffekte einschließt und für das Versagen der Cauchy-Beziehung verantwortlich ist, wird auf den Fall der CsCl-Struktur ausgedehnt. Die Frequenzen der TO-Schwingungsmode für $q = 0$ werden für acht Ionenkristalle sowohl der NaCl- als auch der CsCl-Struktur berechnet. Zum Vergleich werden auch die Werte des Schalenmodells berechnet. Die Ergebnisse werden mit den Infrarotabsorptionsfrequenzen verglichen. Es wird gefunden, daß das deformierbare Schalenmodell bessere Übereinstimmung als das Schalenmodell gibt. Die Ergebnisse sind besonders gut für Kristalle, die ein starkes Versagen der Cauchy-Beziehung zeigen.

1. Introduction

The lattice dynamics of ionic crystals have been intensively studied in recent years. Several models have been suggested to improve upon the original Born-Karman theory [1 to 8]. Of these the deformable shell model [6, 7] includes an effective three-body interaction and accounts for the breakdown of the Cauchy relation. The model has been applied to the study of the dispersion curves for NaI, KI, and KBr and is found to give encouraging results. But for many crystals for which many-body effects are known to be important, experimental dispersion curves are not available. In the present paper we apply the model to a larger group of crystals of both NaCl and CsCl structure, and calculate the infrared absorption frequencies. For this purpose the deformable shell model is extended to include the case of CsCl structure. The parameters of the model are determined according to the procedures discussed in Section 2. For comparison frequencies are also calculated according to the shell model. The results of calculation for eight ionic crystals are given and compared with the experimental values. It is found that the deformable shell model gives distinctly better values than the shell model. The result is particularly striking for those crystals for which the deviation from the Cauchy relation is large.

2. Determination of the Model Parameters

For determining the parameters of a model one has to use the experimental values of elastic constants and the lattice constant. Some authors [9] use the constants at the temperature and pressure at which the experimental frequencies are measured. Others [4] use the constants at the absolute zero of temperature. The two procedures give slightly different values of the parameters. In the present paper we shall calculate the frequencies of normal modes of the crystal according to the quasi-harmonic approximation of Leibfried and Ludwig [10]. For this purpose a more careful evaluation of the model parameters is necessary. It is well known that the frequencies of normal modes are temperature-dependent because of anharmonic effects. A part of this temperature dependence arises due to the thermal expansion of the crystal, and another part is due to the self-energy of the phonons [11, 12]. In the present calculation the first effect is taken account of and the second effect is neglected. Estimates made by Cowley [11] show that for KBr at room temperature the frequency shift due to the first effect is about 12% and that due to the second effect is about 2% for the $q = 0$ TO mode. The corresponding values for NaI are 12% and 6%, respectively. As our main interest is in the investigation of the effect of the many-body interaction implied in the deformable shell model, the neglect of the self-energy shift will not seriously affect our conclusions. To calculate the frequencies of normal modes at T (°K) according to the above quasi-harmonic approximation the proper procedure for the evaluation of the parameters of the model will be to compare the expressions for the elastic constants obtained from the long-wave method with the harmonic elastic constants of the solid at $T = 0$, the solid being under a suitable stress such that its lattice constant is the same as that at T (°K). The experimental values of the harmonic elastic constants can only be obtained for atmospheric pressure. From the pressure derivatives of the elastic constants we can get the required values. Thus we write for the elastic constants obtained from the long-wave method

$$e_{ijkl}^{\text{l.w.}}(r) = \tilde{C}_{ijkl}(\exp) + \frac{\mathrm{d}\,\tilde{C}_{ijkl}}{\mathrm{d}P}(P - P_0) - P\left(\delta_{lj}\,\delta_{ik} + \delta_{il}\,\delta_{jk} - \delta_{ij}\,\delta_{kl}\right), \quad (1)$$

where $\tilde{C}$ is the harmonic elastic constant, $2\,r_0$ is the lattice constant at the temperature at which the normal mode frequencies are to be calculated, P_0 is the atmospheric pressure, and

$$P - P_0 = (\tilde{C}_{11} + 2\,\tilde{C}_{12})\frac{\tilde{r}_0 - r_0}{r_0}. \quad (2)$$

In the above expression $2\,\tilde{r}_0$ is the harmonic value of the lattice constant. Expressing the pressure derivatives in terms of the third-order elastic constants we get for the three elastic constants of a cubic crystal (we put $P_0 \approx 0$) [13]

$$\left.\begin{aligned}
e_{11}^{\text{l.w.}}(r) &= \tilde{C}_{11}(\exp) + (2\,\tilde{C}_{11} + 2\,\tilde{C}_{12} + C_{111} + 2\,C_{112})\,v_0\,, \\
e_{12}^{\text{l.w.}}(r) &= \tilde{C}_{12}(\exp) - (\tilde{C}_{11} + \tilde{C}_{12} - C_{123} - 2\,C_{112})\,v_0\,, \\
c_{44}^{\text{l.w.}}(r) &= \tilde{C}_{44}(\exp) + (\tilde{C}_{11} + 2\,\tilde{C}_{12} + \tilde{C}_{44} + C_{144} + 2\,C_{166})\,v_0\,,
\end{aligned}\right\} \quad (3)$$

where

$$v_0 = \frac{r_0 - \tilde{r}_0}{\tilde{r}_0}.$$

Fig. 1. The positions of the particles a, b, and c for which non-vanishing force constants given by equation (4) exist. Other particles are obtained from symmetry
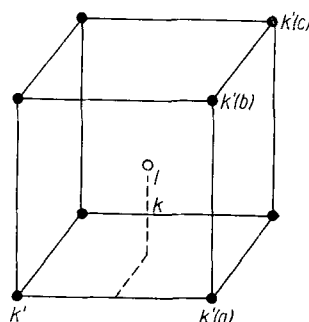
All quantities on the right-hand side are known from experimental measurement of the variation of elastic constants with temperature and pressure, and the value of the coefficient of expansion. The left-hand sides are expressed in terms of the potential function for the interaction between the ions. The parameters of the potential function may therefore be determined from equation (3).

3. Infrared Absorption Frequencies in the Deformable Shell Model

The deformable shell model [6, 7] has been applied to crystals with NaCl structure. The expressions for elastic constants according to the long-wave method and the expression for the dynamical matrix for this structure are given by Basu and Sengupta [6]. As we shall apply the model to several crystals having CsCl structure, the corresponding equations for this structure are developed in the following.

As has been shown by Basu and Sengupta [6] the deformability of the ions leads to three-body force constants between the ions $(l'k')$ and $(l''k'')$ given by

$$\Phi_{ii'}^{(d)}\begin{pmatrix} l' & l'' \\ k' & k'' \end{pmatrix} = \sum_{lkjj'} A(k)\, \Phi_{ij}^{R}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} \Phi_{i'j'}^{R}\begin{pmatrix} l & l'' \\ k & k'' \end{pmatrix} r_j\begin{pmatrix} l' & l \\ k' & k \end{pmatrix} r_{j'}\begin{pmatrix} l'' & l \\ k'' & k \end{pmatrix}, \qquad (4)$$

where $A(k)$ defines the deformability of the k-ions, Φ^{R} is the force constant due to a two-body central repulsive interaction $\Phi(r)$ between the nearest neighbours only, and $r\begin{pmatrix} l' & l \\ k' & k \end{pmatrix}$ is the equilibrium separation between the $(l'\,k')$ and $(l\,k)$ ions. In the above expression the summation extends only to those $(l\,k)$ which are common nearest neighbours to both $(l'\,k')$ and $(l''\,k'')$ ions. For CsCl structure non-vanishing force constants exist only if $k'' = k'$ and $l'' = l'$ or if $l''\,k'$ is an ion of type a, b, or c shown in Fig. 1. The force constant matrices are given by

$$\Phi^{d}\begin{pmatrix} l' \\ k' \end{pmatrix} = 4\, P(k) \begin{vmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}, \qquad (5)$$

$$\Phi^{d}\begin{pmatrix} l' \\ k' \end{pmatrix} = 2\, P(k) \begin{vmatrix} -1 & 0 & -1 \\ 0 & 1 & 0 \\ -1 & 0 & -1 \end{vmatrix}, \qquad (5')$$

$$\Phi^{d}\begin{pmatrix} l' \\ k' \end{pmatrix} = -\, P(k) \begin{vmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{vmatrix}, \qquad (5'')$$

and

$$\Phi^{d}\begin{pmatrix} l' & l' \\ k' & k' \end{pmatrix} = 8\, P(k) \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}, \qquad (5''')$$

where $P(k) = -\, A(k)\, \Phi''^{2}\, r_0^2$ ($2\, r_0$ lattice constant).

With these force constants we can now obtain expressions for elastic constants from the long-wave method. They are given by

$$
e_{11}^{\text{l.w.}} = \frac{\Phi''}{3\,r_0} + 0.3849\,\frac{\Phi'}{r_0^2} + 0.1774\,\frac{e^2}{r_0^4} + \frac{8}{r_0}\left(P(1) + P(2)\right),
$$

$$
e_{12}^{\text{l.w.}} = \frac{\Phi''}{3\,r_0} - 0.7698\,\frac{\Phi'}{r_0^2} - 0.1734\,\frac{e^2}{r_0^4} + \frac{8}{r_0}\left(P(1) + P(2)\right), \tag{6}
$$

$$
e_{44}^{\text{l.w.}} = \frac{\Phi''}{3\,r_0} + 0.3849\,\frac{\Phi'}{r_0^2} - 0.0886\,\frac{e^2}{r_0^4}.
$$

The corresponding expressions for NaCl structure are given in reference [6].

The contribution to the dynamical matrix because of the force constants given by equations (5) to (5''') is

$$
D_{\alpha\alpha}(k''\,k') = 8\,P(k)\,\delta(k''\,k')\,(1 - \cos 2\,q_\alpha\,r_0)\,(1 + \cos 2\,q_\beta\,r_0)\,(1 + \cos 2\,q_\gamma\,r_0),
$$

$$
D_{\alpha\beta}(k''\,k') = 8\,P(k)\,\delta(k''\,k')\,\sin 2\,q_\alpha\,r_0\,\sin 2\,q_\beta\,r_0\,(1 + \cos 2\,q_\gamma\,r_0). \tag{7}
$$

For $q = 0$, deformability has no contribution to the dynamical matrix. Thus, in this case the frequencies of the two optical modes are given by the same expression as in the simple shell model. Assuming only the negative ion to be polarizable we get for the transverse optical mode [1]

$$
(\mu\,\omega_{\mathrm{T}}^2)_{q=0} = R_0 - \frac{e^2\,d^2}{\alpha_e} - \frac{4\,\pi\,e^2\,(z - d)^2\,(\varepsilon_\infty + 2)}{9\,v}. \tag{8}
$$

The meaning of the symbols are the same as in reference [6]. In particular R_0 and d are defined by

$$
R_0 = 2\left(\Phi'' + \frac{2\,\Phi'}{r_0}\right) \qquad \text{for NaCl structure},
$$

$$
= \frac{8}{3}\left(\Phi'' + \frac{2\sqrt{3}}{3}\,\frac{\Phi'}{r_0}\right) \quad \text{for CsCl structure}, \tag{9}
$$

$$
d = \frac{Y\,R_0}{K + R_0}, \tag{9'}
$$

where $-Y\,e$ is the charge on the ion shell and K is the isotropic spring factor which binds the shell to the positive core. The five parameters Φ'', Φ', Y, K, and $(P(1) + P(2))$ are determined in the usual way from the elastic constants interpreted in accordance with equation (3) and the two dielectric constants. It is to be noted that the deformability parameter $(P(1) + P(2))$ does not directly enter the frequency expression (8). Its effect on ω_{T} comes indirectly through R_0 whose value determined from equation (3) and (6) is changed because of the deformability terms.

In Table 1 we have collected the data that have been used to calculate the five parameters for the eight crystals for which all the data were available with sufficient accuracy. In Table 2 we give the values of ω_{T} calculated according to four different models. The first two values correspond to a simple shell model with room temperature values of elastic constants (SM1), and with corrected elastic constants as given by equation (3) (SM2). The last two values correspond to a similar calculation with the deformable shell model (DSM1 and DSM2). The values corresponding to SM2 and DSM2 give the quasiharmonic frequencies.

Table 1

Data used for calculation of the model parameters. e_{11}, e_{12}, and e_{44} are the elastic constants defined by equation (3). The harmonic and the room temperature lattice constants are $2 \tilde{r}_0$ and $2 r_0$, respectively. The numbers within brackets in the second and third column give the references for room temperature and harmonic lattice constants and those in the fourth and fifth column the references for elastic constants and their pressure derivatives, respectively, for the crystal in the corresponding row

Crystal	r (10^{-8} cm)	$\tilde{r}$ (10^{-8} cm)	Room temperature elastic constants (10^{12} dyn/cm^2)			Harmonic elastic constants (10^{12} dyn/cm^2)			Long-wave elastic constants (10^{12} dyn/cm^2)		
			C_{11}	C_{12}	C_{44}	C_{11}	C_{12}	C_{44}	e_{11}	e_{12}	e_{44}
LiF	2.01 [14]	1.99 [14]	0.818 [15]	0.349 [16]	0.565	1.588	0.769	0.685	1.283	0.685	0.643
NaBr	2.981 [14]	2.946 [14]	0.401 [17]	0.101 [18]	0.099	0.507	0.106	0.105	0.370	0.053	0.101
KCl	3.137 [14]	3.108 [14]	0.395 [19]	0.049 [20]	0.063	0.498	0.024	0.068	0.421	0.015	0.070
AgCl	2.772 [22]	2.745	0.597 [21]	0.365 [23]	0.062	0.789	0.409	0.085	0.733	0.355	0.074
CsBr	2.144 [14]	2.116 [14]	0.304 [24]	0.080 [25]	0.074	0.342	0.108	0.106	0.300	0.076	0.083
CsI	2.280 [14]	2.252 [14]	0.246 [25]	0.065 [26]	0.063	0.278	0.085	0.087	0.223	0.051	0.070
TlBr	1.993 [27]	1.968 [27]	0.376 [27]	0.146	0.076	0.472	0.186	0.120	0.378	0.121	0.074
RbCl	3.270 [14]	3.239 [14]	0.365 [28]	0.065 [29]	0.048	0.460	0.076	0.050	0.425	0.053	0.047

Table 2

Values of ω_T calculated according to the shell model (SM) and the deformable shell model (DSM). Columns (2) and (4) give values when room temperature elastic constants are the input data; columns (3) and (5) give values when elastic constants are calculated from equation (3). Experimental values refer to room temperature

Crystal	ω_T (10^{13} s^{-1}) (SM1)	ω_T (10^{13} s^{-1}) (SM2)	ω_T (10^{13} s^{-1}) (DSM1)	ω_T (10^{13} s^{-1}) (DSM2)	ω_T (10^{13} s^{-1}) (experimental)
LiF	5.50	5.98	5.99	5.86	5.78
NaBr	2.48	2.40	2.45	2.53	2.52
KCl	2.50	2.59	2.55	2.75	2.68
AgCl	2.18	2.38	1.49	1.92	1.94
CsBr	0.78	0.71	1.37	1.42	1.37
CsI	0.73	0.41	1.18	1.21	1.17
TlBr	5.43	5.53	8.81	8.51	8.10
RbCl	2.13	2.30	2.08	2.28	2.18

4. Discussion

Of the eight crystals considered here three have CsCl structure and the others have NaCl structure.

In the calculation with the shell model we have determined the values of Φ'' from the experimental values of C_{11}. But we can also calculate them from other linear combination of elastic constants. So there is no uniqueness in the determination of Φ'' and consequently the values of ω_T calculated with the shell model are to some extent ambiguous. But in the case of the deformable shell model there is no such ambiguity, because the three parameters Φ'', Φ', and $\big(P(1) + P(2)\big)$ are determined from the three elastic constants. In order to obtain the values of the elastic constants from equation (3), a knowledge of the harmonic value of the elastic constants as well as the pressure derivatives of the elastic constants is necessary. The harmonic values of the elastic constants can be obtained by an extrapolation of the temperature–elastic constant curve. This can be done only when the elastic constants are measured at various temperatures with sufficient accuracy.

It is noticed from Table 2 that on the whole the deformable shell model with parameters determined according to the procedure outlined in Section 2 (DSM 2) gives distinctly better agreement with the experimental results. The most striking examples are AgCl, TlBr, and LiF. It may be noted that for these crystals the Cauchy-relation breakdown is very pronounced indicating that many-body effects are comparatively large in these cases. In several cases values of ω_T corresponding to DSM1 appear to be slightly better compared to those of DSM 2. But in all these cases deviations for both the models are small and possibly within experimental error. An interesting point to be noted is that the frequencies obtained according to DSM2 are always a few per cent higher than the experimental values. The only exception is AgCl where the difference in the two values is quite small. Such a shift in frequency may occur due to the anharmonic coupling of the phonons. However, the differences are small and within five per cent in all cases.

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