SURFACE MODES WITHIN THE BULK CONTINUA*

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Several types of vibrational surface modes have been found within the bulk continua in calculations for model crystals.

Recently we reported finding, in calculations for model crystals, vibrational surface modes which lie in gaps between "bands" of bulk modes.[1] Since that time we have obtained, in further calculations, modes which are perhaps of still greater interest in that they lie within the bulk "bands." These modes are obtained for wave vectors only along certain symmetry directions within the two-dimensional Brillouin zone associated with the surface. If modes belonging to the same branch but to a different wave vector (q_x, q_y) off the symmetry direction are examined, it is found that the modes are no longer completely localized at the surface, but have degenerated into mixed (or "pseudo surface") modes.

It has been stated in the literature, and appears to be commonly believed, that surface modes cannot exist within a continuum of bulk modes. This premise can be stated more precisely as follows: Suppose that for a particular two-dimensional wave vector (q_x, q_y) there is a continuum of bulk modes (corresponding to different values of q_z) with frequencies ω covering the range $\omega_1 \leq \omega \leq \omega_2$; then a surface mode cannot have a frequency lying within this range.

However, the above premise is not valid along certain symmetry directions: The normal modes for a monatomic crystal with a surface (or two surfaces, if the thickness is finite) are given by the matrix eigenvalue equation

$$\sum_{l_3',\beta} D_{\alpha\beta}(l_3 l_3'; q_x q_y)\xi_\beta(l_3'; p) = \omega_p^2 \xi_\alpha(l_3; p), \quad (1)$$

where ω_p is the frequency for the mode labeled by p, $\xi_\alpha(l_3; p)$ is the corresponding eigenvector which gives the amplitude of vibration in the α direction ($\alpha = x, y, z$) for the l_3th plane parallel to the surface, and $D_{\alpha\beta}(l_3 l_3'; q_x q_y)$ is the dynamical matrix. Suppose, for example, that $q_y = 0$. Then it can be seen from the definition of the dynamical matrix[2] that, for crystals which are invariant under the symmetry operation $y \to -y$,

$$D_{xy}(l_3 l_3'; q_x 0) = D_{yz}(l_3 l_3'; q_x 0) = 0.$$

Along the symmetry direction $q_y = 0$ (q_x axis), there is thus a decoupling of vibrations in the y direction from those in the x and z directions. Consequently, two types of modes will be obtained—those for which $\xi_y = 0$ and those for which $\xi_x = \xi_z = 0$.

Ordinarily, Eq. (1) implies that surface modes should not exist within a bulk continuum: If $\xi_\alpha(l_3)$ is determined for a particular q_x, q_y, and (allowed) ω, if ω lies within a bulk continuum, and if there is no degeneracy, then $\xi_\alpha(l_3)$ will belong to a bulk mode. In the event of an "accidental" degeneracy at ω between a surfacelike mode and a bulk mode, orthogonality requirements should produce a mixing between the two. However, if a decoupling leads to two different types of modes, as discussed above, an "accidental" degeneracy between a surfacelike mode of one type and a bulk mode of the other type will not result in such a mixing. It is therefore possible for a surface mode of one type to exist in a bulk continuum associated with the other type.

Physically, one can visualize the situation as follows: If one attempts to excite a surface vibration with frequency ω lying within a bulk continuum, the excitation will ordinarily decay into bulklike vibrations. But if the bulk vibrations associated with this continuum are polarized in the xz plane, if the surface excitation is polarized in the y direction, and if the wave vector is such that vibrations with these different polarizations are decoupled, then such a decay will not occur.

In Figs. 1(a) and 1(b), we show results from calculations for crystals with free surfaces which are 21 layers thick and composed of particles interacting through a Lennard-Jones potential. The results of Fig. 1(a) are for a monatomic crystal with a (100) surface, and those of Fig. 1(b) are for a crystal with a (111) surface bearing a light adsorbed monolayer. The frequency ω is plotted versus the wave-vector component q_x along the q_x axis. ($\bar{\Gamma}$ is the origin and $\bar{M}$ is the point where the q_x axis intersects the Brillouin zone edge.)

In Fig. 1(a), S_1 is a Rayleigh mode. S_2 is a mode which is polarized mainly in the z direction, like the Rayleigh mode, but is localized primarily in the second layer beneath the surface.[3] In contrast to these two modes, which are

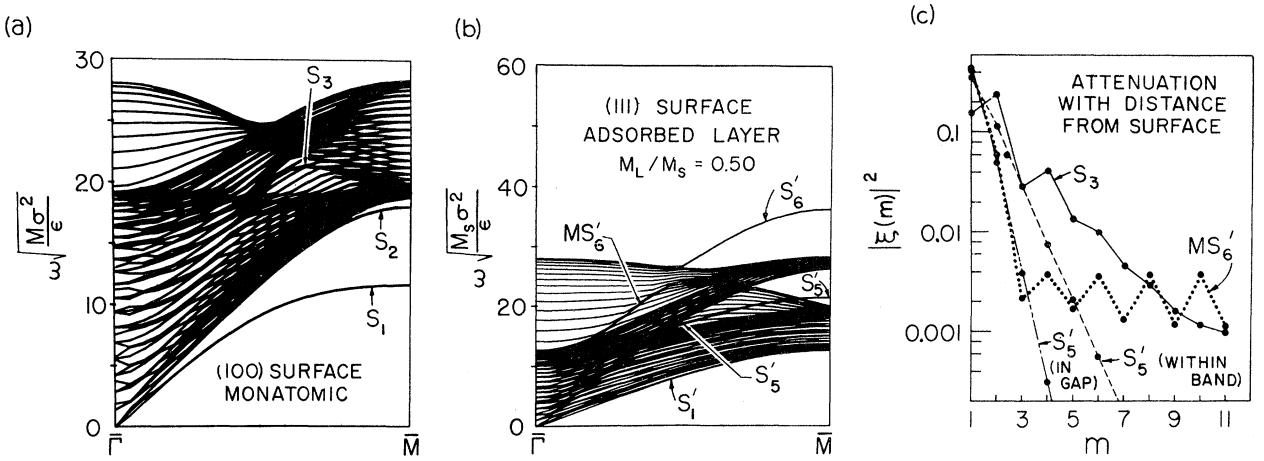

FIG. 1. (a) Frequency versus wave-vector relations along q_x axis (to corner of zone) for 21-layer monatomic crystal with (100) surfaces. M is the atomic mass and ϵ and σ are the potential parameters of the Lennard-Jones potential. The curves were computer generated and no attempt was made to connect them correctly when crossovers between modes occur. (b) Frequency versus wave vector along q_x axis (to center of zone edge) for crystal with (111) surfaces and a light adsorbed layer on each surface; $M_L/M_S = \frac{1}{2}$, where M_L and M_S are the atomic mass for the layer and substrate, respectively. (c) Dependence of the amplitude of vibration $|\vec{\xi}|$ upon the distance from the surface. In each case, the arrows of (a) and (b) indicate the points at which these values of $|\vec{\xi}|^2$ were determined. The eigenvectors are normalized to unity (for the whole 21-layer crystal).

beneath the bulk continuum, S_3 is a surface mode which lies within the continuum. A plot of $|\vec{\xi}|^2 = |\xi_x|^2 + |\xi_y|^2 + |\xi_z|^2$ versus the layer number (with $m = 1$ at the surface) is given in Fig. 1(c). It can be seen that $|\vec{\xi}|^2$ for S_3 falls by more than two orders of magnitude between the surface and the center of the crystal.

In Fig. 1(b), the branch labeled S_6' loses its surface-mode character upon entering the bulk continuum; the branch labeled MS_6' within the continuum is a mixed mode. In contrast, S_5' retains its surface character after it has penetrated well into the continuum, as can be seen from the behavior of its squared amplitude $|\vec{\xi}|^2$ in Fig. 1(c). Plots of $|\vec{\xi}|^2$ for S_5' outside the continuum and for MS_6' are given for comparison.

Several other types of surface modes, not shown here, have been found in bulk continua. In the case of a monatomic crystal with a (100) surface, the Rayleigh modes exist as surface modes within the bulk continuum for most of the $q_x = q_y$ symmetry line. In a region about this line, these modes are still contained in the continuum and are therefore no longer completely localized.[4] Outside this region, the Rayleigh modes fall below the bulk continuum and are again true surface modes. It should be mentioned that along the $q_x = q_y$ direction we have also found *SH* modes (i.e., modes associated primarily with transverse in-plane vibrations) which lie beneath the Rayleigh modes and bulk continuum, so that there are two surface waves along this direction which appear to persist into the long-wavelength limit. These *SH* waves are analogous to the Gulyaev-Bleustein waves recently found for piezoelectric materials.[5] In the case of a monatomic crystal with a (110) surface, we have found *SH* modes which exist as surface modes within the bulk continuum along the q_x axis. In a region around this axis, they become mixed modes, and in other parts of the Brillouin zone they exist as surface modes beneath the bulk bands. Finally, in the case of this surface, there is a mode which, like S_5', is localized at the surface both in a "band gap" and within the continuum.

The results described above seem to imply that surface modes within bulk continua not only are possible but may be a rather common occurrence.

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[1]R. E. Allen, G. P. Alldredge, and F. W. de Wette, Phys. Rev. Letters 23, 1285 (1969).

[2]See, for example, R.E. Allen and F. W. de Wette, Phys. Rev. 179, 873 (1969).

[3]At the point $\overline{M}$, for the (100) surface there is an approximate decoupling between layers parallel to the

surface with respect to vibrations in the z direction, and "single-layer" modes are obtained in which the first layer, the second layer, etc. vibrate almost independently. Similarly, at the point $\bar{X}$ (center of the zone edge) there are "single-layer" modes for in-plane vibrations.

[4]This behavior appears to be related to a result concerning Rayleigh waves in anisotropic elastic media which was obtained by D. C. Gazis, R. Herman, and R. F. Wallis [Phys. Rev. 119, 533 (1960)]. These authors found that for the (100) surface of a cubic crystal, and for certain values of the elastic constants, there is a range of excluded directions of propagation about the [110] direction, but that this direction itself is not excluded.

[5]Yu. V. Gulyaev, Zh. Eksperim. i Teor. Fiz.—Pis'ma Redakt. 9, 63 (1969) [JETP Letters 9, 37 (1969)]; J. L. Bleustein, Appl. Phys. Letters 13, 412 (1969).

OBSERVATION OF SURFACE BOUND STATE AND TWO-DIMENSIONAL ENERGY BAND BY ELECTRON TUNNELING

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Using electron tunneling, we have made direct observation of a surface bound state of electrons localized in a narrow accumulation layer at the InAs-oxide interface. The Landau-level structure of the two-dimensional energy band, associated with the bound state, has been studied in a magnetic field up to 85 kG.

In narrow accumulation or inversion layers at semiconductor surfaces, quantization of electronic motion normal to the surface leads to discrete bound-state energy levels binding electrons to the surface.[1] Corresponding to each surface bound state, there is a band of two-dimensional conduction states, due to a continuum of the electronic motion parallel to the surface, with its band edge at the surface-state binding energy. These states have been referred to as space-charge–induced localized states[2] and also as electric sub-bands.[3] Previously, only experiments on surface transport properties have yielded evidence for their existence.[4] It is the purpose of this Letter to report the first direct observation of these surface bound states and to demonstrate that electron tunneling offers a simple and yet powerful tool for studying the electronic energy structure of these states.

The measurements were made on n-type degenerate InAs-oxide-Pb tunnel junctions using standard techniques.[5] The fabrication procedure for these tunnel junctions has been discussed previously.[6] At present, little is known about the oxide layer, which was thermally grown on the surface of single-crystal InAs. We used Pb films as counterelectrodes so that the tunneling characteristics of superconducting Pb could be used as proof that electron tunneling was the current-carrying mechanism through the junction.[5] The results discussed in this Letter have not been observed in junctions which did not show this proof of tunneling.

We have deduced from tunneling measurements that a narrow accumulation layer of electrons, which may result from positively charged immobile centers in the oxide, exists at the InAs-oxide interface.[7] The two-dimensional energy band corresponding to each surface bound state of the electrons in this accumulation layer may be approximated by[1] $E(k_{\|}) = \hbar^2 k_{\|}^2/2m_{\|}^* + E_b$, where E_b is the surface-state binding energy, $k_{\|}$ is the wave vector parallel to the surface, and $m_{\|}^*$ is the effective mass parallel to the surface. Both E_b and $m_{\|}^*$ have been determined directly from the tunneling results. E_b is determined from the bias at which the two-dimensional band edge is observed in the junction conductance (dI/dV). When a magnetic field is applied normal to the surface, the dI/dV-V curves of the junction exhibit oscillations which reflect the Landau levels of the two-dimensional energy band.[6,8] The period of the oscillations, which equals the Landau-level separation, determines the value of $m_{\|}^*$.

Figure 1 shows the conductance-versus-bias curve of an n-type degenerate ($n = 5.5\times10^{17}/\mathrm{cm}^3$) InAs-oxide-Pb tunnel junction at 4.2°K when the Pb superconductivity is quenched by applying a magnetic field. At a bias equal to the longitudinal optical (LO) phonon energy ($V \approx 30$ mV) of InAs,[9] a decrease in conductance (~2%) is observed in both bias directions. This structure must result from the electron LO-phonon interaction in the InAs electrode. However, the structure is in contrast to the phonon-assisted