Phonons in a quasi-two-dimensional solid: Cesium monolayer on Cu(001)

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The phonon dispersion curves of a well-ordered Cs monolayer epitaxially grown on Cu(001) were measured over the entire Brillouin zone using high-resolution He atom scattering. In addition to the Rayleigh mode an additional perpendicular resonance near the $\bar{\Gamma}$ point and a longitudinal film mode were observed. The appearance of a distinct longitudinal mode, which was not observed for the corresponding monolayer films of Na or K, is attributed to the small interface corrugation seen by the Cs atoms and the phonon velocity mismatch between the film and substrate. Thus the lateral motion of the film is effectively decoupled from the substrate and reveals a quasi-two-dimensional phonon behavior.

Whereas the spectroscopy of molecular normal modes provides a direct way to obtain information on the interatomic forces in molecules the corresponding analysis for solids is rather indirect since the phonon modes involve collective displacements of many atoms and depend on the phonon wave length. Only at the Brillouin zone boundary are the phonon energies directly related to the nearest neighbor interactions. Information on the force field at interfaces can be obtained from an analysis of interface induced phonon modes such as surface phonons[1] or confined interface phonons in periodic super lattices.[2] However, since the corresponding displacement patterns of these modes decay exponentially with the distance from the interface proportional to the wave length they are strictly localized at the interface only in the limit of short wavelengths.

Other localized phonon modes are found for ultrathin films of rare gases as reported by Gibson and Sibener for Xe on Ag(111).[3] Because of the weak lateral interactions the perpendicular mode is without any dispersion. For thicker films several modes appear, which were identified as phonon modes in a rare gas slab,[4] and hence demonstrate the transition from a two-dimensional (2D) system to the surface of a 3D system. In later studies the entire dispersion curves of the Rayleigh mode and the longitudinal mode have also been measured for a Xe monolayer on all the low index copper surfaces.[5–8] The additional observation of the shear horizontal mode for Ar, Kr, and Xe monolayers on Pt(111) as recently reported[9] allows a detailed analysis of lateral interactions in this 2D system.

Surprisingly, localized phonon modes in ultrathin metal films have not yet been observed. Instead the experiments on thin metal film dynamics which were carried out for a number of systems such like Fe/Cu(001),[10] Co/Cu(001),[11] Ni/Cu(001),[12] Pb/Cu(111),[13] and Ni/C(001) (Ref. 14) reveal basically a modified substrate Rayleigh mode. Only in the case of thin alkali metal multilayer films unexpected vibrational properties appear which were observed for epitaxially grown Na films on Cu(001) by Benedek *et al.*[15] and which were later also found for K and Cs films.[16] Due to the large impedance mismatch between the soft alkali metals and the substrate these films can support standing waves with longitudinal polarization directed along the film normal.[17]

In the present He atom scattering (HAS) study of a Cs monolayer epitaxially grown on Cu(001) three phonon film modes—the Rayleigh mode, a longitudinal film mode, and a perpendicular resonance—were observed. Since the longitudinal vibrations are found to be decoupled from the substrate the quasi-2D monolayer phonons provide direct information on the interatomic forces within the metal monolayer.

The HAS apparatus (base pressure 1×10^{-10} mbar) is described in detail elsewhere.[18] After cleaning the Cu(001) substrate by cycles of Ar$^+$-ion sputtering and annealing to 950 K the films were prepared *in situ* by evaporation of cesium from SAES getter dispensers at a rate of 0.2–0.4 ML per minute at a surface temperature of 100 K. The cleanliness of the substrate and the films was checked by x-ray photoelectron spectroscopy. Growth was monitored by measuring the HAS specular intensity during Cs deposition. The characteristic intensity maxima, which appear upon completion of each monolayer[16] reflect a *layer-by-layer* growth mode, so that a single monolayer film could be grown. After annealing at 250 K the intensity and width of the He specular peak was almost identical to that obtained for the clean Cu(001) surface indicating a monolayer film with a small defect density. Due to the weak localization of their valence electrons alkali metal surfaces reveal an extremely small surface corrugation[19] and in the case of the Cs monolayer no He atom diffraction peaks could be detected within the large sensitivity range of the current apparatus of $I_{spec}/I_{min} \approx 10^6$. Therefore the lateral structure of the Cs monolayer had to be characterized by low energy electron diffraction (LEED) which confirmed the structure proposed previously by Cousty *et al.*[20] As shown in Fig. 1(a) Cs forms a quasihexagonal monolayer oriented with its closed packed rows parallel to the $\langle 110 \rangle$ surface directions of the Cu(001) substrate in two domains rotated by 90° against each other. For each domain the Cs-Cs distance along this epitaxial direction amounts to 5.1 Å whereas along the other direction the Cs-Cs bond length is contracted to about 4.8 Å.

The inelastic HAS measurements were performed along the two high symmetry substrate azimuths [100] and [1$\bar{1}$0]. Figure 2 shows some typical time-of-flight (TOF) spectra converted to an energy scale recorded at five angles of incidence. For both directions two well separated sharp energy loss peaks (labeled R and L) and a broad feature (labeled P) were observed.
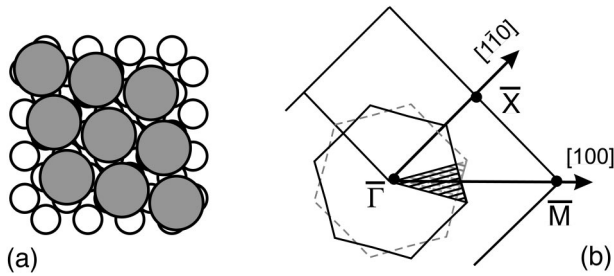
FIG. 1. (a) Structure model for the Cs monolayer on Cu(001) as proposed by Cousty *et al.* (Ref. 20). The actual Cs layer (gray balls) consists of two domains rotated by 90° against each other. (b) Corresponding surface Brillouin zones of the two rotated Cs domains (solid and dashed hexagons) and their orientation relative to the Brillouin zone of the copper substrate. Note that the substrate [100] direction is equivalent for both Cs domains.

Figure 3(a) summarizes the energy and momentum transfer of all the energy loss peaks obtained from over 40 TOF measurements. As shown below in connection with a lattice dynamical calculation the two film modes which extend over the entire Brillouin zone are assigned to the Rayleigh mode (R) and the longitudinal mode (L) with zone boundary energies of about 6 and 5 meV, respectively. Since along the [100] direction the azimuths of both Cs domains coincide as shown in Fig. 1(b) the presence of two phonon modes cannot be caused by the domains but, rather reflects the existence of two different phonon modes. Compared to the [100] direction the observed energy loss peaks are somewhat broader along the [1$\bar{1}$0] direction since in this case somewhat different azimuths of the two domains are measured simultaneously. Upon an increase of the sample temperature from 100 to 200 K a strong decrease of the (incoherent) elastic peak in the TOF spectra was obtained (see Fig. 2). This reflects the small Debye temperature ($\theta_D = 113$ K) of the soft alkali metal films[21] which limits the present measurements to low surface temperatures.

The additional broad energy loss peak P at about 7 meV observed for both azimuth directions is assigned to a perpendicular mode since it appears only for wave vectors close to the Brillouin zone center (see Fig. 3) where the momentum transfer normal to the surface is greatest. Such an assignment is further supported by EELS measurements of the Cs-Cu stretch mode for which an energy of $\hbar\omega_S \approx 6.5$ meV was obtained for submonolayer coverages of Cs on Cu(111).[22]

The theoretical analysis of the lattice dynamics of ultra thin noble gas layers, first introduced by Rouffignac *et al.*,[23] predicts that the longitudinal mode is expected to have a gap at the Brillouin zone center if the film forms a commensurate superstructure. In fact such a gap at the $\bar{\Gamma}$ point has been observed recently for a monolayer of Xe on Cu(111).[8] A careful inspection of the present phonon dispersion curves, however, revealed no evidence for a gap at the Brillouin zone center within the energy resolution of 0.2 meV. This can be understood in terms of the large difference between the lateral spacing of the Cs atoms (≥ 4.8 Å) compared to the copper surface (2.55 Å). Moreover, at the large distance of the film with respect to the substrate surface of about 3 Å (Ref. 24) the Cs atoms experience virtually no lateral corru-
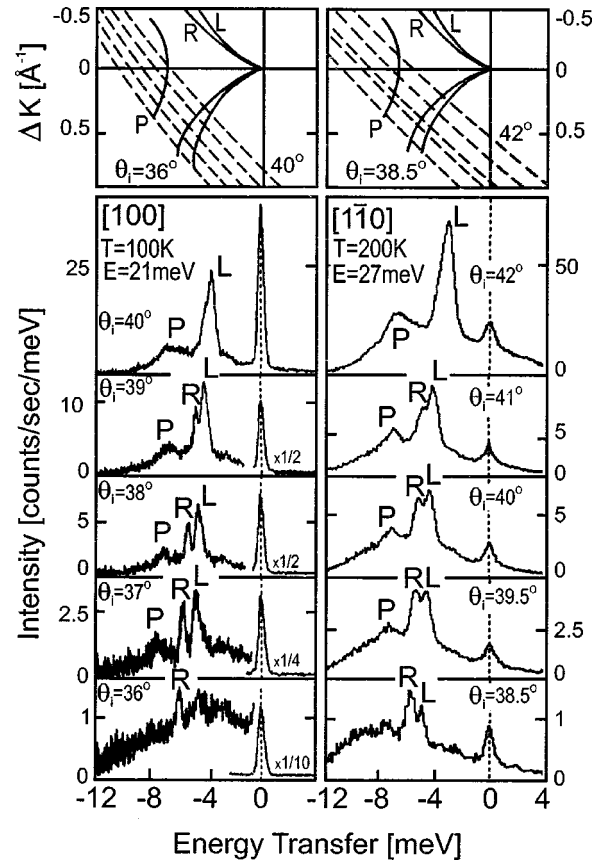

FIG. 2. A series of He-atom time-of-flight (TOF) spectra (converted to an energy transfer scale) for a Cs monolayer on a Cu(001) surface taken along the [100] and [1$\bar{1}$0] directions. The surface temperatures and beam energies were 100 K, 21 meV, and 200 K and 27 eV, respectively. In the top panels the regions covered by the displayed TOF spectra are shown in the $\Delta K - \Delta E$ plane (so-called scan curves). The energy loss peaks are identified by R (Rayleigh mode), L (longitudinal mode), and P (perpendicular resonance).

gation from the substrate as expected from measurements of the frustrated translation mode of isolated Cs atoms on the Cu(001) surface.[25]

When exceeding the Cs coverage slightly above the first monolayer an entirely different behavior was observed. Instead of the Rayleigh mode and the longitudinal mode characteristic nondispersive phonon modes at energies of $\hbar\omega = 2.3$, 1.4, and 1.0 meV appear for films of 2, 3, and 4 ML thickness, respectively. These so-called *organ pipe* modes were previously found for various alkali multilayer films[15,16] and correspond to longitudinal standing waves normal to the surface. A theoretical analysis[17] yielded a power law for the energy dependence of such modes on the number N of layers: $\omega(N) = \omega(1)N^{-\gamma}$. From a fit to the experimental data, values of $\gamma = 1.2 \pm 0.05$ and $\hbar\omega(1) = 5.4 \pm 0.5$ meV were determined. The energy of the fundamental vibration $\hbar\omega(1)$ is in fairly good agreement with the EELS Cs-Cu stretch frequency $\hbar\omega_S = 6.5$ meV and the perpendicular film frequency $\hbar\omega_P \simeq 7$ meV indicating only a small variation of the substrate interaction over a wide range of coverages.

A lattice dynamical analysis was used to identify the phonon mode polarization and the interaction strength within the film. The high desorption temperature of about $T_D \gtrsim 530$ K
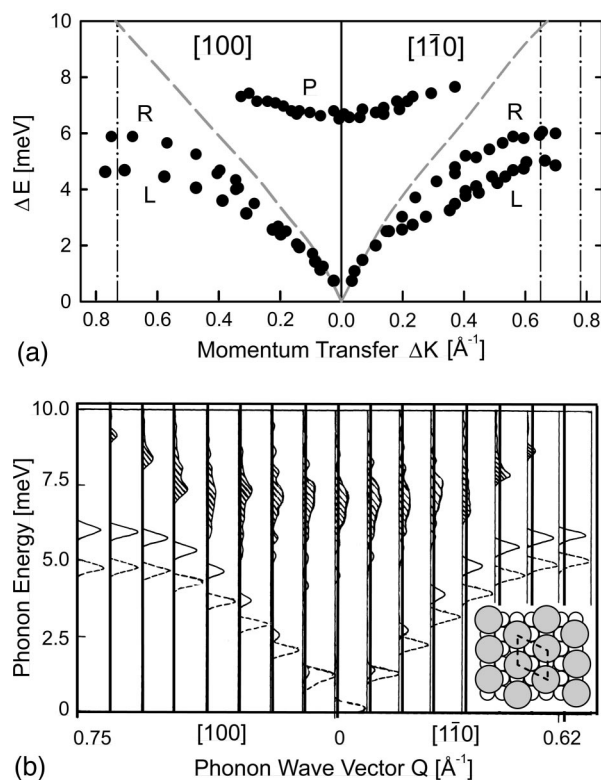
FIG. 3. (a) Measured phonon dispersion curves of a Cs monolayer along the [100] and [1̄10] directions. L and R denote the longitudinal and Rayleigh mode, respectively, and P the perpendicular resonance. The dashed-dotted lines indicate the Brillouin zone boundaries for the two domains of the Cs film and the gray dashed line shows the Rayleigh phonon curve of the undisturbed bare copper surface. (b) The phonon density of states of the Cs atoms calculated from a best fit of the measured dispersion curves for a $c(4 \times 2)$Cs overlayer on Cu(001) (shown in the inset). The calculated vibrational frequency spectrum has been convoluted by a Gaussian of 0.25 meV FWHM. The solid and dashed lines represent displacements perpendicular and parallel to the surface.

for the Cs monolayer using HAS specular reflectivity for detection indicates a vertical binding energy of $E_B \simeq 1.7$ eV to the copper substrate.[26] This strong binding and especially the smaller phonon velocity of the soft but dense Cs film compared to the substrate[27] leads to a ''loading'' of the substrate vibrations[28] so that most of the dynamical motion is concentrated in the layer. To account for the coupling with the substrate a lattice dynamical calculation was performed for a 37 layer slab (35 substrate layers with one Cs layer on each side) using only nearest neighbor radial (β) and tangential (α) force constants, defined by the derivatives of the pair potential with respect to the distances R, $\beta = V''(R)$, and $\alpha = V'(R)/R$. The Cs film was modeled by a $c(4 \times 2)$ superstructure. Because of the negligible lateral corrugation of the substrate holding potential[25] (as discussed above) no tangential force constants were considered for the Cs-Cu interac-

tion. From the measured perpendicular resonance at the $\bar{\Gamma}$ point a force constant of $\beta_{Cs\text{-}Cu} = 55.0$ N/m was determined and the copper substrate was described by a single effective radial force constant of $\beta_{Cu\text{-}Cu} = 28.0$ N/m.[29] To reproduce the measured dispersion curves only the radial Cs-Cs force constant was varied and a value of $\beta_{Cs\text{-}Cs} = 2.2$ N/m was found to provide an excellent fit for both, the Rayleigh mode and the longitudinal mode as displayed in Fig. 3(b).

To compare the Cs interaction in the film with the bulk an effective radial bulk force constant (neglecting α) was determined from a fit to the Cs bulk phonon dispersion curves[30] which yields a value of $\beta_{bulk} = 1.75$ N/m. This indicates a stiffening of the lateral interaction in the film of about 25% which is not unexpected since the nearest neighbor distance in the film is reduced compared to the bulk ($d = 5.24$ Å).

A closer inspection of the displacement patterns for the various phonon modes indicates that the longitudinal mode is strictly localized in the Cs monolayer whereas the Rayleigh mode involves a substantial displacement of the copper substrate atoms. Such a mode mixing with the bulk phonon band is even more pronounced for the perpendicular resonance which results in a broad density of states [shown as the hatched area in Fig. 3(b)].

Attempts to measure corresponding film modes for a monolayer of Na or K on Cu(001) have not been successful. Instead only the Rayleigh modes of the substrate with a slightly reduced frequency due to mass loading, but no longitudinal film mode, were observed. The corresponding slab calculations indicate that due to the reduced mass of these alkali metal atoms their longitudinal film mode shifts towards higher energies and degenerates with the substrate phonon bulk bands.

Since Xe and Cs are very similar in size and mass it is interesting to compare the phonon dynamics of a monolayer for both systems. Whereas in the case of the Xe monolayer on Cu(001) only very weak energy loss peaks were obtained for the longitudinal mode[7] they are anomalous intense for the Cs film over the entire Brillouin zone (see Fig. 2). On the other hand the Xe film has a substantial corrugation leading to intense He-atom diffraction in contrast to the smooth alkali metal surfaces[19] for which no diffraction has been observed. Such an electronic smoothing of the surface in connection with an enhanced excitation probability of the longitudinal surface phonon mode was observed previously also for the bare Cu(001) surface[31] and was explained by a pseudocharge model in which the impact induced distortions of the electron gas are transferred to the phonons.[32] Since for the present system the longitudinal mode is a pure film mode a more elaborate lattice dynamical scattering analysis within the framework of the pseudocharge model would be desirable in order to get detailed information about the lateral interaction in this metallic quasi-2D phonon system.

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