Organ-Pipe Modes of Sodium Epitaxial Multilayers on Cu(001) Observed by Inelastic Helium-Atom Scattering

G. Benedek,[a] J. Ellis, A. Reichmuth,[b] P. Ruggerone, H. Schief,[c] and J. P. Toennies
Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, D-3400 Göttingen, Germany
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Inelastic helium-atom scattering from epitaxial films (2–20 monolayers) of sodium on Cu(001) reveals a large number of nearly dispersionless phonon modes whose frequencies depend on the thickness and scale as the lower harmonics of an open-ended organ pipe. These data provide evidence for confined acoustic resonances, corresponding to longitudinal standing waves normal to the surface with frequencies about 20% larger than in the bulk.

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The surface phonons of the alkali metals, in either monocrystals or supported films, have not yet been studied because of the difficulties in surface preparation. As the simplest of metals with nearly free electrons they are of particular fundamental interest [1]. Although the knowledge of the sound velocities and elastic constants in supported ultrathin films is of high technological relevance [2], few measurements have been reported so far. We have been able to grow layer-by-layer thin epitaxial films of Na on Cu(001) and to measure by means of inelastic helium-atom scattering (HAS) the phonon dispersion curves of films with thickness varying from 1 to 30 monolayers (ML). These data provide evidence for *longitudinal acoustic (LA) resonances confined in the film,* for samples with a number of layers $2 \leq N_L \leq 20$, as well as the Rayleigh wave dispersion curves for thick layers ($N_L \geq 10$) of sodium. Within this thickness range the Na films exhibit a quasihexagonal structure, which gradually evolves for increasing N_L into a (110)-oriented bcc structure with a nearest-neighbor (nn) distance increasing from the substrate-induced value of 3.61 Å to the bulk value of 3.66 Å [3]. Our results indicate that this strain leads to a 20% stiffening of the resonance frequencies with respect to the corresponding ⟨110⟩ LA phonons in the bulk material. An even larger difference is found for the Rayleigh wave velocity along the film surface as compared to that in semi-infinite Na(110).

A HAS investigation of the surface phonon dispersion curves in epitaxially grown multilayers was first reported by Sibener and co-workers [4] for rare gases on a Ag(111) substrate, but the phenomenon presented here was not observed. The eigenmodes of a thick film supported by a stiffer substrate have also been observed by means of Brillouin spectroscopy [5,6] for parallel wave vectors Q larger than the inverse film thickness. Under this condition the eigenmodes are localized in the film, their propagation into the stiffer substrate being forbidden by the acoustic mismatch (Sezawa waves) [7]. Our results reveal that the film eigenmodes can also exist at smaller Q down to 0, even though, unlike Sezawa waves, their frequencies fall into the longitudinal band of the substrate. These modes should therefore be regarded as *resonant* standing waves within the film and are analogous to the quantum size effect seen in the electronic states perpendicular to the surface [8]. The resonance frequencies for a given thickness closely follow an *odd-integer* law like the lower harmonics of an organ pipe with a maximum at the surface and a node at the first substrate layer (*organ-pipe modes*). The only previous, albeit indirect, evidence for such behavior comes from measurements of the loss of monochromatic phonons incident on a helium film from the alkaline-earth fluoride substrate [9]. Saam and Cole [10] attributed the observations to resonances in the helium film for thickness equal to an *odd* multiple of a quarter of the acoustic wavelength in bulk liquid helium. The HAS measurements, however, are a direct evidence of these modes and they cover the range of frequency and film thickness which could not be previously investigated with the Brillouin scattering technique [5–7].

The inelastic HAS measurements have been performed with the apparatus and technique described elsewhere [11]. The incident He beam energy was $E_i = 38$ meV for $N_L = 2$–5 and was reduced to 22 meV for $N_L = 10$–30 in order to improve the resolution close to the elastic peak. The films were prepared *in situ* by evaporation of sodium from a SAES Getter source at a rate of 1 ML every 5 min onto a Cu(100) substrate at $T_s = 60$ and 140 K. The copper surface was prepared in the usual way [11] by repeated cycles of 800-eV argon-ion bombardment and annealing at 800 K. The growth of a well-defined number of multilayers was monitored by measuring the HAS specular intensity as sodium was deposited. The characteristic intensity oscillations, with maxima comparable to the clean-surface signal, indicated a good layer-by-layer growth [12].

Since the hexagonal overlayers, and the subsequent bcc (110) films, grow with one axis oriented along any of the ⟨100⟩ crystallographic directions of the squared substrate, they have two possible equivalent orientations and form in principle a domain structure. The scattering plane was chosen along a ⟨100⟩ direction of the substrate. For the hexagonal structure of the thinnest films the data are along either the $\bar{\Gamma}\bar{M}$ or $\bar{\Gamma}\bar{K}$ direction of the hexagonal

Brillouin zone. For the (110) bcc structure of the thick films the possible directions are either 35.2° ($\bar{\Gamma}\bar{S}$) or 54.8° ($\bar{\Gamma}\bar{S}'$) away from the [001] direction of the bcc (110) Brillouin zone. Actually the observation for $N_L \geq 10$ of a single, sharply defined (standard deviation $\approx 4\%$) and constant Rayleigh wave (RW) velocity indicates either a monodomain overlayer with a uniform orientation during growth, or the lack of any significant anisotropy within the instrumental resolution. The latter case may apply to the hexagonal phase, but not to bcc (110) Na, where the theoretical RW velocities are 905 m/s along $\bar{\Gamma}\bar{S}$ and 1120 m/s along $\bar{\Gamma}\bar{S}'$ [13].

In Fig. 1 we show some selected time-of-flight HAS spectra, converted to an energy-loss scale and taken at incident angles Θ_i close to the specular, for samples of various well-defined thickness (2 to 20 ML). For 2 and 3 ML the features corresponding to the Rayleigh wave of the substrate, indicated by a broken vertical bar, are still visible. For increasing $N_L \geq 10$ the peak corresponding to the Rayleigh wave of the sodium surface, indicated by a solid vertical bar, becomes more and more prominent. The simultaneous presence of both substrate and film Rayleigh waves at $N_L = 5$ indicates the transition. The other features, labeled by a fraction $(2n-1)/N_L$ ($n = 1,2,\ldots$), are associated with the confined resonances of the film. As seen in Fig. 2, where the observed phonon energies are plotted as a function of their parallel wave vector for different film thicknesses, these modes are nearly independent of Q. Their frequencies at $Q = 0$ are very well approximated by

$$\omega = [(2n-1)/N_L]\pi v_L/2a^*, \quad (1)$$

according to an open-ended organ-pipe harmonic sequence, where the prefactor $\pi v_L/2a^*$, with v_L a phase velocity and a^* an effective film interplanar spacing, is constant in a first approximation. The large resonance intensities, comparable to RW intensities especially for the thin layers and small n, indicate that their displacements are normal to the surface. Thus we interpret the $Q = 0$ modes as longitudinal standing waves normal to the surface with wave vector $q_z = \pi(n - \frac{1}{2})/d$, a maximum at the surface and a nodal plane at a distance $d = N_L a^*$ (the effective film thickness) below the surface.

Figure 2 reveals that the lowest ($n = 1$) organ-pipe branches ($\frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \frac{1}{5}, \frac{1}{10}$, etc.) cross the substrate Rayleigh branch (broken line) and approach the Rayleigh branch of the film (solid line). In fact, whenever Q becomes larger than q_z the organ-pipe modes acquire a transverse polarization and transform into either the Rayleigh wave ($n = 1$) or the Sezawa waves ($n \geq 2$). For $N_L = 2$ there is an additional low-lying flat branch at about 1.7 meV which does not fit the organ-pipe scheme. It cannot at present be assigned with certainty. Probably it is due either to interface defects originating from the interface mismatch, or to the frustrated translation modes of isolated Na atoms [14].

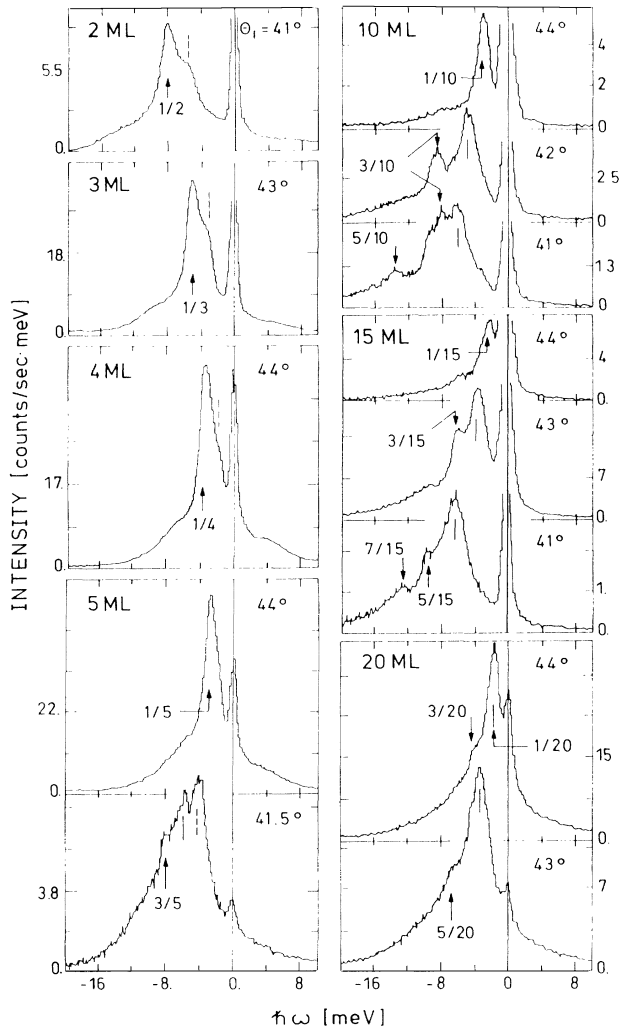

FIG. 1. Inelastic He-atom energy transfer spectra of Na ultrathin films on Cu(001) for $N_L = 2$ to 20 monolayers (ML) along a ⟨100⟩ direction of the substrate. Each fraction $(2n-1)/N_L$ labels the nth organ-pipe mode. The Rayleigh modes of the substrate (broken bar) and of the film (solid bar) are also indicated.

The plot of the experimental frequencies versus the reduced wave vector $2q_z a^*/\pi = (2n-1)/N_L$ shown in Fig. 3 gives approximately the same dispersion law for all thicknesses. The slope at small q_z yields $v_L = 4210$ m/s, which is about 20% larger than the corresponding bulk value ($v_L[110] = 3580$ m/s, from the 90-K neutron data of Wood *et al.* [15], or 3370 m/s, from Farnell's compilation of 300-K elastic constants [13]) obtained from the (110) interplanar spacing of bulk bcc Na (2.99 Å).

In order to account for the observed dispersion and to assess the origin of such a 20% stiffening in the film, we calculated the $Q = 0$ frequencies for waves propagating normal to the surface for a Na slab with one nn interplanar radial force constant f and another force constant f_0 linking the slab to a rigid substrate. By using the value

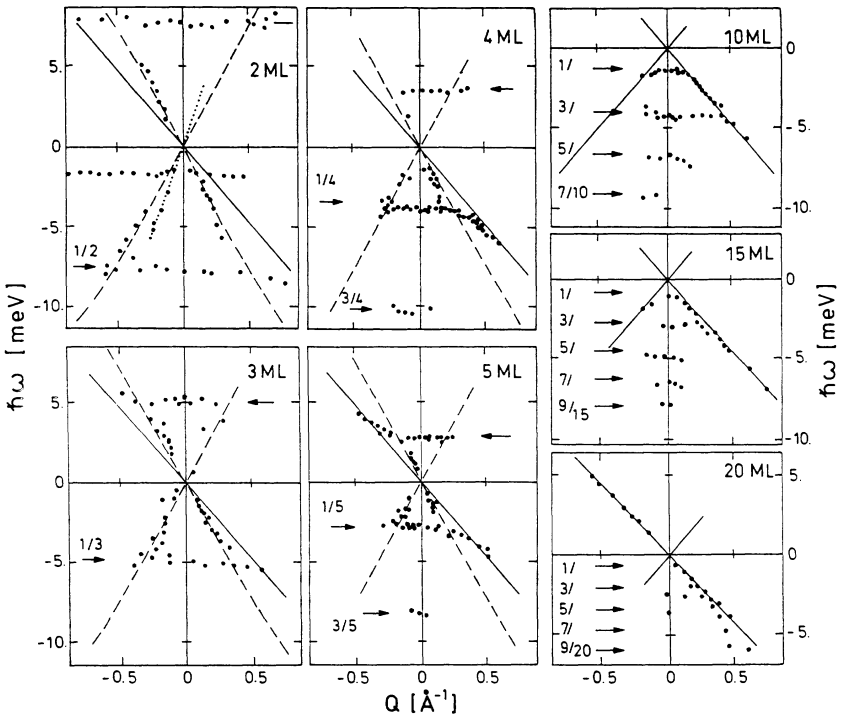

FIG. 2. Measured dispersion curves of Na films (2 to 20 ML) on Cu(001). The arrows indicate the theoretical positions of the organ-pipe modes. The directions of the Rayleigh wave branches in the film (solid line) and in the substrate (broken line) are also shown. For 2 ML a few points correspond to the longitudinal resonance of the substrate (dotted line).

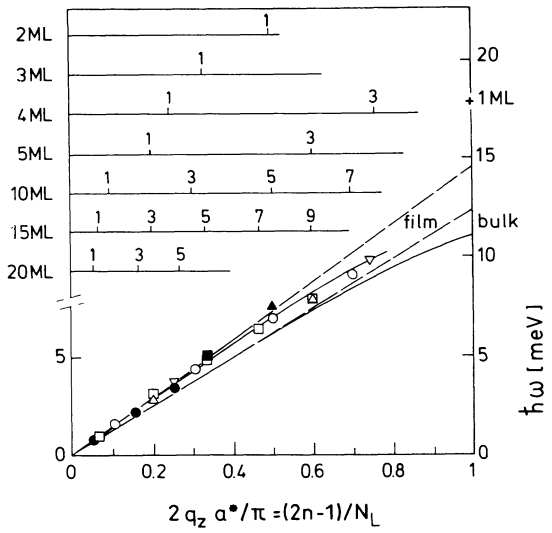

FIG. 3. The dispersion curve of the $Q=0$ organ-pipe modes as function of the reduced wave vector normal to the surface. Different symbols correspond to different thicknesses, as indicated by the above "keyboard." The corresponding monolayer frequency (+) is also given [14]. The dispersion along [110] of the longitudinal mode in bulk sodium (Ref. [15]) is shown for comparison (solid line). The broken straight lines give the slopes at $q_z=0$.

$f_0=28.0$ N/m fitted to the monolayer frequency [14] (17.8 meV), we obtained a very good fit of all the $Q=0$ organ-pipe frequencies with the same film force constant $f=6.6$ N/m for all thicknesses. The calculated values are shown by arrows in Fig. 2. This value of f can be directly compared with the bulk value of $f=5.5$ N/m derived by Wood *et al.* from neutron data [15]. Since another calculation with f_0 also equal to 6.6 N/m gives frequencies (e.g., for $N_L=10$) which are still about 10% stiffer than bulk values, we conclude that the 20% increase of v_L/a^* receives comparable contributions from the coupling to a stiffer substrate and from an intrinsic stiffening within the slab, presumably due to the more compact hexagonal structure.

The Rayleigh wave velocity measured in the thicker films ($N_L=10$–30), $v_R=1360\pm40$ m/s, is also considerably larger (21% or 50%) than predicted for the Na(110) surface in either the $\bar{\Gamma}\bar{S}$ or $\bar{\Gamma}\bar{S}'$ directions [13]. Surprisingly, the Rayleigh wave velocity appears to be independent of the film thickness, even at wavelengths greater than the thickness. Another apparent anomaly of our organ-pipe modes is their negligible Q dependence. This is in disagreement with the pronounced dispersion observed for 3 ML of Kr on Ag(111) [4], but is what one expects for a layered crystal such as graphite [16].

In conclusion, we have presented the first determina-

tion of confined resonances in ultrathin solid films, demonstrating that HAS phonon spectroscopy is not exclusively limited to phonons in the surface plane. The present resolution of HAS is such to provide information on the elastic properties of ultrathin films on the microscopic scale, presently inaccessible to Brillouin scattering. Future HAS investigations should consider the deviations from the regular organ-pipe sequence in order to derive the actual interplanar force constants at different depths. This would be useful for a layer-by-layer assessment of the relaxation and of Friedel oscillations. The recent demonstration that HAS has enough resolution to probe the effects of surface magnetization on the surface phonon frequencies [17] suggests further studies on the organ-pipe modes in thin magnetic layers.

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[a]Present address: Cavendish Laboratory, Madingley Road, Cambridge, CB30HE, United Kingdom.

[b]Permanent address: Dipartimento di Fisica dell'Università di Milano, via Celoria 16, 20133 Milano, Italy.

[c]Present address: Ecole Politecnique Federale, 1015 Lausanne, Switzerland.

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