Long-Wave Optical Vibrations in Simple Ionic Crystals

T. H. K. BARRON

Department of Physical and Inorganic Chemistry, The University, Bristol, England

(Received May 12, 1961)

This paper resolves some of the difficulties recently pointed out by Rosenstock in the theory of the lattice vibrations of ionic crystals of NaCl or CsCl structure. Long optical waves in these crystals (but not in crystals with only short-range forces) are seen to be purely longitudinal and transverse. With the electrostatic approximation, the Lyddane-Sachs-Teller equation $(\omega_l/\omega_t)^2 = \epsilon_0/\epsilon_\infty$ holds independently of the boundary conditions for modes in which the phase of the ionic vibrations is effectively constant over distances which are large compared with the lattice spacing; such modes must be either curl-free or divergence-free, with respective frequencies ω_l and ω_t. If both curl and divergence vanish, the frequency is indeterminate unless boundary conditions are specified, so that there is a singularity but no inconsistency as the wave number $\mathbf{k} \to 0$. When Coulomb retardation is taken into account this singularity disappears, and the frequency at $\mathbf{k}=0$ is found to be ω_t; the range of validity of the Lyddane-Sachs-Teller equation is then $10^{-4} \gtrsim k^{-1} \gtrsim 10^{-6}$ cm.

Reasons are given for believing that the cyclic boundary condition is valid for the thermodynamic properties of large ionic crystals, though this is not proved rigorously; specific boundary conditions may, however, be important in reflection and absorption of infrared radiation.

1. INTRODUCTION

ROSENSTOCK[1] has recently pointed out some popular misconceptions in the theory of the long "optical" vibrations in ionic crystals, and in doing so has raised some interesting problems. Among his points are the following:

I. Even in the limit as the wave vector $\mathbf{k} \to 0$, optical modes as well as acoustic modes are in general neither purely longitudinal nor transverse, except in directions of crystal symmetry. Rosenstock demonstrates this using a two-dimensional model with *short-range* interatomic forces, and concludes that since waves are neither transverse nor longitudinal in this simple example, they will in general be neither transverse nor longitudinal in the complicated examples of real ionic crystals.

II. In contrast, the Lyddane-Sachs-Teller[2] (L.S.T.) equation relates longitudinal and transverse frequencies for long optical waves in binary ionic crystals with central symmetry:

$$(\omega_l/\omega_t) = (\epsilon_0/\epsilon_\infty)^{\frac{1}{2}}, \tag{1}$$

where ϵ_0 and ϵ_∞ are the dielectric constants for low and high frequencies, respectively. Furthermore, this relation has been derived[2] using the cyclic boundary condition; but with this boundary condition Rosenstock claims to show quite generally that at the limit $\mathbf{k}=0$ all optical modes have the same frequency, whether or not we allow for Coulomb retardation. This implies that all long-wave frequencies should tend to the same limit as $\mathbf{k} \to 0$, in contradiction to (1).

III. This contradiction may perhaps be due to the cyclic boundary condition, which in this application may be invalid for two reasons: (i) its validity has been established not for individual normal modes but only for statistical problems involving the normal mode distribution, and (ii) even then, only for crystals with short-range forces. The breakdown of the cyclic boundary condition may mean that the normal modes are

not simple plane waves, and in particular that modes for which $\mathbf{k}=0$ may not exist. Rosenstock accordingly concludes that the L.S.T. relation (1), based as it is by implication upon cyclic boundary conditions and restricted to a range of $\mathbf{k}$ which is small but not precisely defined, cannot be considered quantitatively established.

The present paper resolves some of these problems. It is shown that a short-range force model is not a reliable guide for the behavior of long wave motions in ionic crystals, which are in fact purely longitudinal or transverse for wavelengths which are long compared with the lattice spacing; and that for such waves the derivation of the L.S.T. relation by the "macroscopic" theory of Born and Huang[3] does not depend essentially upon the cyclic boundary condition, but merely on the assumption that long transverse and longitudinal waves exist. Furthermore, allowance for Coulomb retardation in the macroscopic theory leads to three vibrations at $\mathbf{k}=0$ of equal frequency, in agreement with Rosenstock's general theorem, while in an electrostatic model the frequencies for $\mathbf{k}=0$ are indeterminate—a possibility not considered by Rosenstock. The cyclic boundary condition thus does not lead to any inconsistencies, but its validity has yet to be proved.

2. POLARIZATION OF LONG OPTICAL MODES

Let us first consider how the polarization of optical modes comes about in a crystal with only short-range forces. We shall consider throughout cubic crystals with two atoms in a primitive cell, such that each atom is a center of symmetry—i.e., crystals with either NaCl or CsCl structure. For any wave vector $\mathbf{k}$ in the direction of a cubic axis, the directions of polarization are determined by crystal symmetry; there is one longitudinal mode of frequency ω_l and two transverse modes of frequency ω_t. But as $\mathbf{k} \to 0$ ($\lambda \to \infty$), all interacting pairs of atoms are vibrating at approximately the same phase, so that an individual atom vibrating in the direction Oy has only a slight indication from its neighbors

[1] H. B. Rosenstock, Phys. Rev. **121**, 416 (1961).

[2] R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. **59**, 673 (1941).

[3] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954).

as to whether it is taking part in the motion of a transverse wave with wave vector along $0x$ or a longitudinal wave with wave vector along $0y$. It follows that $\omega_l/\omega_t \to 1$ as $\mathbf{k} \to 0$, and that at $\mathbf{k}=0$ the three modes become completely degenerate. This degeneracy is lifted when $\mathbf{k}\neq 0$ by the difference in phase between neighboring primitive cells, *however small this may be*; along certain symmetry directions there will still be degeneracy of the two transverse vibrations, but since the crystal structure is not isotropic the degeneracy in most directions will be wholly lifted, and the vibrations will be neither purely longitudinal nor purely transverse.

The situation is quite different in ionic crystals. Here for small $\mathbf{k}$ the long-range Coulomb forces will feel the effect of a finite wavelength much more strongly than the short-range forces. The approximation of Born and Huang[3] is thus justified, in which as $\mathbf{k} \to 0$ the effect of finite wavelength on the short-range forces (including the Coulomb forces between near neighbors) is neglected, so that they provide merely an *isotropic* restoring force. The polarizing effect is thus due to the Coulomb forces between distant neighbors; and the electric field on an ion due to distant neighbors can be considered as being a part of the macroscopic electric field, and hence as dependent only on the electrical polarization at distant regions. But the macroscopic theory of polarization of a cubic crystal is wholly isotropic, and does not involve the crystal structure. All directions of $\mathbf{k}$ are thus equivalent, and for each the long optical waves are purely longitudinal and transverse. Such waves must be long compared with interionic distances, since otherwise the nonisotropic effect of the short-range forces cannot be neglected.

It should be noted that the above argument does not apply to acoustic waves, since these do not polarize the crystal and consequently Coulomb forces between distant regions are negligible.

3. LYDDANE-SACHS-TELLER RELATION

We now consider the validity of the L.S.T. relation (1) and in particular whether it depends upon the cyclic boundary condition. Here we shall follow the electrostatic treatment of Born and Huang,[3] correcting it where necessary and bringing out explicitly some of the underlying assumptions. Retardation of the Coulomb forces will be discussed in Sec. 4.

The argument of Sec. 2 justifies the isotropic "macroscopic" equations of Born and Huang[3] (p. 82) for all motions of the crystal (whether waves or not) in which the phase of the ionic vibrations is effectively constant over distances large compared with the ionic spacing. These equations are:

$$\ddot{\mathbf{w}} = b_{11}\mathbf{w} + b_{12}\mathbf{E}, \qquad (2)$$

$$\mathbf{P} = b_{21}\mathbf{w} + b_{22}\mathbf{E}, \qquad (3)$$

where $\mathbf{w}$ is proportional to the displacement of the positive ions relative the the negative ions, $\mathbf{E}$ and $\mathbf{P}$

are the macroscopic electric field and polarization, and b_{11}, b_{22}, b_{12}, and b_{21} are constants; the dimensions and amplitude of $\mathbf{w}$ are chosen so that $b_{12}=b_{21}$. From (2) and (3) Born and Huang derive a dispersion formula, the parameters in which can be identified with those in the phenomenological dispersion relation:

$$\epsilon = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/[1-(\omega/\omega_0)^2]; \qquad (4)$$

here ϵ_0 and ϵ_∞ are the low- and high-frequency dielectric constants, and ω_0 can be regarded as defined experimentally by Eq. (4). Thus b_{11}, b_{12}, and b_{22} can be expressed in terms of the quantities ϵ_0, ϵ_∞, and ω_0 derived from experiment.

In order to solve the equations of motion we need, in addition to Eqs. (2) and (3), the electrostatic field equations

$$\text{div } \mathbf{D} \equiv \text{div}(\mathbf{E}+4\pi\mathbf{P}) = 0, \qquad (5)$$

$$\text{curl } \mathbf{E} = 0. \qquad (6)$$

Born and Huang proceed by splitting $\mathbf{w}$ into curl-free and divergence-free components, stating that this splitting is unique, and then identify the two parts with longitudinal and transverse motion, respectively. It is this step that implicitly involves some assumption about boundary conditions, since in fact the splitting is *not* unique; any vector of the form grad ϕ, where ϕ satisfies Laplace's equation $\nabla^2\phi=0$, is both curl-free and divergence-free, and this is precisely the kind of field vector that will be affected by electrostatic boundary conditions.

But the values of ω_l and ω_t do not depend on this assumption. Taking the curl of (2), and using (6), we have

$$(\partial^2/\partial t^2)(\text{curl}\mathbf{w}) = b_{11} \text{ curl}\mathbf{w}, \qquad (7)$$

showing at once that any mode for which the curl does not vanish identically must have an angular frequency, say ω_t, given by

$$\omega_t^2 = -b_{11} = \omega_0^2. \qquad (8)$$

Similarly, taking the divergence of Eqs. (2) and (3), and then eliminating div$\mathbf{P}$ and div$\mathbf{E}$ with the aid of (5), we have

$$(\partial^2/\partial t^2)(\text{div}\mathbf{w})$$
$$= [b_{11} - (4\pi b_{12}b_{21})/(1+4\pi b_{22})](\text{div}\mathbf{w}), \quad (9)$$

showing that any mode for which the divergence does not vanish identically must have an angular frequency, say ω_l, given by

$$\omega_l^2 = -b_{11} + [4\pi b_{12}b_{21}/(1+4\pi b_{22})] = \omega_0^2(\epsilon_0/\epsilon_\infty). \quad (10)$$

For any ionic crystal $\epsilon_0 > \epsilon_\infty$, so that ω_l and ω_t are necessarily different. It is impossible therefore to have modes in which neither the curl nor the divergence vanishes; either the curl or the divergence must vanish identically —or of course both of them may vanish. Pure longitudinal waves are curl-free but not divergence-free, and pure transverse waves are divergence-free but not curl-

free, while waves that have both transverse and longitudinal components are neither. It follows that the only possible wave motions are pure longitudinal waves of frequency ω_l, and pure transverse waves of frequency ω_t; these two frequencies satisfy the L.S.T. relation (1), which has thus been derived without any reference to boundary conditions.

We have still to consider modes for which both curl and divergence vanish. For such modes the electrostatic Eqs. (5) and (6) are both trivial, and (2) and (3) are insufficient to determine the frequency, which can therefore take any values including ω_t and ω_l. The only 'waves' of this type are those for which $\mathbf{k}=0$; the result does not contradict Rosenstock's general proof that in an infinite crystal the optical frequencies for $\mathbf{k}=0$ are all equal, since this depends on the implicit assumption that the frequencies are determinate. Thus we see that mathematically there is a singularity in the frequency as $\mathbf{k} \rightarrow 0$, but physically this is not disquieting for two reasons: (i) we have neglected retardation of the Coulomb forces; (ii) in a finite crystal we cannot let $\mathbf{k} \rightarrow 0$ continuously and, as Rosenstock points out, there may be no modes for which $\mathbf{k}=0$. If such modes do exist in a finite crystal with electrostatic forces their frequencies depend on the physical boundary conditions.[4]

4. RETARDATION OF COULOMB FORCES

We must now determine how far the arguments of Sec. 3 depend upon the electrostatic approximation. When we drop this approximation, we can still retain Eqs. (2), (3), (5), but (6) must be replaced by the remaining Maxwell's equations:

$$\text{curl} \mathbf{E} = -(1/c)(\partial \mathbf{H}/\partial t), \tag{11}$$

$$\text{curl} \mathbf{H} = (1/c)[(\partial/\partial t)(\mathbf{E}+4\pi\mathbf{P})], \tag{12}$$

$$\text{div} \mathbf{H} = 0, \tag{13}$$

where we neglect the difference between $\mathbf{B}$ and $\mathbf{H}$. The equations are still isotropic, so that we still have pure longitudinal and transverse waves. Since we retain Eq. (5) the derivation of ω_l is unaffected; this is not surprising because longitudinal lattice waves do not interact with electromagnetic waves. The transverse modes however do interact strongly in the range of wave vector for which their phase velocities are of the order of the velocity of light, and as $\mathbf{k}$ passes through this range the transverse electromagnetic waves change continuously into transverse lattice waves, and vice versa [see Born and Huang,[3] Fig. 18(a)]. The two transverse frequencies are roots of the equation

$$(k^2c^2/\omega^2) = \epsilon_\infty + [(\epsilon_0-\epsilon_\infty)\omega_0^2/(\omega_0^2-\omega^2)], \tag{14}$$

and as $\mathbf{k} \rightarrow 0$ the frequency of the lattice waves tends to ω_l.

It is encouraging that the longitudinal and transverse

⁴ See, for example, A. A. Maradudin and G. H. Weiss, Bull. Am. Phys. Soc. **6**, 22 (1961).

waves now have the same frequency as $\mathbf{k} \rightarrow 0$, but we must still see what happens when $\mathbf{k}=0$. For $\mathbf{k}=0$, we can write

$$\mathbf{w} = \mathbf{w}_0 e^{i\omega t}, \tag{15}$$

where $\mathbf{w}_0$ is a vector independent of position. Substituting this in (2) and (3) we find that $\mathbf{E}$ and $\mathbf{P}$ are also of the same form:

$$\mathbf{E} = \mathbf{E}_0 e^{i\omega t}, \quad \mathbf{P} = \mathbf{P}_0 e^{i\omega t}, \tag{16}$$

where $\mathbf{E}_0$ and $\mathbf{P}_0$ do not vary with position. Equations (11) and (12) then become, respectively,

$$\partial \mathbf{H}/\partial t = 0, \tag{17}$$

$$\text{curl} \mathbf{H} = (i\omega/c)(\mathbf{E}_0+4\pi\mathbf{P}_0)e^{i\omega t}, \tag{18}$$

and for $\omega \neq 0$ these are compatible only if the electric displacement vanishes:

$$\mathbf{D} \equiv \mathbf{E}+4\pi\mathbf{P} = 0. \tag{19}$$

The effect of Coulomb retardation for $\mathbf{k}=0$ is thus to give us an auxiliary equation, (19), which with (2) and (3) is sufficient to determine the frequency uniquely as ω_l. As Born and Huang have shown, this is also the frequency which both longitudinal and transverse lattice waves have as $\mathbf{k} \rightarrow 0$. The singularity at $\mathbf{k}=0$ found in the electrostatic approximation is thus removed by allowing for Coulomb retardation.

The L.S.T. relationship is therefore valid only over a limited range of wave number, since it breaks down both as $\mathbf{k} \rightarrow 0$ and as $\mathbf{k}$ becomes large. The lower limit of $\mathbf{k}$ can be found from Fig. 18(a) of Born and Huang,[3] which shows that the effect of Coulomb retardation is very small for $k > 10(\omega_0/c) \sim 10^4$ cm^{-1} for a typical ionic crystal. The upper limit is provided by the condition that the wavelength is large compared with interionic spacing, and so the L.S.T. relationship should be valid to a very good approximation in the range

$$10^{-4} \gtrsim \lambda \gtrsim 10^{-6} \text{ cm}.$$

5. BOUNDARY CONDITIONS

A. Size Effects According to the Cyclic Boundary Condition

If the cyclic boundary condition is used, the normal modes have the form of waves in an infinite crystal with the restriction that $\mathbf{k}$ is allowed to have only certain discrete values. For a crystal of linear dimensions of order l, these permitted values of $\mathbf{k}$ form a lattice of points in reciprocal space with lattice spacing of order l^{-1}, one of which is the point $\mathbf{k}=0$.

A complete set of independent modes is given by $\mathbf{k}$ values within the first Brillouin zone, at the boundaries of which $k \sim a^{-1} \sim 3 \times 10^7$ cm^{-1} for a typical ionic crystal. The optical modes are effectively longitudinal and transverse for $k \lesssim 10^{-6}$ cm^{-1}, and the L.S.T. relation holds in the range $k \gtrsim 10^{-4}$ cm^{-1}, so that in a large crystal only one long optical transverse wave in a million

disobeys the L.S.T. relation. In small crystals ($l \lesssim 10^{-4}$ cm) the electrostatic approximation is valid for all **k** except **k**=0, where there are three optical modes each of frequency ω_l; the L.S.T. relation holds for all other long waves. In very small crystals ($l \lesssim 100$ A) long waves are prohibited by the boundary condition, and we no longer have pure longitudinal and transverse waves.

B. Use of the Cyclic Boundary Condition in Statistical Mechanics

Rosenstock[1] has pointed out that the standard proofs of the validity of the cyclic boundary condition for calculating "bulk" thermodynamic properties depend upon the assumption that only short-range forces are present, while in fact it has been widely used—together with the electrostatic approximation—in ionic crystals. This is indeed disquieting, but its validity seems plausible on physical grounds.

In ionic crystals the validity of the cyclic boundary condition could break down in two ways: (i) Because of the long-range forces the frequencies could become indeterminate (as for **k**=0 in the electrostatic approximation); (ii) even if the frequencies are uniquely determined, the motion predicted for the ions may differ from the motion in crystals with realistic physical boundary conditions. We have already seen in Secs. 3 and 4 that the frequencies of long optical waves are uniquely determined, although these waves polarize the crystal and give rise to long-range effects; this being so, it is difficult to see why the frequencies should not be uniquely defined for other modes. It is also worth noting that unique frequencies have been obtained in many detailed calculations (see Rosenstock[1] for references), although this cannot be regarded as conclusive without careful examination to determine whether these calculations do not contain some additional assumption.

If the frequencies are indeed uniquely determined, the cyclic boundary condition predicts a quite definite "bulk" frequency distribution as $l \rightarrow \infty$. Use of the electrostatic approximation will make very little difference, since it only affects about one mode in every 10^6 in a well-populated frequency range. The cyclic boundary condition will be valid if the local motion of ions as $l \rightarrow \infty$ is indistinguishable from the motion of ions in the middle of a crystal with physical boundary conditions. Experimentally it is known that bulk thermodynamic properties exist, and hence that the motion of ions is similar in different internal regions of a crystal. Again it is difficult to see why this motion should be different from that predicted by the cyclic boundary condition, since those modes which might be expected to give the strongest long-distance Coulomb effects (i.e., those which in the interior of the crystal polarize it over regions which are large compared with the ionic

spacing) have frequencies ω_l and ω_t independent of the boundary conditions. (It should be remembered that the results of Sec. 2 were obtained without assuming that the normal modes were plane waves.)

For statistical problems, therefore, the use of the cyclic boundary conditions seems plausible, although admittedly the foregoing arguments are no substitute for a rigorous proof.

C. Interaction of Ionic Crystals with Infrared Radiation

The three main experimental measurements are those of dielectric constant at frequencies well removed from resonance, of selective reflection from surfaces, and of selective absorption in thin films. Dielectric constant is a bulk property, and hence the cyclic boundary condition should be adequate; but both the other measurements obviously may involve surface effects. We can only agree with Rosenstock that the situation here is particularly complicated since, even without allowing for surface effects, the theory of the fine structure of the infrared adsorption spectrum is not simple.[5]

6. SOME OUTSTANDING PROBLEMS

(a) The theory of Born and Huang predicts that transverse optical waves with wavelength $>10^{-2}$ cm should exist in large crystals with frequency ω_t. Are these waves sufficiently coherent for this to be physically meaningful, once we allow for anharmonicity and the imperfections present in even the best experimental crystals? If so, can the waves be detected by any means experimentally?

(b) Can a rigorous proof be found for the validity of the cyclic boundary condition for calculating bulk thermodynamic properties of ionic crystals?

(c) To what extent do surface effects invalidate existing theories[3,5] of the interaction of infrared radiation with ionic crystals?

Note added in proof. A proof of the validity of the cyclic boundary condition for a model representing an ionic crystal is given in a very recent paper on the lattice dynamics of alkali halide crystals[6]; it is also pointed out that the "macroscopic" theory given in Born and Huang[3] is applicable only to optical modes whose wavelengths are short compared with the size of the crystal. I am grateful to Dr. Hardy for sending me a copy of this paper before publication.

---

[5] B. Szigeti, Proc. Roy. Soc. (London) **A252**, 217 (1959); **A258**, 377 (1960).
[6] J. R. Hardy, Phil. Mag. (to be published).