

## Standing-Wave Optical Phonons Confined in Ultrathin Overlayers of Ionic Materials

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High-resolution electron-energy-loss spectra of ultrathin ( $d < 3$  nm) LiBr epitaxial films on Si(100) [W. Gao *et al.*, Solid State Commun. **87**, 1013 (1993)] reveal an anomalous dependence of the frequencies of the macroscopic surface phonons on the layer thickness  $d$ . We present lattice-dynamics calculations of the spectra which prove that this anomalous dependence arises from the excitation of standing-wave optical phonons confined in the film and reflects the dispersion relation of bulk optical vibrations of LiBr in the direction normal to the surface.

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The phonon modes of a crystalline film have been the object of continued interest in surface science. According to the spatial extent of their vibrational amplitude, the modes can be classified as bulklike or as surfacelike and interfacelike modes: The former run over the entire film thickness while the latter remain more or less confined to the surfaces. Thin films of ionic-type materials can support both macroscopic as well as microscopic surface phonons. The former exist merely by virtue of the boundary conditions of classical elasticity theory and electromagnetism imposed at the interfaces of the film seen as an elastic and dielectric continuum, while the latter may arise from the detailed atomic arrangement and the specific force constants at the surfaces.

Among the diverse spectroscopic probes of the phonon modes of a film, high-resolution electron-energy-loss spectroscopy (HREELS) in specular reflection is a powerful technique for probing specifically the surface and interface macroscopic optical phonons of layered materials [1], also called the Fuchs-Kliwer (FK) modes [2]. Recently, Gao *et al.* [3] succeeded in producing high-quality ultrathin LiBr/Si(100) epitaxial layers for investigation by HREELS. Figure 1 is an example of the spectra of Gao *et al.* which exhibit two loss features arising from the two FK modes of the system. Electrostatics predicts that these modes, denoted  $FK^+$  and  $FK^-$ , possess an evanescent electric field extending at a distance of about  $1/Q$  on both sides of the faces of the film [2,4], where  $Q$  is the surface wave vector ( $Q \approx 0.1 \text{ nm}^{-1}$  in Gao's experiments). The inset in Fig. 1 sketches the eigenvectors of the modes. When the thickness  $d$  of the film is much larger than  $1/Q$ ,  $FK^+$  and  $FK^-$  are localized surface and interface modes, respectively. For  $d \ll 1/Q$  the FK modes involve oscillations of all the ions of the film in directions, respectively, parallel and perpendicular to the normal at the surface for  $FK^+$  (longitudinal polarization) and  $FK^-$  (transverse polarization).

In very thin films, the FK phonon frequencies become dependent on the thickness as shown in Fig. 2 where the open circles are the experimental data [3]. The full curves are the predictions of electrostatics based on the sole dielectric functions of LiBr and Si, whereas the crosses

have been deduced from lattice dynamics [5]. It is clear that the  $FK^-$  mode is correctly described by both the macroscopic and microscopic theories for all film thicknesses. However, when  $d$  becomes smaller than 3 nm, the  $FK^+$  branch starts to deviate significantly from the predictions of electrostatics. In this Letter, we demonstrate that this deviation, already pointed out by Gao *et al.* [3], is due to the excitation of longitudinal standing-wave optical phonons ( $LO_n$ ) confined in the LiBr layer, similar to those observed by Raman scattering in semiconductor superlattices [6,7], and which are not described correctly by the dielectric model [8]. Another example of confinement is provided by the recent observation by helium atom scattering (HAS) of long-wavelength *acoustical* standing wave ( $LA_n$ ) in Na/Cu(001) epitaxial layers [9]. The frequency of such standing waves is governed by the boundary conditions they must satisfy. At the free surface of an ionic film, the amplitude of a confined optical or acoustical mode is zero (sinelike) or extremum (cosinelike), respec-

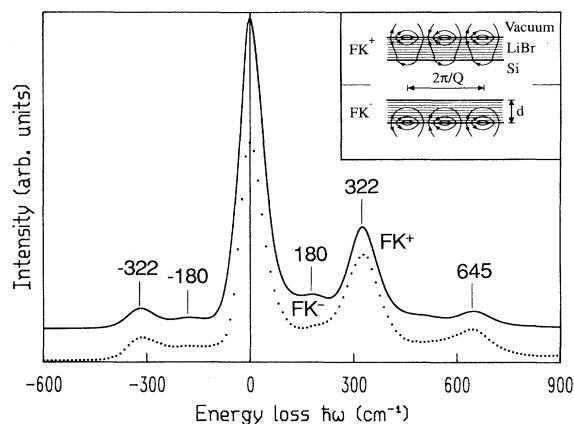


FIG. 1. HREELS spectrum of a 4.8 nm LiBr/Si(100) epitaxial layer obtained with 14.2 eV electrons under an incidence of  $60^\circ$ . The dotted curve shows the experimental data [3]. The full curve is a theoretical spectrum computed with the dielectric approximation, which has been shifted upward for more clarity. The inset shows the electric field lines generated by the two FK modes of the system for  $Qd = 1$ , with the LiBr film being indicated by the shaded areas.

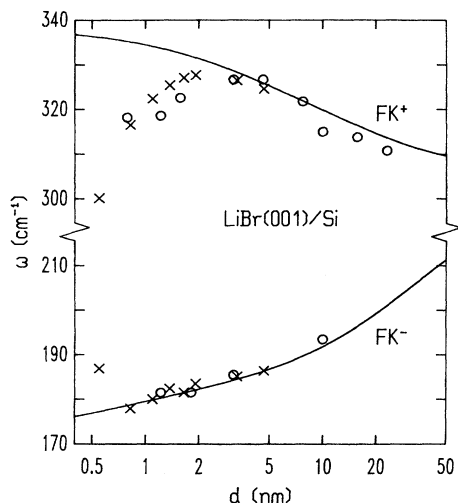


FIG. 2. Positions of the  $FK^+$  and  $FK^-$  loss peaks in the HREELS spectra of LiBr/Si(100) epitaxial layers against film thickness. The experimental results [3] are shown by the open circles. The full curves have been obtained from the dielectric approximation. The crosses are the results of lattice-dynamics calculations performed for films with  $N = 2, 3, \dots, 7, 12,$  and  $17$  ionic planes. The relation between the film thickness and the number of atomic layers is  $d = 0.275N(\text{nm})$ .

tively. At the interface with the substrate, the boundary condition depends on the longitudinal or transverse polarization of the mode. Specific rules are proposed below for determining the frequencies of *all* such long-wavelength confined phonons of an ionic overlayer.

In our applications of the dielectric theory (full curves in Fig. 2), the Si substrate was described by a dielectric constant  $\epsilon_s = 12$ . LiBr received the usual dielectric function  $\epsilon(\omega) = \epsilon_\infty + S\omega_{TO}^2/(\omega_{TO}^2 - \omega^2)$  with  $\epsilon_\infty = 3.22$ ,  $S = 8.73$ , and  $\omega_{TO} = 176 \text{ cm}^{-1}$ , respectively, the high-frequency dielectric constant, the oscillator strength, and the frequency of the transverse optical phonon. These parameters, which are close to those measured from infrared spectroscopy [10], were adjusted so as to best reproduce the frequencies of the FK modes observed experimentally for  $d > 5 \text{ nm}$ . Our lattice-dynamics calculations of the HREELS spectra (crosses in Fig. 2) were based on a shell model [11] fitting the experimental values of the lattice constant, cohesive energy, elastic constants, and the optical constants  $\epsilon_\infty$ ,  $S$ , and  $\omega_{TO}$  of LiBr listed above [12]. The geometry of the LiBr layers was relaxed until the ions reached their equilibrium positions when using Born-Mayer potentials for the short-range interactions. Consistently with the macroscopic approach, the Si substrate was viewed as a dielectric continuum with  $\epsilon_s = 12$ , and the dynamics of the ions was solved in the presence of their image charges [5].

We now discuss why the lattice dynamics succeeds where the dielectric model fails in predicting the positions

of HREELS peaks for ultrathin overlayers (see Fig. 2). In the nonretarded dielectric approximation of relevance here, the frequencies of the  $FK^+$  and  $FK^-$  branches at small surface wave vectors ( $Q \ll 1/d$ ) are the longitudinal  $\omega_{LO}$  and transverse  $\omega_{TO}$  bulk values, respectively, independent of the film thickness. In the lattice-dynamics calculations, a film of LiBr(001) composed of  $N$  atomic layers has  $N$  nondegenerate  $LO_n$  optical branches and  $N$  pairs of doubly degenerate  $TO_n$  modes, with  $n = 1, 2, \dots, N$ . For vanishingly small  $Q$ , the  $FK^+$  and  $FK^-$  modes correspond to the branches  $LO_1$  and  $TO_1$  of highest frequencies. The frequencies of the  $LO_1$  and  $TO_1$  modes depend on  $N$ , as explained below, and converge to the bulk values  $\omega_{LO}$  and  $\omega_{TO}$  at the  $\Gamma$  point for  $N$  larger than about 12. It is only in this large- $N$  limit that the dielectric approximation leads to valid results.

The phonon branches of a film correspond to a surface projection of the dispersion curves of the bulk phonons [13]. For an isolated film of thickness  $d$ , the frequencies at  $Q = 0$  of the  $LO_n$  and  $TO_n$  phonons are approximately those of the bulk LO and TO branches for a wave vector  $k_z$  in the normal direction equal to  $n\pi/d$ . This condition of standing wave in a film was first proposed by Kanellis, Morhange, and Balkanski for GaAs(111) films [14]. In our description of the dynamics of LiBr(001)/Si, image charges of the ions in the substrate occupy the positions the ions would have in a film of double thickness. However, the number of degrees of freedom remains the same as for an isolated film, and only half of the modes of a film with thickness  $2d$  correspond to those of the supported film with thickness  $d$ . The eigenvector analysis provides us with phenomenological quantization rules of the form  $k_z = (2n - \beta)\pi/2d$  for  $LO_n$  and  $k_z = (2n)\pi/2d$  for the  $TO_n$  modes,  $\beta$  being the screening factor  $(\epsilon_s - 1)/(\epsilon_s + 1)$  induced by the substrate. For the longitudinal and transverse acoustical modes, the rules are  $k_z = (2n + \beta)\pi/2d$  for  $LA_n$  and  $k_z = (2n)\pi/2d$  for  $TA_n$ , with now  $n = 0, 1, \dots, N - 1$ . The mode  $TA_0$  corresponds to rigid translations parallel to the surface of all of the ions of the film, and  $LA_0$  is related to the vibration of the film against the massive substrate. Since the image interactions provide a restoring force in the  $z$  direction, the  $LA_0$  mode is a frustrated translation. There is no restoring force from the image ions in the directions parallel to the interface and, for that reason, the  $\beta$  factor does not influence the quantization rules of the transverse modes. For an isolated film ( $\beta = 0$ ) the usual quantization rules of standing waves are recovered for both transverse and longitudinal phonons. For a metallic substrate ( $\beta = 1$ ), the quantization rule of the longitudinal acoustic and optical phonons is that of the organ-pipe modes recently observed by HAS in Na/Cu(001) epitaxial layers [9].

Figure 3 shows the phonon dispersion relations along the [001] direction computed for bulk LiBr. The dots are the phonon frequencies at  $Q = 0$  for LiBr(001)/Si

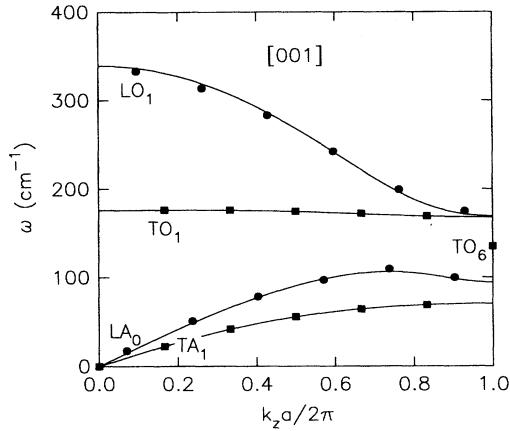


FIG. 3. Phonon dispersion curves along the  $\Gamma X$  direction in bulk LiBr obtained with our shell model ( $a$  is the lattice parameter). The filled symbols give the frequencies of the phonons of a six-layer LiBr(001)/Si relaxed film deduced with the same shell model. They have been positioned at effective wave vectors  $k_z$  fulfilling the quantization rules given in the text. The mode at the origin is  $TA_0$ .

with  $N = 6$  molecular layers ( $d = 1.65$  nm) and with abscissas  $k_z$  given by our quantization rules. They fall close to the bulk-phonon branches, validating these rules. Of course, the mode spectrum of a finite-thickness slab cannot be exactly predicted from the bulk spectrum by the mere quantization of the effective wave vector  $k_z$ . Deviations from this simple rule do occur. In this respect, the frequency of the mode labeled as  $TO_6$  is significantly smaller than that of the bulk TO branch at the zone boundary. This mode, in fact, is the pair of  $S_4$  and  $S_5$  surface microscopic phonons [15]. Notwithstanding these specific spectral features and other minor differences, the fact remains that the simple quantization rules are seen to work rather well in relating the slab modes to bulk-phonon branches even in the ultrathin film limit. The basic physical reason for this appears to be that the long-range Coulomb forces, when calculated by plane-wise summations [15], also reduce to interactions between near-neighbor, neutral atomic planes, so that a single pair of such planes already suffices to sketch the bulk spectrum.

The thickness dependence of the  $LO_1$  and  $TO_1$  frequencies at  $Q = 0$  is directly relevant for our discussion of the positions of the FK loss peaks of LiBr/Si ultrathin films. In these films, the condition  $Q \ll 1/d$  is fulfilled for all the wave vectors probed in a HREELS experiment ( $Q < 0.3$  nm $^{-1}$ ), and the positions of the peaks are a direct measurement of the frequencies of the FK branches at zero  $Q$ . Indeed, the positions of the loss peaks in the computed HREELS spectra of ultrathin films (filled stars in Fig. 4) are very close to the frequencies of the  $LO_1$  and  $TO_1$  modes (open symbols). The quantization rules predict that their frequencies are approximately those of

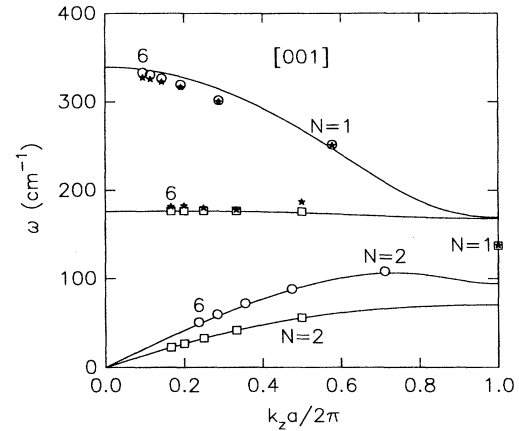


FIG. 4. Frequencies and effective wave vectors  $k_z$  of the  $LO_1$  and  $LA_1$  (open circles),  $TO_1$  and  $TA_1$  (open squares) phonons of relaxed LiBr(001)/Si films composed of  $N = 1, 2, \dots, 6$  atomic planes. The filled stars show the frequencies of the  $FK^+$  and  $FK^-$  loss peaks in the HREELS spectra computed from lattice-dynamics calculations.

the LO and TO bulk phonons at normal wave vectors  $k_z = (2 - \beta)\pi/2d$  and  $\pi/d$ , respectively. The bulk dispersion curves in Fig. 4 indicate that the frequency of  $LO_1$  can be substantially smaller than  $\omega_{LO}$  at the  $\Gamma$  point ( $339$  cm $^{-1}$ ) for a film composed of a few atomic layers, and this explains why the position of the  $FK^+$  loss peak in Fig. 2 deviates so much from  $339$  cm $^{-1}$  for very thin LiBr films. Moreover, one also understands from Fig. 4 why the dielectric approximation worked well for the  $FK^-$  mode, simply because the bulk TO branch has virtually no dispersion along [001]. Therefore, the positions of the FK loss peaks obtained in HREELS for ultrathin films give a measure of the dispersion curve of the LO and TO bulk phonons in the direction normal to the surface.

For a larger film thickness, the FK branches acquire a significant dispersion in the small  $Q$  domain probed by HREELS and, therefore, the corresponding loss peaks in the spectra no longer reflect the position of the  $LO_1$  and the  $TO_1$  standing wave evaluated at the  $\Gamma$  point. At the other end, let us also remark that the  $FK^-$  loss structure computed for  $N = 2$  contains a contribution from the  $LO_2$  mode in addition to the  $TO_1$  phonon when the HREELS spectrum is convoluted with a broadening function simulating the experimental resolution. This explains why the position of the  $FK^-$  loss peak at  $d = 0.6$  nm in Fig. 2 shifts upward.

The calculations carried out for this work were based on several idealizations of epitaxial layers, the strongest among them being the assumption of a perfect-crystal film on a dielectric continuum. In spite of the crudeness of the theoretical approach [16], the shell model calculations reproduced the frequencies of the macroscopic surface phonons of LiBr/Si(100) films surprisingly well. This certainly testifies to the high quality of the epitaxial layers.

Also, the frequencies of the optical phonons of LiBr are below the optical branches of the Si substrate: this optical-frequency mismatch contributes to confine the  $LO_n$  and  $TO_n$  modes in the film and validates our theoretical description.

We note that other experimental data can be interpreted along the same way, as, for instance, the HREELS spectra of native oxides formed on Mg(100) [17]. At high oxygen exposures corresponding to the formation of a two-layer MgO film, two surface loss peaks were observed at 660 and 550  $\text{cm}^{-1}$ . These values are close to the frequencies  $\omega_{LO_1} = 690$  and  $\omega_{LO_2} = 581 \text{ cm}^{-1}$  that can be deduced from the phonon dispersion curves of bulk MgO measured by neutron scattering [18] when applying the simple quantization rules given above. Lattice-dynamics calculations have confirmed this assignment [19]. In another closely related context, a thickness dependence of the LO frequency was observed by infrared absorption spectroscopy (IRAS) for the case of ultrathin Al oxide layers [20], and the values converged to the bulk  $\omega_{LO}$  of  $\text{Al}_2\text{O}_3$  crystal only for  $d > 4 \text{ nm}$ . These observations could reflect the dispersion of the LO branch of bulk  $\text{Al}_2\text{O}_3$  along the [111] direction, for which there exist no experimental measurements [21].

In conclusion, we have shown that the anomalous thickness dependence of the FK phonons of an ultrathin film results from the discreteness of optical modes confined in the film and is a manifestation of the dispersion of the bulk-phonon branches of the film material in the direction normal to the surface.

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