

Application of the three body force shell model to the lattice dynamics of calcium oxide

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Abstract. The lattice dynamics of CaO has been studied on the basis of the three body force shell model, which takes into account the effect of many body interactions in the lattice potential. The dispersion curves obtained by plotting ω vs q agree fairly well with the experiments. It is concluded that the value of the molecular electronic polarizability of the solid must be much smaller than that determined experimentally which suggests that the interaction system in the solid may have a substantial covalent character.

Keywords. Calcium oxide; three body force shell model; molecular electronic polarizability.

1. Introduction

The alkaline earth oxide crystals are predominantly ionic in character and their lattice dynamics can be studied on the basis of the same theoretical models which are applicable to alkali halides. The dielectric properties of the latter class of compounds are most simply explained in terms of the shell model of Dick and Overhauser (1958) which has been suitably developed by Woods *et al* (1960) for the study of the vibrational properties of these solids. This approximate model has been recently improved by Nusslein and Schroder (1967) by including a radial breathing motion of the shell and by Verma and Singh (1969) by including three body forces between ion pairs. The two resulting models viz., the breathing shell model (BSM) and the three body force shell model (TSM) have been shown to be approximately equivalent by Cochran (1971) and by Verma (1972), the main difference between the two being only in their mathematical structure and not in their physical contents. Both these models have been successfully applied to the study of phonon dispersion in various ionic crystals and they seem to have established themselves as meaningful simple phenomenological models of ionic solids. Some recent studies (Singh and Upadhyaya 1972, Verma and Agarwal 1973 and Upadhyaya and Singh 1972) concern the alkaline earth oxide crystals MgO and CaO on which the experimental phonon dispersion relations are available.

As pointed out by Agarwal and Verma (1972) the original formulation of the TSM suffered from a discrepancy in respect of the definition of shell and core charges and electronic polarizations of the ions. The discrepancy which becomes serious when we apply the model to the divalent alkaline earth oxides, was later removed by Verma and Agarwal (1973). An application of the corrected theory to MgO has led to excellent results. However, the electronic polarizability of Mg^{2+} is so negligibly small as com-

pared to that of O^{2-} that MgO is more suited for the one-ion polarizable version of the TSM. As against this the electronic polarizability of Ca^{2+} is sufficiently large making CaO a good test case for checking the applicability of the two-ion polarizable version of the TSM to this class of compounds.

The model parameters of the TSM are usually calculated from the values of the elastic constants, the long wave optical vibration frequencies and the electronic polarizabilities of the constituent ions of the solid. The polarizabilities of the ions are determined from the molecular polarizabilities usually by means of the additivity rule, the validity of which is questionable (Pirenne and Kartheuser 1964). It is therefore felt that the electronic polarizabilities are the most doubtful among the input data used in the model. This is why we have derived the dispersion curves of CaO for a number of different sets of values of the electronic polarizabilities of the two ions. In this paper we are reporting results for three different sets of polarizability values obtained by successively reducing the polarizabilities of the two ions in the same ratio. The model used is the one described by Verma and Agarwal (1973). In section 2 we give a brief description of the model and in section 3 the results with a short discussion.

2. Theory

The TSM equations can be put in matrix notation in the form:

$$\begin{aligned} M\omega^2 U &= (\mathcal{Z}\mathbf{C}'\mathcal{Z}+R)U + (\mathcal{Z}\mathbf{C}'\mathcal{Y}+T)W \\ O &= (\mathcal{Y}\mathbf{C}'\mathcal{Z}+T^T)U + (\mathcal{Y}\mathbf{C}'\mathcal{Y}+S)W \end{aligned} \quad (1)$$

with

$$\mathcal{Z}\mathbf{C}'\mathcal{Z} = \mathcal{Z}(\mathcal{Z}+12f(a))\mathbf{C}+\mathbf{V} \quad (2)$$

where $f(a)$ is a function related to overlap integrals of electron wave functions, \mathbf{V} is the matrix of the force constants derived from the purely three body part of the lattice potential as expressed by Lundqvist (1955) and \mathcal{Z} is set equal to 2. The other terms in equations (1) and (2) have the same meanings as in the shell model of Cowley *et al* (1963).

The definition (2) of the modified coulomb matrix implies definitions of shell and core charges such that the expressions for the electronic and distortion polarizabilities become

$$a_\kappa = \frac{e^2 y_\kappa^2 \mathcal{Z}(\mathcal{Z}+12f(a))}{k_\kappa + S_0} \quad (3)$$

$$d_\kappa = \frac{e y_\kappa \sqrt{\mathcal{Z}(\mathcal{Z}+12f(a))}}{k_\kappa + S_0} \quad (4)$$

where $\kappa (=1, 2)$ designates the type of the ions, and k_κ is the isotropic spring constant coupling the core and shell of the κ -type ion.

For wave vectors along the three high symmetry directions in the cubic solid, equation (1) leads to three quadratic equations in ω^2 which can be easily solved to give the frequencies of vibration ω for each wave vector \mathbf{q} ($q=2\pi/\lambda$). The expression for ω^2 in the long wave length limit can be used to obtain the expressions for the elastic constants and the long wave optical vibration frequencies. These relations read as under:

$$C_{11} = \frac{e^2}{4a_0^4} \left[-5.112 \mathcal{Z}(\mathcal{Z}+12f(a)) + A + 9.3204 \mathcal{Z} \left(a \frac{df}{da} \right) \right] \quad (5)$$

$$C_{12} = \frac{e^2}{4a_0^4} \left[0.226 \mathcal{Z}(\mathcal{Z} + 12f(a)) - B + 9.3204 \mathcal{Z} \left(a \frac{df}{da} \right) \right] \quad (6)$$

$$C_{44} = \frac{e^2}{4a_0^4} \left[2.556 \mathcal{Z}(\mathcal{Z} + 12f(a)) + B \right] \quad (7)$$

$$\mu\omega_L^2 = R'_0 + \frac{8\pi}{3} \cdot \frac{e^2}{v} \cdot \frac{\mathcal{Z}'^2}{f_L} \left\{ \mathcal{Z}(\mathcal{Z} + 12f(a)) + 6 \left(a \frac{df}{da} \right) \right\} \quad (8)$$

$$\mu\omega_T^2 = R'_0 - \frac{4\pi}{3} \cdot \frac{e^2}{v} \cdot \frac{1}{f_T} \left\{ \mathcal{Z}'^2 \cdot \mathcal{Z}(\mathcal{Z} + 12f(a)) \right\} \quad (9)$$

where

$$\left. \begin{aligned} f_L &= 1 + \frac{8\pi}{3} \cdot \frac{\alpha}{v} \cdot \frac{1}{\mathcal{Z}(\mathcal{Z} + 12f(a))} \left\{ \mathcal{Z}(\mathcal{Z} + 12f(a)) + 6 \left(a \frac{df}{da} \right) \right\} \\ f_T &= 1 - \frac{4\pi}{3} \cdot \frac{\alpha}{v} \\ \mathcal{Z}' &= 1 - d_2 + d_1 \\ R'_0 &= R_0 - e^2 \left(\frac{d_1^2}{\alpha_1} + \frac{d_2^2}{\alpha_2} \right) \\ R_0 &= (e^2/v) (A + 2B) \end{aligned} \right\} \quad (10)$$

$v=2a^3$ is the volume of the unit cell in the equilibrium configuration and A and B are the force parameters derived from the short range repulsion which is supposed to act entirely through the shells and to be significant only for nearest neighbours. The equilibrium condition with the assumed potential is

$$B = -1.165 \mathcal{Z}(\mathcal{Z} + 12f(a)) \quad (11)$$

Equations (3) or (4), (5) to (9) and (11) constitute the eight constraints to determine the eight parameters of the theory viz., A , B , $f(a)$, $(a df/da)$, \mathcal{Y}_1 , \mathcal{Y}_2 , and k_1 , k_2 or d_1 , d_2 . These parameters are then used to determine the elements of the matrices in equation (1) for any chosen value of the wave vector. Equation (1) can then be solved to determine ω .

3. Results and discussion

The input data are given in table 1 and the model parameters derived from them are listed in table 2. These parameters were used to calculate the vibration frequencies for a number of wave vectors along the three high symmetry directions which have been plotted against q in figure 1 together with the experimental points of Vijayaraghavan and Iyengar (1971).

It is clear from the figure that the best agreement is obtained for the smallest value of the polarizabilities used which corresponds to a molecular polarizability of 2.446 \AA^3 as against 2.9 \AA^3 reported by Tessman *et al* (1953). It has been proved by Verma and Agarwal (unpublished) that the Lorentz-Lorenz relation used in the calculation of molecular polarizabilities of solids is somewhat modified in the presence of three body forces in the interaction system and the corrected equation leads to polarizability values greater or smaller than the TKS values according as the Cauchy discrepancy $C_{12}-C_{44}$ is positive or negative. The corrected molecular polarizability thus calculated is 2.70

Table 1. Input data

Constants	Values	References
$C_{11}(10^{11} \text{ dyne cm}^{-2})$	22.34	Son and Bartels 1972
$C_{12}(10^{11} \text{ dyne cm}^{-2})$	5.93	
$C_{44}(10^{11} \text{ dyne cm}^{-2})$	8.1	
Lattice constant (10^{-8} cm)	2.4033	Vijayaraghavan and Iyengar 1971
$\omega_L(10^{13} \text{ rad sec}^{-1})$	10.83	
$\omega_T(10^{13} \text{ rad sec}^{-1})$	5.65	

Table 2. Model parameters

$A=31.3975$, $B=-3.9242$, $(a \text{ d}f/\text{d}a)=-0.06734$, $f(a)=-0.0263$

$\alpha=2.9 \text{ \AA}^3$	$\alpha=2.7 \text{ \AA}^3$	$\alpha=2.446 \text{ \AA}^3$
$\alpha_1=0.35 \times 10^{-24} \text{ cm}^3$	$\alpha_1=0.48 \times 10^{-24} \text{ cm}^3$	$\alpha_1=0.396 \times 10^{-24} \text{ cm}^3$
$\alpha_2=2.55 \times 10^{-24} \text{ cm}^3$	$\alpha_2=2.22 \times 10^{-24} \text{ cm}^3$	$\alpha_2=2.05 \times 10^{-24} \text{ cm}^3$
$d_1=0.0166$	$d_1=0.0198$	$d_1=0.0297$
$d_2=0.2999$	$d_2=0.2946$	$d_2=0.2948$
$\gamma_1=-5.33$	$\gamma_1=-6.10$	$\gamma_1=-3.37$
$\gamma_2=-2.14$	$\gamma_2=-1.90$	$\gamma_2=-1.75$

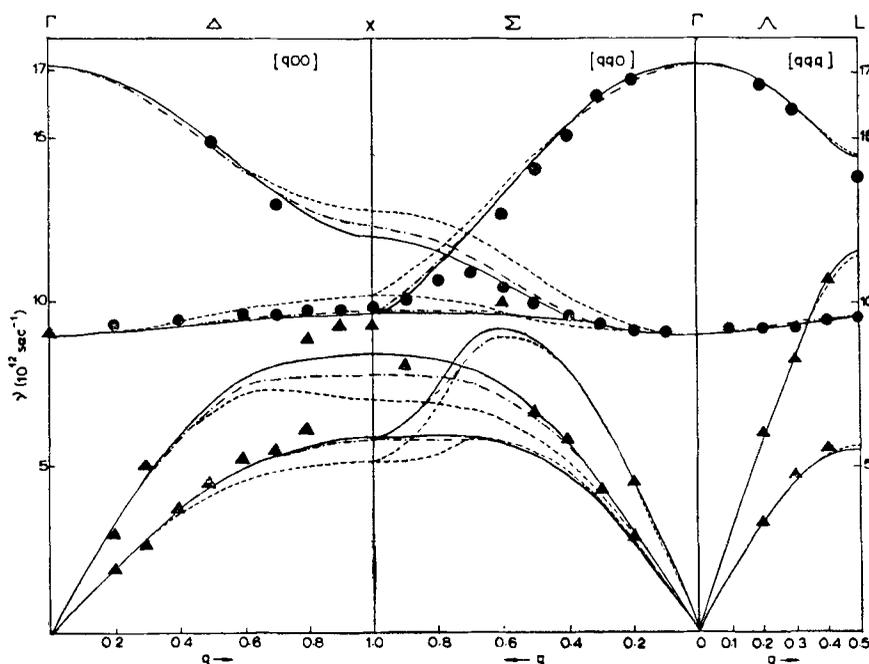


Figure 1. Vibration frequencies for a number of wave vectors along three high symmetry directions *vs q*. Circles and triangles, experimental points of Vijayaraghavan and Iyengar (1971). — for $\alpha=2.446 \text{ \AA}^3$; - · - · - for $\alpha=2.7 \text{ \AA}^3$; - - - - for $\alpha=2.9 \text{ \AA}^3$

\AA^3 . The dispersion curves however show that an exact agreement will perhaps be obtained for a molecular polarizability nearly equal to 2.2\AA^3 , which is much smaller than the corrected value. A look at the work of Pirenne and Kartheuser (1964) shows that the polarizability for the ions may be much smaller than those obtained from the Lorentz-Lorenz relation if some additional interactions like the covalent binding are also operative. The present study thus shows that either the molecular electronic polarizability of CaO is actually equal to nearly 2.2\AA^3 demanding a lower value of the high frequency dielectric constant of the solid than the experimental values reported (Tessman *et al* 1953), or there is a substantial contribution of covalent binding in the interaction system of the solid.

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