Observation of Surface Optical Phonons in NaF(001) by Inelastic He-Atom Scattering

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Previous time-of-flight experiments at 20-meV He beam energies, which provided the dispersion curve of Rayleigh surface phonons, have been extended to 90-meV energies on NaF(001) along ⟨100⟩. Despite a large multiphonon background from the Rayleigh phonons it has been possible to detect small peaks due to optical surface phonons. The results provide the first direct experimental evidence in the dispersion curves of microscopic surface optical modes.

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Inelastic scattering of He atoms from crystal surfaces has been recently used for the first direct observation of surface phonons over the entire surface Brillouin zone.[1] The dispersion curves of Rayleigh waves have now been determined from time-of-flight (TOF) spectra in five ionic crystals, a semiconductor, and the three noble metals.[2-5] More recently electron energy-loss spectroscopy (EELS) has also been employed and the dispersion of acoustical surface modes in a clean Ni(100) surface and optical modes with an oxygen overlayer have been obtained.[6] He scattering has a resolution ten times better than EELS and no drawbacks due to surface charging. Still, it has until now been considered to be relatively insensitive to surface optical modes. Unlike neutrons, He atoms interact with crystal nuclei via the surrounding electrons at relatively large distances, from which, in the absence of net charge, they can only weakly couple to the optical-mode counterphase motion of oppositely charged ions.[7]

Notwithstanding these unfavorable conditions, we have been able to obtain the first extensive evidence of microscopic optical surface vibrations in an ionic crystal using He scattering. The dispersion curves of the two optical modes, which are polarized in the scattering plane defined by the incident and outgoing wave vectors (sagittal plane), and are denoted by S_4 (mainly longitudinal) and S_2 (mainly transverse), have been measured in NaF(001) along ⟨100⟩ out to the zone boundary.[8] We have observed also the quasi-longitudinal acoustic surface mode S_6 in the region of strong hybridization with S_4.[8] Microscopic surface optical modes have been theoretically predicted by Lucas as early as 1968,[9] but no clear experimental evidence was given until now.

The apparatus, the crystal-surface preparation, and the procedure used in the present experiment are the same as those thoroughly described in Ref. 2. Compared to the previous investigation of NaF(001) Rayleigh waves,[2] we have used a lower surface temperature ($T_s = 180$ K) and a higher beam-source temperature ($T_{\mathrm{He}} \simeq 450$ K) resulting in a larger incident momentum ($k_i = 13.36$ Å^{-1}; $E_i = 93.0$ meV). At this energy a multiphonon background arises on the phonon creation side and the lower-energy part of the phonon spectrum including Rayleigh waves is broadened by multiphonon processes.

Most of the spectra have been recorded for incident angles $\theta_i (\theta_f = 90° - \theta_i)$ in the range 30 to 40° where we expect a resonance enhancement of the scattering intensity due to the in-plane inelastic resonances $(m,n)_v = (1,1)_v$ (m,n are reciprocal-lattice-vector indices) with the atom-surface bound states $v = 0, 1, 2$.[10] Several sequences of TOF spectra were obtained by varying θ_i in steps of 0.3° or 0.2° in order to check the reproducibility of the spectral features and to follow the rapid changes in angular locations of the resonances. Here, however, we observed that inelastic resonances possibly show visible effects only when in tune with a surface mode, these effects consisting in reshaping and slightly amplifying the response of optical modes. Still, the optical-mode features were observable also out of resonance; in particular, a few zone-boundary modes have been detected in a nonresonant region around $\theta_i \sim 52°$.

In Fig. 1(a), we show an example of TOF spectrum taken at the incident angle $\theta_i = 38.3°$. The same spectrum is plotted in Fig. 1(b) as a function of the phonon frequency ω ($\omega < 0$ for phonon creation processes) and compared with another spectrum taken at a slightly larger incident angle ($\theta_i = 38.5°$). The two spectra look very similar, except for small differences in the shape of the peaks at $\omega \simeq -3.8$ and -4.9×10^{13} rad s^{-1}. From a comparison with the calculated one-phonon reflection coefficient [Fig. 1(b)] we see that these two peaks fall in the positions where the creation of two surface optical modes S_4 and S_2 are predicted, while the major peaks correspond to Rayleigh waves

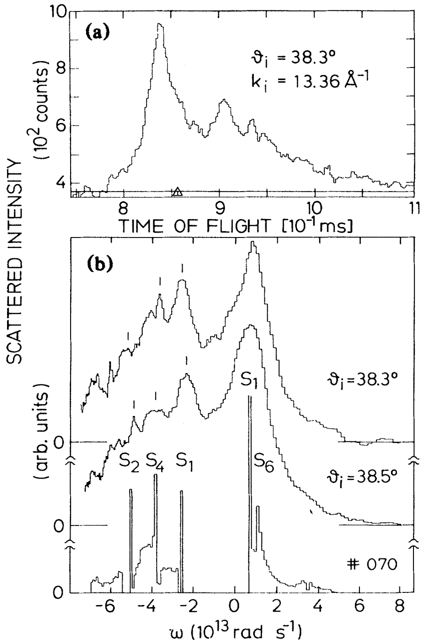

FIG. 1. (a) Time-of-flight spectrum of He scattered from the NaF (001) surface along ⟨100⟩ for an incident angle $\theta_i = 38.3°$ and momentum $k_i = 13.36$ Å^{-1}. (b) The same spectrum is plotted as a function of phonon frequency together with another spectrum taken at slightly larger θ_i and compared with the theoretical one-phonon reflection coefficients. S_1 labels the Rayleigh waves, S_2 and S_4 the optical surface modes, and S_6 the quasilongitudinal acoustic surface mode. Vertical bars mark the structures attributed to resolved surface modes.

(S_1), of which two are observed corresponding to two different Brillouin zones.

The theoretical spectrum has been obtained by use of a Morse potential for the He-surface interaction, the eikonal approximation for the scattering process, with no resonance effect included,[11] and the Green's-function method for surface dynamics.[8] We show only the result for $\theta_i = 38.3°$ as the calculated spectrum for $\theta_i = 38.5°$ is almost identical. Thus the observed shape change of the S_2 and S_4 peaks produced by such a small angular variation is hardly significant, although the sharpening of S_2 for $\theta_i = 38.5°$ may be attributed to the resonance $(m,n)_v = (1,1)_0$.

In the sequence of spectra shown in Fig. 2, the intensity of the larger peak is shared between the Rayleigh mode S_1 and the quasilongitudinal surface acoustic mode S_6. The S_2 mode is no longer visible, while the Lucas mode S_4 has an oscillating intensity with the sharpest maximum at 39.8°. The enhancement at this angle is probably connected with the inelastic resonance $(1,1)_1$ and a predicted large surface-phonon density of states. The gradual shift of the S_4 frequency with increasing θ_i gives a picture of the dispersion of the sagittal Lucas mode.

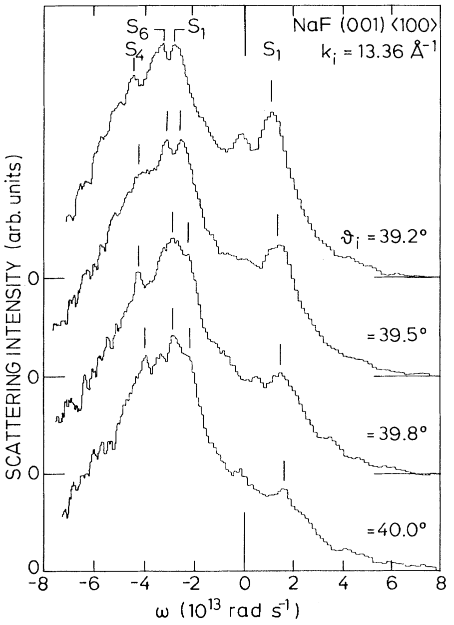

FIG. 2. A series of inelastic He-scattering spectra taken at increasing incident angles. Vertical bars mark the features that are attributed to resolved surface modes.

The experimental points corresponding to frequency and parallel-momentum transfers of the observed peaks in the optical region are plotted in Fig. 3 (solid circles) together with the calculated surface-phonon dispersion curves[8] (solid lines) and the surface-projected bulk-phonon continuum (cross-hatched region). The reproducibility of the experimental points and their close correspondence to the theoretical dispersion curves provides compelling evidence that we are observing optical surface modes. The group of points found at one half of the zone around $\omega \simeq 3\times10^{13}$ rad s^{-1}, and attributed to S_6, is rather dispersed. It seems, however, that S_4 and S_6 do not follow the complex hybridization scheme indicated by the theory. Rather, and more simply, the S_4 branch goes continuously up to the zone edge, whereas S_6 bends down and connects with $\underline{S}_8$. In LiF(001) the Rayleigh wave frequency at the $\bar{M}$ point was found to be about 11% below the theoretical value.[2] A 17% larger F$^-$ polarizability at the surface was assumed in order to remove the discrepancy. A similar discrepancy is not found in NaF(001), since here the F$^-$ ions are not involved in $\bar{M}$-point Rayleigh wave motion, because they are lighter than the Na$^+$ ions. Conversely, it is not surprising that some misfit occurs for NaF(001) optical branches. Perhaps this misfit could be removed by a simple adjustment of the surface F$^-$ polarizability. We note also that the Chen, Alldredge, and de Wette slab calculation, based on the shell model, gives the S_2 mode much closer to the LO band bottom[12] in disagreement with the present data. This

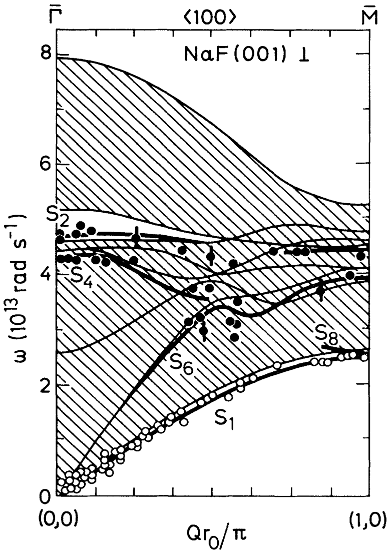

FIG. 3. Calculated surface-phonon dispersion curves for sagittal polarization in NaF(001) along ⟨100⟩ (solid lines) and surface-projected bulk bands (cross-hatched regions). Solid circles are the present experimental data obtained with a high-energy He beam ($k_i = 13.36$ Å^{-1}); open circles are previous data obtained with a lower-energy beam ($k_i \simeq 6$ Å^{-1}; from Ref. 2). The representative error bars indicate the energy half width of the He beam.

illustrates further how sensitive certain surface modes are to the details of bulk dynamical models.

We want to stress a few relevant differences between the situation existing in NaF(001) and in other crystals studied to date. Optical modes could not be resolved in the initial investigation of LiF with a low-energy He beam. In both cases, NaF and LiF, the fluorine ion has the larger interaction with He because of its larger size; but in NaF it moves predominantly in the optical modes, as a result of its lighter mass, while in LiF it moves mostly in the acoustic modes. Thus in NaF(001) a more intense scattering from optical modes is expected. A similar situation occurs in KCl(001), where experimental points lying along the crossing mode S_8 have already been reported.[2] Furthermore we note that in crystals having a large acoustic-optical gap, surface optical modes can be highly localized. From this point of view NaF(001) represents a challenging case: Here only small gaps exist as a result of the almost equal ionic masses, and most of the optical surface modes are just resonant (mixed) modes.[12]

We can estimate the scattering intensity for a localized surface optical mode from a simple theory for Rayleigh modes, which predicts that the relative intensity falls off with Q as $\exp(-Q^2/Q_c^2) \times n(\omega(Q))$, where $n(\omega(Q))$ is the Bose temperature factor.[13] The exponential cutoff factor Q_c relates to the steepness of the coupling potential. For the alkali halide LiF(001) $Q_c^2 = 2.4$ Å^{-2}, whereas for Ag(111) $Q_c^2 = 0.56$ Å^{-2}.[13] For nearly equal ionic masses, the above expression qualitatively holds also for optical modes, as they can be regarded as a prolongation into the next Brillouin zone of the acoustic branches, with wave vector $(2\pi/r_0) - Q$. Thus, if we take account of the differences in Q_c, the zone-center optical modes are expected to undergo an intensity reduction similar to that of zone-boundary modes in metals.

The results presented here call attention to the experimental difficulties of detecting small structures superimposed on a large multiphonon background which are to be expected in extending He time-of-flight spectroscopy to studying modes of higher frequency such as the extrinsic optical modes of adsorbates on metals. Here EELS has a definite advantage since for the same Debye-Waller factor

$$\frac{m}{M_{\text{surf}}} \frac{E_{iz} k_B T_{\text{surf}}}{(k_B \Theta_D)^2}$$

(m is the projectile particle mass, M_{surf} is the surface atom mass, T_{surf} is the surface temperature, and Θ_D is the surface Debye temperature), which determines the amount of multiphonon background,[14] the perpendicular electron energy E_{iz} can be 3 orders of magnitude larger because of its lower mass, compared to the He atom. The present experiments demonstrate, however, that He scattering may provide useful information up to energies of about 0.6 eV, which can be readily achieved by heating the beam source to 2600 K.

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