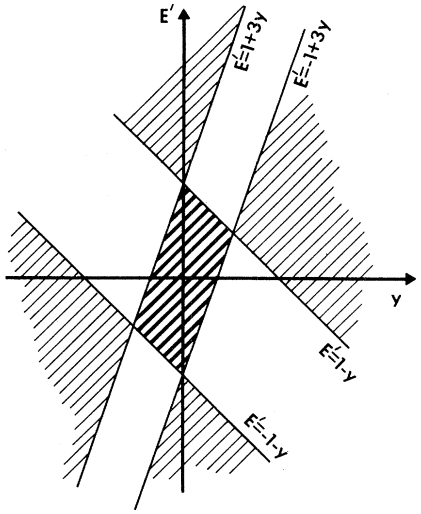

FIG. 2. Bounds on the density of states. $E'=E/|V_2|$, $y=V_1/|V_2|$. Shaded regions are forbidden, unshaded allowed. The heavily shaded region is the region to which the inequality (6) applies.

gap.

Our conclusion is that for such an idealized model (which we do not believe to be oversimplified to the point of being irrelevant to real physical systems) the existence of the gap is not dependent on periodicity of the structure. Note that the results are not compatible with the existence of localized states throughout the gap, as is often postulated, although these would presumably be introduced by defects and/or the slight deviations of bond configurations from the ideal values here assumed.

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Surface and Pseudosurface Modes in Ionic Crystals*

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The nature of the surface and pseudosurface modes in ionic-crystal slabs is clarified, and some apparent discrepancies among the previous studies are resolved. The first shell-model calculations of surface-mode spectra are reported; the results for NaCl are significantly different from those obtained with the rigid-ion model. A new type of long-wavelength optical surface mode has been found in the shell-model results for RbF.

Several theoretical treatments of optical surface modes in ionic crystals have appeared recently,[1-7] and it has been stated that there appear to be discrepancies among the results of these treatments.[3,5,7] In the present Letter the nature of the surface modes will be clarified, and these results reconciled.

Until the present, two methods have been used in calculations of optical surface modes in ionic crystals: The first is the continuum approximation, first used by Fuchs and Kliewer[1] for a slab with two flat surfaces, and subsequently used by Englman and Ruppin[2,3] for crystals with other geometries. The second method involves lattice-dynamical calculations for a slab-shaped crystal based on the rigid-ion model of Kellermann.[8] Such calculations were first carried out by Lucas[4] for $\bar{q}=0$, where $\bar{q}$ is the two-dimensional wave vector associated with propagation parallel to the surfaces. Subsequently Tong and Maradudin[5] carried out a calculation for values of $\bar{q}$ lying throughout the first two-dimensional Brillouin zone.

In reconciling the results of these treatments, it is necessary to recognize three limitations of the continuum approximation: First, it is valid only at large wavelengths (small $\bar{q}$) in a thick

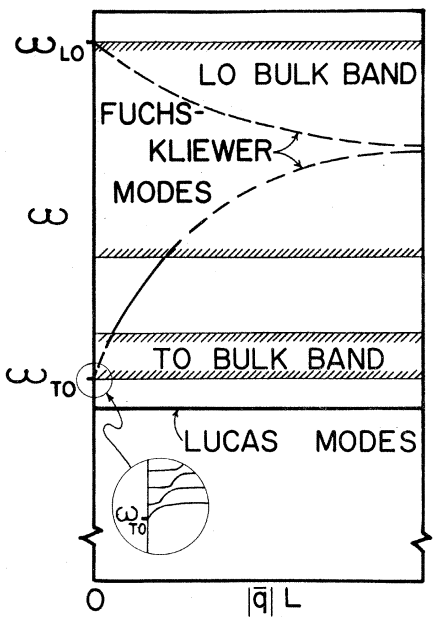

FIG. 1. Schematic drawing of the LO (longitudinal optical) and TO (transverse optical) bulk bands, and of the Fuchs-Kliewer (FK) and Lucas modes, in a thick slab at long wavelengths (of the order of the slab thickness L). Here ω is the vibrational frequency; ω_{LO} and ω_{TO} are, respectively, the limiting frequencies of the LO and TO bulk modes as $\vec{q}\to 0$, where $\vec{q}$ is the three-dimensional propagation vector for bulk modes in an infinite crystal. It is assumed that $|\bar{q}|^{-1}$ is large compared to an atomic spacing, but not so large that retardation effects must be taken into account. In the present drawing it is assumed that the bottom of the LO bulk band lies beneath the asymptotic frequency toward which the FK modes converge; as indicated in the text, it is likely that this will ordinarily be the case. The dashed lines indicate that the FK modes are pseudosurface modes within the bulk bands. As schematically depicted in the circular inset, these dashed lines actually represent a locus of interaction among hybridizing branches. (See Ref. 7).

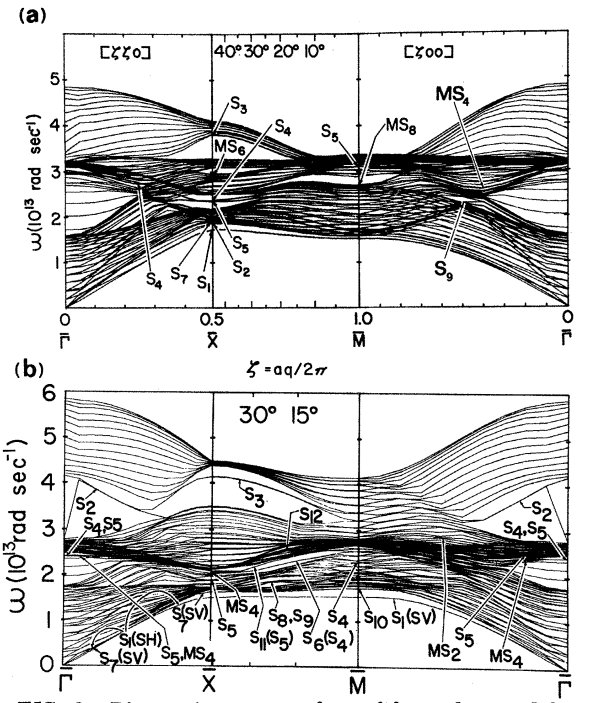

FIG. 2. Dispersion curves for a fifteen-layer slab of NaCl with (100) surfaces, calculated with (a) an eleven-parameter shell model and (b) the rigid-ion model of Ref. 5. Each pair of surface modes is labeled S_i $(i=1,2,\cdots)$ according to an arbitrary scheme; modes with the same label in (a) and (b) are not necessarily related. Here $\bar{\Gamma}$ is the origin, $\bar{M}$ a corner, and $\bar{X}$ the center of an edge of the square Brillouin zone associated with the (100) surface. The curves are computer-generated for a finite mesh of $\bar{q}$ points, and crossovers between branches are not always taken into account.

slab since otherwise the atomicity of the crystal is important. Second, even at large wavelengths this approximation is valid only for determining deeply penetrating surface modes since the atomicity is again important for "microscopic" surface modes which penetrate only a few atomic spacings. Third, the spreading of the bulk optical modes into "bands," as depicted in Fig. 1, is absent in the continuum approximation.[9] Consequently, what appears to be a surface mode in the continuum treatment may actually be a pseudosurface mode lying within the bulk bands, as indicated by the dashed lines of Fig. 1.

In view of these limitations of the continuum model, it is not difficult to reconcile the results for slab-shaped crystals: Fuchs and Kliewer[1] found a pair of surface modes whose penetration depth becomes large as $\bar{q}\to 0$. Lucas[4] found two pairs of surface modes with a very small penetration depth at the point $\bar{q}=0$. He did not find the Fuchs-Kliewer (FK) modes because they are no longer surface modes at $\bar{q}=0$, and his modes were not found by Fuchs and Kliewer because the continuum treatment overlooks "microscopic" surface modes.

Tong and Maradudin[5] found the FK modes and the Lucas modes in their calculations; but there was some difficulty in understanding the behavior of these modes, which led to misinterpretations, mainly because computational limitations restricted the number of values of $\bar{q}$ that could be examined. The actual behavior is as follows: At the point $\bar{\Gamma}$ in Fig. 2(b), both pairs of Lucas modes (labeled by S_4 and S_5) are pure surface modes because they are rigorously decoupled

from the bulk acoustic modes surrounding them. (They are associated with vibrations parallel to the surface, whereas the bulk modes are associated with vibrations perpendicular to the surface.) However, for points slightly removed from $\bar{\Gamma}$ along the symmetry line $\bar{\Gamma}\bar{M}$ (the line discussed in Ref. 5), the Lucas modes split, with the upper pair (S_5) remaining pure surface modes and the lower pair (MS_4) becoming pseudosurface modes. [See the right-hand side of Fig. 2(b).] The reason for this behavior is that the acoustic bulk modes surrounding these modes are polarized within the sagittal plane, and so is MS_4; S_5, however, is polarized perpendicular to the sagittal plane and is thus still rigorously decoupled from the bulk modes.[10] Similar behavior occurs along the symmetry line $\bar{\Gamma}\bar{X}$ on the left-hand side of Fig. 2(b). For points off these symmetry lines, both S_4 and S_5 degenerate into pseudosurface modes.[11]

The remaining pair of surface modes found by Tong and Maradudin, with no attenuation at $\bar{\Gamma}$, are the FK modes, labeled S_2 in Fig. 2(b). As the origin is approached, these modes penetrate more and more deeply, and their degeneracy is broken by the finite thickness of the slab. The lower member of the FK pair goes to the frequency ω_{TO} (bottom of transverse optical, or TO, band) and the upper member to the frequency ω_{LO} (top of longitudinal optical, or LO, band), in agreement with the results of Ref. 1. This behavior is not shown in Fig. 2(b), whose graphs are computer generated for a finite mesh of $\bar{q}$ values, but it is indicated in Fig. 1.

There is one significant difference between the continuum and lattice-dynamical results for the FK modes at large wavelengths: In the continuum results they are pure surface modes, whereas in the lattice-dynamical results they are pseudosurface modes in the region where they lie within the bulk bands.[12] As indicated in Fig. 1, each FK branch actually becomes a locus of interaction among hybridizing modes as it passes into the bulk bands.[13] Such behavior is typical of a series of pseudosurface modes. At short wavelengths (large $\bar{q}$), the FK modes S_2 again enter the bulk bands as pseudosurface modes, labeled MS_2 on the right-hand side of Fig. 2(b).

There is thus no discrepancy among the various treatments with respect to the long-wavelength surface modes.[14] Furthermore, although the results of Fig. 2 are specifically for the (100) surface of NaCl, one expects that these modes will frequently show up in much the same way for other surface orientations and other ionic materials: The FK modes are essentially classical electromagnetic waves in a dielectric slab (with retardation neglected). The Lucas modes are "peeled off" from the bottom of the TO bulk bands by the perturbation associated with short-range changes in the force constants of atoms very near the surface,[15] and one expects that they will frequently occur in other realistic models and in real crystals. Moreover, one expects that microscopic surface or pseudosurface modes similar to the Lucas modes will often occur in spherical, cylindrical, etc. crystals, since the surface of a macroscopic sphere or cylinder is almost flat on a microscopic scale.

We now turn to a discussion of the shell-model results. The method of calculation will be described in detail elsewhere; here we mention only that an eleven-parameter shell model was used, with the values of the parameters determined by Schmunk and Winder.[16] This model, as opposed to the rigid-ion model, takes the polarizabilities of the ions into account and consequently yields results which are in far better agreement with the experimentally determined dispersion curves for the bulk. Consequently, it should also provide a much better picture of the true surface-mode spectra for NaCl than does the Kellermann rigid-ion model.[17]

As can be seen from a comparison of Figs. 2(a) and 2(b), there are a number of significant differences between the shell-model and rigid-ion results. The main difference is that the FK modes never appear as pure surface modes in the shell-model results. Instead, they are always buried within the bulk bands as pseudosurface modes, whose existence is indicated in Fig. 2(a) by the disturbance near $\bar{\Gamma}$ in the LO bulk band. On the basis of these results for NaCl, and results of calculations for RbF which are currently in progress, it appears that the FK modes will ordinarily be pseudosurface modes, rather than surface modes, over most or all of the two-dimensional Brillouin zone.

The Rayleigh modes S_1 also show different behavior in the shell-model results: They retain the same polarization (primarily SV) along $\bar{X}\bar{M}$, and do not cross S_7 along $\bar{\Gamma}\bar{X}$. (In the rigid-ion model, S_1 changes from SV to SH along $\bar{M}\bar{X}$ and crosses S_7 along $\bar{\Gamma}\bar{X}$).

The Lucas modes S_4 and S_5 are still present at the origin $\bar{\Gamma}$. The pair of modes S_5, which are again symmetry decoupled from the surrounding bulk modes along the symmetry lines $\bar{\Gamma}\bar{X}$ and $\bar{\Gamma}\bar{M}$,

persist to the edge of the Brillouin zone along both these lines, as indicated in Fig. 2(a). The other pair of Lucas modes (S_4,MS_4) are again mixed with the bulk modes even along these symmetry lines, except in the gap near $\bar{X}$ and in the long, narrow gap extending from $\bar{\Gamma}$ to about midway to $\bar{X}$, where they are pure surface modes as indicated in Fig. 2(a).

There are considerable differences between the shell-model and rigid-ion results with respect to the gaps within the bulk bands and, as a consequence, with respect to the surface modes lying within these gaps.

We mention that the Lucas modes have also been found in the shell-model calculations for RbF which are now in progress. For this material there is a large gap between the optical and acoustic bands, and both pairs of Lucas modes are pure surface modes from the origin to the edge of the Brillouin zone. In addition, a third type of long-wavelength optical surface mode has been found in RbF (distinct from the Lucas and FK modes), which lies in a small gap near the origin between the LO and TO bands. The new pair of modes is "peeled off" from the LO bands as the Lucas modes are "peeled off" from the TO bands, and their penetration depth at the origin is small.

We wish to thank Dr. W. E. Jones and Professor R. Fuchs for conversations which were very helpful in clarifying the behavior of the FK modes at large wavelengths. We are also indebted to Dr. Jones for a copy of his dissertation.

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[9]As indicated in Fig. 1, and also evident in Fig. 2, for a given value of $\bar{q}$ there are "bands" of bulk modes corresponding roughly to different values of q_z. If the modes were to exhibit no dispersion, as in the continuum model of Ref. 1, then each band would reduce to a single line; i.e., in Fig. 1 the LO band would reduce to a line at ω_{LO} and the TO band to a line at ω_{TO}.

[10]S_4 is a pure surface mode at the single point $\bar{M}$ since it is also symmetry decoupled from the surrounding bulk modes at this point. (S_4 is polarized normal to the surface: the bulk modes, parallel to the surface.) Also, S_6 in Fig. 2(b) is, in effect, an extension of S_4, and S_{11} an extension of S_5.

[11]Similar behavior in the case of a monatomic crystal has been previously described [R. E. Allen, G. P. Alldredge, and F. W. de Wette, Phys. Rev. Lett. 24, 301 (1970)].

[12]The Fuchs-Kliewer modes are somewhat analogous to the Damon-Eshbach surface spin waves which are actually pseudosurface waves lying within the bulk continuum [T. Wolfram and R. E. de Wames, Phys. Rev. Lett. 24, 1489 (1970)].

[13]The behavior of the Fuchs-Kliewer modes within the bulk bands was first pointed out in Ref. 7.

[14]The various short-wavelength surface modes of Fig. 2, first found in Ref. 6, will be discussed elsewhere.

[15]In Ref. 7, it was found that when these short-range changes are partially neglected, the Lucas modes disappear.

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[17]In the results of Fig. 2(a), the relaxation of the surface ions is neglected. If the surface relaxation is large, it may produce appreciable shifts in the surface-mode frequencies, but the most prominent features of the surface-mode spectrum (i.e., those discussed in the text) should not be affected very much. In the results of Fig. 2(b), the surface relaxation is taken into account (differing somewhat from that in Ref. 5), but it is very small and has little effect on the frequencies.