

Phonon dispersion measurements and first-principles calculations for the Au(110) surface

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(Received 24 July 1989)

We have measured the dispersion of surface phonons on the (1×2) reconstructed Au(110) surface along the high-symmetry directions using momentum resolved electron-energy-loss spectroscopy. The frequencies of surface modes at high-symmetry points of the surface Brillouin zone have been calculated with force constants determined from first-principles self-consistent total-energy calculations and are in excellent agreement with the experimental data. "Glue-model" calculations which predicted an experimentally not observed dipole active mode peeling off the top of the bulk phonon band seem to overestimate the bonding strength of atoms near the surface.

The clean (110) surface of Au undergoes a (1×2) reconstruction. The structure of this surface has been the subject of extensive investigations using different experimental techniques.¹⁻⁹ All experiments favor the missing row model, i.e., every other row of Au atoms along $[110]$ is missing. Concerning the surface relaxation, however, glancing-incidence x-ray diffraction² and high-resolution electron microscopy³ experiments suggested an outward relaxation of the first layer whereas, on the other hand, the results of low-energy electron-diffraction¹ (LEED), ion-scattering,^{4,5} and He-diffraction experiments⁶ indicated a contraction of the top interlayer spacing. Recent reanalysis of this system with electron microscopy⁸ and with x-ray diffraction⁹ now also indicates a contraction. So the controversy as to the direction of the relaxation seems to have been settled in favor of an $\sim 18\%$ contraction between the first and second layers. This is also in good agreement with recent first-principles calculations.¹⁰

The reconstruction, the very open surface structure, and the large contraction should have a major influence on the surface-phonon modes. Qualitatively, one may distinguish two different effects. On the one hand, the smaller coordination at the surface should lead to a reduction of the bonding strength of surface atoms, and hence, the surface-phonon modes peel off the bottom of the bulk phonon band. The Rayleigh phonon is the classical example. On the other hand, the large contraction between the first and second layers should lead to an increase in the bonding strength at the surface which gives rise to an enhanced frequency of the Rayleigh mode at the zone boundary or even result in new surface modes above the top of the bulk phonon band. Examples for such modes are phonons localized at step edges.¹¹ A recent molecular-dynamics study¹² of the Au(110) surface predicted also high-frequency modes above the top of the bulk phonon band. The interaction potential was constructed by a phenome-

nological many-body force scheme called the "glue-model," which is very similar to the embedded-atom method.¹³ Experimentally the surface-phonon dispersion was measured so far only by He scattering.¹⁴ The high-frequency modes predicted by the glue model were, however, not accessible to this method.

Here, we report on electron-energy-loss spectroscopy (EELS) measurements and on first-principles calculations of the surface phonons on the (1×2) reconstructed Au(110) surface and find good agreement between theory and experiment. Both experiment and the first-principles calculations exclude the high-frequency modes above the bulk phonon band predicted by the glue model.

The sample was cleaned by repeated cycles of Ne-ion sputtering and heating to 900 K. After final annealing ~ 1 h at 450 K we observed the sharpest (1×2) LEED structure. Auger-electron spectroscopy (AES) and also EELS spectra showed no traces of surface contaminations. Phonon spectra were recorded using high-resolution EELS. Spectra were recorded at different impact energies and scattering angles to selectively tune into high scattering cross sections for the different phonon modes. The energy resolution in the reflected beam was set to 23–28 cm^{-1} full width at half maximum. We measured the phonon dispersion along the $[001]$ ($\bar{\Gamma}\bar{Y}$) and the $[\bar{1}10]$ ($\bar{\Gamma}\bar{X}$) azimuth. Sample spectra are shown in Fig. 1 and the complete dispersion is displayed in Fig. 2. The diffuse elastic intensity for the scattering plane along $[001]$ (suppressed in Fig. 1) is rather high compared to the diffuse elastic intensity along $[\bar{1}10]$ directions. This is caused by a one-dimensional disorder perpendicular to the chain orientation. This disorder was also observed before in scanning tunneling microscopy (Ref. 7), LEED (Ref. 1), and x-ray diffraction² experiments.

As shown in Figs. 1 and 2 (solid circles), we observe three surface-phonon modes. Along the $\bar{\Gamma}\bar{X}$ direction the

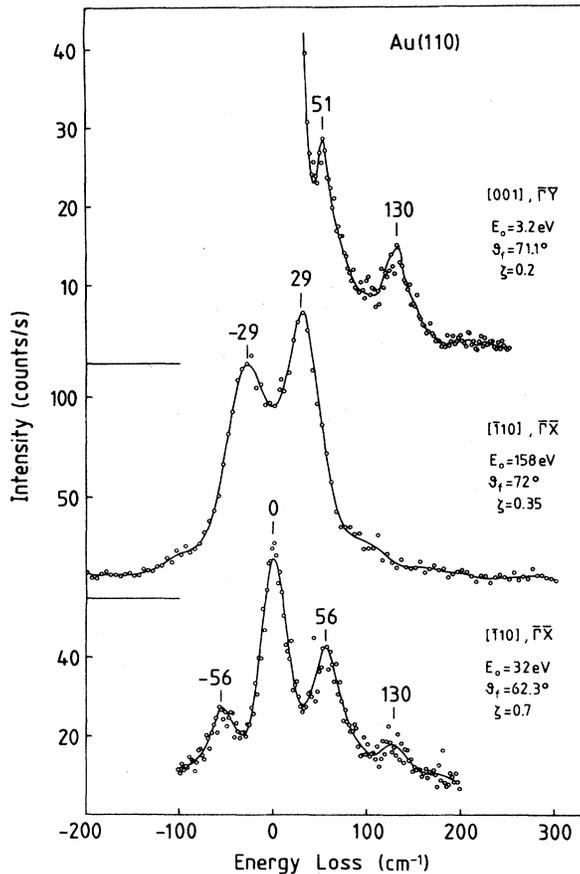


FIG. 1. Sample spectra with the scattering plane aligned along [001] ($\bar{\Gamma}$ - \bar{Y}) and $[\bar{1}10]$ ($\bar{\Gamma}$ - \bar{X}) directions, respectively. ζ is the wave vector in reduced units, where $\zeta=1$ refers to the Brillouin-zone boundary.

Rayleigh phonon runs up to a frequency of 56 cm^{-1} at \bar{X} (at room temperature). At $\sim 50 \text{ cm}^{-1}$ we measure a rather dispersionless surface resonance in both directions. This resonance arises due to a "backfolding" of the Brillouin zone on the reconstructed surface (inset in Fig. 2). Along [001] this mode originates from a mode near \bar{Y}' on the unreconstructed surface [$S_3(\bar{Y}')$]. This mode is vertically polarized at \bar{Y}' and has been observed on several (110) surfaces.¹⁵ Because of the reconstruction the mode is folded back to the $\bar{\Gamma}$ point of the reconstructed surface and appears as a resonance mode there. Because of the reconstruction the \bar{Y}' - \bar{S}' direction of the reciprocal space is also folded onto the $\bar{\Gamma}$ - \bar{X} direction. Since the above-mentioned mode near \bar{Y}' exists all the way along the \bar{Y}' - \bar{S}' direction on the unreconstructed surface the backfolding causes the resonance near 50 cm^{-1} along $\bar{\Gamma}$ - \bar{X} . Furthermore, we observe along the $\bar{\Gamma}$ - \bar{X} and $\bar{\Gamma}$ - \bar{Y} directions a surface resonance between 125 and 145 cm^{-1} . The data points show a large energy spread depending on the scattering conditions used. Measurements at room temperature and at 100 K resulted in the same frequency values within the experimental error. Despite extensive searching a surface phonon above the bulk phonon band (above 157 cm^{-1}) was not observed in the whole course

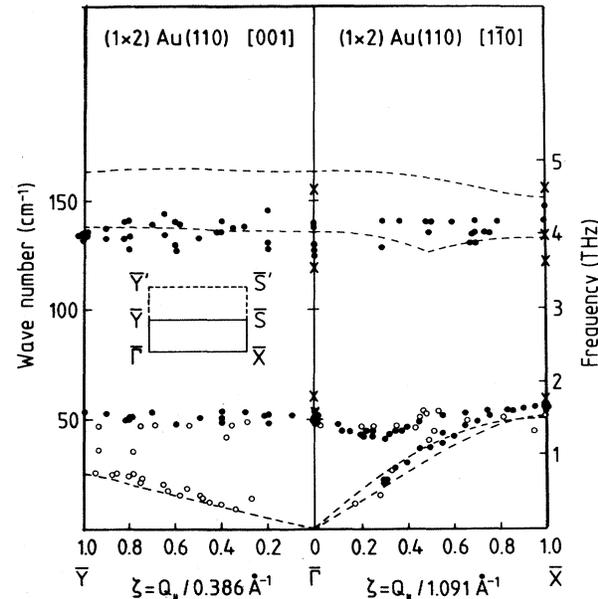


FIG. 2. Phonon dispersion of the (1×2) reconstructed gold surface along $\bar{\Gamma}$ - \bar{X} and $\bar{\Gamma}$ - \bar{Y} directions. Our EELS results (filled circles) and first-principle calculations (crosses at $\bar{\Gamma}$ and \bar{X}) are compared to He scattering data (open circles) and glue-model calculations (dashed curves).

of experiments and can be excluded. The two observed surface resonances (around 50 and 135 cm^{-1}) are not dipole active.

It is interesting to compare these results with the He-scattering data¹⁴ (open circles in Fig. 2). In the energy range accessible to both methods, the Rayleigh phonon (along $\bar{\Gamma}$ - \bar{X}) and the mode at $\sim 50 \text{ cm}^{-1}$ are in good agreement. Even the small dip of the $\sim 50\text{-cm}^{-1}$ mode along $\bar{\Gamma}$ - \bar{X} around $\zeta=0.3$ is consistently measured by He scattering and EELS. Further on we can see the complementary capacities of both methods: He scattering resolves also the Rayleigh phonon along the $\bar{\Gamma}$ - \bar{Y} direction because of its better energy resolution, whereas EELS has access to the high-frequency mode at $\sim 135 \text{ cm}^{-1}$ which will be essential for the comparison with the theoretical models.

The comparison of surface phonons calculated within the semiempirical glue model¹² to the measured dispersion shows that the Rayleigh phonons are reasonably reproduced by this molecular-dynamics study (dashed curves in Fig. 2). However, at $\bar{\Gamma}$ the measured surface resonance at 50 cm^{-1} is not reproduced. At the $\bar{\Gamma}$ point these calculations predict surface resonances at 28 and 80 cm^{-1} (not shown in Fig. 2). In the high-frequency regime the glue model predicts two modes above the calculated bulk phonon maximum at 137 cm^{-1} and at 165 cm^{-1} at $\bar{\Gamma}$. The mode at 165 cm^{-1} is even predicted to be dipole active. However, our dipole spectra showed no dipole-active mode. For a comparison of the unexpected high-frequency modes predicted by the glue model to the experimental data we have to take into account that the bulk phonon maximum obtained by the glue model calculations

is 17% lower than the (true) bulk phonon maximum ($\omega_{\max} = 157 \text{ cm}^{-1}$) measured by neutron diffraction.¹⁶ The measured band between 125 and 145 cm^{-1} is a band of surface resonances, below the bulk phonon maximum, whereas both *calculated* modes are true surface modes, above the *calculated* bulk phonon band at 130 cm^{-1} . The correspondence of the calculated mode at 137 cm^{-1} to the observed-loss band between 125 and 145 cm^{-1} is therefore fortuitous. The mode at 165 cm^{-1} is predicted to be *z* polarized and should therefore be observed with a higher-scattering cross section than the *y*-polarized mode at 137 cm^{-1} . Since we find no mode at all above the bulk phonon band we conclude that the glue model overestimates the bonding strength at the surface.

A calculation of surface modes based on the use of bulk force constants¹⁷ also fails completely for this surface. The calculations predict for \bar{Y} a surface instability not seen experimentally. Furthermore, the surface resonances at 43 and 58 cm^{-1} for the $\bar{\Gamma}$ point are not in agreement with the observed modes. In addition, no strong resonance around 120 cm^{-1} is present in these calculations.

The comparison between experimental results and theoretical predictions based on bulk force constants or the semiempirical glue model clearly demonstrates the need for first-principles calculations of surface phonons. Total-energy calculations based on density-functional theory have recently successfully determined the equilibrium geometry of the (1×2) missing row structure.¹⁰ Since this method includes the full microscopic electron screening at the surface and contains no adjustable parameters to be fitted to the experiment, the results are expected to provide an accurate description of the surface dynamics. The method allows for the determination of the force-constant matrices coupling the various atoms in the unit cell. This goes beyond conventional frozen phonon calculations. Because of the calculation of force-constant matrices, no assumptions about the polarization vectors of the surface modes have to be made. Having calculated the surface force constants we set up the dynamical matrix for a Au(110) slab 153 layers thick. The coupling between the inner layers of our slab were described using parameters determined from measured bulk phonon dispersion curves,¹⁷ whereas the couplings involving the first three layers, which are strongly affected by the reconstruction, are determined from our microscopic calculations. Details of the method can be found in Ref. 14 and references given there. While previous calculations have been restricted to the $\bar{\Gamma}$ point¹⁴ in the surface Brillouin zone, we present here results for the \bar{X} point as well. Spectral densities for the \bar{X} point are shown in Fig. 3, obtained by weighting the frequencies with the square of the vibration amplitude of the last layer atoms.

Some of the interplanar surface force constants obtained from our microscopic first-principles calculations differ by 50–100% from those obtained with bulk atomic force constants.¹⁷ These changes are localized at the surface and result from the large inward relaxation of the first layer of atoms which accompanies the reconstruction. With these changes surface resonances at $\bar{\Gamma}$ were predicted at 53 cm^{-1} with *z* polarization, 60 cm^{-1} with *x* polarization, and at 53 cm^{-1} , 117 cm^{-1} , and 156 cm^{-1} with *y*

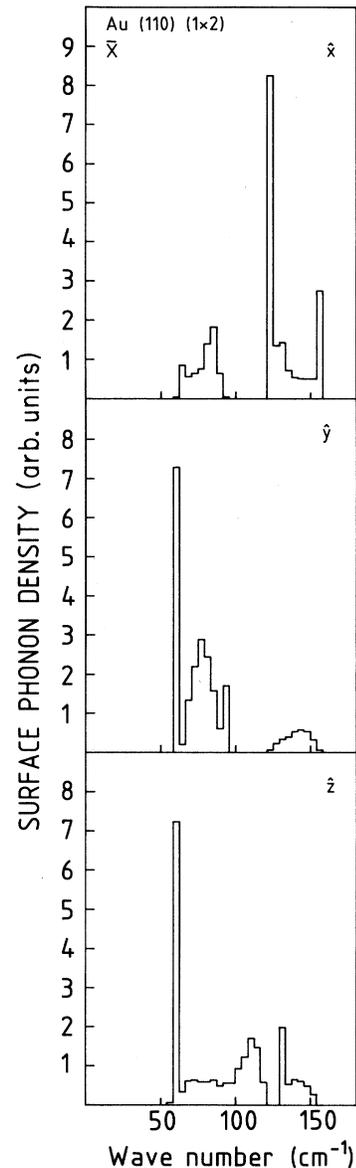


FIG. 3. Theoretical results for the surface-phonon density of states at the \bar{X} point of Au(110) for various polarizations. The *z* direction corresponds to the [110] direction (surface normal), the *y* direction corresponds to [001], and *x* corresponds to $[\bar{1}10]$.

polarization. The directions *x*, *y*, and *z* denote the crystallographic directions $[\bar{1}10]$, [001], and [110], and the polarization vectors refer only to the last layer atoms. Among these resonances the very strong modes at 53 and 117 cm^{-1} are in agreement with the experimental results given in Fig. 2, whereas the 60-cm^{-1} mode is not resolved experimentally because it is so close to the strong 53-cm^{-1} loss.

For the \bar{X} point the calculations indicate two strong surface modes at 59 cm^{-1} with *z* and *y* polarization, respectively, and one at 121 cm^{-1} with *x* polarization. A weaker surface resonance with *z* polarization is present at 132 cm^{-1} as well as one with *x* polarization at 156 cm^{-1} .

The low-lying mode is again in excellent agreement with the experiment. A value of 58 cm^{-1} was measured at a temperature of 110 K. The modes at 121, 132, and 156 cm^{-1} (at \bar{X}) correspond to the broadband of observed losses between 125 and 145 cm^{-1} along the $\bar{\Gamma}$ - \bar{X} direction. Depending on the scattering conditions, varying contributions of the three modes are picked up. Another resonance shows up at 94 cm^{-1} , which is not seen experimentally because it has y polarization and thus belongs to the class of shear horizontal modes which are not accessible in our experiment.

Preliminary results for the \bar{Y} point again indicate a resonance around 120 cm^{-1} . Furthermore, the instability observed with bulk force constants is no longer present. In contrast to the glue model, we do not find surface modes

well above the upper bulk band edge at any of the high-symmetry points of the Brillouin zone, which is in agreement with the experiment. It is therefore concluded that, at least for gold surfaces, only microscopic first-principles calculations provide a correct description of the surface dynamics.

Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This work was supported by the Director for Energy Research and the Office of Basic Energy Sciences including a grant of computer time on the Cray computers at the Lawrence Livermore Laboratory and by NATO collaborative research Grant No. RG(86/0516).

¹W. Moritz and D. Wolf, *Surf. Sci.* **88**, L29 (1979); **163**, L655 (1985).

²I. K. Robinson, *Phys. Rev. Lett.* **50**, 1145 (1983).

³L. D. Marks, *Phys. Rev. Lett.* **51**, 1000 (1983).

⁴M. Copel and T. Gustafsson, *Phys. Rev. Lett.* **57**, 723 (1986).

⁵J. Möller, K. J. Snowdon, W. Heiland, and H. Niehus, *Surf. Sci.* **178**, 475 (1986).

⁶M. Manninen, J. K. Nørskov, and C. Umrigar, *Surf. Sci.* **119**, L393 (1982).

⁷G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, *Surf. Sci.* **131**, L379 (1983).

⁸T. Hasegawa, N. Ikarashi, K. Kobayashi, K. Takayanagi, and K. Yagi, in *Structure of Surfaces II*, edited by J. F. van der Veen and M. A. Van Hove, Springer Series in Surface Sciences, Vol. 11 (Springer, Berlin, 1988), p. 43.

⁹I. K. Robinson and E. Vlieg (unpublished).

¹⁰K. M. Ho and K. P. Bohnen, *Europhys. Lett.* **4**, 345 (1987).

¹¹H. Ibach and D. Bruchmann, *Phys. Rev. Lett.* **41**, 958 (1978).

¹²X. Q. Wang, G. L. Chiarotti, F. Ercolessi, and E. Tosatti, *Phys. Rev. B* **38**, 8131 (1988).

¹³S. M. Foiles, M. I. Baskes, and M. S. Daw, *Phys. Rev. B* **33**, 7983 (1986).

¹⁴A. M. Lahee, J. P. Toennies, Ch. Wöll, K. P. Bohnen, and K. M. Ho, *Europhys. Lett.* (to be published).

¹⁵S. Lehwald, F. Wolf, H. Ibach, B. M. Hall, and D. L. Mills, *Surf. Sci.* **192**, 131 (1988).

¹⁶F. Ercolessi, M. Parrinello, and E. Tosatti, *Philos. Mag. A* **58**, 213 (1988).

¹⁷*Metals: Phonon States and Electron States and Fermi Surfaces*, Landolt Börnstein, edited by K.-H. Hellwege and J. L. Olsen, New Series, Vol. 13 (Springer, New York, 1981).