Surface Phonons on Stepped Pt(111) Surfaces

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The experimental observation phonons localized to step edges on platinum $6(111)\times(11\bar{1})$ surfaces is reported. Their frequency is *above* the maximum frequency of the bulk phonon spectrum.

Surface phonons, i.e., phonons with the amplitude of vibration localized to atoms near the surface of a material, have been considered in the theory of lattice dynamics for some time.[1-3] Low-frequency acoustic surface waves on solids (Rayleigh waves) even have become a matter of some technical relevance.[4] In the high-frequency regime the only surface phonons accessible to experimental observations so far were the Fuchs-Kliewer surface phonons[5] on ionic crystals.[6-8] These optical surface phonons are nonradiative polarization waves in a dielectric material with the geometry of a slab or semi-infinite half-space. They are analogous to the surface plasmons of a free-electron gas. As the typical decay length of the amplitude of vibration for Fuchs-Kliewer phonons is $\sim q_{\parallel}^{-1}$ ($q_{\parallel}$ being the wave vector parallel to the surface) their frequency is insensitive to the specific physical properties of the outermost surface layer for the small $q_{\parallel}$ accessible in the experiment.[6-8]

In this Letter we report the first experimental observation of surface phonons reflecting truly microscopic properties of the surface. The phonons are associated with the step atoms of a clean stepped Pt$[6(111)\times(11\bar{1})]$ surface. Evidence for the surface character of the phonons is provided by the following observations: (i) The frequency of the surface phonons is above the maximum frequency of the bulk spectrum. (2) *In situ* comparison to a flat Pt(111) surface shows no evidence for the phonons on the flat surface. (3) Small amounts of CO adsorbed on the step atoms shift the frequency substantially.

The experimental technique used in the experiments is electron-energy-loss spectroscopy (EELS).[9] In previous studies using this technique the observation of characteristic losses was limited to frequencies above $\hbar\omega \sim 300$ cm^{-1} (37 meV) due to the lack of resolution and high background intensity in the vicinity of the elastically reflected beam. Lattice phonons on metal surfaces therefore could not be observed. In this study we employ a more advanced version of a single-pass electron spectrometer with cylindrical condensers as energy-dispersing elements. For this spectrometer the background intensity is less than 10^{-3} of the no-loss intensity for losses above $\hbar\omega = 150$ cm^{-1} (18.5 meV).

For an *in situ* comparison of a flat and a stepped surface two crystals with different orientations were mounted on the manipulator. The crystals were cut by spark erosion from single-crystal rod after Laue orientation to a precision of ± 0.5° The crystals were cleaned in ultrahigh vacuum by oxygen treatment and annealing to high temperatures by standard procedures which have been controlled using Auger and LEED (low-energy electron diffraction) analysis. The EELS spectra were recorded in specular reflection with a primary energy of 6 eV at an angle of incidence of 70° from the normal. Typical results for the clean surfaces are shown in the upper panel of Fig. 1. The dotted line represents the flat surface and characterizes also the background due to the tail of the elastically reflected electrons. The spectrum of the stepped $6(111)\times(11\bar{1})$ surface shows a characteristic loss with a maximum at 205 cm^{-1}. This loss was found to be extremely sensitive to contamination. Even at pressures of 10^{-10} Torr only a few minutes of observation were available. The spectra were therefore recorded immediately after flashing with the sample temperature still considerable above room temperature ($T \sim 500$ K). The additional small losses in the spectrum are due to beginning CO contamination and represent a fractional coverage of ~ 0.001. Other common components of a UHV residual gas like H_2, CO_2, CH_4, and H_2O do not adsorb on Pt at this temperature. From a previous study of CO adsorption on the same stepped surface where EELS spectra and flash-desorption spectra were compared it was learned that up to exposures of ~ 0.4 L (1 L = 10^{-6} Torr sec), CO adsorbs on top of the step atoms.[10] We therefore purposely dosed the sample with CO. A typical example referring to an exposure of ~ 0.1 L of CO is shown in the lower panel of Fig. 1. Here the phonon loss is substantially changed and the metal-carbon vibration (370 cm^{-1}) and the CO-stretching vibration (2050 cm^{-1}) are observed in addition. We estimate the amount of adsorbed CO by

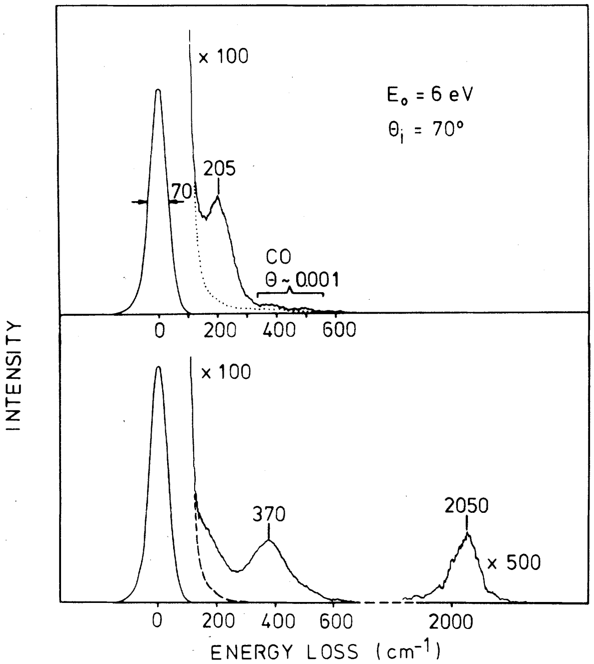

FIG. 1. Upper panel: EELS spectrum of a "clean" stepped Pt[6(111)×(11$\bar{1}$)] surface. The dotted line is the spectrum of the flat surface when the elastic intensity is scaled to the stepped surface. Lower panel: Spectrum after dosing with 0.1 L of CO.

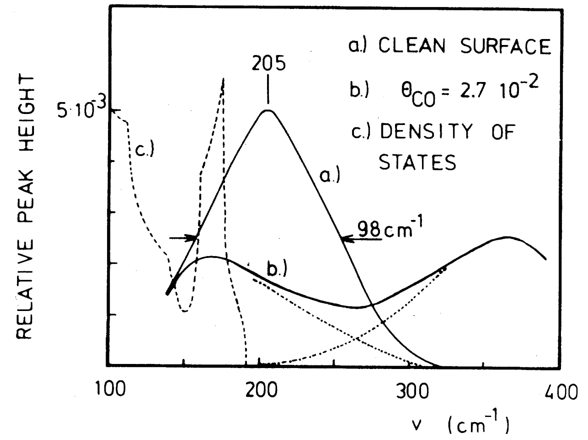

FIG. 2. Loss spectra of the clean and CO-dosed stepped surface. The bulk density of states is shown for comparison.

two considerations. (i) Assuming a sticking coefficient of 1 we calculate an upper limit of 3.8 $\times 10^{13}$ cm^{-2} CO surface molecules. (ii) The amount of CO adsorbed at 0.1 L relative to the saturation exposure may be calculated from flash-desorption traces.[10] With a saturation coverage of 7.5 $\times 10^{14}$ cm^{-2} we obtain a coverage 4×10^{13} cm^{-2}. As this amount of CO is adsorbed on the step atoms the fractional coverage of the atoms on the step edges is 0.16. Higher CO exposures up to 0.4 L corresponding to fractional step-atom coverages of 0.5 did not alter the spectrum except for an increase in the CO losses.

For the purpose of further discussion we have replotted the phonon losses on an enlarged scale after subtracting the background as observed on the flat surface (Fig. 2). We also show the bulk-phonon density of states as calculated by Dutton, Brockhouse, and Miller.[11] As seen from Fig. 2 the maximum of the surface-phonon loss is well above the maximum bulk frequency and even more above the frequency regime where the bulk density of states peaks. The half-width of the phonon loss is about 28 cm^{-1} larger than the half-width of the specularly reflected beam. After CO exposure, the intensity of the phonon losses is depleted in the high-frequency range and now peaks where the bulk density of states is high.

Prior to a more detailed discussion of these results some consideration must be paid to the mechanism of the electron-phonon interaction. The intensity of the phonon losses was found to have the angular dependence of the elastic intensity when moving the analyzer out of the specular position. This is indicative of a dipole scattering mechanism.[12,13] The phonon losses in Fig. 2 are therefore caused by phonons near the center of the surface Brillouin zone. Apparently the necessary dipole moment is provided by the step atoms. We note that step atoms contribute a considerable static dipole moment as well which is observed as a reduction in the work function of stepped surfaces[14] {−0.4 eV for the Pt[6(111) ×(11$\bar{1}$)] surface}. The theory of Evans and Mills[12] allows us to calculate the effective ionic charge characterizing the dipole moment of surface phonons from the intensity of the loss relative to the specularly reflected intensity. If we assume that the edge atoms only carry the effective charge we calculate $e^* = 0.45e \pm 0.1e$ per edge atom, which is somewhat larger than the static ionic charge of 0.2e calculated from the work-function change.[14] These numbers are an upper estimate as more atoms than the edge atoms vibrate and contribute to the dipole moment of the phonon. While the dynamic effective charge of the step atoms provides a coupling mechanism to surface phonons it provides also coupling to all those bulk phonons with which the dipole-active step atoms move in phase. This condition is fulfilled for six different wave vectors parallel to the surface and arbitrary $q_\perp$. Energy losses due to bulk phonons therefore should resemble closely the density of states. We believe that this effect causes the observed loss spectrum in the case where the step atoms bind CO molecules (Fig. 2).

A very puzzling aspect of the results is the fact that the surface phonon has a higher frequency of vibration than all bulk phonons which is at variance with the common belief. While a theory of surface phonons associated with step edges is not available the implications of this effect may be elucidated with the help of the simple model of a monoatomic linear chain with nearest-neighbor interactions. In this model no localized surface vibration exists unless the force constant between the surface atom and the next atom is 33% higher than the bulk coupling constant. When we apply this simple model to the platinum case we calculate the force constant for the edge atoms to be 1.7 times the bulk force constant.[1] Therefore the observation of a surface phonon as high as reported here is indicative of very substantial increase in the force constants for the edge atoms. It suggests a major rearrangement in the electronic configuration of edge atoms possibly connected with a geometric contraction in order to maintain a high binding energy with the seven nearest neighbors. This indeed could give rise to a change in the force constants by a factor $12/7=1.71$ just as estimated from the experimental data. Once CO is adsorbed on the platinum step atoms the force constant should relax to the bulk value which is consistent with the observed depletion of the loss intensity around 205 cm^{-1}. As seen from Fig. 2, however (and also for higher coverages, there is still some loss intensity above the bulk phonon range when CO is adsorbed. This may be correlated to the fact that the CO adsorption on the step atoms saturates at a fractional coverage of 0.5 for steric reasons.

The linear-chain model also allows up to make a rough estimate of the degree of localization of the phonon to the step edges. Assuming the force constants as calculated from the frequency shift, the atom in the second layer of the linear chain has a mean-square amplitude of vibration of $\sim e^{-2}$ of the surface atom. Thus the degree of localization should be rather high and the phonons reported here may therefore be considered as edge phonons.

Finally we note that the observation of edge phonons and the depletion of their intensity with exposure to an adsorbate seems to provide a very elegant method for determining whether the adsorbate is adsorbed at the steps or on the terraces.

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