

Surface Elastic Waves in Cubic Crystals*

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A theoretical investigation of surface elastic waves in cubic crystals has been carried out using a theory developed by Stoneley. The range of elastic constants for which Rayleigh type surface waves exist on a (100) free surface has been determined. For other allowed values of the elastic constants generalized Rayleigh waves exist which are characterized by complex attenuation constants. In either case waves may not be propagated in certain directions parallel to the surface depending on the values of the elastic constants. A lattice dynamical theory of surface waves has been developed for a monatomic simple cubic lattice with nearest and next nearest neighbor central forces and angle-bending forces involving successive nearest neighbors. The surface waves exhibit dispersion when the wavelength is comparable to the lattice spacing. In the case of Rayleigh waves a critical wavelength exists, in general, such that for shorter wavelengths the atomic displacements show a reversal in phase between successive layers parallel to the surface.

I. INTRODUCTION

THE existence and properties of elastic waves on the surface of a solid have been the subject of investigation since the time of Lord Rayleigh.¹ Seismologists such as Stoneley² and Press and Ewing³ have been interested in the possible interpretation of seismic waves in terms of various types of surface waves in either a semi-infinite solid or a material made up of many layers. In engineering applications of crystal plates⁴ such as to frequency control, surface waves have been considered as limiting cases of extensional or flexural modes at high frequencies. The properties of many semiconductor devices are strongly influenced by surface characteristics, e.g., the mobilities of electrons and holes in surface layers. An understanding of surface waves and their interaction with current carriers may contribute to our knowledge of these mobilities. Finally, the physical properties of very small crystal particles may be in part determined by surface modes of vibration. For example, specific heats and optical absorption coefficients of very finely powdered crystals may exhibit effects due to surface waves.

The first investigation of surface waves was carried out by Lord Rayleigh¹ who discussed the case of waves at the surface of a semi-infinite isotropic medium. These waves are characterized by an exponential decrease of displacement amplitude with increasing distance from the surface and as customary will be referred to as

Rayleigh surface waves. For straight-crested Rayleigh waves in an isotropic medium the displacement of a point executes an ellipse in the sagittal plane, i.e., the plane normal to both the bounding surface and the wave front. Another type of "surface" wave, which has been treated by Love,⁵ involves transverse shear deformation and occurs in an isotropic slab of infinite length and breadth resting on a different semi-infinite isotropic medium.

The existence of surface elastic waves in anisotropic media has been investigated by Stoneley⁶ who considered the special case of cubic symmetry. Other work on surface waves in anisotropic media includes that of Gold⁷ on cubic crystals, that of Deresiewicz and Mindlin⁴ on monoclinic crystals, and that of Synge.⁸

Stoneley showed that in cubic crystals Rayleigh-type surface waves exist for certain values of the three elastic constants c_{11} , c_{12} , and c_{44} but not for others. In the latter cases a real phase velocity is associated with attenuation constants which are complex rather than real. This implies that the displacements contain components which vary with distance from the free surface as the product of a trigonometric function and an exponentially decaying function. Surface waves of this type will be referred to as generalized Rayleigh waves. Synge⁸ has recently given a formal treatment of the various types of surface waves which may occur in anisotropic media. Synge found that surface waves may not propagate in certain directions for particular values of the elastic constants.

Another approach to vibration problems in crystals is provided by considering the material as a lattice of interacting discrete particles rather than a continuum. Theories of surface modes of vibrations in crystals have

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¹ Lord Rayleigh, Proc. London Math. Soc. **17**, 4 (1887).

² R. Stoneley, Monthly Notices Roy. Astron. Soc. Geophys. Suppl. **5**, 343 (1949).

³ F. Press and M. Ewing, Trans. Am. Geophys. Union **32**, 677 (1951).

⁴ H. Deresiewicz and R. D. Mindlin, J. Appl. Phys. **28**, 669 (1957).

⁵ A. E. H. Love, *Some Problems of Geodynamics* (Cambridge University Press, London, 1926), Chap. XI, p. 160.

⁶ R. Stoneley, Proc. Roy. Soc. (London) **A232**, 447 (1955).

⁷ L. Gold, Phys. Rev. **104**, 1532 (1956).

⁸ J. L. Synge, J. Math. and Phys. **35**, 323 (1957).

been discussed from the discrete atomic point of view by Lifshitz and Rosenzweig⁹ and by Wallis.¹⁰ Lifshitz and Rosenzweig employed a technique comparable to that used by Montroll and Potts¹¹ in their investigation of localized vibrational modes at point defects. They found that two types of surface modes may exist in diatomic crystals, one analogous to Rayleigh waves and a second type derived from the optical branch and having no analog in continuum theory. This second type of surface mode was also found by Wallis.

The work of Lifshitz and Rosenzweig⁹ is primarily formal, and it is not clear that their method is easily adapted to calculations based on realistic models. The work of Wallis¹⁰ is based on very specialized models. For these models the surface modes disappear if the lattice becomes monatomic and are replaced by ordinary bulk modes.

In the present paper we report the results of an investigation of surface elastic waves in cubic crystals from both the continuum and discrete particle points of view. We employ methods which are sufficiently flexible so that detailed calculations can be carried out for realistic models. Using Stoneley's⁶ continuum treatment of cubic crystals we have studied the nature of the surface wave displacements, velocities and attenuation constants for various possible values of the elastic constants c_{11} , c_{12} , and c_{44} . The discrete particle method has been applied to the study of surface wave characteristics in the monatomic simple cubic lattice. Nearest and next nearest neighbor central forces and angle-bending forces involving successive nearest neighbors were assumed. For wavelengths long in comparison with the interatomic distance the discrete particle theory, as to be expected, yields results equivalent to those of the continuum theory. When the wavelength becomes comparable to the interatomic distance the particle theory leads to dispersion, whereas the continuum results remain nondispersive for all wavelengths, since the continuum solutions can be scaled.

II. CONTINUUM THEORY

A. Frequency Equation

Our treatment of the continuum theory of surface waves in cubic crystals is based on that of Stoneley. We present only those of his results which are needed in the subsequent discussion.

Consider a semi-infinite continuum of cubic symmetry bounded by a principal plane $z=0$ which is free of traction. At any point x, y, z in the medium the displacement components u, v, w , are assumed to be of the form

$$(u, v, w) = (U, V, W) \exp[-qz + i(lx + my - ct)], \quad (1)$$

where c is the phase velocity, κ the wavenumber, and q the attenuation constant. Substituting Eq. (1) into the equations of motion [see Stoneley⁶ Eq. (4)] one obtains a set of linear homogeneous algebraic equations for the amplitudes U, V, W whose nontrivial solution requires that

$$\begin{vmatrix} g_1 l^2 + m^2 - p^2 - q^2 & lm(g_2 + 1) & lq(g_2 + 1) \\ lm(g_2 + 1) & l^2 + g_1 m^2 - p^2 - q^2 & mq(g_2 + 1) \\ lq(g_2 + 1) & mq(g_2 + 1) & p^2 + g_1 q^2 - 1 \end{vmatrix} = 0 \quad (2)$$

where

$$\begin{aligned} g_1 &= c_{11}/c_{44}, \\ g_2 &= c_{12}/c_{44}, \\ p^2 &= \rho c^2/c_{44}, \end{aligned} \quad (3)$$

in which the c_{ij} are the well-known elastic constants and ρ is the density.

Equation (2) is a bicubic in q and p . Thus to a given velocity-ratio p correspond three values of the square of the attenuation constant q . The displacements u, v , and w given by Eq. (1) decrease toward zero as z increases provided that the constants q_j are positive real numbers or complex numbers with positive real parts. This is possible if all three of q_j^2 as given by Eq. (2) are either positive or complex. The amplitudes U_j, V_j , and iW_j corresponding to any q_j are given by

$$\frac{U_j}{\xi_j} = \frac{V_j}{\eta_j} = \frac{iW_j}{\zeta_j} = K_j, \quad j=1, 2, 3, \quad (4)$$

where

$$\begin{aligned} \xi_j &= (l^2 + g_1 m^2 - p^2 - q_j^2)(p^2 + g_1 q_j^2 - 1) - m^2 q_j^2 (g_2 + 1)^2, \\ \eta_j &= lm(g_2 + 1)[q_j^2(g_2 + 1 - g_1) + 1 - p^2], \\ \zeta_j &= lq_j(g_2 + 1)[m^2(g_2 + 1 - g_1) - l^2 + p^2 + q_j^2]. \end{aligned} \quad (5)$$

Thus under the stated restrictions on q_j , the general values of the displacements which satisfy the equations of motion and, in addition, tend to zero as z tends to infinity are given by

$$(v, u, iw) = \sum_{j=1,2,3} (\xi_j \eta_j \zeta_j) K_j \times \exp[-q_j z + i(lx + my - ct)]. \quad (6)$$

The ratios of the K_j are determined by use of the boundary conditions which are that the stresses on the boundary plane vanish. [See Stoneley⁶ Eqs. (10).]

Substituting Eqs. (6) into Stoneley's Eqs. (10) one obtains a homogeneous linear system of equations with three unknown variables K_j . A nontrivial solution is obtainable if

$$D(p) = |f_{ij}| = 0, \quad (i, j=1, 2, 3), \quad (7)$$

where

$$\begin{aligned} f_{1j} &= l\zeta_j - q_j \xi_j, \\ f_{2j} &= m\zeta_j - q_j \eta_j, \\ f_{3j} &= l\xi_j + m\eta_j + (c_{11}/c_{12})q_j \zeta_j. \end{aligned} \quad (8)$$

⁹ I. M. Lifshitz and L. N. Rosenzweig, J. Exptl. Theoret. Phys. **18**, 1012 (1948).

¹⁰ R. F. Wallis, Phys. Rev. **105**, 540 (1957).

¹¹ E. W. Montroll and R. B. Potts, Phys. Rev. **100**, 525 (1955).

Equation (7) may be used for the determination of the velocity ratio p , for given elastic constants and direction of propagation, as follows. For an assumed value of p three values of q_j are computed from Eq. (2) and the corresponding values of ξ_j, η_j, ζ_j from Eqs. (5). These values are entered in Eq. (7) and the zero of D , considered as a function of p alone, is determined by a suitable approximation technique. In the present investigation an "interval halving" technique was used which determines a root in a given range of the independent variable within a specified small relative error. When the velocity ratio p , satisfying Eq. (7) is determined, the corresponding displacement components are derived according to Eqs. (6). The numerical computations were performed on an IBM 704 electronic digital computer.

B. General Remarks

The characteristic Eq. (7) pertains to the general case of wave propagation along any arbitrary direction $(l, m, 0)$ on the plane $z=0$. There is no *a priori* assurance that any root p of this equation corresponds to a physically acceptable surface wave. The nature of the attenuation constants q_j which are involved in the formal solution of the problem determines whether or not this solution actually describes a surface wave. If all the q_j involved in the solution are positive real then the displacement components decay exponentially with z , a case defined in the introduction as that of Rayleigh-type waves. However, two of the three roots q_j^2 of the bicubic Eq. (2) may be complex conjugate. The corresponding attenuation constants q_j are also complex conjugate and the displacements associated with these q_j may be expressed in terms of products of trigonometric and exponentially decaying functions of z (generalized Rayleigh-type). Finally, if one or more of the three roots q_j^2 of the bicubic are negative, the corresponding q_j are pure imaginary. The displacements associated with pure imaginary q_j do not decay with z and hence no surface wave is possible in this case.

As seen from the derivation of the general characteristic equation, for an arbitrary direction of propagation, all three waves associated with the three attenuation constants q_j must, in general, be superimposed in order to satisfy the boundary conditions. Furthermore, the displacement components u and v are not necessarily proportional to l and m . As a result, the movement of every point in the continuum, as described by Eqs. (6), is along an ellipse which is, in general, inclined with respect to the sagittal plane. Exceptions discussed by Stoneley⁶ are the case of isotropy and the two symmetric cases, $(l=1, m=0)$ and $(l=m=1/\sqrt{2})$. As pointed out by Stoneley, only two of the three waves associated with the three attenuation constants q_j are necessary in these special cases for the possible composition of Rayleigh-type surface waves. Furthermore, the motion corresponding to these waves is executed in the sagittal plane and is uncoupled from motion associated with the

third attenuation constant, which is perpendicular to this plane. The latter motion accounts for Love-type waves which will not be discussed in this paper.

The three special cases of physical or geometric symmetry are the only ones considered in detail by Stoneley because of the considerable computational difficulties involved in the case of any other arbitrary direction of propagation. Only one such direction was considered by Stoneley for NaCl in order to demonstrate the characteristics of motion in the general case. However, in his investigation of a limited number of materials, Stoneley gave an indication of what is to be expected from a more detailed investigation of Rayleigh-type waves. He found that such waves are possible for some materials of cubic symmetry, e.g., NaCl. They are not obtainable in other materials, e.g., Al, for which the attenuation constants are complex for $l=1$, say.

As mentioned in the introduction, complex attenuation constants yield displacements whose amplitude varies with the distance from the free surface as the product of trigonometric and decreasing exponential functions. Waves which involve such displacements were defined as generalized Rayleigh surface waves. It is natural to ask what circumstances lead to one or the other type of surface wave. In order to answer this and other questions we have conducted an analytical and numerical investigation, in the entire range of permissible elastic constants, as discussed in the following sections.

C. Investigation of the Stable Region of Elastic Constants

As is well known, the elastic constants cannot be completely arbitrary if they are to correspond to a physically stable material under arbitrary conditions of strain. A well established criterion of stability is afforded by the condition that the strain energy be a positive definite quadratic function of the strain components.¹² This is true if the 6×6 matrix of elastic constants c_{ij} is positive definite. A necessary and sufficient condition for this occurrence is that the discriminants of the matrix c_{ij} be positive.¹³ For a cubic crystal the latter condition yields the inequalities

$$\begin{aligned} c_{11} &> 0, \\ c_{11} - c_{12} &> 0, \\ c_{11} + 2c_{12} &> 0, \\ c_{44} &> 0, \end{aligned} \quad (9)$$

which determine the "stable region" of elastic constants. In the plane $g_1 = c_{11}/c_{44}$ versus $g_2 = c_{12}/c_{44}$ the stable region is the sector which includes the positive g_1 axis

¹² A. E. H. Love, *Theory of Elasticity* (Dover Publications, New York, 1944), p. 99.

¹³ R. A. Frazer, W. J. Duncan, and A. R. Collar, *Elementary Matrices* (The MacMillan Company, New York, 1946), p. 30.

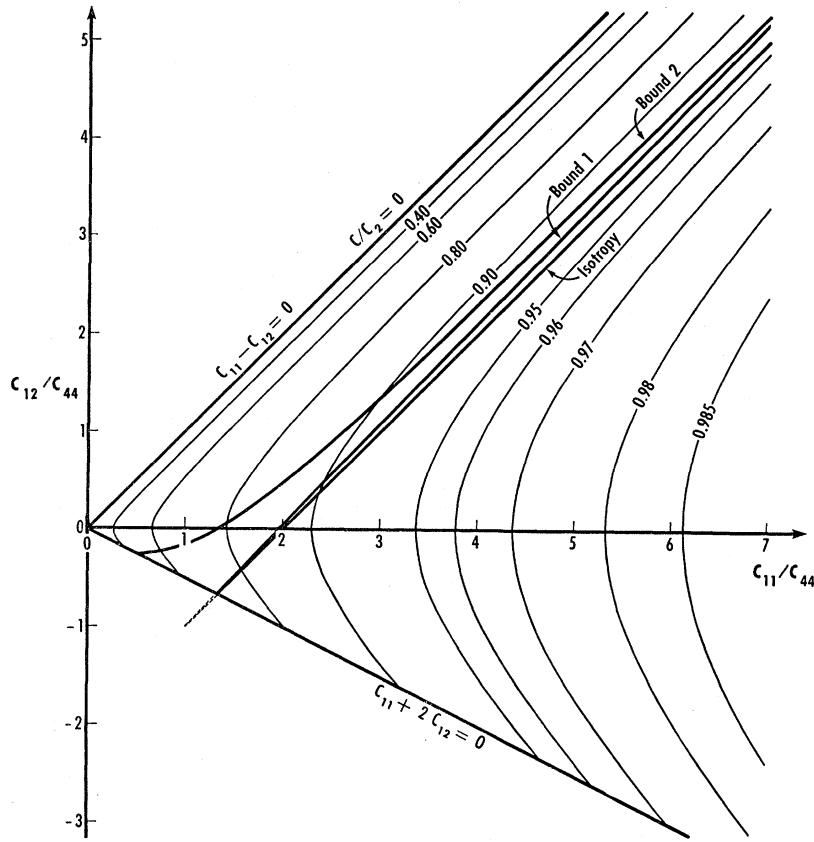


FIG. 1. Region of stability of cubic crystal continua. The bound 1 separates materials for which only Rayleigh surface waves exist from those in which generalized Rayleigh waves may be propagated in some or all directions. Excluded directions of propagation are observed for materials above bound 2. Also shown in this figure are the line of isotropy and contours of constant normalized phase velocity, c/c_2 , for waves in the (100) direction.

and is bounded by the lines

$$g_1 - g_2 = 0,$$

and

$$g_1 + 2g_2 = 0,$$

(10)

as shown in Fig. 1.

We now seek to establish the bound, or bounds, between subregions of the stable region corresponding to materials which propagate the two different types of surface waves, i.e., the Rayleigh and generalized Rayleigh type. To this end we recall that the type of the wave is determined from the nature of the associated attenuation constants. It has already been mentioned that, in general, these constants are the roots of the cubic Eq. (2), provided that this equation and Eq. (7) are simultaneously satisfied for an appropriate value of the frequency parameter, p . It is rather difficult to investigate the nature of the roots q_j for the general case of arbitrary direction of propagation. This is so because p cannot be obtained explicitly in terms of the q_j , and also, because the q_j are obtained from a cubic equation. However, in the special cases of propagation in the (100) and (110) directions these difficulties disappear, and one can perform a reasonably thorough investigation of the attenuation constants. This investigation is fairly adequate for our purposes since it is reasonable to expect that any phenomena observed here display some sort of

continuity as the direction of propagation varies from (100) to (110). Consequently we now direct our attention to these two special cases.

For waves in the (100) direction, the frequency equation degenerates into

$$(1 - p^2)(g_1^2 - g_2^2 - g_1 p^2) - p^4 g_1(g_1 - p^2) = 0 \quad (11)$$

and the attenuation constants of the two superimposed waves are obtained from an equation quadratic in q^2 , namely,

$$(g_1 - p^2 - q^2)(1 - p^2 - g_1 q^2) + q^2(g_2 + 1)^2 = 0, \quad (12)$$

as discussed by Stoneley.⁶ A transition from Rayleigh-type to generalized Rayleigh-type waves occurs when the two roots q_j^2 of Eq. (12) change from positive real into complex. A condition for the transition is obtained by setting the discriminant of Eq. (12) equal to zero. Thus, one obtains a possible bound, hereafter designated as bound 1a, from the simultaneous solution of Eq. (11) and the discriminant of Eq. (12) which is obtained, after reduction, in the form

$$d_1 = p^4(g_1 - 1)^2 + 2(g_1 + 1)(g_1 + g_2)(g_2 + 2 - g_1)p^2 + (g_1 + g_2)(g_2 - g_1)(g_2 + 2 - g_1)(g_2 + 2 + g_1) = 0. \quad (13)$$

The approximate position of bound 1a can be estimated by observing that in the plane g_1 versus g_2 the straight

line

$$g_2 + 2 - g_1 = 0, \quad (14)$$

or

$$c_{12} + 2c_{44} - c_{11} = 0, \quad (15)$$

corresponds to the isotropic case. The left-hand side of Eq. (13) is positive if Eq. (14) is satisfied, hence, one always obtains Rayleigh-type waves for an isotropic material, in accordance with Rayleigh's results.¹ The left-hand side of Eq. (13) is a quadratic in p^2 and hence it is positive if its discriminant is negative. This discriminant is

$$d_2 = 16g_1(g_2 + 1)^2(g_1 + g_2)(g_2 + 2 - g_1), \quad (16)$$

and it is negative if

$$g_2 + 2 - g_1 < 0. \quad (17)$$

It follows that only Rayleigh-type surface waves may exist for materials corresponding to points below the isotropic line, Fig. 1, and hence bound 1a is located above this line. Eliminating p between Eqs. (13) and (11) one obtains an implicit function of g_1 and g_2 . Points of bound 1a have been determined by selecting a value for g_2 and computing the corresponding value of g_1 by iteration. For $g_1 \gg 1$ and $g_2 \gg 1$ it may be ascertained that the bound 1a is approximated by its asymptote

$$g_1 = g_2 + s, \quad (18)$$

where

$$s \approx 1.778.$$

It remains to be checked whether or not the attenuation constants obtained on either side of bound 1a correspond to amplitudes actually decreasing with increasing distance from the free surface. In the region of generalized Rayleigh waves, i.e., $d_1 < 0$, it is always possible to obtain two complex conjugate q_j with positive real parts which yield displacements attenuated with z , as may be seen from Eqs. (6). In the region of Rayleigh waves, i.e., $d_1 > 0$, the two values of q_j^2 obtained from the quadratic Eq. (12) must be both positive. A check of the coefficients of Eq. (12) reveals that this is so in the entire region $d_1 > 0$. In fact, the sum and product of the two roots q_1^2 and q_2^2 are

$$q_1^2 + q_2^2 = [g_1(g_1 - p^2) + (1 - p^2) - (g_2 + 1)^2]/g_1, \quad (19)$$

and

$$q_1^2 q_2^2 = (g_1 - p^2)(1 - p^2)/g_1.$$

In view of the location of bound 1a we may assume

$$g_1 > g_2 + s, \quad (20)$$

and

$$g_1 > 1.$$

Then, under the verifiable assumption that $p < 1$, we

obtain

$$\begin{aligned} g_1(g_1 - p^2) + (1 - p^2) - (g_2 + 1)^2 \\ > (g_1 - 1) + (g_1 + g_2)(g_1 - 2 - g_2) > 0, \quad (21) \\ (g_1 - p^2)(1 - p^2) > (g_1 - 1)(1 - p^2) > 0. \end{aligned}$$

Hence, surface waves are always possible in the (100) direction, on both sides of bound 1a.

A similar investigation can be carried for waves in the (110) direction, leading to the derivation of bound 1b analogous to bound 1a. Bound 1b separates materials which are characterized by Rayleigh type and generalized Rayleigh type waves in the (110) direction. Following Stoneley⁶ the frequency equation for this direction is

$$(1 - p^2)[g_1 g_3 - g_2^2 - p^2 g_1] - p^4 g_1 (g_3 - p^2) = 0, \quad (22)$$

where

$$g_3 = (1/2)(g_1 + g_2 + 2). \quad (23)$$

The squares of the corresponding attenuation constants are the roots of the quadratic equation

$$(g_3 - p^2 - q^2)(1 - p^2 - g_1 q^2) + q^2(g_2 + 1)^2 = 0. \quad (24)$$

The discriminant of Eq. (24) may be obtained in the form

$$d_3 = A p^4 + B p^2 + C, \quad (25)$$

where

$$\begin{aligned} A &= (g_1 - 1)^2, \\ B &= (g_2 + 2 - g_1)(g_1^2 - 3g_1 + 2g_2 + 2g_1 g_2), \\ C &= (1/4)(g_2 + 2 - g_1) \\ &\quad \times (4g_2^3 - g_1^3 - 8g_1 g_2 + 8g_2^2 - 8g_1 - 3g_1^2 g_2 - 6g_1^2). \end{aligned} \quad (26)$$

A transition from Rayleigh-type to generalized Rayleigh-type waves occur across a bound, hereafter designated as bound 1b, which is determined from a simultaneous solution of Eq. (22) and one derived by setting $d_3 = 0$. Again, it is seen that the line of isotropy lies within the Rayleigh region ($d_3 > 0$). The bound 1b is estimated by eliminating p between Eqs. (22) and (25) and computing g_1 as a function of g_2 , by iteration. It lies slightly to the right of bound 1a, for relatively small values of g_1 and g_2 , it crosses bound 1a in the neighborhood of $g_1 \approx 9$, $g_2 \approx 7.2$ and tends to an asymptote

$$\begin{aligned} g_1 &= g_2 + s', \quad g_1 \gg 1, \\ s' &\approx 1.7037. \end{aligned} \quad (27)$$

Just as in the case of waves in the (100) direction, we find that surface waves are always possible in the (110) direction. In the region $d_3 > 0$ both the sum and the product of the two q_j^2 , namely,

$$\begin{aligned} q_1^2 + q_2^2 &= [g_1(g_3 - p^2) + (1 - p^2) - (g_2 + 1)^2]/g_1, \\ q_1^2 q_2^2 &= (g_3 - p^2)(1 - p^2)/g_1, \end{aligned} \quad (28)$$

are always positive. In the region $d_3 < 0$ it is always possible to take two complex conjugate q_j with positive real parts.

It has already been mentioned in the preceding that it is rather difficult to conduct an investigation of waves in an arbitrary direction of propagation along the line used for the two directions of symmetry. It is conjectured, and verified by our computations, that bounds between regions of Rayleigh type and generalized Rayleigh type waves, which may be established for various directions of propagation between (100) and (110), lie in the neighborhood of the very closely spaced bounds 1a and 1b. For all practical purposes the lower of the two bounds, i.e., the one with smaller g_2 for the same g_1 , may be considered as a physical bound beyond which generalized Rayleigh-type waves appear for some directions of propagation. This lower bound, designated as bound 1, is shown in Fig. 1. In the range of g_1 and g_2 in this figure bound 1 coincides with bound 1b.

D. Excluded Directions of Propagation

While computing the phase velocity for various materials and different directions of propagation, it was discovered that some materials are characterized by the existence of an excluded range of directions of propagation. In this range no surface waves are possible of either the Rayleigh or the generalized Rayleigh type. The excluded directions are generally in the vicinity of the (110) direction. It has been observed that for the materials in question one of the attenuation constants tends to zero as the angle of the direction of propagation with the (100) direction increases from zero to some critical value θ_c . Beyond θ_c it is not possible to obtain the three surface waves which are needed in order to satisfy the boundary conditions. All of the materials examined which involve an excluded range of directions of propagation are within the region of generalized Rayleigh waves, and it is the real attenuation constant which vanishes at θ_c . The question arises whether or not it is possible to establish, within the stable region of elastic constants, a bound between subregions which are characterized by the presence or absence of excluded directions of propagation. The answer is affirmative and such a bound, denoted as bound 2, is shown in Fig. 1. This bound is essentially a contour along which the condition

$$\theta_c = \pi/4, \quad (29)$$

is satisfied. It is conjectured, and verified by numerical computations, that this contour leaves all other possible contours of $\theta_c < \pi/4$ above itself in Fig. 1.

All the materials corresponding to elastic constants which lie above bound 2 are characterized by the existence of an "excluded sector" of directions of propagation, in the vicinity of the (110) direction. It should be remarked, however, that a surface wave can always propagate along the (110) direction, although this direction is within the excluded sector. This is because the Rayleigh or generalized Rayleigh wave in the (110) direction is uncoupled from the wave corresponding to the third attenuation constant which vanishes at θ_c .

According to the preceding discussion the bound 2 is determined from the simultaneous solution of Eq. (22) and the equation

$$(1/2) (g_1 - g_2) - p^2 = 0. \quad (30)$$

Eliminating p from these two equations one obtains

$$2(2 - g_1 + g_2)(g_1 g_2 + g_1 - g_2^2)^2 - g_1(g_1 - g_2)^2(g_2 + 1) = 0. \quad (31)$$

The line of g_2 as a function of g_1 given by Eq. (31) has been computed numerically and is shown in Fig. 1. It intersects the axis g_1 at $g_1 = 4/3$ and tends to an asymptote

$$g_1 = g_2 + s'', \quad g_1 \gg 1, \\ s'' \approx 1.7939. \quad (32)$$

A comparison of this asymptote with the asymptotes of bounds 1 and 1a of the preceding section shows that bound 2 crosses these bounds at some points. This implies that excluded directions may exist also for materials of the Rayleigh region, for relatively large elastic parameters g_1 and g_2 (i.e., relatively incompressible materials). No further investigation of the region of large g_1 and g_2 has been deemed necessary at the present, since no real materials of cubic symmetry have been found in that region.

E. Numerical Computations

The phase velocity and attenuation constants were computed for different directions of propagation between (100) and (110) and for various cubic crystals. The materials considered include typical metallic substances (Cu, Al), alkali-halides (NaCl, KCl) and materials of special crystallographic structure (diamond, β -brass). The elastic constants of all these materials, as well as all other known cubic crystals lie within a rather limited region in the plane g_1, g_2 , as shown in Fig. 2. Very few substances have a negative c_{12} , or g_2 . Virtually all of the simple elements lie within the generalized Rayleigh region, and most of them above bound 2. Most of the alkali-halides are within the Rayleigh region. The values of elastic constants for all these materials were taken from Trent and Stone,¹⁴ Mason,¹⁴ and Huntington.¹⁵

Figure 3 contains a plot of the phase velocity ratio, p , versus the angle θ of the direction of propagation with (100) for some of the aforementioned materials. It is seen that the phase velocity varies very slowly with θ in the case of the alkali halides, whereas its variation is more pronounced in the case of materials which are characterized by the existence of excluded directions of propagation. The variation of the phase velocity appears to be more rapid in the neighborhood of θ_c . In any case,

¹⁴ American Institute of Physics Handbook (McGraw-Hill Book Company, Inc., New York, 1957), pp. 2-56, 3-81, and 3-83.

¹⁵ *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 276.

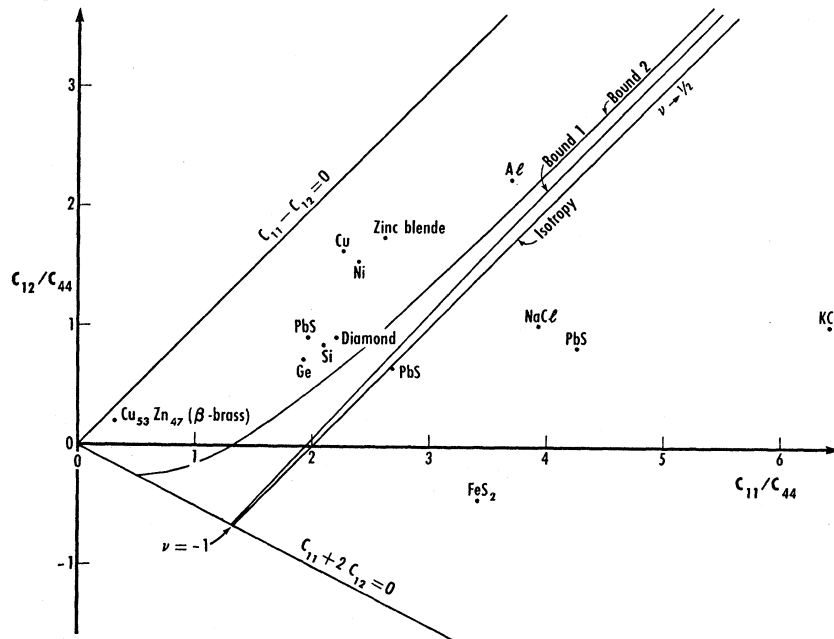


FIG. 2. Position of various materials with respect to bounds 1 and 2. The values for the elastic constants are taken from references 14 and 15. It may be noted that there are wide variations in the measured values for the elastic constants of PbS.

the minimum phase velocity is within 30% of the maximum phase velocity for all the materials considered here. Having obtained the phase velocity ratio p , one can compute immediately the corresponding attenuation constants q_i from the cubic Eq. (2). Figures 4 and 5 contain plots of q_i versus θ for a material in the Rayleigh region, KCl, and a material in the generalized Rayleigh region, Cu.

Since the phase velocity does not vary too much with θ , one can obtain an estimate of the phase velocities

which are to be expected in a given crystal by considering the velocity in the (100) direction. For this purpose we have plotted contours of equal phase velocity in Fig. 1, for surface waves propagating in the (100) direction. It may be ascertained that these contours are symmetric about the g_1 axis, since the frequency Eq. (11) is even in g_2 . All contours intersect the lower bound of the stable region and tend asymptotically to

$$g_1 = g_2 + h, \quad g_2 \gg 1, \quad (33)$$

where h varies with the value of p , i.e., it is different

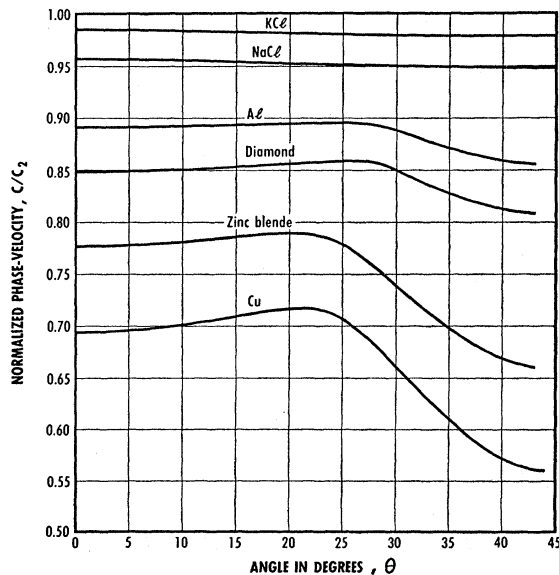


FIG. 3. Normalized phase velocity, c/c_2 , versus angle between the direction of propagation and the (100) direction, θ , for various materials as given by the continuum theory.

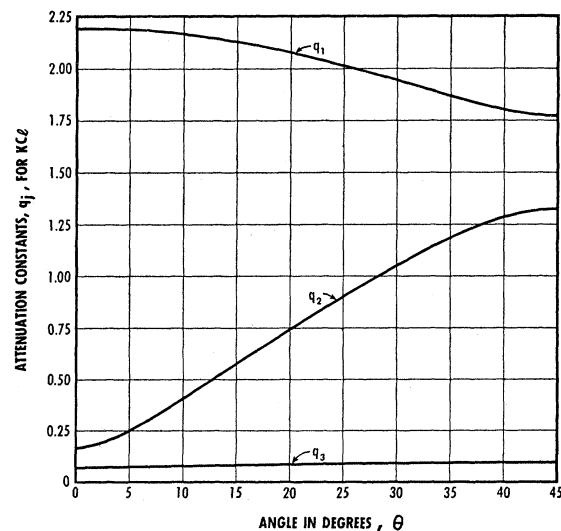


FIG. 4. Attenuation constants, q_i , versus angle between the direction of propagation and the (100) direction, θ , as given by the continuum theory, for KCl.

for different contours. The line of isotropy is the asymptotic line of the contour $p \approx 0.955$. Since the line of isotropy does not intersect contours with p smaller than about 0.68, one obtains immediately an upper and lower bound for the phase velocity of Rayleigh waves in isotropic materials. The upper bound $p \approx 0.955$ corresponds to an incompressible isotropic material, and the lower bound $p \approx 0.68$ to a material on the verge of instability with a Poisson's ratio equal to -1 . In the case of anisotropy, for $g_2 = 0$ and for $g_1 \rightarrow \infty$ the phase velocity ratio p tends to 1.

III. DISCRETE PARTICLE THEORY

A. Frequency Equation

Consider a monatomic simple cubic lattice composed of particles with mass M and nearest neighbor distance a . We assume Hooke's law interaction of nearest and next-nearest neighbors due to central forces characterized by force constants α and β , respectively. We also assume forces due to angular stiffness of a system of three consecutive nearest neighbors which form a right angle in the equilibrium configuration. These angular stiffness forces are characterized by a force constant γ . No account is taken of changes in geometry and force constants caused by lattice distortion near the free surface. We shall use a coordinate system with axes parallel to the principal axes of symmetry and assume that the material extends to positive infinity in the z direction and is bounded by a plane perpendicular to this direction. In the absence of body forces the equations of motion can be written in the form¹⁶

$$\begin{aligned}
 M\ddot{u}_{l,m,n} = & \alpha(u_{l+1,m,n} - 2u_{l,m,n} + u_{l-1,m,n}) \\
 & + \beta(u_{l+1,m+1,n} + u_{l-1,m+1,n} + u_{l+1,m-1,n} \\
 & + u_{l-1,m-1,n} + u_{l+1,m,n+1} + u_{l-1,m,n+1} \\
 & + u_{l+1,m,n-1} + u_{l-1,m,n-1} - 8u_{l,m,n}) \\
 & + (\beta + \gamma)(v_{l+1,m+1,n} + v_{l-1,m-1,n} \\
 & - v_{l-1,m+1,n} - v_{l+1,m-1,n} + w_{l+1,m,n+1} \\
 & + w_{l-1,m,n-1} - w_{l+1,m,n-1} - w_{l-1,m,n+1}) \\
 & + 4\gamma(u_{l,m+1,n} + u_{l,m-1,n} + u_{l,m,n+1} \\
 & + u_{l,m,n-1} - 4u_{l,m,n}), \quad (34)
 \end{aligned}$$

with corresponding similar equations for the equilibrium of the y and z components of forces. In the preceding Eq. (34), u , v , and w are the components of displacement in the x , y , and z directions and l , m , and n are integers specifying the corresponding coordinates of a particle in the equilibrium configuration with respect to some arbitrary origin. The determination of the central force contribution is straightforward.¹⁷ The components of the angular stiffness forces are determined by differentiating the expression for the strain energy due to angular deformation with respect to the respective

¹⁶ It should be noted that l and m have not the same meaning here as in the continuum discussion where they represent direction cosines.

¹⁷ E. W. Montroll, J. Chem. Phys. **15**, 575 (1947).

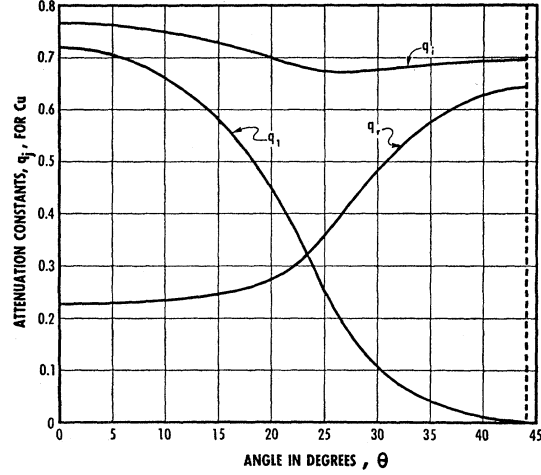


FIG. 5. Attenuation constants, q_i , versus angle between the direction of propagation and the (100) direction, θ , as given by the continuum theory, for Cu.

displacement components. Thus, for example, the strain energy due to the deformation of the angle composed by the particles $(l, m+1, n)$, (l, m, n) , and $(l+1, m, n)$ is

$$E = (\gamma/2)[(u_{l,m+1,n} - u_{l,m,n}) + (v_{l+1,m,n} - v_{l,m,n})]^2, \quad (35)$$

and the corresponding contribution to the x component of force on the particle (l, m, n) is

$$-\frac{\partial E}{\partial u_{l,m,n}} = \gamma[(u_{l,m+1,n} - u_{l,m,n}) + (v_{l+1,m,n} - v_{l,m,n})]. \quad (36)$$

We seek a solution of Eqs. (34) of the type

$$(u, v, w)_{l,m,n} = (U, V, W) \exp[-qn + i(\phi_1 l + \phi_2 m + \omega t)]. \quad (37)$$

Introducing Eqs. (37) in Eqs. (34), one obtains,

$$d_{ij}X_j = 0, \quad (38)$$

where

$$\begin{aligned}
 d_{11} = & M\omega^2 + 2\alpha(\cos\phi_1 - 1) \\
 & + 4\beta(\cos\phi_1 \cos\phi_2 + \cos\phi_1 \cosh q - 2) \\
 & + 8\gamma(\cos\phi_2 + \cosh q - 2), \\
 d_{12} = d_{21} = & -4 \sin\phi_1 \sin\phi_2 (\beta + \gamma), \\
 d_{13} = d_{31} = & -4 \sin\phi_1 \sinh q (\beta + \gamma), \\
 d_{22} = & M\omega^2 + 2\alpha(\cos\phi_2 - 1) \\
 & + 4\beta(\cos\phi_1 \cos\phi_2 + \cos\phi_2 \cosh q - 2) \\
 & + 8\gamma(\cos\phi_1 + \cosh q - 2), \\
 d_{33} = & -[M\omega^2 + 2\alpha(\cosh q - 1) \\
 & + 4\beta(\cosh q \cos\phi_1 + \cosh q \cos\phi_2 - 2) \\
 & + 8\gamma(\cos\phi_1 + \cos\phi_2 - 2)], \\
 d_{33} = d_{32} = & -4 \sin\phi_2 \sinh q (\beta + \gamma), \\
 X_1 = & U, \quad X_2 = V, \quad X_3 = iW.
 \end{aligned} \quad (39)$$

A nontrivial solution of Eqs. (38) requires that

$$|d_{ij}|=0. \quad (40)$$

For a given set of force constants and wave numbers ϕ_1 and ϕ_2 , Eq. (40) constitutes a relationship between the frequency ω and the attenuation constant q . Since it is a cubic in $\cosh q$, to a given frequency ω correspond, in general, three attenuation constants q_j with possible physical interest. As in the case of the continuum theory, a surface wave results only if the q_j which are involved in the solution have real parts greater than zero. This condition is satisfied, for real $\cosh q_j$, if

$$|\cosh q_j| > 1. \quad (41)$$

The case $\cosh q_j > 1$ yields a positive real q_j and hence a Rayleigh-type surface wave, i.e., one whose displacement amplitude decreases monotonically and exponentially away from the surface. The case $\cosh q_j < -1$ corresponds to a q_j of the type

$$q_j = q_{j0} + i\pi, \quad (42)$$

where q_{j0} is positive real. The associated wave is a special case of the generalized Rayleigh surface wave involving phase reversal between successive layers in the direction normal to the free surface. The amplitudes U_j , V_j , and (iW_j) corresponding to a particular q_j are determined by

$$\frac{U_j}{\xi_j} = \frac{V_j}{\eta_j} = \frac{iW_j}{\zeta_j} = K_j, \quad (43)$$

where

$$\begin{aligned} \xi_j &= d_{22}d_{33} - d_{32}d_{23}, \\ \eta_j &= d_{23}d_{31} - d_{21}d_{33}, \\ \zeta_j &= d_{21}d_{32} - d_{31}d_{22}. \end{aligned} \quad (44)$$

The general solution of the equations of motion, corresponding to surface waves, is given by

$$(u, v, iw) = \sum_{j=1,2,3} (\xi_j, \eta_j, \zeta_j) K_j \times \exp[-q_j n + i(\phi_1 l + \phi_2 m + \omega t)], \quad (45)$$

where the K_j are to be determined from the boundary conditions. The boundary is formed by removal of all particles on one side of the boundary layer, which is assumed to be the one defined by $n=0$. The boundary conditions express the vanishing of the components of forces, on a given particle, which arise from interaction with any of the removed particles. In our particular model the only particles which are affected are those of

the boundary layer, $n=0$. Thus one obtains

$$\begin{aligned} &\beta(u_{l+1,m,-1} + u_{l-1,m,-1} - 2u_{l,m,0}) \\ &+ \beta(w_{l-1,m,-1} - w_{l+1,m,-1}) + 4\gamma(u_{l,m,-1} - u_{l,m,0}) \\ &+ \gamma(w_{l-1,m,0} - w_{l+1,m,0} \\ &\quad + w_{l-1,m,-1} - w_{l+1,m,-1}) = 0, \\ &\beta(v_{l,m+1,-1} + v_{l,m-1,-1} - 2v_{l,m,0}) \\ &+ \beta(w_{l,m-1,-1} - w_{l,m+1,-1}) + 4\gamma(v_{l,m,-1} - v_{l,m,0}) \\ &+ \gamma(w_{l,m-1,0} - w_{l,m+1,0} \\ &\quad + w_{l,m-1,-1} - w_{l,m+1,-1}) = 0, \end{aligned} \quad (46)$$

and

$$\begin{aligned} &\alpha(w_{l,m,-1} - w_{l,m,0}) + \beta(w_{l+1,m,-1} + w_{l-1,m,-1} \\ &+ w_{l,m+1,-1} + w_{l,m-1,-1} - 4w_{l,m,0}) \\ &+ \beta(u_{l-1,m,-1} - u_{l+1,m,-1} + v_{l,m-1,-1} - v_{l,m+1,-1}) \\ &+ 2\gamma(w_{l+1,m,0} + w_{l-1,m,0} + w_{l,m+1,0} \\ &+ w_{l,m-1,0} - 4w_{l,m,0}) \\ &+ \gamma(u_{l+1,m,0} - u_{l-1,m,-1} + u_{l-1,m,-1} - u_{l-1,m,0}) \\ &+ \gamma(v_{l,m+1,0} - v_{l,m-1,-1} + v_{l,m-1,-1} - v_{l,m-1,0}) = 0. \end{aligned}$$

If Eqs. (45) are substituted into Eqs. (46) one obtains

$$\sum_j T_{ij} K_j = 0, \quad (i, j = 1, 2, 3), \quad (47)$$

where

$$\begin{aligned} T_{1j} &= 2\xi_j [\beta(\exp q_j \cos \phi_1 - 1) + 2\gamma(\exp q_j - 1)] \\ &\quad - 2\zeta_j [\beta \exp q_j \sin \phi_1 + \gamma(\exp q_j + 1) \sin \phi_1], \\ T_{2j} &= 2\eta_j [\beta(\exp q_j \cos \phi_2 - 1) + 2\gamma(\exp q_j - 1)] \\ &\quad - 2\zeta_j [\beta \exp q_j \sin \phi_2 + \gamma(\exp q_j + 1) \sin \phi_2], \\ T_{3j} &= 2\xi_j \sin \phi_1 [\beta \exp q_j + \gamma(\exp q_j - 1)] \\ &\quad + 2\eta_j \sin \phi_2 [\beta \exp q_j + \gamma(\exp q_j - 1)] \\ &\quad + \zeta_j \{ \alpha(\exp q_j - 1) + 2\beta[\exp q_j (\cos \phi_1 + \cos \phi_2) - 2] \\ &\quad + 4\gamma[\cos \phi_1 + \cos \phi_2 - 2] \}. \end{aligned} \quad (48)$$

The secular equation which must be satisfied in order to have nontrivial solutions of Eqs. (47) is

$$|T_{ij}| = 0. \quad (49)$$

For a direction of propagation specified by ϕ_1 and ϕ_2 the frequency ω and attenuation constants q_j are determined by the simultaneous solution of Eqs. (40) and (49). In order to carry out the calculation for a given material it is necessary to know the values of the force constants α , β , γ . The latter can be related to the elastic constants and the interatomic spacing, a , by expanding displacement components such as $u_{l+i, m+j, n+k}$ in power series about $u_{l,m,n}$, substituting into Eqs. (34) and comparing the results with the continuum equations of motion. The results are

$$\begin{aligned} c_{11} &= (\alpha + 4\beta)/a, \\ c_{12} &= 2\beta/a, \\ c_{44} &= (2\beta + 4\gamma)/a. \end{aligned} \quad (50)$$

It may be noted that if power series expansions of the displacement components are substituted in Eqs. (46)

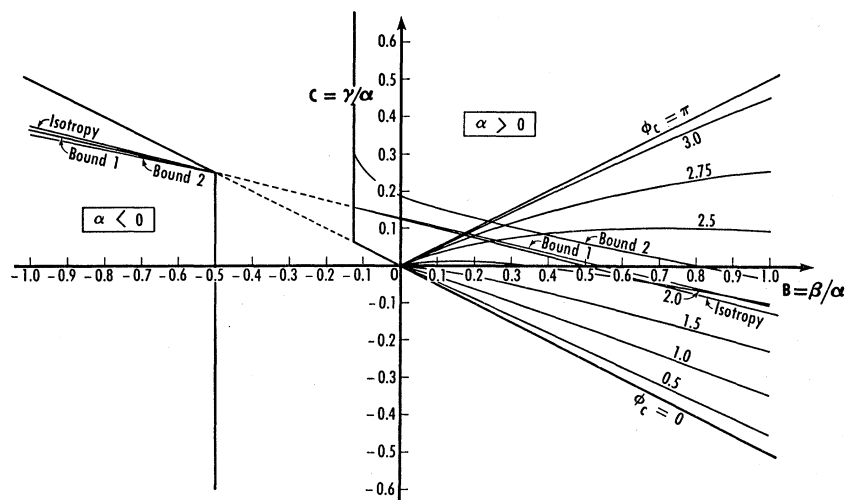


FIG. 6. Diagram showing the region of stability of simple cubic lattices, and the position of bounds 1 and 2 and the line of isotropy within this region. Also shown are contours of constant critical wave number ϕ_c . The meaning of ϕ_c is that for greater wave numbers, the atomic displacements show a reversal in phase between successive layers parallel to the surface.

and use is made of Eqs. (50), one obtains the continuum boundary conditions.

The force constants α , β , γ must satisfy conditions for the stability of the lattice which are analogous to the conditions imposed on the elastic constants in continuum theory. By substituting Eqs. (50) into Eqs. (9) and introducing the ratios $B = \beta/\alpha$ and $C = \gamma/\alpha$, one obtains the following stability conditions:

$$\alpha > 0: \quad B > -(1/8), \quad (51)$$

$$C > -(B/2);$$

and

$$\alpha < 0: \quad B < -(1/2), \quad (52)$$

$$C < -(B/2).$$

One therefore has two regions of stability in the B - C plane. It is unlikely on physical grounds that the nearest neighbor force constant is negative, however, so the stable region of importance is specified by Eqs. (51).

The entire stable region is shown in Fig. 6. Also shown in this figure is the mapping of the bounds 1 and 2 which were discussed in the preceding sections. It should be noted that these bounds as indicated correspond to wavelengths large in comparison with the interatomic distance, in which case the lattice theory matches the results of the continuum theory. As the wavelength decreases the positions of these bounds may change in the plane B versus C .

B. Numerical Computations

Calculations of the surface mode frequencies and attenuation constants for the monatomic simple cubic lattice discussed above have been made for various values of the force constants α , β , and γ which are consistent with the existence of Rayleigh waves in the continuum limit. Only waves propagating in the (100) direction were considered.

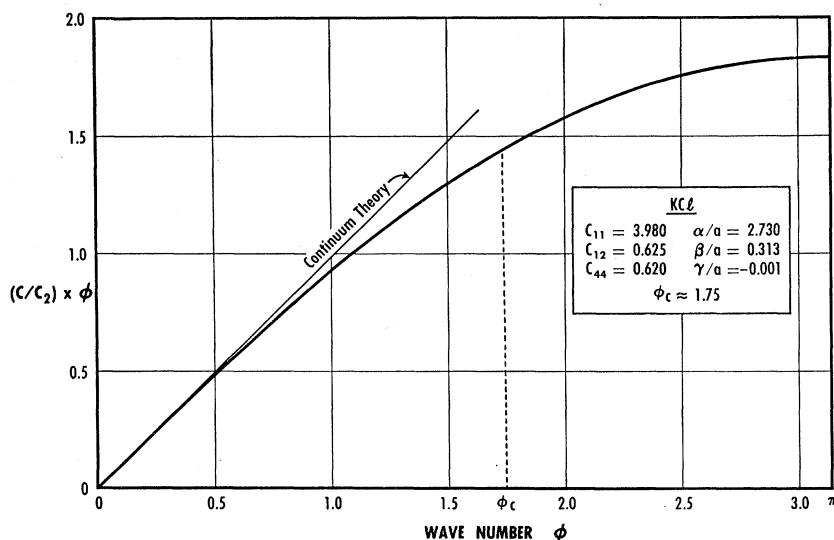


FIG. 7. Dispersion curve of normalized frequency versus the dimensionless wave number ϕ , as given by the lattice theory for waves in the (100) direction in a KCl crystal.

A typical result for the normalized frequency,

$$(c/c_2)\phi = \omega[M/(2\beta + 4\gamma)]^{1/2}, \quad (53)$$

as a function of the wavenumber $\phi = \phi_1$ is plotted in Fig. 7. The physical parameters were chosen to fit the data for potassium chloride which is nearly monatomic in so far as atomic masses are concerned and which crystallizes in a simple cubic array. For small values of ϕ , ω is proportional to ϕ and the phase velocity $\omega a/\phi$ is nearly constant with the value given by continuum theory. For values of ϕ such that the wavelength is of the order of a lattice spacing, dispersion becomes apparent, and ω is no longer proportional to ϕ . The phase velocity decreases continuously as ϕ ranges from zero to its maximum value, π . The qualitative behavior of the dispersion curve in Fig. 7 is similar to that shown by the bulk modes of vibration in cubic lattices.

The dependences of $\cosh q_1$ and $\cosh q_2$ on ϕ are shown in Fig. 8 for KCl. For small ϕ both $\cosh q_1$ and $\cosh q_2$ are greater than unity and q_1 and q_2 can be taken to be real and positive. At a certain value of ϕ , which we shall call the critical wavenumber ϕ_c , the value of $\cosh q_1$ approaches infinity. Beyond the critical wavenumber the value of $\cosh q_1$ is less than -1 so that q_1 has the form $q_{10} + i\pi$, where q_{10} is real. Consequently for $\phi > \phi_c$ the surface modes are of the special generalized Rayleigh type in which the displacement components corresponding to q_1 are 180° out of phase between adjacent layers parallel to the surface.

The value of the critical wavenumber ϕ_c can be determined fairly simply for surface waves propagating in the (100) direction. For this direction Eq. (40) factors into two equations, one linear and one quadratic in $\cosh q$. The quadratic equation is the equation of interest, and the critical wavenumber occurs when the coefficient of the $(\cosh q)^2$ term vanishes. The value of ϕ_c is therefore determined by

$$(B \cos \phi_c + 2C)[1 + 2B(\cos \phi_c + 1)] + 2(B + C)^2 \sin^2 \phi_c = 0. \quad (54)$$

In Fig. 6 the values of the critical wavenumber are shown as contours in the B - C plane. The regions of stability are also indicated as well as the bounds for the various types of surface waves in the continuum limit. The values of ϕ_c range from 0 to π , the former occurring for $B = -2C$ and the latter for $B = 2C$. It should be noted that the critical wavenumber ϕ_c has the physical significance discussed in the preceding paragraph provided that $\cosh q_j$ as determined from Eqs. (40) and (49) are real and greater than unity in magnitude. The contours for constant ϕ_c were only drawn for the important section of the stable region corresponding to positive primary central forces, i.e., $\alpha > 0$.

IV. DISCUSSION

The results of the continuum calculations reported in this paper are restricted to surface waves on (001) sur-

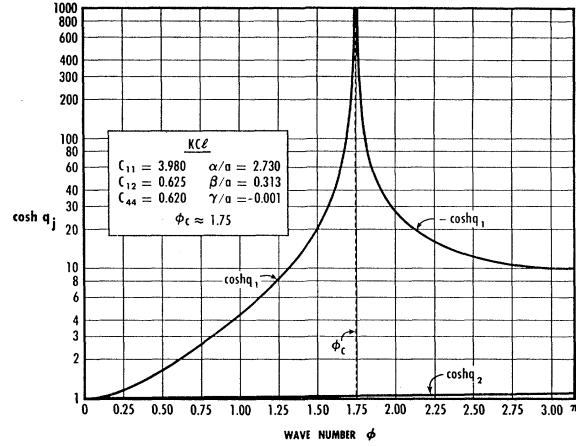


FIG. 8. Variation of the hyperbolic cosine of the attenuation constants, $\cosh q_j$, versus the dimensionless wave number ϕ , as given by the lattice theory for waves in the (100) direction in a KCl crystal.

faces of cubic crystals but are otherwise quite general within the framework of linear elasticity theory. Using Fig. 1 one can readily determine what types of surface waves exist for any cubic material for which the elastic constants are known. Thus, in the region below bound 1 in Fig. 1, Rayleigh-type surface waves exist. Above bound 1 generalized Rayleigh waves may exist which have displacement amplitudes decreasing from the surface as do products of trigonometric and exponentially decaying functions. Between bounds 1 and 2 generalized Rayleigh waves exist for all directions of propagation in a (001) surface. Above bound 2, surface waves do not exist in a range of directions of propagation about the (110) direction, although a surface wave is always possible in the (110) direction itself.

The continuum treatment presented here has assumed that the elastic constants and density of a crystal do not deviate from their bulk values in the region near the surface. Such deviations may be expected to be small for crystals of macroscopic size and should not seriously modify our results.

The discrete lattice theory of surface waves discussed in this paper is restricted to (001) surfaces of cubic crystals just as is the continuum theory. The lattice theory is further restricted by microscopic considerations which limit the applicability of the results. For example, we have considered only the monatomic simple cubic lattice which, to our knowledge, occurs only rarely in nature. Despite the paucity of materials for application, calculations on the monatomic simple cubic lattice are important for establishing qualitative phenomena and providing a basis for comparison with results on more complicated lattices. Furthermore, the qualitative behavior of low-frequency (acoustic branch) elastic waves is a little different in monatomic and diatomic cubic crystals.

Our results show that surface waves in discrete lattices

exhibit dispersion, i.e., a variation of the phase velocity with wavelength. This behavior is very similar to that found with bulk vibrational modes. We have also found for the monatomic cubic lattice considered here that a critical wavenumber generally exists in the Rayleigh wave region. For wavenumbers greater than the critical wavenumber the atomic displacements exhibit a phase reversal between successive layers parallel to the surface.

A sufficient number of interactions has been chosen in our model to permit the fitting of an arbitrary set of elastic constants. Since the interactions are assumed to be short-range, however, one must hold certain reservations concerning the validity of the quantitative results

for ionic crystals such as NaCl or KCl where long-range Coulomb forces are important.

Work is currently underway on the generalization of the lattice theory to face- and body-centered cubic lattices as well as to diatomic cubic lattices and the diamond and zinc-blende lattices. It is hoped that a unified treatment can be obtained of both Rayleigh-type waves and the optical surface waves.

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Decrease of *F*-Center Photoconductivity Upon Bleaching*

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A quantitative study of the rapid decrease in photoconductivity accompanying the relatively less rapid bleaching of *F* centers in additively colored KCl is reported. The experimental observations agree, except during very early stages of bleaching, with an equation for the variation of sensitivity with total light absorbed derived upon the assumption that negative-ion vacancies are created and traps of smaller cross section are filled during bleaching. Except during early stages, where several kinds of traps may be present in low concentration, only one kind of trap other than the negative-ion vacancy need be considered.

The effects of added divalent ions, both positive and negative, upon photoconductivity are reported.

INTRODUCTION

WHEN *F* centers in an additively colored alkali halide crystal are destroyed by irradiation with light which they absorb, the photoconductivity of the crystal is reduced relatively much more than is the optical absorption.^{1,2} In one experiment previously reported,² for example, the photoconductivity was reduced by about 80% during bleaching, while the number of *F* centers, as given by the absorbance, was decreased by only 10%. The decrease in photoconductivity produced by bleaching is hereafter referred to as *fatigue*.

The sensitivity of a photoconductor depends both upon the ratio of conduction electrons produced to quanta absorbed (that is, upon the quantum efficiency, η) and upon the average lifetime of a conduction electron, τ . Oberly ascribed the fatigue to a decrease of η with bleaching, and proposed that two types of *F* centers may exist: a soft center which is photoconducting and readily bleached by light ($\eta=1$), and a hard

center which is not photoconducting ($\eta=0$), nor capable of being bleached, but continues to absorb light. Accordingly, the photoconductivity would undergo a sharper decrease during bleaching than the optical density and approach a zero value as the "soft" centers are destroyed. Markham³ attributed the diminishing photoconductivity to a decreasing τ instead of η , and suggested that the decreased electron lifetime was caused by an increase in negative-ion vacancy concentration as *F* centers were decomposed.

This report describes experiments carried out to provide quantitative information regarding the fatigue of photoconductivity during bleaching. The data were consistent with equations for the variation in sensitivity with light absorbed, developed upon the assumption that as bleaching proceeds traps of small cross section, initially present in the crystal, are filled and negative-ion vacancies of large cross section are created. There appears to be no necessity to assume the existence of two types of *F* centers.

EXPERIMENTAL

(a) Sample Preparation

All measurements were conducted at room temperature in the *F* band of single crystals of KCl. The

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¹ J. J. Oberly, Phys. Rev. **84**, 1257 (1951).

² G. W. Neilson and A. B. Scott, *Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 297.

³ J. J. Markham, Phys. Rev. **86**, 433 (1952).