

## Optical lattice vibrations in finite ionic crystals: I

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**Abstract.** A theory for the properties of long-wave optical vibration modes in finite ionic crystals of arbitrary shape is given. Neglecting retardation effects, it is found that in finite specimens there exist transverse and longitudinal bulk modes as well as surface modes, which are neither transverse nor longitudinal and which have intermediate frequencies. Explicit solutions are given for diatomic crystal samples with one, two and three dimensions finite. The modifications which arise from more complex unit cells and polarizable ions are given. A detailed calculation of the properties of long-wave optical phonons in finite specimens of strontium titanate is presented.

### 1. Introduction

In this series of papers we present a theory of long-wave optical phonons and of polaritons (phonons strongly coupled to photons) (Hopfield 1958) in ionic crystals of finite size and arbitrary shape. The major conclusion is that the energies and modes of vibrations are essentially size and shape dependent. The same is true for their primary experimental diagnostics, light absorption, *to the extent that one can fairly say that a theory which does not take into account the size and shape of the specimen can only partially explain absorption and transmission results.*

We have earlier published concisely some of our results (Englman and Ruppin 1966) for phonons, that is without retardation taken into account, and in the first part we cover the same subject, now, however, in an extended and a more detailed form. While the optical transverse phonons cannot properly be decoupled from photons, nevertheless much of the current thinking and discussion of infra-red absorption is in terms of phonons (rather than polaritons). There is, further, a region in the Brillouin zone of vibrations (wavelengths shorter than that of the reststrahlen, though still longer than lattice spacings) where long-wave phonons are respectable. These two reasons justify, in our view, the separate presentation of the phonon problem in this first part. In the following two parts the all-important shape and size dependence of polaritons is treated. There, some of the results appropriate for the limiting case of pure phonons will be rederived.

The basis of our investigation is the existence of the long-range Coulomb forces in ionic crystals which cause the frequencies of the long-wave optical phonons to depend on the size and on the shape of the specimen (Englman and Ruppin 1966). This effect is important for phonons with wavelengths comparable with the dimensions of the crystal. Some related experiments, which show shape-dependent frequencies, have been performed on thin slabs (Berreman 1963) and on approximately needle-shaped (Hass 1964) and spherical (Tsuboi *et al.* 1962, Axe and Pettit 1966) specimens. A feature common to all experiments is the appearance of lattice absorption at frequencies other than  $\omega_T$  (the long-wave transverse optical frequency), which is the only absorption frequency in the theory of large crystals (Born and Huang 1954) (disregarding the structure arising from anharmonic effects). The frequencies at which absorption is found to occur in finite crystals are usually found to lie within (and on the boundaries of) the region between  $\omega_T$  and  $\omega_L$  (the long-wave longitudinal optical frequency).

A first explicit calculation of a shape-dependent frequency was given by Fröhlich (1949), who obtained the frequency of optical phonons of infinite wavelength for the case of a spherical specimen of a diatomic ionic crystal. This frequency is, as will be shown in the present work, the lowest in a series of optical surface modes of the spherical crystal. So far, only the simplest case, that of the diatomic crystal slab, has received a complete theoretical treatment (Fuchs and Kliewer 1965). We present now a general theory which will apply to

specimens of arbitrary shapes and from which all the long-wave optical modes of vibration can be calculated. In this treatment, as well as in the theoretical works cited above, retardation effects are neglected.

## 2. Finite diatomic crystals

We discuss first the properties of long-wave optical phonons in simple diatomic ionic crystals. The equations of motion of the lattice are

$$M_{\kappa} \ddot{U}_{\alpha} \binom{l}{\kappa} = - \sum_{l' \kappa'} \Phi_{\alpha\beta} \binom{l l'}{\kappa \kappa'} U_{\beta} \binom{l'}{\kappa'} \quad (1)$$

where  $\mathbf{U} \binom{l}{\kappa}$  is the displacement of the atom of type  $\kappa$  in the  $l$ th unit cell from its equilibrium position and  $\Phi_{\alpha\beta} \binom{l l'}{\kappa \kappa'}$  are the atomic force constants.

For a lattice obeying periodic boundary conditions the normal modes of vibration are plane waves, and in the long-wavelength limit the two optical frequencies are given by (Kellerman 1940)

$$\omega_{\text{T}}^2 = \omega_0^2 - \frac{4\pi}{3} \quad \omega_{\text{L}}^2 = \omega_0^2 + \frac{8\pi}{3}. \quad (2)$$

The squared frequency is measured here in units of  $e^2/\mu V$ , where  $V$  is the volume of the unit cell and  $\mu$  is the reduced mass of the two atoms. The presence of the long-range Coulomb interaction causes the splitting between the longitudinal branch and the transverse branch, which would otherwise be degenerate with a single frequency  $\omega_0$ .

From (1) we go over to the equations of motion of the relative displacement of the positive and the negative ions. Assuming  $\exp(-i\omega t)$  for the time dependence these are

$$\mu \omega^2 f_{\alpha}(l) = \sum_{l' \beta} \Phi_{\alpha\beta}(ll') f_{\beta}(l') \quad (3)$$

where  $\mathbf{f}(l) = \mathbf{U} \binom{l}{+} - \mathbf{U} \binom{l}{-}$  is the relative displacement of the ions. The force constants contain a part arising from short-range forces and a part arising from the long-range Coulomb forces. The contribution of the short-range forces is independent of the shape of the crystal. Here, and throughout our work, we neglect the variation of the short-range force constants for the atoms lying at the surface of the crystal. The modes affected by this surface effect have short wavelengths, while our concern is the long-wavelength modes. Thus we write the equations (3) in the form

$$\mu(\omega^2 - \omega_0^2) f_{\alpha}(l) = \sum'_{l' \beta} \Phi_{\alpha\beta}^{\text{C}}(ll') f_{\beta}(l') \quad (4)$$

where now only the Coulomb force constants appear.

For vibrations with wavelength long compared with the lattice constant  $\mathbf{f}(l)$  can be replaced by a continuous function  $\mathbf{f}(\mathbf{r})$  of the coordinate  $\mathbf{r}$  and the summation in (4) replaced by an integral over the volume of the crystal. The equations of motion thus take the form

$$\mu(\omega^2 - \omega_0^2) f_{\alpha}(\mathbf{r}) = \frac{1}{V} \sum_{\beta} \int' \Phi_{\alpha\beta}^{\text{C}}(\mathbf{r}, \mathbf{r}') f_{\beta}(\mathbf{r}') d^3r' \quad (5)$$

where the prime on the integral sign means that the neighbourhood of the point  $\mathbf{r} = \mathbf{r}'$  is to be excluded from the domain of integration (since the summation in (4) was over  $l' \neq l$ ). Using the explicit form of the Coulomb force constants

$$\Phi_{\alpha\beta}^{\text{C}}(\mathbf{r}, \mathbf{r}') = \frac{\partial^2}{\partial r_{\alpha} \partial r_{\beta}'} \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} = - \frac{\partial^2}{\partial r_{\alpha} \partial r_{\beta}} \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \quad (6)$$

and the relation

$$\Delta \frac{1}{|\mathbf{r}-\mathbf{r}'|} \equiv \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \frac{1}{|\mathbf{r}-\mathbf{r}'|} = -4\pi\delta(\mathbf{r}-\mathbf{r}') \quad (7)$$

we can write (5) in the form

$$\left( \omega^2 - \omega_0^2 + \frac{4\pi}{3} \right) \mathbf{f}(\mathbf{r}) = -\text{grad div} \int \frac{\mathbf{f}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r' \quad (8)$$

where again  $\omega^2$  is measured in units of  $e^2/\mu V$ . This is an integral equation whose eigenfunctions  $\mathbf{f}(\mathbf{r})$  are the vibration amplitudes of the ions in long-wave optical modes and whose eigenvalues give the frequencies of these modes. The integration in (8) is over the whole volume of the crystal.

The last equation can also be derived in a different way, starting from the equation of motion for the relative displacement of the ions

$$\mu \ddot{\mathbf{f}} = -\mu\omega_0^2 \mathbf{f} + e \left( \mathbf{E} + \frac{4\pi}{3} \mathbf{P} \right) \quad (9)$$

where  $\mu\omega_0^2$  is the force constant of the short-range interaction and  $(4\pi/3)\mathbf{P}$  is the local field correction to the macroscopic field  $\mathbf{E}$ .  $\mathbf{P}$ , the dipole moment per unit volume, is equal to the product of the dipole moment of a unit cell,  $e\mathbf{f}$ , and the density of the unit cells,  $1/V$ .  $\mathbf{E}$  is equal to  $-\text{grad } \phi$ , where  $\phi$ , the potential created by the distribution of dipoles of density  $\mathbf{P}(\mathbf{r})$ , is given by

$$\phi(\mathbf{r}) = - \int \left\{ \text{grad} \frac{1}{|\mathbf{r}-\mathbf{r}'|} \cdot \mathbf{P}(\mathbf{r}') \right\} d^3r' = - \int \text{div} \frac{\mathbf{P}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r'. \quad (10)$$

Combining (9) and (10) we again obtain the basic integral equation (8). Operating on (8) with the operators  $\text{div}$  and  $\text{curl}$ , respectively, the following equations are obtained:

$$\begin{aligned} \left( \omega^2 - \omega_0^2 - \frac{8\pi}{3} \right) \text{div } \mathbf{f}(\mathbf{r}) &= 0 \\ \left( \omega^2 - \omega_0^2 + \frac{4\pi}{3} \right) \text{curl } \mathbf{f}(\mathbf{r}) &= 0. \end{aligned} \quad (11)$$

From the requirement that both these equations must be satisfied simultaneously, we conclude that there are three possible types of solution.

$$(i) \quad \text{div } \mathbf{f}(\mathbf{r}) = 0 \quad \text{and} \quad \omega^2 = \omega_0^2 - \frac{4\pi}{3} \quad (12)$$

which are transverse modes whose frequency is equal to  $\omega_T$ , the transverse optical frequency of the infinite crystal.

$$(ii) \quad \text{curl } \mathbf{f}(\mathbf{r}) = 0 \quad \text{and} \quad \omega^2 = \omega_0^2 + \frac{8\pi}{3} \quad (13)$$

which are longitudinal modes and their frequency is equal to  $\omega_L$ , the longitudinal optical frequency of the infinite crystal.

$$(iii) \quad \text{div } \mathbf{f}(\mathbf{r}) = 0 \quad \text{and} \quad \text{curl } \mathbf{f}(\mathbf{r}) = 0 \quad (14)$$

which are neither transverse nor longitudinal modes and, as will be shown later, their frequencies depend on the shape of the crystal.

### 3. The surface modes

We discuss first the third type of mode, satisfying equation (14), which will be called the surface mode for reasons which will become clear later. Quite generally, these modes will be of the form  $\mathbf{f} = \text{grad } \phi$ , where  $\phi$  is a solution of the Laplace equation  $\Delta\phi = 0$ . Explicit

expressions for the solutions and the eigenfrequencies can be given for crystals whose boundary surfaces are given by the equations  $\xi_1 = \text{const.}$ , where  $\xi_1, \xi_2, \xi_3$  are curvilinear coordinates such that  $|\mathbf{r} - \mathbf{r}'|^{-1}$  can be expanded in the form (Morse and Feshbach 1953)

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = -4\pi \frac{h_1'}{h_2' h_3'} \sum_q W_q^*(\xi_2', \xi_3') W_q(\xi_2, \xi_3) \frac{y_{1q}(\xi_1) y_{2q}(\xi_1')}{\Delta(y_{1q}, y_{2q})} \rho(\xi_2', \xi_3') \quad (15)$$

where  $W_q(\xi_2, \xi_3) y_{iq}(\xi_1)$  are solutions of the Laplace equation;  $h_i$  is the scale factor for the coordinate  $\xi_i$  ( $h_i'$  is the corresponding factor for the primed coordinate  $\xi_i'$ );  $\Delta$  is the Wronskian of the two 'radial' solutions  $y_{1q}(\xi_1')$  and  $y_{2q}(\xi_1')$  involving their derivatives, given by  $\Delta = y_{1q} y_{2q}' - y_{1q}' y_{2q}$ ; and the density function  $\rho(\xi_2, \xi_3)$  is defined by

$$\int \int W_q^*(\xi_2, \xi_3) W_p(\xi_2, \xi_3) \rho(\xi_2, \xi_3) d\xi_2 d\xi_3 = \delta_{qp}. \quad (16)$$

We distinguish two cases.

(i) The solid has one boundary surface  $\xi_1 = \xi_1^0$ . The solutions of (8) which satisfy (14) are then given by

$$\mathbf{f}_q(\mathbf{r}) = \text{grad}\{W_q(\xi_2, \xi_3) y_{1q}(\xi_1)\} \quad (17)$$

where  $y_{1q}(\xi_1)$  is the solution of the 'radial equation' which is regular at the origin and everywhere inside the solid. To obtain the eigenvalues the integral equation (8) has to be written in terms of the curvilinear coordinates in the form

$$\left(\omega^2 - \omega_0^2 + \frac{4\pi}{3}\right) f_j(\mathbf{r}) = \frac{1}{h_j} \frac{\partial}{\partial \xi_j} \int \sum_i \frac{1}{h_i'} \left(\frac{\partial}{\partial \xi_i'} \frac{1}{|\mathbf{r} - \mathbf{r}'|}\right) f_i(\mathbf{r}') h_1' h_2' h_3' d\xi_1' d\xi_2' d\xi_3'. \quad (18)$$

By substituting expression (17) for  $\mathbf{f}$  and integrating by parts, the integral on the right-hand side can be transformed into a surface integral over the surface  $\xi_1 = \xi_1^0$ . Using the expansion (15) and the orthogonality relation (16) the surface integral can be evaluated. It is then found that  $\omega_q$ , the frequency corresponding to the solution  $\mathbf{f}_q(\mathbf{r})$ , is given by

$$\omega_q^2 - \omega_0^2 + \frac{4\pi}{3} = -4\pi \left\{ \frac{y_{1q}' y_{2q}}{\Delta(y_{1q}, y_{2q})} \right\}_{\xi_1^0}. \quad (19)$$

The subscript  $\xi_1^0$  denotes that the expression in the curly brackets has to be evaluated at  $\xi_1 = \xi_1^0$ .

(ii) The solid has two boundary surfaces,  $\xi_1 = \xi_1^I$  and  $\xi_1 = \xi_1^{II}$  (where  $\xi_1^I > \xi_1^{II}$ ). In this case the solutions of (8) and (14) will be linear combinations of

$$\mathbf{f}_q^1(\mathbf{r}) = \text{grad}\{W_q(\xi_2, \xi_3) y_{1q}(\xi_1)\} \quad (20)$$

and

$$\mathbf{f}_q^2(\mathbf{r}) = \text{grad}\{W_q(\xi_2, \xi_3) y_{2q}(\xi_1)\}. \quad (21)$$

We substitute these two functions successively into the integral equation (18) and apply the same procedure as before, the only modification being that near the inner surface  $\xi_1 = \xi_1^{II}$  we have to use, instead of (15), the expansion

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = -4\pi \frac{h_1'}{h_2' h_3'} \rho(\xi_2', \xi_3') \sum_q W_q^*(\xi_2', \xi_3') W_q(\xi_2, \xi_3) \frac{y_{1q}(\xi_1') y_{2q}(\xi_1)}{\Delta(y_{1q}, y_{2q})}. \quad (22)$$

We obtain

$$\left(\omega^2 - \omega_0^2 + \frac{4\pi}{3}\right) \mathbf{f}_q^1(\mathbf{r}) = -4\pi \left(\frac{y_1' y_2}{\Delta}\right)_{\xi_1^I} \mathbf{f}_q^1(\mathbf{r}) + 4\pi \left(\frac{y_1' y_1}{\Delta}\right)_{\xi_1^{II}} \mathbf{f}_q^2(\mathbf{r}) \quad (23)$$

$$\left(\omega^2 - \omega_0^2 + \frac{4\pi}{3}\right) \mathbf{f}_q^2(\mathbf{r}) = -4\pi \left(\frac{y_2' y_2}{\Delta}\right)_{\xi_1^I} \mathbf{f}_q^1(\mathbf{r}) + 4\pi \left(\frac{y_2' y_1}{\Delta}\right)_{\xi_1^{II}} \mathbf{f}_q^2(\mathbf{r}). \quad (24)$$

From the secular equation of this system of two linear equations the following eigenvalues are obtained:

$$\omega_{g\pm}^2 - \omega_0^2 + \frac{4\pi}{3} = -2\pi \left\{ \left( \frac{y_1' y_2}{\Delta} \right)_{\xi_1^I} - \left( \frac{y_2' y_1}{\Delta} \right)_{\xi_1^{II}} \right\} \pm 2\pi \left[ \left\{ \left( \frac{y_1' y_2}{\Delta} \right)_{\xi_1^I} + \left( \frac{y_2' y_1}{\Delta} \right)_{\xi_1^{II}} \right\}^2 - 4 \left( \frac{y_1' y_1}{\Delta} \right)_{\xi_1^{II}} \left( \frac{y_2' y_2}{\Delta} \right)_{\xi_1^I} \right]^{1/2}. \quad (25)$$

#### 4. The longitudinal modes

Longitudinal solutions of (8), i.e. solutions which satisfy (13), will have the form

$$\mathbf{f}^L(\mathbf{r}) = \text{grad } \psi(\mathbf{r}) \quad (26)$$

where  $\psi(\mathbf{r})$  is any scalar function which vanishes on the surface of the crystal:

$$\psi(S) = 0. \quad (27)$$

Substituting  $\mathbf{f}^L(\mathbf{r})$  into the integral equation (8) we obtain

$$\begin{aligned} \left( \omega^2 - \omega_0^2 + \frac{4\pi}{3} \right) \text{grad } \psi(\mathbf{r}) &= \text{grad} \int \left\{ \text{grad}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \cdot \text{grad}' \psi(\mathbf{r}') \right\} d^3 r' \\ &= \text{grad} \int \psi(\mathbf{r}') \left( \text{grad}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \cdot d\mathbf{s}' \right) \\ &\quad - \text{grad} \int \psi(\mathbf{r}') \Delta' \frac{1}{|\mathbf{r} - \mathbf{r}'|} d^3 r' \end{aligned} \quad (28)$$

where the primed operators act on the primed coordinates.

Using (27) and (7) we find that  $\mathbf{f}^L(\mathbf{r})$  is indeed an eigenfunction and with the proper eigenvalue  $\omega^2 = \omega_0^2 + 8\pi/3$ . The longitudinal modes can also be shown (Ruppin and Englman 1967) to be orthogonal to the surface modes, i.e. if  $\mathbf{f}^S(\mathbf{r})$  is a surface mode then

$$\int \{ \mathbf{f}^{L*}(\mathbf{r}) \cdot \mathbf{f}^S(\mathbf{r}) \} d^3 r = 0. \quad (29)$$

#### 5. The transverse modes

Transverse solutions of (8), i.e. solutions which satisfy (12), will have the form

$$\mathbf{f}^T(\mathbf{r}) = \text{curl } \mathbf{v}(\mathbf{r}) \quad (30)$$

where  $\mathbf{v}(\mathbf{r})$  is any vectorial function whose tangential components vanish on the surface of the crystal:

$$v_t(S) = 0. \quad (31)$$

Substituting  $\mathbf{f}^T(\mathbf{r})$  into (8) we obtain

$$\begin{aligned} \left( \omega^2 - \omega_0^2 + \frac{4\pi}{3} \right) \text{curl } \mathbf{v}(\mathbf{r}) &= \text{grad} \int \left\{ \text{grad}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \cdot \text{curl}' \mathbf{v}(\mathbf{r}') \right\} d^3 r' \\ &= \text{grad} \int \text{div}' \left\{ \frac{\text{curl}' \mathbf{v}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right\} d^3 r' \\ &= \text{grad} \int \frac{\text{curl}' \mathbf{v}(\mathbf{r}') \cdot d\mathbf{s}'}{|\mathbf{r} - \mathbf{r}'|}. \end{aligned} \quad (32)$$

The last surface integral vanishes because of (31), so that  $\mathbf{f}^T(\mathbf{r})$  is an eigenfunction with the eigenvalue  $\omega^2 = \omega_0^2 - 4\pi/3$ .

The transverse modes are orthogonal to the surface modes and to the longitudinal modes:

$$\int \{\mathbf{f}^{\text{T}*}(\mathbf{r}) \cdot \mathbf{f}^{\text{S}}(\mathbf{r})\} d^3r = \int \{\mathbf{f}^{\text{T}*}(\mathbf{r}) \cdot \mathbf{f}^{\text{L}}(\mathbf{r})\} d^3r = 0. \quad (33)$$

## 6. Examples

### 6.1. Sphere

The appropriate curvilinear coordinates are, of course, spherical coordinates

$$\xi_1 \equiv r, \quad \xi_2 \equiv \theta, \quad \xi_3 \equiv \phi. \quad (34)$$

The boundary surface of the crystal is given by  $r = R$ . The radial parts of the solutions of the Laplace equation are

$$y_{1l} = r^l, \quad y_{2l} = r^{-(l+1)} \quad (35)$$

and the angular part is

$$W_{lm} = y_{lm}(\theta, \phi) \quad (36)$$

so that, according to (17), the surface modes are given by

$$\mathbf{f}_{lm}^{\text{S}} = \text{grad}\{r^l y_{lm}(\theta, \phi)\} \quad l = 1, 2, 3, \dots \quad (37)$$

The frequencies of these modes as obtained from (19) and (35) are

$$\omega_l^2 = \omega_0^2 - \frac{4\pi}{3} + 2\pi \frac{l}{l + \frac{1}{2}} \quad l = 1, 2, 3, \dots \quad (38)$$

The lowest frequency (with  $l = 1$ ) is equal to  $\omega_0$  and, as  $l$  increases, the frequencies converge from below to the frequency  $\omega_{\text{S}}$  given by

$$\omega_{\text{S}}^2 = \omega_0^2 + \frac{2\pi}{3} \quad (39)$$

which lies exactly midway between  $\omega_{\text{T}}^2$  and  $\omega_{\text{L}}^2$ . The surface mode of lowest order ( $l = 1$ ) describes a vibration having a constant amplitude over the whole sphere. This is the mode which was first discussed by Fröhlich (1949). In all the higher surface modes ( $l = 2, 3, \dots$ ) the amplitude of vibration decreases as  $r^{l-1}$  with increasing distance from the surface.

Two sets of orthogonal transverse modes (having zero divergence and frequency  $\omega_{\text{T}}$ ) corresponding to the two perpendicular directions of polarization are given by

$$\mathbf{f}_{lms}^{\text{T}1} = \text{curl}\{\mathbf{r}y_{lm}(\theta, \phi)j_l(k_{ls}r)\} \quad (40)$$

$$\mathbf{f}_{lms}^{\text{T}2} = \frac{1}{k_{ls}} \text{curl} \text{curl}\{\mathbf{r}y_{lm}(\theta, \phi)j_l(k_{ls}r)\} \quad (41)$$

where  $k_{ls}$  is the  $s$ th root of the equation

$$j_l(k_{ls}R) = 0. \quad (42)$$

Of course, because of the degeneracy orthogonal linear combinations of solutions of the type (40) and (41) could serve equally well. A set of orthogonal longitudinal modes, having vanishing curl and frequency equal to  $\omega_{\text{L}}$ , is given by

$$\mathbf{f}_{lms}^{\text{L}}(\mathbf{r}) = \text{grad}\{y_{lm}(\theta, \phi)j_l(k_{ls}r)\} \quad (43)$$

where  $k_{ls}$  is defined as above.

### 6.2. Spherical shell

For a crystal having the shape of a spherical shell, with outer radius  $R_1$  and inner radius  $R_2$ , the surface modes will be given by linear combinations of the form

$$\mathbf{f}_{lm}^{\text{S}}(\mathbf{r}) = A \text{grad}\{r^l y_{lm}(\theta, \phi)\} + B \text{grad}\{r^{-(l+1)} y_{lm}(\theta, \phi)\}. \quad (44)$$

The corresponding frequencies, obtained from (25) and (35), are

$$\omega_{i\pm}^2 = \omega_0^2 + \frac{2\pi}{3} \pm \frac{2\pi}{2l+1} \left\{ 1 + 4l(l+1) \left( \frac{R_2}{R_1} \right)^{2l+1} \right\}^{1/2}. \quad (45)$$

Here, unlike the case of the spherical crystal, half of the surface mode frequencies have values higher than  $\omega_S$ , but again the frequencies converge, when  $l \rightarrow \infty$ , to the value  $\omega_S$ . Transverse and longitudinal solutions are

$$\mathbf{f}_{ims}^{T1}(\mathbf{r}) = \text{curl}\{\mathbf{r}y_{lm}(\theta, \phi)f_i(k_{is}r)\} \quad (46)$$

$$\mathbf{f}_{ims}^{T2}(\mathbf{r}) = \frac{1}{k_{is}} \text{curl} \text{curl}\{\mathbf{r}y_{lm}(\theta, \phi)f_i(k_{is}r)\} \quad (47)$$

$$\mathbf{f}_{ims}^L(\mathbf{r}) = \text{grad}\{y_{lm}(\theta, \phi)f_i(k_{is}r)\} \quad (48)$$

where  $f_i(k_{is}r)$  is a linear combination of spherical Bessel and Neumann functions

$$f_i(k_{is}r) = Aj_i(k_{is}r) + Bn_i(k_{is}r) \quad (49)$$

which vanishes on both surfaces:

$$f_i(k_{is}R_1) = f_i(k_{is}R_2) = 0. \quad (50)$$

It follows that  $k_{is}$  has to be a root of the equation

$$\frac{j_i(k_{is}R_2)}{j_i(k_{is}R_1)} = \frac{n_i(k_{is}R_2)}{n_i(k_{is}R_1)}. \quad (51)$$

We note that in the limiting case of a spherical shell with vanishingly small inner radius ( $R_2 \rightarrow 0$ ) we do not obtain the modes or eigenvalues of a full sphere. This does not offend physical intuition since the solutions given for the spherical shell cease to be valid when the inner radius becomes of the same order of magnitude as the lattice spacing.

### 6.3. Cylinder

We use cylindrical coordinates

$$\xi_1 \equiv r, \quad \xi_2 \equiv \phi, \quad \xi_3 \equiv z.$$

The boundary surface of the crystal is given by  $r = R$ . The radial parts of the solutions of the Laplace equation are

$$y_{1mk} = I_m(kr), \quad y_{2mk} = K_m(kr) \quad (52)$$

where  $I_m$  and  $K_m$  are modified Bessel functions. The angular part is

$$W_{mk} = \exp(im\phi) \exp(ikz). \quad (53)$$

The surface modes, according to (17), have the form

$$\mathbf{f}_{mk}^S = \text{grad}\{\exp(im\phi) \exp(ikz)I_m(kr)\}. \quad (54)$$

Their frequencies, as obtained from (19), are

$$\omega_{mk}^2 = \omega_0^2 - \frac{4\pi}{3} + 4\pi kRI_m'(kR)K_m(kR). \quad (55)$$

They cover only the lower half of the range between  $\omega_T^2$  and  $\omega_L^2$  (figure 1). Two sets of transverse solutions are

$$\mathbf{f}_{mks}^{T1} = \text{curl}\{\mathbf{a}_z J_m(\alpha_{ms}r) \exp(im\phi) \exp(ikz)\} \quad (56)$$

where

$$J_m(\alpha_{ms}R) = 0$$

and

$$\mathbf{f}_{mks}^{T2} = \text{curl curl}\{\mathbf{a}_z J_m(\beta_{ms}r) \exp(im\phi) \exp(ikz)\} \quad (57)$$

where

$$J_m'(\beta_{ms}R) = 0.$$

$\mathbf{a}_z$  is a unit vector in the  $z$  direction.

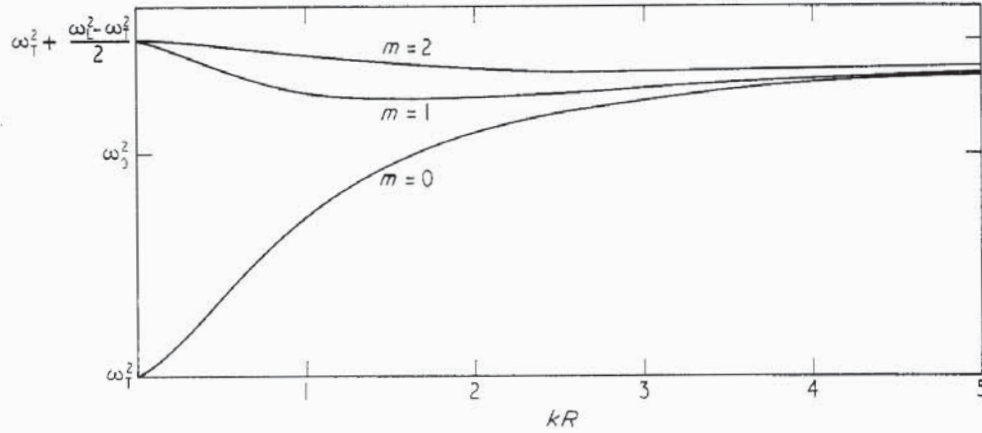


Figure 1. The square of the frequencies of the surface modes of a cylindrical crystal.

Longitudinal solutions are

$$\mathbf{f}_{mks}^L(\mathbf{r}) = \text{grad}\{J_m(\alpha_{ms}r) \exp(im\phi) \exp(ikz)\}. \quad (58)$$

#### 6.4. Cylindrical shell

For a long cylindrical shell (outer radius  $R_1$ , inner radius  $R_2$ ) the surface modes will be linear combinations of the form

$$\mathbf{f}_{mk}^S(\mathbf{r}) = A \text{grad}\{\exp(im\phi) \exp(ikz) I_m(kr)\} + B \text{grad}\{\exp(im\phi) \exp(ikz) K_m(kr)\}. \quad (59)$$

Their frequencies, as obtained from (25) and (52), are given by

$$\begin{aligned} \omega_{mk\pm}^2 = \omega_0^2 - \frac{4\pi}{3} + 2\pi\{K_m(kR_1)I_m'(kR_1)kR_1 - I_m(kR_2)K_m'(kR_2)kR_2\} \\ \pm 2\pi[\{K_m(kR_1)I_m'(kR_1)kR_1 + I_m(kR_2)K_m'(kR_2)kR_2\}^2 \\ - 4I_m(kR_2)I_m'(kR_2)kR_2K_m(kR_1)K_m'(kR_1)kR_1]^{1/2}. \end{aligned} \quad (60)$$

These values lie between  $\omega_T^2$  and  $\omega_L^2$ , but are not restricted to the lower half of this region as was the case for a solid cylinder. Figure 2 shows  $\omega_{mk\pm}^2$  as a function of  $kR$  for a shell with inner radius  $R$  and outer radius  $2R$ .

The transverse and the longitudinal solutions are

$$\mathbf{f}_{mks}^{T1} = \text{curl}\{\mathbf{a}_z F_m(\alpha_{ms}r) \exp(im\phi) \exp(ikz)\} \quad (61)$$

$$\mathbf{f}_{mks}^{T2} = \text{curl curl}\{\mathbf{a}_z G_m(\beta_{ms}r) \exp(im\phi) \exp(ikz)\} \quad (62)$$

$$\mathbf{f}_{mks}^L = \text{grad}\{F_m(\alpha_{ms}r) \exp(im\phi) \exp(ikz)\}. \quad (63)$$

$F_m(\alpha_{ms}r)$  is a linear combination of Bessel and Neumann functions  $J_m(\alpha_{ms}r)$  and  $N_m(\alpha_{ms}r)$  which vanishes at the boundaries:

$$F_m(\alpha_{ms}R_1) = F_m(\alpha_{ms}R_2) = 0. \quad (64)$$

From this it follows that  $\alpha_{ms}$  is the  $s$ th root of the equation

$$\frac{J_m(\alpha_{ms}R_2)}{J_m(\alpha_{ms}R_1)} = \frac{N_m(\alpha_{ms}R_2)}{N_m(\alpha_{ms}R_1)}. \quad (65)$$



$G_m(\beta_{ms}r)$  is a linear combination of  $J_m(\beta_{ms}r)$  and  $N_m(\beta_{ms}r)$  whose derivative vanishes at the boundaries

$$G_m'(\beta_{ms}R_1) = G_m'(\beta_{ms}R_2) = 0 \quad (66)$$

from which we see that  $\beta_{ms}$  is the  $s$ th root of the equation

$$\frac{J_m'(\beta_{ms}R_2)}{J_m'(\beta_{ms}R_1)} = \frac{N_m'(\beta_{ms}R_2)}{N_m'(\beta_{ms}R_1)} \quad (67)$$

### 6.5. Slab

The slab geometry was discussed by Fuchs and Kliewer (1965), who obtained the normal modes and the frequencies by solving a one-dimensional integral equation. In

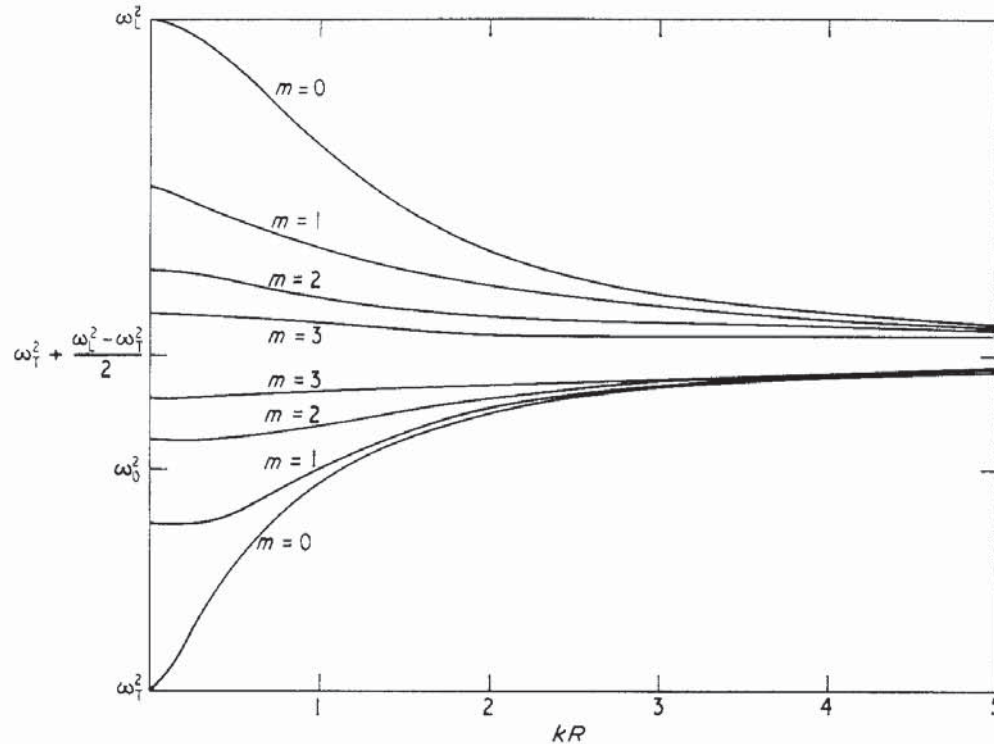


Figure 2. The square of the frequencies of the surface modes of a cylindrical shell with inner radius  $R$  and outer radius  $2R$ .

fact, for this geometry the general three-dimensional integral equation (8) reduces (by assuming the solutions to obey periodic boundary conditions in the two long directions) to a one-dimensional integral equation.

It is interesting to note that the solutions for a slab can be obtained from those of the cylindrical shell of the same thickness, in the limit of infinite radius. Thus, the surface mode frequencies of the slab can be obtained from (60) by going over to the limit  $R_1, R_2 \rightarrow \infty$ , but keeping the thickness fixed, i.e.  $R_1 - R_2 = 2a$ .

Using the relations

$$I_m(x) \xrightarrow{x \rightarrow \infty} \frac{1}{(2\pi x)^{1/2}} \exp(x), \quad K_m(x) \xrightarrow{x \rightarrow \infty} \left(\frac{\pi}{2x}\right)^{1/2} \exp(-x) \quad (68)$$

we obtain the result

$$\omega_{k\pm}^2 = \omega_0^2 + \frac{2\pi}{3} \pm 2\pi \exp(-2ka) \quad (69)$$

which agrees with the results of Fuchs and Kliewer (1965). The eigenfunctions for the slab can be obtained from those of the cylindrical shell, (59), (61), (62), (63), by the same procedure.

## 7. Boundary conditions

From our treatment above it is not apparent that the solutions of the basic integral equation (8) satisfy any specific boundary conditions at the surface of the crystal. In fact, because the eigenfunctions are solutions of the integral equation, they automatically obey the boundary conditions required by electrostatic theory, i.e. the tangential components of the electric field and the normal component of the displacement field are continuous at the surface:

$$(E_{\text{in}})_t = (E_{\text{out}})_t \quad (70)$$

$$(E_{\text{in}})_n + 4\pi P_n = (E_{\text{out}})_n. \quad (71)$$

Here  $\mathbf{E}_{\text{in}}$  is the field inside the solid, which is related to the vibration amplitude  $\mathbf{f}$  by (9) in the following way:

$$E_{\text{in}} = \left\{ \frac{\mu}{e} (\omega_0^2 - \omega^2) - \frac{4\pi}{3} \frac{e}{V} \right\} \mathbf{f}. \quad (72)$$

We can rederive the frequencies of the surface modes (19) by imposing on the eigenfunctions the boundary conditions (70), (71). The field inside the crystal associated with a surface mode of type (17) is given by

$$\mathbf{E}_{\text{in}}^q = \left\{ \frac{\mu}{e} (\omega_0^2 - \omega_q^2) - \frac{4\pi}{3} \frac{e}{V} \right\} \text{grad}\{W_q(\xi_2, \xi_3)y_{1q}(\xi_1)\}. \quad (73)$$

The field outside the crystal has to satisfy the equations

$$\text{div } \mathbf{E}_{\text{out}} = 0, \quad \text{curl } \mathbf{E}_{\text{out}} = 0 \quad (74)$$

and will thus have the form

$$\mathbf{E}_{\text{out}}^q = A \text{grad}\{W_q(\xi_2, \xi_3)y_{2q}(\xi_1)\} \quad (75)$$

since  $y_{2q}(\xi_1)$  is regular for  $\xi_1 > \xi_1^0$ . Applying the first boundary condition (70) we obtain the value of  $A$ :

$$A = \left\{ \frac{\mu}{e} (\omega_0^2 - \omega_q^2) - \frac{4\pi}{3} \frac{e}{V} \right\} \frac{y_{1q}(\xi_1^0)}{y_{2q}(\xi_1^0)}. \quad (76)$$

The second boundary condition (71) thus becomes

$$\left\{ \frac{\mu}{e} (\omega_0^2 - \omega_q^2) - \frac{4\pi}{3} \frac{e}{V} \right\} y_{1q}' + 4\pi \frac{e}{V} y_{1q}' = \left\{ \frac{\mu}{e} (\omega_0^2 - \omega_q^2) - \frac{4\pi}{3} \frac{e}{V} \right\} \frac{y_{1q}}{y_{2q}} y_{2q}' \quad (77)$$

where all the functions are evaluated at  $\xi_1 = \xi_1^0$ . Measuring the squared frequency in units of  $e^2/\mu V$  we find that this is identical with our previous result (19) (which was obtained by substituting the eigenfunctions (17) into the integral equation (8)).

The electric fields associated with the longitudinal modes and with the transverse modes can also be shown to obey the boundary conditions (70) and (71).

## 8. Complex cubic structures

The preceding discussion was restricted to diatomic crystals. We now extend the treatment to include the case of ionic crystals with more than two atoms per unit cell, but still having cubic symmetry. The difficulty that one meets in these crystals is that we do not have a unique optical vibrational coordinate (like the relative displacement of the ions in diatomic crystals). The contributions of the individual ionic motions to any normal mode depend on the long-range (as well as on the short-range) forces present, and these differ for different surface modes. It will be shown that the integral equation (8) still determines the spatial dependence of the vibration amplitudes and that the displacements of the various

ions in the unit cell depend on the solutions of that integral equation. The equations of motion are

$$M_{\kappa}\omega^2 U_{\alpha} \left( \begin{matrix} l \\ \kappa \end{matrix} \right) = \sum_{l'\kappa'\beta} \left\{ \Phi_{\alpha\beta}^S \left( \begin{matrix} l l' \\ \kappa \kappa' \end{matrix} \right) + \Phi_{\alpha\beta}^C \left( \begin{matrix} l l' \\ \kappa \kappa' \end{matrix} \right) Z_{\kappa} Z_{\kappa'} \right\} U_{\beta} \left( \begin{matrix} l' \\ \kappa' \end{matrix} \right) \quad (78)$$

where  $Z_{\kappa}$  is the charge of the  $\kappa$ th ion in units of  $e$ ,  $\Phi_{\alpha\beta}^S$  are the force constants of the short-range interaction and  $\Phi_{\alpha\beta}^C$  are the Coulomb force constants, given by

$$\Phi_{\alpha\beta}^C \left( \begin{matrix} l l' \\ \kappa \kappa' \end{matrix} \right) = - \left( \frac{\partial^2}{\partial r_{\alpha} \partial r_{\beta}} \frac{e^2}{r} \right)_0. \quad (79)$$

The last expression is to be evaluated in the equilibrium configuration, i.e. for

$$r = \left| \mathbf{R} \left( \begin{matrix} l \\ \kappa \end{matrix} \right) - \mathbf{R} \left( \begin{matrix} l' \\ \kappa' \end{matrix} \right) \right| = |\mathbf{R}(l) + \mathbf{R}(\kappa) - \mathbf{R}(l') - \mathbf{R}(\kappa')| \quad (80)$$

where

$$\mathbf{R} \left( \begin{matrix} l \\ \kappa \end{matrix} \right) = \mathbf{R}(l) + \mathbf{R}(\kappa) \quad (81)$$

is the position vector of the undisplaced  $\kappa$ th atom in the  $l$ th unit cell.

We shall now redistribute the two terms in the sum (78) so as to obtain two new force constants (equation (89) below), one of which causes no spatial variation in the vibration amplitudes and the other, long-range term, whose value per ionic charge depends only on the separation between the unit cells of the ions (but not on the actual separation of the ions).

We first expand the displacements in the form

$$U_{\beta} \left( \begin{matrix} l' \\ \kappa' \end{matrix} \right) = U_{\beta} \left( \begin{matrix} l' \\ \kappa' \end{matrix} \right) + \{\mathbf{R}(l') - \mathbf{R}(l)\} \cdot \text{grad } U_{\beta} \left( \begin{matrix} l' \\ \kappa' \end{matrix} \right). \quad (82)$$

We can assume that  $\text{grad } U_{\beta}$  is evaluated at an appropriate intermediate point such that the last equation holds exactly. Now,  $|\text{grad } \mathbf{U}|$  is of the order of magnitude of  $|\mathbf{U}|/\lambda$ , where  $\lambda$  is the wavelength characterizing the variation of  $\mathbf{U} \left( \begin{matrix} l \\ \kappa \end{matrix} \right)$  with  $l$ . Our treatment is restricted to long waves, i.e. to  $\lambda \gg r_0$ , where  $r_0$  is the lattice constant. The short-range part of the right-hand side of (78) becomes therefore, in this approximation,

$$\sum_{\kappa'\beta} K_{\alpha\beta}(\kappa\kappa') U_{\beta} \left( \begin{matrix} l \\ \kappa' \end{matrix} \right) \quad (83)$$

where terms of the order of magnitude of  $r_0/\lambda$  were neglected, and where

$$K_{\alpha\beta}(\kappa\kappa') = \sum_{l'} \Phi_{\alpha\beta}^S \left( \begin{matrix} l l' \\ \kappa \kappa' \end{matrix} \right) \quad (84)$$

which is taken to be independent of  $l$  (since we always neglect surface effects arising due to the short-range forces).

If we expand the Coulomb force constants in the form

$$\Phi_{\alpha\beta}^C \left( \begin{matrix} l l' \\ \kappa \kappa' \end{matrix} \right) = \Phi_{\alpha\beta}^C \left( \begin{matrix} l l' \\ \kappa \kappa' \end{matrix} \right) + \{\mathbf{R}(\kappa') - \mathbf{R}(\kappa)\} \cdot \text{grad } \Phi_{\alpha\beta}^C \left( \begin{matrix} l l' \\ \kappa \kappa' \end{matrix} \right) \quad (85)$$

and use the expansion (82), we find that, for long waves, the Coulomb part of the right-hand side of (78) can be separated into two sums. One sum extends only over the near neighbourhood of the  $l$ th cell and can therefore be written, in analogy with (83), in the form

$$\sum_{\kappa'\beta} H_{\alpha\beta}(\kappa\kappa') U_{\beta} \left( \begin{matrix} l \\ \kappa' \end{matrix} \right). \quad (86)$$

The second sum, which is of genuine long-range character, is

$$\sum'_{l'\kappa'} \Phi_{\alpha\beta}^c(l'l') Z_{\kappa} Z_{\kappa'} U_{\beta} \left( \begin{matrix} l' \\ \kappa' \end{matrix} \right) \quad (87)$$

where

$$\Phi_{\alpha\beta}^c(l'l') \equiv \Phi_{\alpha\beta}^c \left( \begin{matrix} l & l' \\ \kappa & \kappa \end{matrix} \right). \quad (88)$$

The equations of motion thus become

$$M_{\kappa} \omega^2 U_{\alpha} \left( \begin{matrix} l \\ \kappa \end{matrix} \right) = \sum_{\beta\kappa'} \{ F_{\alpha\beta}(\kappa\kappa') \delta_{l'l'} + \Phi_{\alpha\beta}^c(l'l') Z_{\kappa} Z_{\kappa'} \} U_{\beta} \left( \begin{matrix} l' \\ \kappa' \end{matrix} \right) \quad (89)$$

where now the  $F_{\alpha\beta}$  contain the pure short-range repulsion force constants and also that part of the Coulomb force constants which is of short-range nature:

$$F_{\alpha\beta}(\kappa\kappa') = K_{\alpha\beta}(\kappa\kappa') + H_{\alpha\beta}(\kappa\kappa'). \quad (90)$$

The equations (89) hold for crystals of any symmetry. We now assume that the unit cell has cubic symmetry, and that only central forces act between the atoms.  $F_{\alpha\beta}$  will then be diagonal, provided that each atom lies at a point of no less than  $D_2$  symmetry with the same directions of twofold axes of rotation for all atoms. In this case we find that the equations of motion (89) are separable in the sense that we can write their solutions in the form

$$U_{\alpha} \left( \begin{matrix} l \\ \kappa \end{matrix} \right) = f_{\alpha}^{\lambda}(l) Q_{\alpha}(\kappa) \quad (91)$$

where  $f^{\lambda}(l)$  is an eigenfunction of the Coulomb part of (89), i.e.

$$\sum_{\beta l'} \Phi_{\alpha\beta}^c(l'l') f_{\beta}^{\lambda}(l') = \lambda f_{\alpha}^{\lambda}(l). \quad (92)$$

This equation can be transformed into the integral form

$$\left( \lambda + \frac{4\pi}{3} \right) \mathbf{f}^{\lambda}(\mathbf{r}) = - \text{grad div} \int \frac{\mathbf{f}^{\lambda}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r'. \quad (93)$$

Substituting (91) into (89) and using the symmetry assumed for the lattice we have

$$M_{\kappa} \omega_{\lambda}^2 Q_{\alpha}^{\lambda}(\kappa) = \sum_{\kappa'} \{ F_{\alpha\alpha}(\kappa\kappa') + \lambda Z_{\kappa} Z_{\kappa'} \} Q_{\alpha}^{\lambda}(\kappa') \quad (94)$$

where the index  $\lambda$  was added to the displacements and to the frequencies to stress their dependence on the eigenvalues of the integral equation (93).

We now apply this procedure to calculate explicitly the frequencies of the long-wave optical modes and the displacements of the atoms in these modes for finite specimens of strontium titanate. The lattice dynamics of the infinite crystal (i.e. using periodic boundary conditions) has been thoroughly studied by Cowley (1964). We use the parameters given by him for the rigid-ion model. (Analogous calculations could be made, however, with greater labour, by using the more exact shell model.) The Coulomb coefficients given by Cowley (1964) consist, in the long-wave limit, of two parts.

(i) A term which depends on the direction of the wave vector. This term has the value  $-4\pi/3$  (in units of  $e^2/V$ ) for transverse modes and  $8\pi/3$  for longitudinal modes. For surface modes in finite specimens it will take intermediate values. In fact, this term is just the eigenvalue  $\lambda$  of the integral equation (93). Since the eigenvalues  $\lambda$  always lie in the region between  $-4\pi/3$  and  $8\pi/3$  (their specific values in this region depending on the shape of the crystal), we solve the equations of motion, and present the solutions, for all values of  $\lambda$  in this range.

(ii) A term which is independent of the direction of the wave vector. This term gives the deviation of local field factor from the Lorentz  $4\pi/3$  value (Slater 1950). This term is included in our formulation of the equations of motion (94) in the force constants  $F(\kappa\kappa')$  which also contain, of course, the pure short-range force constants ( $R_{\kappa\kappa'}$  in Cowley's notation).

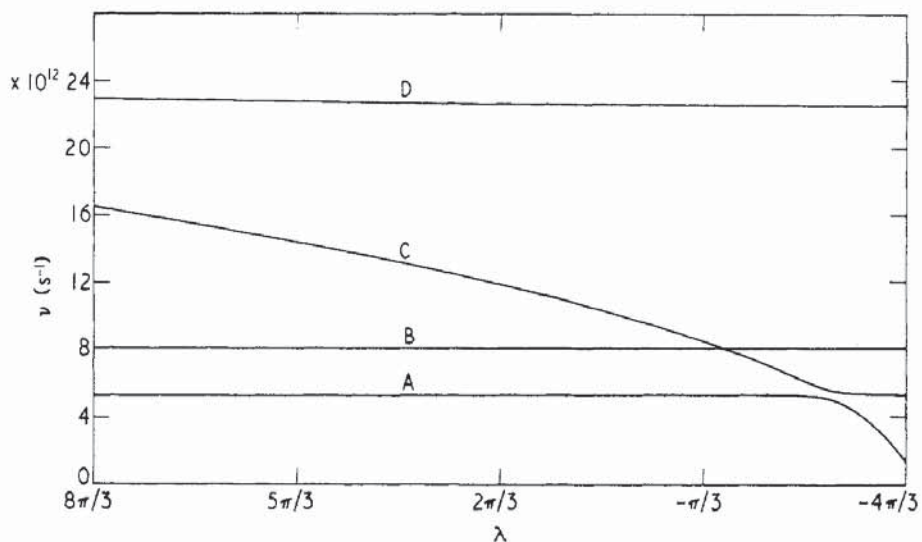


Figure 3. Frequencies of the long-wave optical phonons in finite crystals of  $\text{SrTiO}_3$ , as obtained from the rigid-ion model.

Figure 3 shows the frequencies of the long-wave optical phonons as a function of  $\lambda$ . For  $\lambda = 8\pi/3$  these are the frequencies of the longitudinal phonons and for  $\lambda = -4\pi/3$  they are those of the transverse phonons. (Of course they do not coincide with the exact experimental value owing to the limitations of the rigid-ion model which we are using.) Given a finite specimen having a simple shape one can find the frequencies of the optical surface modes in the following way. First one solves the integral equation (93) and finds the appropriate eigenvalues  $\lambda$  for this geometry. These can be taken directly from our previous

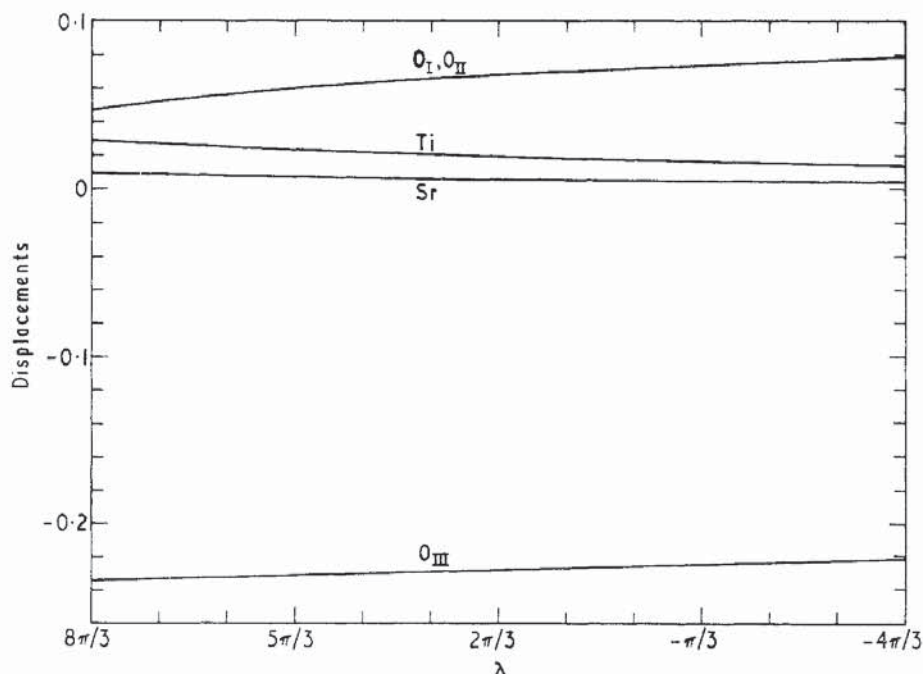


Figure 4. Displacements of atoms in mode D.

results (19), (25). Having found the values of  $\lambda$ , one obtains from figure 3 the related frequencies.

One optical mode (namely at  $\mathbf{k} = 0$  of species  $\Gamma_{25}$  and designated B in figure 3) is not polar. In this mode two oxygen ions move in opposite senses while all the other ions do not move, so that no dipole moment arises. This mode exhibits no size and shape effects and its frequency is the same for all values of  $\lambda$ . The highest mode (species  $\Gamma_{15}$ , D in figure 3) is well separated from the other  $\Gamma_{15}$  modes and shows only a slight dependence on  $\lambda$ . The displacements of the atoms in this mode as a function of  $\lambda$  obtained from (94) are shown in figure 4. The most prominent size and shape effects are exhibited by the  $\Gamma_{15}$  modes designated A and C. Figures 5 and 6 show the displacements of the ions in these modes. The displacements behave quite smoothly for most values of  $\lambda$ , but undergo violent changes in the region near  $\lambda = -\pi$  owing to the strong mixing of the two modes in this region (see figure 3). Examining figures 5 and 6 we find that the pattern of displacements of the atoms in mode A near  $\lambda = 8\pi/3$  is similar to that of mode C for  $\lambda = -4\pi/3$ , and, vice versa, the pattern of displacements of mode C near  $\lambda = 8\pi/3$  is similar to that of mode A at  $\lambda = -4\pi/3$ . This behaviour is typical of two approaching energy levels which belong to the same symmetry species. In the region of nearest approach the change of pattern occurs rather abruptly.

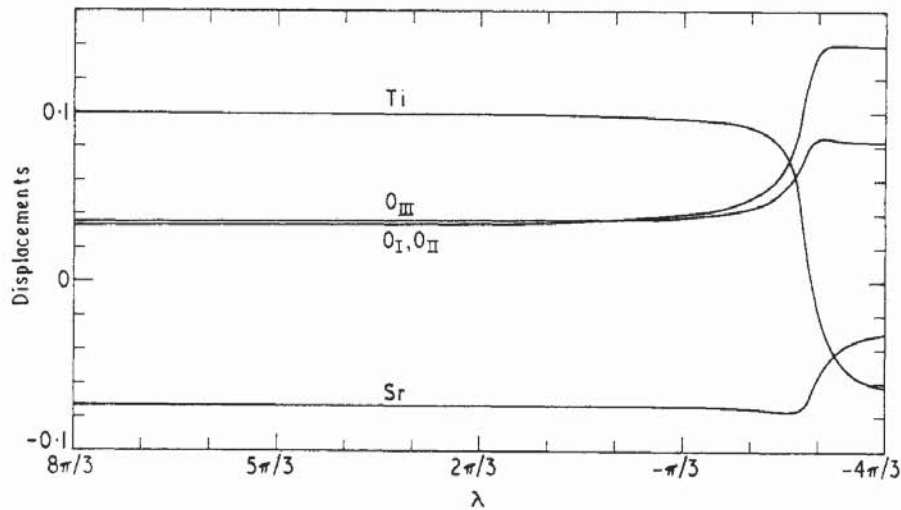


Figure 5. Displacements of atoms in mode A.

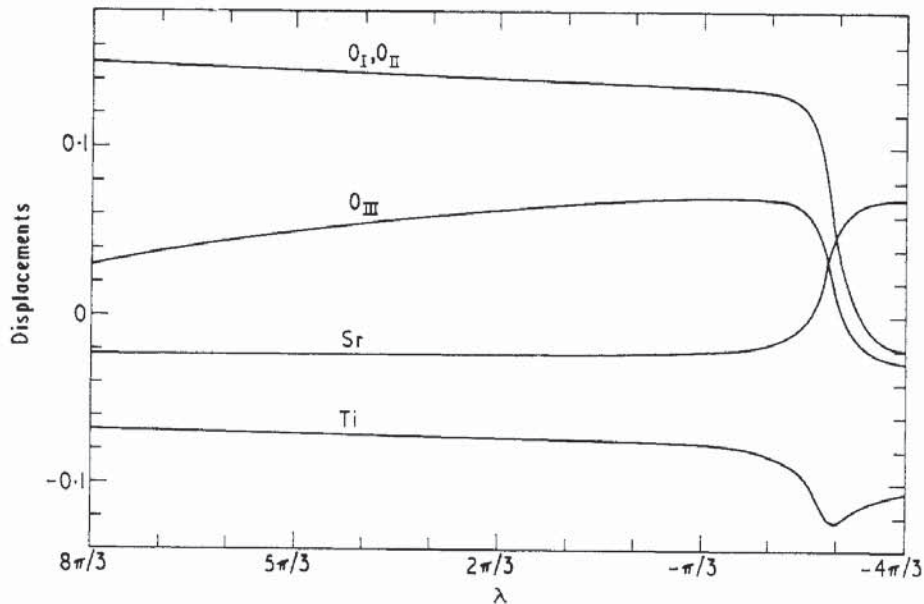


Figure 6. Displacements of atoms in mode C.

Up to this point it was assumed that the ions are not polarizable, i.e. the rigid-ion model was used. The polarizabilities of the ions can be accounted for by using the shell model (Tolpygo 1950, Dick and Overhauser 1958). In this model each ion is replaced by a shell of charge  $Ye$  and a core of charge  $Xe$ , where  $(X+Y)e = Ze$  is the net charge on the ion. Equations (93) and (94) can still be used (for cubic crystals), with  $\kappa$  now, taking the values 1, 2, ...,  $2S$  (where  $S$  is the number of ions per unit cell), and with  $Z_\kappa$  and  $M_\kappa$  being the charge and mass respectively of the  $\kappa$ th constituent (core or shell).

As an example we obtain the optical phonon frequencies of finite diatomic polarizable crystals. Woods *et al.* (1960) have shown that the frequencies of the long-wave optical phonons in alkali halide crystals are given by

$$\omega^2 = \omega_0'^2 + \frac{\lambda}{1 + \alpha\lambda/V} \frac{(Z'e)^2}{\mu V} \quad (95)$$

where  $\mu\omega_0'^2$  and  $Z'e$  are the effective short-range force constant and effective charge respectively, which can both be expressed in terms of the force constants of the model.  $\alpha$  is the sum of the polarizabilities of the two ions and is related to the high-frequency dielectric constant by

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi}{3V} \alpha. \quad (96)$$

For the transverse branch  $\lambda$  has the value  $-4\pi/3$  and for the longitudinal branch  $\lambda = 8\pi/3$ . Since the equations of motion (94) have the same structure as the equations for the infinite crystal, the result (95) will hold also for finite crystals. The only difference is that in the latter case  $\lambda$  is determined from the integral equation (93). For surface modes  $\lambda$  takes values intermediate between  $-4\pi/3$  and  $8\pi/3$ .

## 9. Crystals of lower symmetry

For ionic crystals with many atoms in the unit cell and with symmetry lower than cubic, equations (89) still apply; however, a simple separation of the solutions in the form (91) is in general not possible. We write (89), which still applies, in the form

$$\omega^2 M_\kappa^{1/2} U_\alpha \begin{pmatrix} l \\ \kappa \end{pmatrix} = \sum_{\beta l' \kappa'} \left\{ \frac{F_{\alpha\beta}(\kappa\kappa')}{(M_\kappa M_{\kappa'})^{1/2}} \delta_{ll'} + \Phi_{\alpha\beta}^c(ll') \frac{Z_\kappa Z_{\kappa'}}{(M_\kappa M_{\kappa'})^{1/2}} \right\} M_{\kappa'}^{1/2} U_\beta \begin{pmatrix} l' \\ \kappa' \end{pmatrix}. \quad (97)$$

We can attempt to achieve some sort of separation of this equation in two different ways.

(i) We assume the solution to have the form

$$M_\kappa^{1/2} U_\alpha \begin{pmatrix} l \\ \kappa \end{pmatrix} = \sum_\mu w_\alpha^\mu(\kappa) v^\mu(l) \quad (98)$$

where  $\mathbf{w}^\mu(\kappa)$  are the eigenvectors of the following 'short-range equation':

$$\omega_\mu^2 w_\alpha^\mu(\kappa) = \sum_{\beta\kappa'} \frac{F_{\alpha\beta}(\kappa\kappa')}{(M_\kappa M_{\kappa'})^{1/2}} w_\beta^\mu(\kappa'). \quad (99)$$

Substituting (98) in (97), multiplying by  $w_\alpha^\mu(\kappa)$ , summing over  $\alpha$  and  $\kappa$ , and using the orthonormality relation

$$\sum_{\alpha\kappa} w_\alpha^\mu(\kappa) w_\alpha^{\mu'}(\kappa) = \delta_{\mu\mu'} \quad (100)$$

we have

$$(\omega^2 - \omega_\mu^2) v^\mu(l) = \sum_{\mu' l'} \Phi_M^{\mu\mu'}(ll') v^{\mu'}(l'). \quad (101)$$

We have here defined a modified Coulomb force constant

$$\Phi_M^{\mu\mu'}(ll') = \sum_{\substack{\alpha\kappa \\ \beta\kappa'}} w_\alpha^\mu(\kappa) \Phi_{\alpha\beta}^c(ll') \frac{Z_\kappa Z_{\kappa'}}{(M_\kappa M_{\kappa'})^{1/2}} w_\beta^{\mu'}(\kappa') \quad (102)$$

which represents the energy of Coulomb interaction between the cells  $l$  and  $l'$  when the displacements in the cells are solutions of the short-range problem (99). Since we are dealing with long waves only we can replace equations (101) by integral equations

$$(\omega^2 - \omega_{\mu}^2)v^{\mu}(\mathbf{r}) = \sum_{\mu'} \frac{1}{V} \int \Phi_{\mathbf{M}^{\mu\mu'}}(\mathbf{r}, \mathbf{r}')v^{\mu'}(\mathbf{r}') d^3r'. \quad (103)$$

This is a set of  $3S$  conjugate integral equations ( $S$  is the number of atoms in the unit cell) from which the eigenfrequencies are determined.

(ii) We assume the solution to have the form

$$M_{\kappa}^{1/2}U_{\alpha} \begin{pmatrix} l \\ \kappa \end{pmatrix} = \sum_{\lambda} f_{\alpha}^{\lambda}(l)q^{\lambda}(\kappa) \quad (104)$$

where  $\mathbf{f}^{\lambda}(l)$  are the eigenvectors of the 'long-range equation'

$$\lambda f_{\alpha}^{\lambda}(l) = \sum_{\beta l'} \Phi_{\alpha\beta}^{\mathcal{C}}(ll')f_{\beta}^{\lambda}(l') \quad (105)$$

(which can be converted into the integral form (93)). Substituting (104) in (97), multiplying by  $f_{\alpha}^{\lambda}(l)$ , summing over  $\alpha$  and  $l$  and using the orthonormality relation

$$\sum_{\alpha l} f_{\alpha}^{\lambda}(l)f_{\alpha}^{\lambda'}(l) = \delta_{\lambda\lambda'} \quad (106)$$

we obtain the following equation for the frequencies:

$$\omega^2 q^{\lambda}(\kappa) = \sum_{\lambda'\kappa'} F_{\mathbf{M}^{\lambda\lambda'}}(\kappa\kappa')q^{\lambda'}(\kappa') \quad (107)$$

where we have defined a modified short-range force constant

$$F_{\mathbf{M}^{\lambda\lambda'}}(\kappa\kappa') = \sum_{\alpha\beta l} f_{\alpha}^{\lambda}(l) \left\{ \frac{F_{\alpha\beta}(\kappa\kappa')}{(M_{\kappa}M_{\kappa'})^{1/2}} + \lambda' \frac{Z_{\kappa}Z_{\kappa'}}{(M_{\kappa}M_{\kappa'})^{1/2}} \delta_{\alpha\beta} \right\} f_{\beta}^{\lambda'}(l). \quad (108)$$

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