

Nature of Vibrational Modes in Ionic Crystals

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The principal purpose of this paper is to discuss the nature of the modes of vibration in a solid. The following is found: (1) Waves in lattices are in general neither transverse nor longitudinal; in particular, they need not be transverse or longitudinal when the propagation vector \mathbf{k} is very small. (2) The relationship $\omega_l/\omega_t = (\epsilon_0/\epsilon_\infty)^{1/2}$ for "longitudinal" and "transverse" modes in ionic crystals applies, if at all, in a region of small, but nonzero, wave vector \mathbf{k} . (3) The derivation of this relationship is based, at least implicitly, on the use of cyclic boundary conditions. (4) The use of cyclic boundary conditions is valid in statistical problems for crystals without long-range forces, but has never been justified for systems with Coulomb forces. (5) If cyclic boundary conditions are nonetheless used, it can be simply shown that for $\mathbf{k}=0$, $\omega_l/\omega_t=1$.

I. INTRODUCTION

THE over-all purpose of this paper is to discuss the nature of the modes of vibration of a solid. We are particularly interested in solids in which long-range forces, which appear to complicate the situation considerably, are important.

The problem is by no means a new one, and it has in fact been discussed from many different, and not necessarily mutually consistent, viewpoints. Chronologically, elasticity theory came first, and introduced into the field much of the vocabulary that is still used; later, lattice dynamics was developed as a classical theory involving coupled harmonic oscillators; it proved to be valid, as far as it went, in quantum theory as well, on account of the particularly close correspondence that occurs between classical and quantum mechanics for oscillators; however, the earliest, and still the most detailed, work in lattice dynamics dealt with models involving short-range forces only, and some of the results of this work tended to be accepted as valid for crystals with long-range forces, without obvious justification. Finally, many people were led into this field by a primary interest in optical problems—the interaction of light with either individual atoms or with the lattice as a whole, or perhaps with both; these are much more involved problems essentially quantum mechanical in nature, but with the interaction of the light with the lattice often superimposed on it in a semiclassical way.

Specifically, the following things are done here. In Sec. II it is pointed out that the waves in the lattice which constitute the usual modes need be neither transverse nor longitudinal, not even when the propagation vector \mathbf{k} is very small, and that when $\mathbf{k}=0$ the very concept of transverse or longitudinal polarization is meaningless. In Sec. III the frequently used relationship $\omega_l/\omega_t = (\epsilon_0/\epsilon_\infty)^{1/2}$ is discussed. (Notation: ω_l , ω_t are the frequencies, respectively, of the "longitudinal" and "transverse" vibrations, and ϵ_0 , ϵ_∞ the dielectric constants, respectively, for zero frequency and for high frequencies.) It is shown that this relationship contradicts not only the results of Sec. II (somewhat superficially), but, more important, that it disagrees with a counter-example whose validity is established under rather general conditions. In Sec. IV reasons for this

discrepancy are examined and discussed; among the items suspected of being responsible are the effects of polarizability, of retardation, of size and shape dependence, of the order and method of mathematically performing limiting processes, and of using simplified boundary conditions. It is shown that the last of these may be responsible, since no mathematical, or even plausible, justification has ever been presented for the use of cyclic boundary conditions in crystals with long-range forces. In Sec. V the results are summarized and discussed. In Appendix I an example, which is used throughout the paper, is worked out in detail. Appendix II amplifies the discussion of Sec. II.

II. POLARIZATION OF WAVES

It seems rather commonly believed that waves in solids are either transverse or longitudinal. This belief, even when restricted to waves whose propagation vector is small, is not always justified.

There is no simple reason for believing this for short waves, for their properties depend in detail on the atomic forces; but in fact it is not even true for long waves (often called "acoustical" or "elastic" waves) which can be described with reference to the bulk properties of the solid only. ("Acoustic" waves are usually defined as low-frequency waves of long wavelength or small propagation vector.) The question of "acoustic" waves has been discussed by deLaunay¹ who shows that even these waves in nonisotropic cubic crystals are transverse or longitudinal only in the (100), (110), (111) directions. An equivalent result can be straightforwardly obtained from the classical work of Green² as expounded by Love.³

¹ J. deLaunay, *J. Chem. Phys.* **21**, 1975 (1953), see p. 1997.

² G. Green, *Trans. Cambridge Phil. Soc.* **7**, 121 (1842).

³ A. E. H. Love, *A Treatise on the Mathematical Theory of Elasticity* (reprinted by Dover Publications, New York, 1944). Relation (23) on page 299 gives the necessary condition for transverse waves. This expression for the strain energy function W is found to agree with the general one for cubic crystals (last line of Sec. 109, p. 160) when the condition $c_{11}-c_{12}=2c_{44}$ (isotropy) holds, because then the corresponding coefficients in the two expressions are equal; and also when propagation is in the (100), (110), or (111) directions, because then all the nonvanishing strain components themselves become equal. I am indebted to Dr. Jules deLaunay for calling this work to my attention.

It should be realized that a certain amount of subtlety is required to make any sense at all out of statements about the polarization of waves of infinite wavelength. A transverse (longitudinal) wave is defined as one in which the atomic, or material, displacements are perpendicular (parallel) to the direction of propagation (i.e., to the propagation vector \mathbf{k}); and if the wavelength is infinite (propagation vector 0) then the entire concept becomes meaningless; a vector cannot be perpendicular (or parallel) to a vanishing vector or, physically speaking, if a displacements are the same everywhere in a crystal, then no direction of propagation can be defined at all. Thus statements about elastic waves, or even nonelastic waves of "long" wavelength such as the above, make sense only for small propagation vector but not in the limit of propagation vector approaching 0; if it is to make any sense there, a way of going to the limit must be defined.

D -dimensional crystals of n atoms per unit cell are known to have nD frequencies (or "modes") for each wave vector \mathbf{k} . The "acoustic" or "elastic" waves discussed by deLaunay¹ and others arise for small \mathbf{k} and are D in number. The $(n-1)D$ other solutions that arise are often called "optical" modes. (This is a misleading designation since it seems to imply that they are optically observable, which is never obvious and usually not true. A mode can be optically observable only if the dipole moment of each cell changes in course of a vibration, and then only if contributions from each cell add, rather than cancel as they often do. We shall discuss this matter further in Secs. IV and V.)

In the literature we have found no study from the standpoint of lattice dynamics of *all* the modes that arise for small \mathbf{k} (and not just of the "acoustic" ones); we therefore thought that this would be worth doing in detail, if only for some special model. We therefore proceed to do this for the simplest possible nontrivial crystal model. Our main interest there is in the eigenfunctions themselves, rather than in the eigenvalues (frequencies) as is usual.

In looking for a model which is nontrivial for our purposes, we do not object to restricting ourselves to small wave numbers (except to zero wave number); we are primarily interested in the relationship between propagation vector \mathbf{k} and the atomic displacement vector, and in the difference there between the so-called "acoustical" waves and the "optical" waves. To exhibit these features, our crystal must have at least two dimensions (one dimensional crystals have only one direction of any sort) and to get more than one mode whose frequency does not approach 0 as \mathbf{k} approaches 0, we choose two atoms per unit cell. Also, we must include interaction between nearest and next nearest neighbors, for if the latter are omitted, then the problem is known to degenerate into a one-dimensional one. The simplest example to work out that is, to our purposes, nontrivial is therefore the two-dimensional

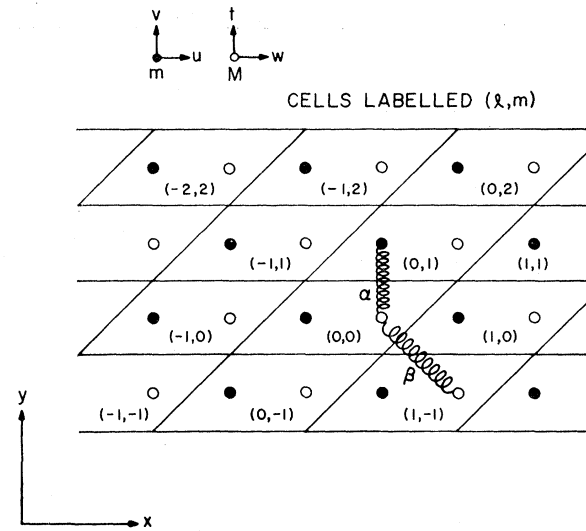


FIG. 1. The crystal model in our example.

diatomic lattice with first and second neighbor interaction.

The notation is explained by reference to Fig. 1. Cells are labelled by indices l, m , each cell containing one atom of mass m whose displacements in the x and y directions are called u_{lm} and v_{lm} , respectively, and one atom of mass M whose displacement in the x direction and y direction are called w_{lm} and t_{lm} . The Hooke's law force constant for first and second neighbor interactions are called α and β , respectively. We write $Q^2 = m/M$, $\sigma = \beta/\alpha$, and

$$\begin{aligned} u_{lm} &= e^{i\omega t} e^{i(l\varphi_1 + m\varphi_2)} U m^{-\frac{1}{2}}, \\ v_{lm} &= e^{i\omega t} e^{i(l\varphi_1 + m\varphi_2)} V m^{-\frac{1}{2}}, \\ w_{lm} &= e^{i\omega t} e^{i(l\varphi_1 + m\varphi_2)} W M^{-\frac{1}{2}}, \\ t_{lm} &= e^{i\omega t} e^{i(l\varphi_1 + m\varphi_2)} T M^{-\frac{1}{2}}, \end{aligned} \quad (1)$$

for the usual normal mode transformation. U, V, W , and T are constants, ω is the frequency, and φ_1 and φ_2 can be related to the propagation vector $\mathbf{k} = (k_1, k_2)$ by equating $e^{i(l\varphi_1 + m\varphi_2)} = e^{i(k_1 x + k_2 y)}$, and observing from Fig. 1 that $x = 2la + y$, $y = ma$ so that $\mathbf{k} = (1/2a)[\varphi_1, 2\varphi_2 - \varphi_1]$, a being the distance between nearest neighbors. The four linear algebraic equations which result from inserting (1) into the Newtonian equations of motion and which define U, V, W, T can then be written

$$(H - \lambda)\psi = 0, \quad (2)$$

with

$$\lambda = (mM)^{\frac{1}{2}} \omega^2 / \alpha, \quad \psi = \begin{pmatrix} U \\ W \\ V \\ T \end{pmatrix},$$

and H a 4×4 matrix whose elements, which are functions of the φ 's, or k 's, are written down in Appendix I. The solution to Eq. (1), valid for small \mathbf{k} , is obtained by perturbation theory in Appendix I.

The results are as follows. The eigenvalues are found to be

$$\begin{aligned}(Q+Q^{-1})\lambda_1 &= [1+2\sigma]a^2(k_1^2+k_2^2)+a^2(k_1^2-k_2^2)(1+\xi^2)^{\frac{1}{2}}, \\ (Q+Q^{-1})\lambda_2 &= [1+2\sigma]a^2(k_1^2+k_2^2)-a^2(k_1^2-k_2^2)(1+\xi^2)^{\frac{1}{2}}, \\ (Q+Q^{-1})\lambda_3 &= 2(Q+Q^{-1})^2-[1-(Q^2+Q^{-2})\sigma] \\ &\quad \times a^2(k_1^2+k_2^2)+a^2(k_1^2-k_2^2)(1+\eta^2)^{\frac{1}{2}}, \quad (3) \\ (Q+Q^{-1})\lambda_4 &= 2(Q+Q^{-1})^2-[1-(Q^2+Q^{-2})\sigma] \\ &\quad \times a^2(k_1^2+k_2^2)-a^2(k_1^2-k_2^2)(1+\eta^2)^{\frac{1}{2}},\end{aligned}$$

with $\eta = \frac{1}{2}(Q^2+Q^{-2})\xi$, $\xi = 4\sigma k_1 k_2 / (k_1^2 - k_2^2)$, and the corresponding eigenfunctions

$$\begin{aligned}\psi_1^c &= (Q^2+1)^{-\frac{1}{2}}c_+(\xi) \begin{bmatrix} \xi Q \\ \xi \\ [1-(1+\xi^2)^{\frac{1}{2}}]Q \\ [1-(1+\xi^2)^{\frac{1}{2}}] \end{bmatrix}, \\ \psi_2^c &= (Q^2+1)^{-\frac{1}{2}}c_-(\xi) \begin{bmatrix} \xi Q \\ \xi \\ [1+(1+\xi^2)^{\frac{1}{2}}]Q \\ [1+(1+\xi^2)^{\frac{1}{2}}] \end{bmatrix}, \\ \psi_3^c &= (Q^2+1)^{-\frac{1}{2}}c_+(\eta) \begin{bmatrix} \eta \\ -\eta Q \\ [1-(1+\eta^2)^{\frac{1}{2}}] \\ -[1-(1+\eta^2)^{\frac{1}{2}}]Q \end{bmatrix}, \\ \psi_4^c &= (Q^2+1)^{-\frac{1}{2}}c_-(\eta) \begin{bmatrix} \eta \\ -\eta Q \\ [1+(1+\eta^2)^{\frac{1}{2}}] \\ -[1+(1+\eta^2)^{\frac{1}{2}}]Q \end{bmatrix},\end{aligned} \quad (4)$$

with

$$c_{\pm}(\xi) = [1 + (1 + \xi^2)^{-\frac{1}{2}}] / 2^{\frac{1}{2}} \xi.$$

In all these formulas, the signs are correct as they stand whenever $\xi > 0$ but are to be reversed when $\xi < 0$. We note that Eq. (4) resolves the ambiguity of defining the polarization of waves as 0 wave vector is approached: it states that, and how, the polarization depends on the direction of the approach.

As to the eigenvalues λ , we may observe that for $\mathbf{k} = 0$, we have $\lambda_1 = \lambda_2$, and $\lambda_3 = \lambda_4$.

As for the eigenfunctions, or atomic displacements, we observe first of all, that for each mode, $U/V = W/T$. According to Eq. (4) we have explicitly

$$\begin{aligned}U_1/V_1 &= W_1/T_1 = \xi / [1 - (1 + \xi^2)^{\frac{1}{2}}], \\ U_2/V_2 &= W_2/T_2 = \xi / [1 + (1 + \xi^2)^{\frac{1}{2}}], \\ U_3/V_3 &= W_3/T_3 = \eta / [1 - (1 + \eta^2)^{\frac{1}{2}}], \\ U_4/V_4 &= W_4/T_4 = \eta / [1 + (1 + \eta^2)^{\frac{1}{2}}].\end{aligned}$$

This means that the motion of one atom in any given cell is always either parallel or antiparallel to that of the other atom. By looking at the ratio U/W , or V/T , we see that modes 1 and 2 are parallel and modes 3 and 4 are antiparallel.

Next, we ask whether the various modes are perpendicular to each other. The condition for this would be,

for modes 1 and 2,

$$u_1 u_2 + v_1 v_2 + w_1 w_2 + t_1 t_2 = 0,$$

or, since we have already shown that the two atoms in any cell move always parallel or antiparallel in any given mode, more simply $u_1 u_2 + v_1 v_2 = 0$ or, by (1) $U_1 U_2 + V_1 V_2 = 0$, which, by the use of (4), is found to hold true. Thus modes 1 and 2 are mutually perpendicular and similarly modes 3 and 4 can be shown to be mutually perpendicular. On the other hand, any low-frequency modes are perpendicular to the high-frequency modes only if special conditions hold ($\sigma = 0$, or $m = M$, or $k_1 = 0$ or $k_2 = 0$).

Finally, we ask whether and under what conditions any mode is transverse or longitudinal. The condition that mode i be longitudinal is

$$U_i / V_i = k_1 / k_2.$$

Substituting from (4) we find

modes 1 and 3 are longitudinal if and only if $k_2 \rightarrow 0$,

modes 2 and 4 are longitudinal if and only if $k_1 \rightarrow 0$,

and, since mode 1 is perpendicular to 2 and 3 perpendicular to 4,

modes 2 and 4 are transverse if and only if $k_2 \rightarrow 0$,

modes 1 and 3 are transverse if and only if $k_1 \rightarrow 0$.

In summary, then, we may say that the "acoustical" modes (the ones whose frequency approaches 0 as \mathbf{k} approaches 0) agree with deLaunay (who started from the standpoint of the elasticity theory) and the other modes show behavior very similar to the acoustic ones: for any given small \mathbf{k} , the low-frequency modes are perpendicular to each other, and the high-frequency modes are perpendicular to each other, but any one mode is longitudinal or transverse only for certain special crystallographic directions. The two acoustic frequencies are seen to be equal to zero at $\mathbf{k} = 0$, and approach that value in a continuous way as a finite \mathbf{k} is permitted to approach zero; and the two other ("optical") frequencies are seen to be equal to each other at $k = 0$ and they, too, approach the value they take on at $k = 0$ in a continuous way as a finite \mathbf{k} is permitted to approach zero.

The preceding development constitutes, among other things, a counter-example to the commonly believed theorem that all lattice waves are either transverse or longitudinal. The counterexample here is confined to small \mathbf{k} , and it might therefore still be conjectured that the theorem may be valid when \mathbf{k} is *not* small. In fact, it is not valid. For a counter-example applicable for all \mathbf{k} , turn to Appendix II.

III. ARE THE FREQUENCIES OF "TRANSVERSE" AND "LONGITUDINAL" MODES SIMPLY RELATED?

We are now prepared to consider the "well-known" relation

$$\omega_l / \omega_t = (\epsilon_0 / \epsilon_{\infty})^{\frac{1}{2}}. \quad (5)$$

We shall find that serious difficulties arise when either its quantitative assertions or its physical implications are compared with our previous results, and with simple but general extensions of our previous results. We shall devote most of the rest of this paper to establishing and then explaining these contradictions.

Relation (5) was first obtained by Lyddane, Sachs, and Teller⁴ and later obtained as a consequence of a more general phenomenological treatment of long waves by Huang.^{5,6} LST define ω_t and ω_l as the frequency of "the transverse vibration" and "the longitudinal vibration," respectively, ϵ_0 as the dielectric constant for zero frequency and ϵ_∞ as the dielectric constant for high frequencies (essentially the square of the index of refraction). Both papers make it clear that they are considering long waves and, in particular, the ones whose frequencies do not approach zero there; the limit of \mathbf{k} close to zero⁷ is thus clearly implied. Neither paper seems to have any doubt about the transverse and longitudinal nature of the waves or the method of going the limit. LST, however, are clearly talking about propagation perpendicular or parallel to a crystal face, in which, as we have seen from at least one example (preceding section) waves are indeed often transverse or longitudinal.

We shall first attempt to discuss the situation by means of our example of Sec. II. The model, let us repeat here, is that of a diatomic two-dimensional lattice with interaction between first and second neighbors, and the work is valid for small \mathbf{k} for the "optical" as well as the acoustic modes. The two squared frequencies in our calculation that correspond to ω_l^2 and ω_t^2 in LST and BH are λ_3 and λ_4 (for λ_1 and λ_2 are the "elastic" or "acoustical" modes). We note two things:

(1) ω_l is equal to ω_t (in the limit of $\mathbf{k}=0$, and nearly equal for small \mathbf{k}) or $\omega_l/\omega_t=1$; this clearly contradicts Eq. (5).

(2) Except for the main crystallographic directions, the vibrations corresponding to λ_3 and λ_4 are neither transverse nor longitudinal, neither at $\mathbf{k}=0$ (where the concept is, strictly speaking, meaningless) nor for small \mathbf{k} (as shown in Appendix I) nor presumably in the case when \mathbf{k} is not small (as shown in Appendix II). Having established these apparent contradictions, we must of course investigate to what extent our example is relevant to the case envisaged by LST and BH.

LST and BH are concerned with real three-dimensional ionic crystals with long- as well as short-

range interactions; our model is in every respect simpler than theirs (two dimensions and short-range forces only). Thus if our example contradicts a supposedly general result, that result may be considered to have been proven wrong; but a result specially derived from our model will not necessarily be valid for real solids. In other words the results of Appendix I are not to be taken literally in a quantitative way, since they derive from a special model, but are of importance wherever they contradict a supposedly general theorem.

First consider statement (2), the less important one of the two. It contradicts nothing in LST (although it would seem to detract from the implied generality of the treatment), but does appear to contradict the statement that "the independent vibrational modes can be taken as transverse and longitudinal waves of different wave numbers and directions of propagation."⁸ Be this as it may, we can certainly conclude that since waves are neither transverse nor longitudinal in our simple example, they will in general be neither transverse nor longitudinal in the complicated cases of real ionic crystals.

By contrast, statement (1) would seem to be of the kind that had little general probative value. If two frequencies happen to be equal in some simple special case, the "corresponding" frequencies surely need not be equal in all cases. However, we shall now proceed to show that statement (1) is true under circumstances much more general than implied by our example. In fact, we show that, under fairly general conditions, all nonacoustical vibrations have the same frequency for $\mathbf{k}=0$.

We do restrict ourselves to diatomic crystals of cubic symmetry and of structure such that each atom is a center of symmetry. (This includes the NaCl and CsCl structure but not the ZnS structure). Temporarily only, we also restrict ourselves to two-dimensional crystals as illustrated in Fig. 2. Let us call the two kinds of atoms in the crystal A and B . When $\mathbf{k}=0$, all A atoms move the same way in all cells, and all the B atoms move the same way in all cells. We might say that the motion is rigid motion of the B sublattice relative to the A sublattice; it will cause no confusion if we omit phrase beginning with the word "relative" henceforth. Consider now the forces that act on one particular A atom. The force exerted by any other A atom vanishes, for forces arise only from relative displacements and these are all 0 between pairs of A atoms. The forces exerted by the B atoms, on the other hand, do not vanish, but they have the property that motion of the B sublattice in the x direction causes a force on the A atom which is purely in the x direction. Physically, this can be seen from Fig. 2: for each atom B_1 located at equilibrium position (x_0, y_0) , there exists another atom B_2 located at equilibrium position $(x_0, -y_0)$; if the B sublattice moves in the x direction, both B_1 and

⁴ R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. **59**, 673 (1941); referred to as LST.

⁵ Kun Huang, Proc. Roy. Soc. (London) **A208**, 352 (1951).

⁶ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), Sec. 7; referred to as BH.

⁷ LST make it clear that they are speaking of small \mathbf{k} , but not $\mathbf{k}=0$ (although they do not use that language, nor make the point that the concept of transversality or longitudinality would be meaningless there). They specify that the wavelength must be large, but much smaller than the dimensions of the crystal.

⁸ See reference 6, p. 87.

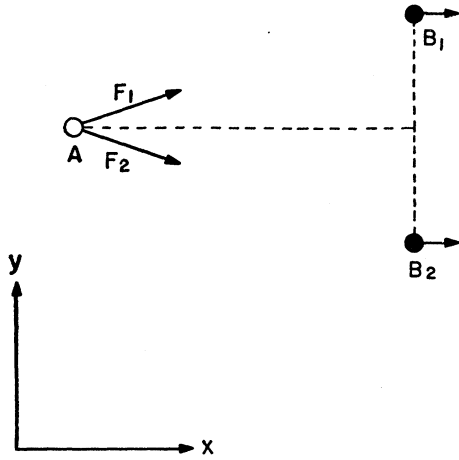


FIG. 2. Forces when $k=0$ (two dimensions). F_i is the force exerted on particle A by particle B_i . The resultant of the F_i is in the x direction.

B_2 may exert forces on the A atom at the origin; the x components of these two forces add, the y components cancel, leaving a net force in the x direction only. In this way all B atoms can be grouped into pairs, such that each pair has a net force on the A atom at the origin which will be in the x direction only. Any motion of the B sublattice in the x direction will thus remain in the x direction, and one of the modes of vibration for $k=0$ can therefore be described entirely without regard to the y direction. This is actually a complete description of one of the nonacoustical modes with $k=0$: the B sublattice moves in the x direction alone, and its frequency is determined by the sum of the restoring forces in the x direction. Since we have not specified the details of this force, we cannot compute the frequency here; but we do know, purely from symmetry, that there will exist a second mode, in which the B sublattice moves in the y direction alone, that than the restoring force, now directed in the y direction alone, on that motion will be of the same strength as it was in the other case, and that the frequency of these two modes will therefore be the same.

At this point it is important to realize the generality of the argument in the preceding paragraph. Atom B_1 and B_2 are not necessarily nearest neighbors of atom A ; rather, no assumption whatever has been made about their distance from A ; similarly nothing was said about the nature of the forces (central or noncentral, velocity dependent or independent, etc.). The resulting forces on A from any pair B_1 and B_2 can thus be added to the resulting forces from any other pair, and all forces that act on A can thus be accounted for, regardless of the nature of the force and particularly of the range of the force; forces of infinite range (e.g., Coulomb forces) are included.

(Formally, the force in the y direction on atom A due to motion in the x direction of all the B atoms appears in the element M_{23} of the dynamical matrix M

in Eq. (A2.5). It is identically 0 there because interaction in that model is included only to second neighbors. If, e.g., fourth neighbors had been included, a term $\sin ak_2 e^{iak_1} + 2 \sin ak_1 e^{-ik_1} [\cos 2ak_2 + \cos ak_1 e^{iak_2}]$ would appear there; in conformance with the argument in the preceding paragraph, this term goes to 0 as k goes to 0).

The proof is easily extended from two dimensional to three dimensional diatomic lattices as illustrated by Fig. 3. The only difference is that the cancellation of forces in the directions other than that of the direction of motion occurs not pair-wise but quartet-wise. Since there are three possible directions of motion, there are three independent modes of the vibration, all of the same frequency. Again there is no restriction in the argument concerning the nature and range of the forces in the crystal, and Coulomb forces in ionic crystals, in particular, are included.

Our conclusion may be summarized by saying that the diatomic three-dimensional crystals with atoms which are centers of symmetry have six modes of vibration for $k=0$: the frequency of three of these is 0 (in agreement with elasticity theory) and the frequencies of the three other modes are all equal,^{9,10} in disagreement with relation (1).

IV. DISCUSSION

The results of the preceding section disagree not only with relation (5), but also with some features of several explicit calculations of lattice frequencies.^{6,11-13} It does agree with others.¹⁴⁻¹⁷ The results of R¹⁷ agree because they were obtained for the sodium chloride lattice essentially by carrying out in detail the steps outlined in the preceding paragraphs here; the papers referred to in references 14-17 do not include long range forces, except perhaps sometimes by unjustified implication. The results of references 6, 7, 11-13 do not agree among each other. In attempting to disentangle the situation, we consider the following matters which could, one might think, be responsible.

- (a) polarizability,
- (b) electrostatics versus electrodynamics,
- (c) size and shape dependence, and the order of performing limiting processes,
- (d) boundary conditions.

⁹ The limiting value of ω_l/ω_t is also discussed by H. Fröhlich, *Theory of Dielectrics* (Oxford University Press, New York, 1958), p. 149 ff. Fröhlich points out that the ratio is unity for crystals small with respect to the wavelength, and size and shape-dependent for larger crystals; see our discussion, particularly Sec. IV c.

¹⁰ When the three "optical" frequencies are equal and the three acoustical ones zero, the sum rule $\sum_{i=1}^8 \omega_i^2(k) = 18a/\beta\bar{M}$, which is valid for all k [R. Brout, *Phys. Rev.* **113**, 43 (1958)], gives directly $\omega^2(0) = 6a/\beta\bar{M}$ for the optical ones (β =compressibility, \bar{M} =reduced mass). But it should be pointed out that the specific form of the right-hand side of Brout's sum rule depends directly on the assumed nature of the short-range forces (in Brout's paper, repulsive interaction between nearest neighbors only).

(a) BH attributes the discrepancy of their results with K's to K's failure to consider the electrical polarizability of the ions. This disagreement is, however, entirely quantitative; qualitatively, both papers get two different non-0 frequencies for $\mathbf{k}=0$. What K, and also I, R, and many other authors, have ignored, and what is also ignored in the present paper, is the so-called "electronic" polarizability, which arises from the fact that ions are not truly charged point masses, but are charged objects of finite size, whose charge is therefore subject to distortion by electromagnetic forces. The "ionic" polarizability, which arises from the displacement from equilibrium of the ions themselves, is properly accounted for automatically in the lattice dynamical problem in all cases. Physically, neglect of the electronic polarizability means setting $\epsilon_\infty=1$ (at high frequencies, the dielectric constant is entirely due to electronic motion, since the ions are too heavy to participate in the motion); but $\epsilon_0 \neq 1$, and hence the right-hand side of Eq. (5) will still differ from unity.

The present result—one single nonzero frequency—can therefore not be attributed to our own refusal to consider the electronic polarizability explicitly.

(b) The question has been raised whether for $\mathbf{k}=0$ the forces can be considered as purely electrostatic ones, or whether "retardation" must be taken into account. Introduction of retardation would in effect make the forces velocity-dependent. Much discussion has been devoted to this point,^{12,13-18} but it is probably fair to say that no solution acceptable to all has been given. However, we may cite I,¹¹ who is aware of the existence of the problem but uses only electrostatics in this calculation, and gets two, rather than one, nonzero frequencies for $\mathbf{k}=0$. By contrast, K treats the retardation problem in detail; but he, too, gets two different frequencies for $\mathbf{k}=0$. In both cases, the value of the frequencies for \mathbf{k} small but not 0 do approach the $\mathbf{k}=0$ values smoothly. (It is agreed that the retardation is negligible for \mathbf{k} not equal to 0.) Furthermore, as pointed out in Sec. III above, velocity dependent forces are not excluded in our argument that lead to equal optical frequencies.

We conclude that our failure to consider retardation

¹¹ M. Iona, Phys. Rev. **60**, 822 (1941); referred to as I. This paper treats the KCl lattice as monatomic; therefore our $\mathbf{k}=0$ appears at his points (000) and (π, π, π) .

¹² E. W. Kellerman, Phil. Trans. Roy. Soc. **238**, 513 (1940); referred to as K.

¹³ R. H. Lyddane and K. F. Herzfeld, Phys. Rev. **54**, 846 (1938); referred to as LH. ^{13a} A. D. B. Woods, W. Cochran, and B. N. Brockhouse, Phys. Rev. **119**, 980 (1960).

¹⁴ M. Born and Th. v. Karman, Physik Z. **13**, 279 (1912). ¹⁵ M. Born and M. G. Mayer, *Handbuch der Physik*, edited by S. Flügge (Verlag Julius Springer, Berlin, 1933), Vol. 24, Part 2.

¹⁶ M. Blackman, Proc. Roy. Soc. (London) **A159**, 416 (1937).

¹⁷ H. B. Rosenstock, J. Phys. Chem. Solids **4**, 201 (1958), referred to as R. Note particularly top, p. 203. This paper treats the NaCl lattice as 8-atomic; our $\mathbf{k}=0$ therefore corresponds to the frequencies there called ω_1 and ω_2 .

¹⁸ J. H. Thompson, Proc. Roy. Soc. (London) **A149**, 487 (1935).

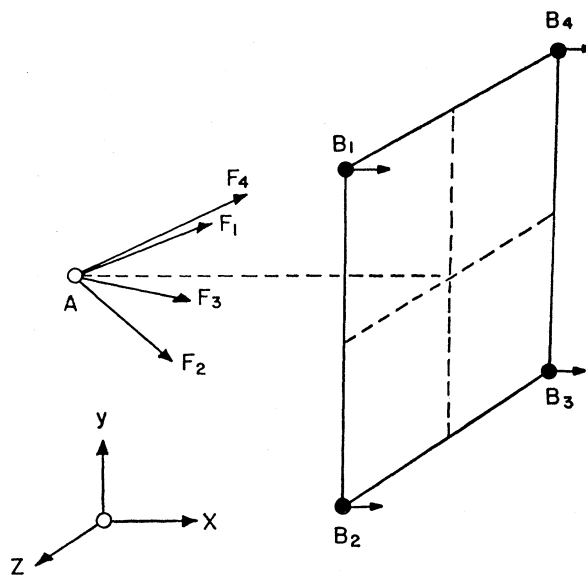


FIG. 3. Forces when $\mathbf{k}=0$ (three dimensions). F_i is the force exerted on particle A by particle B_i . The resultant of the F_i is in the x direction.

explicitly cannot account for our obtaining only one single nonzero frequency at $\mathbf{k}=0$.

(c) LH¹⁹ have noticed that results for lattice frequencies are dependent on the size and shape assumed for the crystal. This is a consequence of the long-range nature of the Coulomb forces which makes the summation processes only conditionally convergent. There are, as has been observed, several quantities in such a calculation that must be computed by some process of approaching infinity: the three space coordinates (and the order and method used here might make a difference) and in addition the wavelength.²⁰ It should be said however that the wavelength does not "approach infinity" in the usual sense of mathematical analysis: the basic quantity is the wave vector \mathbf{k} , to whose reciprocal the wavelength is proportional, and which does not "approach" zero in a continuous way, but in finite and well-defined steps. There should therefore be no difficulty in letting the wavelength *approach* infinity; rather, there is nothing wrong with *setting* k equal to zero.

In our case no explicit assumption at all has been made about the crystal size and shape, but it is important to realize that implicitly such assumptions are contained in our tacit assumption that the modes for which $\mathbf{k}=0$ actually exist. More will be said about this matter in (d) below; at this point let us merely emphasize that the existence of modes with $\mathbf{k}=0$ is not obvious.

(d) All explicit calculations concerning ionic crystal frequencies, except one recent one-dimensional one,²¹ have used the assumption of cyclic boundary condi-

¹⁹ See reference 13, p. 354.

²⁰ See reference 12, p. 598.

²¹ H. B. Rosenstock, J. Phys. Chem. Solids **15**, 50 (1960).

tions. This problem of boundary conditions has been discussed for many years.^{22,23} It is generally believed that the validity of cyclic boundary conditions is established at least for statistical problems—i.e., for problems in which only the total number of frequencies in a finite, though arbitrarily small, frequency interval is of interest, but not necessarily for problems in which one is interested in individual modes. At this point we wish to make two points:

First, that the above restriction is an important one for the present case, and

Second, that proofs that have been given for the validity of cyclic boundary conditions are invalid for crystals with long range forces.

The first statement is perhaps most clearly justified by asserting that the modes for which $\mathbf{k}=0$ do not exist in the absence of cyclic boundary conditions (strictly speaking, they might exist in certain special cases, such as when certain crystal parameters take on special values, but the probability of such an occurrence is zero). This is shown affirmatively for one-dimensional ionic crystals in reference 21 and follows *a fortiori* for three-dimensional ones. Yet the modes for which \mathbf{k} equals zero are the ones which are generally alleged¹⁵ to be the only ones that give rise to optical phenomena (see, however, reference 17). In a negative sense we point out that the existing justification for cyclic boundary conditions (Lederman²⁴ and Peierls²⁵) concern themselves only with the numbers of eigenvalues in a range but not with the changes caused in individual eigenvalues by changing boundary conditions, and certainly not at all with the detailed nature of any eigenfunctions.²⁶

The second statement, which asserts that no rigorous justification for the correctness of cyclic boundary condition exist at all for crystals with long-range forces, has, as far as we know, not been made recently, and in fact the opposite seems to be generally assumed.²³ Ledermann's²⁴ original proof for this is rather clear about the matter, however. He essentially establishes the theorem that the correct frequency distribution g is related to the distribution g_c obtained from cyclic boundary conditions by

$$g(\lambda) = g_c(\lambda)[1 + O(b/(i+b))],$$

where b is the number of boundary particles and i the

number of interior particles. L carefully defines the boundary particles as particles which have one or more "active" neighbors missing, and as "active neighbors" of a particle those particles that exert a force on it. If interaction is short range, "active neighbors" and the word "neighbors" in the ordinary sense are synonymous and $O(b/(i+b)) = O(1/N)$, with N^3 the number of atoms in the crystal. This is the usual interpretation of L 's theorem. If, however the forces are of infinite range, then all particles in the lattice are "active neighbors" of any particle, all particles become, by definition boundary particles, $O(b/(i+b)) = O(1)$, and the theorem derived is devoid of useful content. Similarly, Peierls' proof is dependent on the assumption that "a disturbance starting from a point a distance d from the nearest surface will propagate in the same manner as in an infinite crystal for a time less than d/c , where c is the maximum velocity of sound." This statement is correct only when the interactions are of short range; for long-range interaction, infinity, or more precisely the velocity of light, would have to be substituted for the velocity of sound. Thus this proof also fails to establish a relationship between the behavior of the finite lattice and the lattice with cyclic boundary conditions when long-range forces occur.

We have thus established that cyclic boundary conditions have been used in all earlier calculations of lattice frequencies, either explicitly or by implication (this includes both the papers devoted to the calculation of frequency spectra and general papers such as LST), and also that no justification for this exists in crystals in which Coulomb forces exist. It is perhaps to the point to add that this flaw is likely to be an important one because lattice sums, whose values are strongly dependent on small systematic changes in the positions of all particles, appear (either explicitly or by implication) in all these works. We can therefore conclude that the incorrect treatment of boundaries may well be responsible for the contradictory results that have been found.

(Parenthetically, let us reiterate what we hinted in point (c) above: that our own calculation in Sec. III is also based on cyclic boundary conditions. It follows that the result obtained there—viz., three equal "optical" frequencies—cannot be applied to ionic crystals either. But we should point out clearly that Sec. III does provide a general proof of the equality of "optical" frequencies for all cases in which cyclic boundary conditions are valid).

V. SUMMARY

The situation may, then, be summarized as follows. The vibrational modes for any given \mathbf{k} are, in general, neither transverse nor longitudinal. In particular, \mathbf{k} being very small is not a sufficient condition for transversality or longitudinality, neither for the low-frequency ("acoustic" or "elastic") waves nor for the high-frequency ("optical") ones; even when \mathbf{k} is very

²² For a comparatively recent discussion, see H. B. Rosenstock, J. Chem. Phys. **23**, 2415 (1955).

²³ BH (reference 6), Appendix IV.

²⁴ W. Lederman, Proc. Roy. Soc. (London) **A182**, 362 (1944).

²⁵ R. E. Peierls, Proc. Natl. Inst. Sci. (India) **20**, 121 (1954); or reference 23.

²⁶ The nature of the modes in the absence of cyclic boundary conditions are examined in one simple case (short-range forces of a special kind) in H. B. Rosenstock, J. Chem. Phys. **27**, 1194 (1957). In that case, the usual modes are still sine or cosine waves, differing from their form in the case of cyclic boundary conditions only in their phases. This particularly simple result is a consequence of the simple model there used and should not be expected to remain if long range forces are included. See also reference 22.

small, waves will be transverse or longitudinal only in special directions or if the crystal is isotropic, or for special models. For $\mathbf{k}=0$ the concept of transverse or longitudinal waves becomes, strictly speaking, meaningless.

However, if one confines oneself to certain special crystallographic directions (e.g., the (110) direction in cubic crystals), modes may be correctly called transverse and longitudinal. Doing so, Lyddane, Sachs, and Teller have derived the relationship (5), $\omega_l/\omega_t = (\epsilon_0/\epsilon_\infty)^{1/2}$, for the two "optical" frequencies at a value of \mathbf{k} which is implied to be small, but not specifically defined. In contrast, we have shown that for $\mathbf{k}=0$, the three "optical" frequencies of an ionic crystal of alkali halide structure are all equal. Our calculation is straightforward and independent of the force model assumed, provided only that the harmonic approximation is retained, and includes, in particular, forces of infinite range (Coulomb). The discrepancy is resolved by pointing out that both the present calculation and the earlier calculations of LST and most other writers are predicated upon cyclic boundary conditions. It is pointed out that no justification has ever been adduced for the use of cyclic boundary conditions in crystals with forces of infinite range, and that what use cyclic boundary conditions have (which is considerable) is restricted to short range force models. It follows that a mode for which $\mathbf{k}=0$ (i.e., in which, at any one time, each cell in the crystal looks exactly like any other cell) need not even exist, and that although the motion of the ions will still be describable in terms of normal modes (provided only that the harmonic approximation is retained) these need not be of the form $\sin(\mathbf{k}\cdot\mathbf{x})$ or $\cos(\mathbf{k}\cdot\mathbf{x})$; the very definition of the propagation vector \mathbf{k} is based on this form of the normal modes.¹⁻³ We must thus conclude that Eq. (5), based, as it is by implication, upon the use of cyclic boundary conditions and restricted in its validity as it is to a range of \mathbf{k} which is small but not precisely defined, cannot be considered quantitatively established; and that if it could be shown that cyclic boundary conditions are valid for ionic crystals (which has never been done), then relation (5) would be in complete disagreement with a simple calculation which shows that for $\mathbf{k}=0$, ω_l and ω_t are equal.

The situation is particularly complicated in connection with optical problems, because the mode with $\mathbf{k}=0$ is generally believed to be the only one that interacts with light. Recent work in which boundary conditions were taken into account correctly has shown, to be sure, that this belief is not exactly correct; but accepting this belief would, besides being incorrect, seem to be inconsistent with adoption of Eq. (5) (which refers to a region of \mathbf{k} in which \mathbf{k} is small, but certainly not 0). It is, in other words, not clear just what the values of the frequency are in those ranges of \mathbf{k} that may be important for optical phenomena, and to what approximation, if any, relation (5) may apply there.

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APPENDIX I. COMPUTATIONS FOR SECTION II

The matrix H in Eq. (1) can be written

$$H = \begin{pmatrix} rQ^{-1} & -p^* & -\sigma g'Q^{-1} & 0 \\ -p & rQ & 0 & -\sigma g'Q \\ -\sigma g'Q^{-1} & 0 & rQ^{-1} & -q^* \\ 0 & -\sigma g'Q & -q & rQ \end{pmatrix}, \quad (A1)$$

with

$$\begin{aligned} r &= 2 + \sigma(2 - f), \\ f &= \cos\varphi_2 + \cos(\varphi_1 - \varphi_2), \quad g' = \cos\varphi_2 - \cos(\varphi_2 - \varphi_1), \\ p &= 1 + e^{i\varphi_1}, \quad q = e^{i\varphi_2} + e^{i(\varphi_1 - \varphi_2)}. \end{aligned} \quad (A2)$$

We are to solve (1) for small φ . There it becomes, by expanding and keeping terms up through φ^2 ,

$$(H^0 + H' - \lambda)\psi = 0, \quad (A3)$$

with

$$\begin{aligned} H' &= i\varphi_1 H_{\text{imag}}' + A + \sigma B, \\ H^0 &= 2 \begin{pmatrix} Q^{-1} & -1 & 0 & 0 \\ -1 & Q & 0 & 0 \\ 0 & 0 & Q^{-1} & -1 \\ 0 & 0 & -1 & Q \end{pmatrix}, \\ H_{\text{imag}} &= \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}, \\ A &= \begin{pmatrix} 0 & \varphi_1^2/2 & 0 & 0 \\ \varphi_1^2/2 & 0 & 0 & 0 \\ 0 & 0 & 0 & h \\ 0 & 0 & h & 0 \end{pmatrix}, \\ B &= \begin{pmatrix} hQ^{-1} & 0 & gQ^{-1} & 0 \\ 0 & hQ & 0 & -gQ \\ -gQ^{-1} & 0 & hQ^{-1} & 0 \\ 0 & -gQ & 0 & hQ \end{pmatrix}, \\ h &= g + \varphi_2^2, \quad g = \frac{1}{2}\varphi_1(\varphi_1 - 2\varphi_2). \end{aligned}$$

(A3) is approached by first solving it for $\varphi=0$, viz.,

$$(H^0 - \lambda^0)\psi^0 = 0, \quad (A4)$$

and then proceeding by perturbation theory. The eigenvalues of (A4) are obtained by solving the determinantal equation

$$|H^0 - \lambda^0| = 0;$$

the solutions are

$$\lambda_1^0 = \lambda_2^0 = 0, \quad \lambda_3^0 = \lambda_4^0 = 2(Q + Q^{-1}). \quad (A5)$$

The eigenvectors are then found by substituting these values for λ^0 back into (A4). We find that the ones

corresponding to $\lambda^0=0$ can be written

$$\psi_1^0 = (Q^2+1) \begin{bmatrix} Q \\ 1 \\ 0 \end{bmatrix}, \quad \psi_2^0 = (Q^2+1) \begin{bmatrix} 0 \\ 0 \\ Q \\ 1 \end{bmatrix},$$

and the ones corresponding to $\lambda^0=2(Q+Q^{-1})$ as

$$\psi_3^0 = (Q^2+1) \begin{bmatrix} 1 \\ -Q \\ 0 \\ 0 \end{bmatrix}, \quad \psi_4^0 = (Q^2+1) \begin{bmatrix} 0 \\ 0 \\ 1 \\ -Q \end{bmatrix}. \quad (\text{A6})$$

Any linear combination of ψ_1^0 and ψ_2^0 , and of ψ_3^0 and ψ_4^0 would be equally satisfactory for describing the solutions to the zero-order problem, and the next task in the perturbation theoretic treatment is to find the "correct" linear combinations ψ_i^c of zero-order eigenfunctions—i.e., that linear combination to which the perturbed problem reduces if the perturbation is permitted to disappear ($\varphi \rightarrow 0$). The general formulas for the ψ_i^c , as well as the other formulas needed for the degenerate perturbation theory, are collected by Condon and Shortley,²⁷ for example. On account of the matrix H_{imag} we must carry the calculation to second order if we desire accuracy to φ^2 . The eigenvalues are found to be as given by Eq. (2) and the corresponding "correct" linear combinations of eigenfunctions by (3).

APPENDIX II. ORTHOGONALITY, TRANSVERSALITY, AND LONGITUDINALITY FOR ALL \mathbf{k}

We first show that, for any given \mathbf{k} , the modes are always orthogonal or, in a certain sense, perpendicular to each other. (This has nothing directly to do with whether any one mode is transverse or longitudinal or neither, i.e., with whether any one mode is perpendicular or parallel to \mathbf{k} or neither.) In every lattice dynamical problem with harmonic forces one obtains, after eliminating time dependence and performing the partially diagonalizing transformation suggested by translational symmetry, an eigenvalue equation of the form (2), which we now write as

$$(H - \lambda^{(i)})\psi^{(i)} = 0. \quad (\text{A7})$$

H , called the dynamical matrix, is a Hermitian $nD \times nD$ matrix if we are dealing with a D -dimensional crystal with n atoms per unit cell, and $\psi^{(i)}$ and $\lambda^{(i)}$ are its eigenvectors and eigenvalues, respectively ($i=1, 2, \dots, nD$). Each element in ψ describes the displacement of one of the n atoms in one of the D directions in space. It can then be shown²⁸ that the eigenvectors are

²⁷ E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, New York, 1953), Secs. 8, 9.

²⁸ Replace i by j in (A7), take the Hermitian conjugate, and postmultiply by $\psi^{(i)}$; from this subtract the equation that results from premultiplying (A7) by $\psi^{(j)}$. The result is $(\lambda^{(j)} - \lambda^{(i)})\psi^{(j)*}\psi^{(i)} = 0$ as was to be demonstrated. In connection with the behavior of lattice waves, this standard theorem of matrix theory has been discussed by J. deLaunay, Gordon Research Conference on Physics and Chemistry of Metals, 1959 (unpublished).

orthogonal,

$$\psi^{(j)*}\psi^{(i)} = 0 \quad (\text{A8})$$

unless the corresponding eigenvalues are equal, $\lambda^{(i)} = \lambda^{(j)}$. If the lattice is monatomic, $n=1$, (A8) simply implies that for any given \mathbf{k} the displacement vectors of two different modes are perpendicular to each other; but when $n>1$, this simple interpretation cannot be made.

To show now that the modes are in general neither transverse nor longitudinal, we chose the example of the monatomic two-dimensional square lattice.²⁹ Without even specifying the forces, we can write

$$H = \begin{pmatrix} A & C \\ C & B \end{pmatrix}$$

in (A7); upon solving the resulting secular equation for $\lambda^{(i)}$ and substituting these back into (A7) we find

$$a^{(1)} = Z + (Z^2 + 1)^{1/2}, \quad (\text{A9})$$

$$a^{(2)} = Z - (Z^2 + 1)^{1/2}, \quad (\text{A10})$$

where we have written

$$\psi^{(i)} = \begin{pmatrix} U^{(i)} \\ V^{(i)} \end{pmatrix}, \quad a^{(i)} = V^{(i)}/U^{(i)}, \quad (i=1, 2)$$

and

$$Z = (B - A)/2C. \quad (\text{A11})$$

Solving (A9) for Z gives

$$Z = (a^{(1)2} - 1)/2a^{(1)}. \quad (\text{A12})$$

Now, for concreteness, specify that forces exist between first and second neighbors and that their ratio is σ . Then (A11) becomes²⁹

$$Z = (\cos k_1 - \cos k_2)/2\sigma \sin k_1 \sin k_2,$$

and combining this with (A12) gives

$$(a^{(1)2} - 1)/2a^{(1)} = (\cos k_1 - \cos k_2)/2\sigma \sin k_1 \sin k_2. \quad (\text{A13})$$

The condition that mode 1 be longitudinal is that the ratio k_2/k_1 be equal to the ratio $V^{(1)}/U^{(1)} = a^{(1)}$, which requires, from (A13), that

$$(a^{(1)2} - 1)/2a^{(1)} = (\cos k_1 - \cos a^{(1)}k_1)/2\sigma \sin k_1 \sin a^{(1)}k_1. \quad (\text{A14})$$

But this cannot be generally true; for if (A14) should hold for some specific k_1 and σ , it will certainly not hold if either of these parameters is changed slightly. Mode 1 is therefore not longitudinal (except possibly at isolated points in \mathbf{k} space for certain special values of the force constants), and the same can be shown for mode 2 in the same way; and the orthogonality relation (A8) then implies that neither mode 2 nor mode 1 can be transverse, either (subject to the same accidental exceptions). Having shown that modes are, in general, neither transverse nor longitudinal in case of one very simple model, the same follows *a fortiori* for more complicated crystals.

²⁹ E. W. Montroll, *J. Chem. Phys.* **15**, 575 (1947).