On the other hand, the first and second difficulties are of a more serious nature for they do occur in the weak-coupling limit. Because our results are essentially insensitive to the actual computation scheme [compare Eqs. (31) and (42), and also Eq. (6.21) of reference 6], we do not feel that our solution of the basic equation (5) could be in serious error, at least in the weak-coupling limit. Moreover, the predicted transition temperatures are not remarkably sensitive to the errors, or approximations, which do remain in our treatment, with the possible exception of the cases in which zone boundary perturbations are too extensive at the Fermi surface (such as Bi, Sb, $\cdots$), so that the free-electron Fermi sphere is a very poor approximation. This suggests strongly that the results derived here are exactly the logical conclusions of the original assumptions of the BCS theory. Consequently, what serious difficulties, such as the isotope effect, are to be found, seem to us to require either a new look at the basic assumptions of the theory, possibly using a different interaction taking into account more complex diagrams than the lowest order diagrams implicitly contained in the BCS's treatment, or re-examination of the experimental evidence.

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Effect of an Impurity Layer on Surface Waves*

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We study here the effects of a homogeneous impurity mass layer on the surface waves of a semi-infinite monatomic square lattice with nearest and next nearest neighbor central springs. In the long-wavelength limit the impurity layer does not alter the surface waves from those of a pure semi-infinite lattice. However, depending upon the ratio of the impurity mass to the host mass, and for wavelengths shorter than a critical wavelength, the long-wavelength surface wave may disappear and new surface waves with frequencies either higher or lower than the spectrum of the pure infinite lattice may appear. The relationship of this model to the analogous one- and three-dimensional problems is discussed. We expect this theory to be applicable to problems such as the effect of an oxide layer on the surface vibrations of a crystal.

I. INTRODUCTION

DURING the past several years a number of powerful experimental techniques for the study of the details of the vibration spectra of solids have become available. Specifically, analysis of the inelastic scattering of slow neutrons from crystals[1] has enabled plots of $\omega(\mathbf{k})$ (frequency as a function of wave number in a Brillouin zone) to be made in various directions in $\mathbf{k}$ space for many solids. Visscher[2] has discussed the application of the Mössbauer effect for similar determinations.

Along perhaps more conventional lines, Jacobsen[3] and Bömmel and Dransfeld[4] have produced strong microwave phonon beams in solids and plans exist for extending this technique to higher frequencies. One may therefore hope that an extension to infrared frequencies is not too far off. Changes in the velocities of propagation of elastic energy due to dispersion of both volume and surface waves could then be studied.

The existence of these high-frequency techniques makes it desirable to have a more detailed picture of the short-wavelength (dispersive) portion of the lattice vibration spectra of real crystals than was needed to interpret insensitive average properties such as the specific heat.

Various aspects of this problem have been studied by many authors: Montroll and Potts[5] and their collaborators and Lifshitz[6] and his collaborators have studied the nature of localized vibrational modes due to point impurities; Lax[7] and Cochran *et al.*[8] have clarified the nature of the dispersion of the volume

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[1] For a review of this field see L. S. Kothari and K. S. Singwi, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. 8.

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[3] E. H. Jacobsen, Phys. Rev. Letters **2**, 249 (1959).

[4] H. E. Bömmel and K. Dransfeld, Phys. Rev. Letters **1**, 234 (1958).

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[6] I. M. Lifshitz, J. Exptl. Theoret. Phys. (USSR) **17**, 1017, 1076 (1947) and other papers.

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[8] W. Cochran, Proc. Roy. Soc. (London) **A253**, 260 (1959); A. D. B. Woods, W. Cochran, and B. N. Brockhouse, Phys. Rev. **119**, 980 (1960).

modes in certain types of crystals; Wallis,[9] Lifschitz and Rosenzweig,[10] and Gazis, Herman, and Wallis[11] have studied surface waves in two- and three-dimensional bounded but otherwise perfect lattices.

In this article we shall use a few simple models to study qualitatively the modifications that are introduced in the surface wave spectrum of a semi-infinite two-dimensional monatomic square lattice by the existence of an impurity atom layer on the surface. We will show that the surface wave dispersion curve $\omega(k)$, where k is wave number parallel to the edge of the lattice, is the same as that of a lattice without the impurity layer for long wavelengths, i.e., to terms linear in k. At short wavelengths diverse possibilities exist depending upon the ratio of the mass of a surface impurity atom to that of a host atom: The surface wave which exists at long wavelengths will have its frequency shifted compared to that of a pure lattice and may even disappear for short enough wavelengths; new surface waves will appear with frequencies which, depending upon the mass ratio, may be either higher or lower than those of waves associated with the volume of the lattice for the same wavelength. The stiffer a lattice is, the less likely it is to exhibit impurity-induced short-wavelength surface waves.

The results will be schematically extended to more realistic cases by analogy with work on point imperfections.

II. TWO-DIMENSIONAL MODEL

We consider here the simplest nontrivial model of a semi-infinite monatomic square lattice with an impurity layer on its surface. The mass of each host atom is M and the impurity mass is M'. We assume nearest-neighbor central springs (spring constant α) and next-nearest-neighbor central springs (spring constant γ). The equations of motion for the x and y displacement components u_{lm}, v_{lm} of the atom at the lattice point l, m within the lattice are

$$\begin{aligned}M\ddot{u}_{lm}=&\alpha(u_{l+1,m}+u_{l-1,m}-2u_{l,m})\\&+(\gamma/2)(u_{l+1,m+1}+u_{l+1,m-1}+u_{l-1,m+1}\\&+u_{l-1,m-1}-4u_{l,m})\\&+(\gamma/2)(v_{l+1,m+1}-v_{l-1,m+1}-v_{l+1,m-1}\\&\qquad+v_{l-1,m-1}),\\M\ddot{v}_{lm}=&\alpha(v_{l,m+1}+v_{l,m-1}-2v_{l,m})\\&+(\gamma/2)(v_{l+1,m+1}+v_{l+1,m-1}+v_{l-1,m+1}\\&+v_{l-1,m-1}-4v_{l,m})\\&+(\gamma/2)(u_{l+1,m+1}-u_{l-1,m+1}-u_{l+1,m-1}\\&\qquad+u_{l-1,m-1}).\end{aligned}\tag{1}$$

We assume the lattice to fill the lower half-plane ($y\leqslant 0$). The equations of motion of a surface atom are thus

$$\begin{aligned}M'\ddot{u}_{l0}=&\alpha(u_{l+1,0}+u_{l-1,0}-2u_{l,0})\\&+(\gamma/2)(u_{l+1,-1}+u_{l-1,-1}-2u_{l,0})\\&\qquad+(\gamma/2)(-v_{l+1,-1}+v_{l-1,-1}),\\M'\ddot{v}_{l0}=&\alpha(v_{l,-1}-v_{l,0})+(\gamma/2)(v_{l+1,-1}+v_{l-1,-1}-2v_{l,0})\\&\qquad+(\gamma/2)(-u_{l+1,-1}+u_{l-1,-1}).\end{aligned}\tag{2}$$

The method of solution has been indicated by Stonely[12] and in reference 11. We use a form of solution that satisfies the unperturbed equations and has the proper asymptotic behavior at $-\infty$:

$$\begin{aligned}u_{lm}&=U\exp(ikl+qm-i\omega t),\\v_{lm}&=V\exp(ikl+qm-i\omega t).\end{aligned}\tag{3}$$

These forms substituted in the unperturbed equations yield a pair of homogeneous linear equations for the amplitudes U and V. The condition for solution (vanishing of the determinant of the coefficients) gives a relationship between ω^2 and q: for a fixed ω^2 there are two values of $\cosh q$:

$$\cosh q=[-\eta\pm(\eta^2-\xi\rho)^{\frac{1}{2}}]/\xi,\tag{4}$$

where

$$\begin{aligned}\xi&=4\Gamma(\cos k+\Gamma),\\\eta&=(1+2\Gamma\cos k)[\Omega^2-2(1+\Gamma)+\cos k]+\cos k,\\\rho&=[\Omega^2-2(1+\Gamma)+\cos k]^2-4\Gamma^2\sin^2k-\cos^2k,\end{aligned}$$

and $\omega^2=(\alpha/M)\Omega^2$, $\Gamma=\gamma/\alpha$. One could now write out expressions for the amplitudes U, V.

We satisfy the surface equations with a linear combination of the two solutions above:

$$\begin{aligned}u_{lm}&=\sum_{j=1}^{2}A_jU_j\exp(ikl+q_jm-i\omega t),\\v_{lm}&=\sum_{j=1}^{2}A_jV_j\exp(ikl+q_jm-i\omega t).\end{aligned}\tag{5}$$

The resulting pair of linear homogeneous equations for the A_j has a condition for solution which finally gives implicitly the dispersion curve $\omega(k)$ of the surface waves:

$$\begin{aligned}0=&(e^{q_1}-e^{q_2})\{4\Gamma^2\sin^2k\sinh q_1\sinh q_2(\mathcal{P}\Omega^2-\Gamma)\\&+(\mathcal{P}\Omega^2-1-\Gamma)[2(1-\cos k)\\&+2\Gamma(1-\cos k\cosh q_1)-\Omega^2][2(1-\cos k)\\&+2\Gamma(1-\cos k\cosh q_2)-\Omega^2]\}+2\sinh q_1\\&\times[2(1-\cos k)+2\Gamma(1-\cos k\cosh q_2)-\Omega^2]\\&\times\{(\mathcal{P}\Omega^2-\Gamma)(\mathcal{P}\Omega^2-\Gamma-1)+(\mathcal{P}\Omega^2-\Gamma)\\&\times(1+\Gamma\cos k)e^{q_2}+(\mathcal{P}\Omega^2-\Gamma-1)\Gamma\cos k e^{q_1}\end{aligned}$$

[9] R. F. Wallis, Phys. Rev. **116**, 302 (1959).

[10] I. M. Lifschitz and L. N. Rosenzweig, J. Exptl. Theoret. Phys. (USSR) **18**, 1012 (1948).

[11] D. C. Gazis, R. Herman, and R. F. Wallis, Phys. Rev. **119**, 533 (1960).

[12] R. Stonely, Proc. Roy. Soc. (London) **A232**, 447 (1955).

$$+e^{q_1+q_2}\Gamma(\Gamma+\cos k)\}-2\sinh q_2[2(1-\cos k)+2\Gamma(1-\cos k\cosh q_1-\Omega^2]\times\{(\mathcal{P}\Omega^2-\Gamma)(\mathcal{P}\Omega^2-1-\Gamma)+(\mathcal{P}\Omega^2-\Gamma)\times(1+\Gamma\cos k)e^{q_1}+(\mathcal{P}\Omega^2-\Gamma-1)\Gamma\cos k e^{q_2}+e^{q_1+q_2}\Gamma(\Gamma+\cos k)\},\quad (6)$$

where $\mathcal{P}=1-M'/M$. One must check that the dispersion values $\omega(k)$ give q_j's with positive real parts in order that our solutions be interpretable as surface waves.

Equation (6) cannot be solved explicitly for $\omega(k)$. However we may understand the qualitative features of the solutions from an analysis of two limiting cases: (a) k small (the continuum limit); (b) $k=\pi$ (the edge of the zone).

(a) k Small

We may derive the results for k small (long wavelength) either by making the continuum approximation in the equations of motion (1) and (2) and solving the problem anew, or by assuming k and q_j are small in Eqs. (4) and (6). As concerns Eq. (4) we merely note that for small k it is homogeneous in q^2, k^2, and ω^2, and that k and q_j are of the same order of magnitude, i.e., the penetration depth of a surface wave is about the same size as the wavelength parallel to the surface of the medium. Keeping the pertinent lowest-order terms, Eq. (6) becomes

$$\begin{aligned}&(\alpha+\gamma)[(\alpha+\gamma)K^2-\gamma Q_1^2-\rho\omega^2]\\&\quad\times[(\alpha+\gamma)K^2-\gamma Q_2^2-\rho\omega^2]+4\gamma^3K^2Q_1Q_2\\&\quad+[1/(Q_1+Q_2)][2\gamma^2K^2+2Q_1Q_2\gamma(\alpha+\gamma)]\\&\quad\times\{[(\alpha+\gamma)K^2-\gamma Q_1^2-\rho\omega^2]Q_2\\&\quad-[(\alpha+\gamma)K^2-\gamma Q_2^2-\rho\omega^2]Q_1\}\\&=2a(\rho-\rho')\omega^2(Q_1+Q_2)\\&\quad\times\{\gamma[(\alpha+\gamma)K^2-\rho\omega^2+\gamma Q_1Q_2]+\alpha\gamma Q_1Q_2\}\\&\qquad+2a^2(\rho-\rho')^2\omega^4[(\alpha+\gamma)K^2-\rho\omega^2+\gamma Q_1Q_2].\quad(7)\end{aligned}$$

We have introduced the following notation convenient for a continuum:

$$K=k/a,\quad Q_j=q_j/a,\quad \rho=M/a^2,\quad \rho'=M'/a^2,$$

and a is the lattice constant. In the absence of an impurity layer the right-hand side of Eq. (7) becomes zero and the equation is the two-dimensional analog of the continuum treatment of reference 11. When the q_j^2 are eliminated, this unperturbed equation is homogeneous in K^2 and ω^2, and if we divide by an appropriate power of K^2, only ω^2/K^2 will occur. Thus, as expected, the long-wavelength surface waves show no dispersion in the absence of an impurity layer. Each solution of the unperturbed problem may give rise to a surface wave. It can be shown that long-wavelength surface waves occur only for $\Gamma=\gamma/\alpha<\frac{1}{2}$.

The form of the right-hand side of Eq. (7) is

$$aKf(\omega^2/K^2)+a^2K^2g(\omega^2/K^2),$$

and we note that it does not depend only upon (ω^2/K^2) but also on K in the combination aK. We do not expect $f(\omega^2/K^2)$ and $g(\omega^2/K^2)$ to be extraordinarily large even though they contain the factors $\rho-\rho'$ and $(\rho-\rho')^2$, respectively. Near a root of the left-hand side, $\omega^2/K^2=C_1^2$, we may write Eq. (7) schematically as

$$(C_1^2-\omega^2/K^2)=aKF(\omega^2/K^2)+a^2K^2G(\omega^2/K^2),$$

where again $F(\omega^2/K^2)$ and $G(\omega^2/K^2)$ are not excessively large. Assuming $aK\ll 1$ we may correct the unperturbed result to first order in aK by using $\omega^2/K^2=C_1^2$ on the right-hand side. The result,

$$\omega^2/K^2\cong C_1^2-aKF(C_1^2),$$

shows that except for impurity masses of purely mathematical interest the surface wave dispersion curve is unchanged in the long-wavelength limit. Allowing the impurity mass to grow indefinitely would effectively replace the free-boundary condition by a fixed-boundary condition and certainly cause modifications of all normal modes of the system.

(b) $k=\pi$

In this case Eq. (6) reduces to

$$(\mathcal{P}\Omega^2-\Gamma-\Gamma e^{q_1})[\mathcal{P}\Omega^2-1-\Gamma+(1-\Gamma)e^{q_2}]=0,\quad(8)$$

where

$$\begin{aligned}\cosh q_1&=(\Omega^2-4-2\Gamma)/2\Gamma,\\ \cosh q_2&=[2(1+\Gamma)-\Omega^2]/2(1-\Gamma),\\ \sinh q_1&=\pm(1/2\Gamma)[(\Omega^2-4)(\Omega^2-4-4\Gamma)]^{\frac{1}{2}},\\ \sinh q_2&=\mp[1/2(1-\Gamma)][(\Omega^2-4)(\Omega^2-4\Gamma)]^{\frac{1}{2}}.\end{aligned}$$

Here the top signs are for $\Omega^2>4+4\Gamma$ and the bottom signs are for $\Omega^2<4\Gamma$ and may be derived from the condition that $\cosh q_j$ and $\sinh q_j$ have the same sign. The regions $\Omega^2<4\Gamma$ and $\Omega^2>4+4\Gamma$ are the only ones giving rise to surface waves, as can be seen by examining the expressions for $\sinh q_1$ and $\sinh q_2$. In order to satisfy Eq. (8), one of its brackets must vanish. Using the expressions for $\sinh q_j$ and $\cosh q_j$, we thus find a surface wave if either of the following is satisfied:

$$(2\mathcal{P}-1)\Omega^2=-4\pm[(\Omega^2-4)(\Omega^2-4-4\Gamma)]^{\frac{1}{2}},\quad(9a)$$

$$(2\mathcal{P}-1)\Omega^2=\pm[(\Omega^2-4)(\Omega^2-4\Gamma)]^{\frac{1}{2}},\quad(9b)$$

where the top signs are for $\Omega^2>4+4\Gamma$ and the bottom signs are for $\Omega^2<4\Gamma$. It is instructive to examine these equations graphically. We will do this for the case $\Omega^2<4\Gamma$, Eq. (9b) and will then state the results for all the cases.

$\Omega^2<4\Gamma$, *Eq. (9b)*

We plot the left-hand side (lhs) and right-hand side (rhs) separately as functions of Ω^2 (see Fig. 1). The lhs is a straight line through the origin whose slope increases with increasing impurity mass and has the

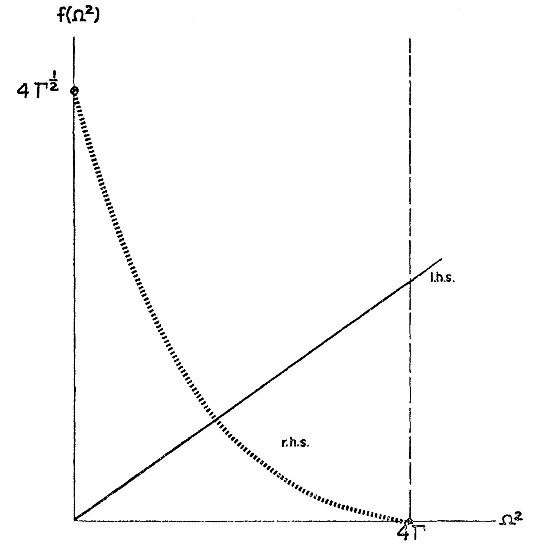

FIG. 1. A plot of the left- and right-hand sides of Eq. (9b) for the case $\Omega^2 < 4\Gamma$.

value one for $M = M'$. The rhs depends only upon Γ and approaches the origin as $\Gamma \to 0$. The case we are studying is the extension of the single long-wavelength surface wave to the Brillouin zone boundary. It is interesting to note that this branch disappears for short wavelengths if $M' < M/2$, i.e., there is no intersection if $\mathcal{P} > \frac{1}{2}$, or $M' < M/2$ for any value of Γ.

We will now state the results obtained by analyzing all four cases for all relevant values of $\mathcal{P}$, and $0 < \Gamma < 1$.

SUMMARY

S-1. $\mathcal{P} < -\frac{1}{2}(1 - \Gamma + [1 - \Gamma]^{\frac{1}{2}})$. There are two low-frequency surface modes. As Γ increases, or the lattice has more resistance to shear motions, the minimum $\mathcal{P}$ increases, and $\to 0$ as $\Gamma \to 1$.

S-2. $-\frac{1}{2}(1 - \Gamma + [1 - \Gamma]^{\frac{1}{2}}) < \mathcal{P} < \Gamma/[2(1+\Gamma)]$. There is one low-frequency surface mode—the extension of the long-wavelength mode.

S-3. $\Gamma/[2(1+\Gamma)] < \mathcal{P} < \frac{1}{2}$. There is one low-frequency and one high-frequency surface mode.

S-4. $\frac{1}{2} < \mathcal{P} < \frac{1}{2} + \Gamma^{\frac{1}{2}}/[2(1+\Gamma)]$. There is only one high-frequency surface mode.

S-5. $\frac{1}{2} + \Gamma^{\frac{1}{2}}/[2(1+\Gamma)] < \mathcal{P} < 1$. There are two high-frequency surface modes. We note that as Γ increases it requires an ever lighter mass to cause the second high-frequency mode to appear.

We have also studied in more detail the particularly simple case $\Gamma = \frac{1}{2}$. As mentioned above there are no long-wavelength surface waves for $\Gamma = \frac{1}{2}$. It is easy to show that no high-frequency surface waves can occur for this case if $k < (2\pi/3)$. This is the critical wave number k_c discussed in reference 11 such that for $k < k_c$ the displacements of adjacent layers parallel to the surface are in phase, whereas for $k > k_c$ the displacements of adjacent layers are 180° out of phase. There is a value of k_c for each value of Γ. In Tables I and II we give the information necessary to sketch the dispersion curves for low- and high-frequency surface waves, respectively, in the region $k \geq 2\pi/3$. We show here the values of $\mathcal{P}$ giving surface waves for particular values of Ω^2 below and above the volume dispersion curves for both $k = \frac{2}{3}\pi$ and $k = \pi$. For a particular impurity mass parameter $\mathcal{P}$, we may interpolate in these tables and find the values of Ω^2 giving surface waves for $k = \frac{2}{3}\pi$ and $k = \pi$. Smooth curves may then be drawn between corresponding pairs of Ω^2 at these two limiting k values. Examination of the tables reveals the interesting fact that two high-frequency surface waves exist for values of $\mathcal{P}$ as low as 0.526. For $0.526 < \mathcal{P} < 0.736$ one of these waves joins the volume band between $k = 2\pi/3$ and $k = \pi$. We also see that a low-frequency surface wave exists for $\mathcal{P} < 0.549$ which joins the volume band between $k = \frac{2}{3}\pi$ and $k = \pi$ if $0.5 < \mathcal{P} < 0.549$.

TABLE I. Low Ω^2. Values of the mass impurity parameter $\mathcal{P}$ for which low-frequency surface waves exist. Several squared frequencies Ω^2 are shown for the minimum and maximum wave numbers $k = 2\pi/3$, $k = \pi$ allowing surface waves for a lattice with $\Gamma = \frac{1}{2}$.

$k = 2\pi/3$			$k = \pi$		
Ω^2	$\mathcal{P}_1$	$\mathcal{P}_2$	Ω^2	$\mathcal{P}_1$	$\mathcal{P}_2$
1.5	0.549	−1.216	2.0	0.500	−1.212
1.0	−0.093	−2.392	1.5	−0.124	−1.951
0.5	−1.380	−5.829	1.0	−0.366	−3.437
			0.5	−1.792	−7.888

III. DISCUSSION

The results of Sec. II may be understood in terms of a competition between the attempt of the surface impurities to form localized modes characteristic of the semi-infinite, one-dimensional lattices that they end, and the attempt of the pure semi-infinite solid to exhibit a Rayleigh-type wave with its short-wavelength dispersion. This latter tendency is frustrated for short wavelengths if the surface mass is sufficiently small (see S-4 and S-5). It is significant of the competition that high-frequency surface modes will only form for $k > k_c$ because of the 180° phase shift in the relative amplitudes of atoms in adjacent layers parallel to the surface for those k. When a surface wave is excited the displacements of the atoms in a row perpendicular to the surface (u_{lm}, v_{lm} for l fixed and $m \leq 0$) resemble closely the corresponding pattern for a short wavelength mode of a semi-infinite, one-dimensional monatomic lattice with a mass impurity at its end, and such a chain will exhibit an impurity mode for some impurity masses.

The appearance of two low (S-1) or two high (S-5) frequency surface modes is evidence of the fact that both the "longitudinal" and "transverse" branches of the volume spectrum can produce localized modes. This effect is more clearly brought out by an analysis of surface waves for the Rosenstock-Newell (RN)

model.[13] These results were briefly reported some time ago by the present author[14] and a sketch of some of them appears in the Appendix. The well known simplification of the RN model is the decoupling of the x and y equations of motion. A further characteristic of the model is the absence of long-wavelength surface waves. In the Appendix it is seen that both x and y motions may give rise to surface waves (caused by mass and spring impurities) for appropriate strengths of the different impurities. Particularly interesting here is the competition between the impurity spring and impurity mass parameters which may minimize surface dispersion effects. In this connection it should be noted that surface spring constants may be expected to be greater than volume spring constants according to quantum mechanical calculations for small graphite platelets[15]; the order of magnitude to be expected for the ratio is 1.5.

The effects of surface impurities on the surface waves of a three-dimensional crystal should be dominated by the fact that, as in the two-dimensional case, the boundary is of one lower spatial dimension than the volume of the material, i.e., we again have a set of coupled parallel semi-infinite one-dimensional lattices. In the long-wavelength region we should still find no impurity effects. (Our argument to this effect for two dimensions would seem to be easily generalizable to three dimensions.) For short wavelengths the one-dimensional impurity tendency should still produce surface modes. An interesting question to be answered concerns the modification by the impurities of the surface wave number region not admitting surface waves for a pure lattice, as discussed in references **11**, 12, and by Synge.[16]

Some points worthy of attention for realistic models of surfaces are:

(1) The effect of thicker surface layers. Here one may expect that where one surface layer gives rise to a surface wave, two or more layers will cause a number of surface waves less than or equal to the number of layers. It would be helpful to study the analogous linear chain with the same number of impurity atoms at one end.

(2) The effect of surface roughness. The details of this problem will be difficult but one may expect that roughness will lead to a scattering out of surface waves into volume waves and the formation of modes localized near points on the surface.

(3) The effect of corners and edges (a type of roughness). This problem has been studied for the diatomic square and cubic RN lattices by Wallis., He exhibits corner and edge modes, using a perturbation-theory approach. We have studied the same problem using a square piece of the model of the Appendix. We find that symmetrized combinations of simple exponential-type solutions are possible only if we introduce particular values of a second type of impurity mass at the corners. For any other corner mass value, one might say that the equations do not separate and a Green's function method of solution is appropriate.

Finally we point out that a complete study of surface excitations should start with a finite lattice and use periodic boundary conditions parallel to the surface. In this way one would discover waves of mixed surface and volume character as well as pure surface and volume waves. That such waves are possible can be seen by examining the vibrations of a finite linear monatomic chain with nearest and next nearest neighbor restoring springs and no surface impurities. It can be shown using a method of Slater[17] that the normal modes of such a system are linear combinations of two sinusoidal modes and combinations of one sinusoidal mode and one exponential mode. No purely localized modes exist. It is probable that semilocalized modes are much more prevalent than surface modes. This idea has also been indicated by Synge.[15]

Detailed three-dimensional calculations are tedious and should await experimental impetus.

TABLE II. High Ω^2. Values of the mass impurity parameter $\mathcal{P}$ for which high-frequency surface waves exist. Several squared frequencies Ω^2 are shown for the minimum and maximum wave numbers $k=2\pi/3$, $k=\pi$ allowing surface waves for a lattice with $\Gamma=\frac{1}{2}$.

$k=2\pi/3$			$k=\pi$		
Ω^2	$\mathcal{P}_1$	$\mathcal{P}_2$	Ω^2	$\mathcal{P}_1$	$\mathcal{P}_2$
4.5	0.526	0.141	6.0	0.736	0.167
5.0	0.613	0.259	6.5	0.758	0.278
5.5	0.666	0.338	7.0	0.777	0.338
6.5	0.734	0.448	8.0	0.806	0.427
8.5	0.807	0.582	10.0	0.846	0.545
			20.0	0.924	0.774

APPENDIX

We present here a brief outline of surface wave considerations for the Rosenstock-Newell model. Consider a semi-infinite square monatomic lattice filling the half-plane $y\leqslant 0$, with nearest-neighbor central and noncentral springs α and β and particle mass M. We introduce central and noncentral impurity springs α' and β' between adjacent surface atoms and a surface atomic mass M'. The equations of motion for the x components of displacement are:

(a) volume,

$$M\ddot{u}_{lm}=\alpha(u_{l+1,m}+u_{l-1,m}-2u_{l,m})+\beta(u_{l,m+1}+u_{l,m-1}-2u_{l,m}); \quad \text{(A1)}$$

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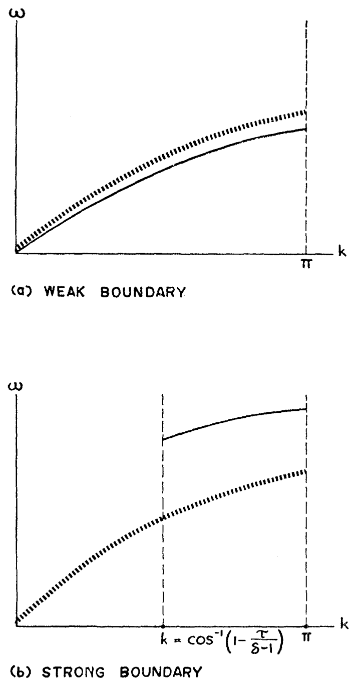

FIG. 2. Dispersion curves for surface waves for a crystal with a surface spring impurity. The dotted line is the dispersion curve for an infinite lattice with

$$k_x = k, \quad k_y = 0.$$

(b) surface,

$$M'\ddot{u}_{l0} = \alpha'(u_{l+1,0} + u_{l-1,0} - 2u_{l,0}) + \beta(u_{l,-1} - u_{l,0}).$$

The usual form of solution,

$$u_{lm} = \exp\left[ikl + \begin{Bmatrix} q \\ q+i\pi \end{Bmatrix} m - i\omega t\right],$$

leads to the eigenvalue condition

$$\begin{Bmatrix} \coth(q/2) = \epsilon, \\ \tanh(q/2) = \epsilon, \end{Bmatrix} \tag{A2}$$

and

$$M\omega^2/2\alpha = 1 - \cos k + \tau(1 \mp \cosh q),$$

where

$$\epsilon = 1 + \tau / [(\eta - \delta)(1 - \cos k) + \tau(\eta - 1)(1 \mp \cosh q)],$$

and

$$\eta = M'/M, \quad \delta = \alpha'/\alpha, \quad \tau = \beta/\alpha.$$

The upper signs and bracketed expressions are for low-frequency surface waves and the upper signs are for high-frequency waves.

We sketch the forms of the dispersion curves for a few simple cases. Figure 2 shows the results for $\eta = 1$ (a pure crystal with the inevitable spring impurity). In the strong-boundary case the mode does not appear "out of thin air" but rises out of the volume band for $k_y = \pi$.

Figure 3 shows the results for $\eta = \delta$. Here the competition between the mass impurity and the spring impurity causes q to have a value independent of k. Thus the surface wave dispersion curve is parallel to the infinite lattice curve with $k = k_x$, $k_y = 0$, but is displaced upward. For motion in the y direction the results shown in Fig. 3 have the same form except that τ is replaced by $1/\tau$ and $\delta \to \delta' = \beta'/\beta$. This replacement may cause significant quantitative changes because $\tau \ll 1$ in many realistic cases.

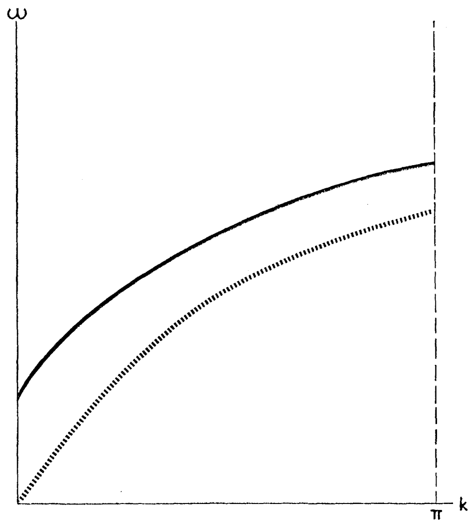

FIG. 3. Dispersion curve for surface waves for a crystal with both mass and spring surface impurities. The strengths of the impurities are connected by the relation $\eta = \delta$.