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Measurements of surface phonon frequencies on Al(110) for comparison with recent *ab initio* calculations

J. P. Toennies and Ch. Wöll
Max-Planck-Institut für Strömungsforschung, D-3400 Göttingen, Bunsenstrasse 10, Federal Republic of Germany

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High-resolution He-atom time-of-flight spectroscopy has been used to measure the dispersion curves of surface phonons on Al(110) in the two high-symmetry directions out to the zone boundaries. The experimental frequencies are compared with the results of the recent pseudopotential calculation of surface forces by Ho and Bohnen [Phys. Rev. Lett. **56**, 934 (1986)]. The largest difference between experiment and theory is at $\bar{X}$ where the experiment is smaller by 15%.

The anomalous surface phonon mode, which has been discovered by high-resolution He-atom scattering on the close-packed (111) surface of noble and transition metals,[1-6] has not yet been understood from a theoretical point of view. The occurrence of this unexpected surface phonon branch could be traced back to a strong softening of the lateral intralayer force constant between atoms in the surface plane.[7] The softening is typically 50% but can be as large as 70% as in the case of the 23×1 reconstructed Au(111) surface.[3] It has been qualitatively explained by a surface-induced reduction in (sp)-d hybridization. Whereas, for the bulk the stiffening effect of (sp)-d hybridization on the frequencies of phonons has been demonstrated by a microscopic theory,[8] only qualitative considerations are available for the surface of transition metals, which even suggest opposite results.[9]

One way to test this explanation is to study a nearly-free-electron metal such as aluminum. The Al(110) surface is especially interesting because it is the first metal surface for which extensive *ab initio* calculations have been reported by Ho and Bohnen.[10] In these calculations the pseudopotential approach within the local density functional formalism was used to determine total energies for displacements at the symmetry points $\bar{X}$, $\bar{Y}$, and $\bar{S}$. Fitting of a force-constant scheme to these energies then allowed for the prediction of phonon frequencies at the high-symmetry points. These theoretical results do not, in fact, appear to predict an anomalous mode referred to above but do show a rather strong dependence of the surface phonon frequencies on the interlayer surface relaxation, which has been measured[11] to be $\Delta d_{1,2}=(-8.5\pm1.0)\%$, $\Delta d_{2,3}=(+5.5\pm1.5)\%$, and $\Delta d_{3,4}\approx0\%$. The calculations show that relaxation has the effect of raising the frequencies of the transverse polarized modes by about 10% and lowering the longitudinal modes by a somewhat smaller amount. The largest effect is to raise the frequency of the shear horizontal mode S_2 by about 30% but unfortunately this mode cannot be observed by either electron or He-atom scattering. By experimentally studying Al(110) with the high resolution provided by He-atom scattering, we can test the accuracy of the *ab initio* theory as well as its implications for the *sp-d* hybridization model for the anomaly observed in the noble and transition metals.

The He-atom time-of-flight scattering apparatus has been described in detail elsewhere.[2,12] Two different crystals were prepared by mechanical polishing down to 1 μm and subsequent cycles of annealing and Ne-atom sputtering in a ultrahigh vacuum-UHV chamber with a base pressure of 5×10^{-11} mbar. After repeated sputtering and annealing the surface concentration of oxygen measured with a cylinder mirror Auger analyzer was less than 2% and the surface exhibited sharp low-energy electron diffraction (LEED) patterns. A reconstruction or a multidomain structure as reported by Noonan and Davis[11] was not observed. However, elastic scattering of He atoms, which is more sensitive to surface topology than electrons, revealed a large amount of disorder in agreement with several LEED studies.[11,13,14] The angular half width of the specularly scattered He atoms was measured as a function of incident energy in the range from 10 to 50 meV. An analysis of these results according to the procedure proposed by Lu and Lagally[15] indicates the presence of randomly distributed steps with a mean separation of about 15 Å. The rough state of this surface is commonly attributed to an instability with respect to formation of (111) facets, as confirmed by pronounced rainbows in the He-atom angular distributions. The quality of the surface could not be improved by annealing close to the melting point. A second crystal gave similar results.

In Fig. 1 we present some typical time-of-flight spectra transformed to an energy abscissa for the $\bar{\Gamma}$-$\bar{X}$ direction (parallel to the rows). For small Q vectors the peak S_1, corresponding to excitation of a Rayleigh phonon, is quite sharp, but at $\bar{X}$ the peak is less well defined, although a precision in locating the peak of about ±0.2 meV is still possible. The second peak at larger energies, denoted by E, is probably related to a high density of states at the lower edge of the surface projected longitudinal bulk phonon band. As the signal to noise ratio is rather poor, we considered only peaks with a half width of equal to or greater than that of the incident beam.

In Fig. 2 we present spectra for the $\bar{\Gamma}$-$\bar{Y}$ direction. From the peaks in the spectra two experimental phonon dispersion curves can be constructed, denoted by S_1 and S_3. Their separation was only possible for wave vectors greater than 0.4 Å^{-1}. The polarization of these modes cannot be determined experimentally with certainty, but a comparison with experimental data for the same direction on a Pd(110) surface seems to indicate that the lower

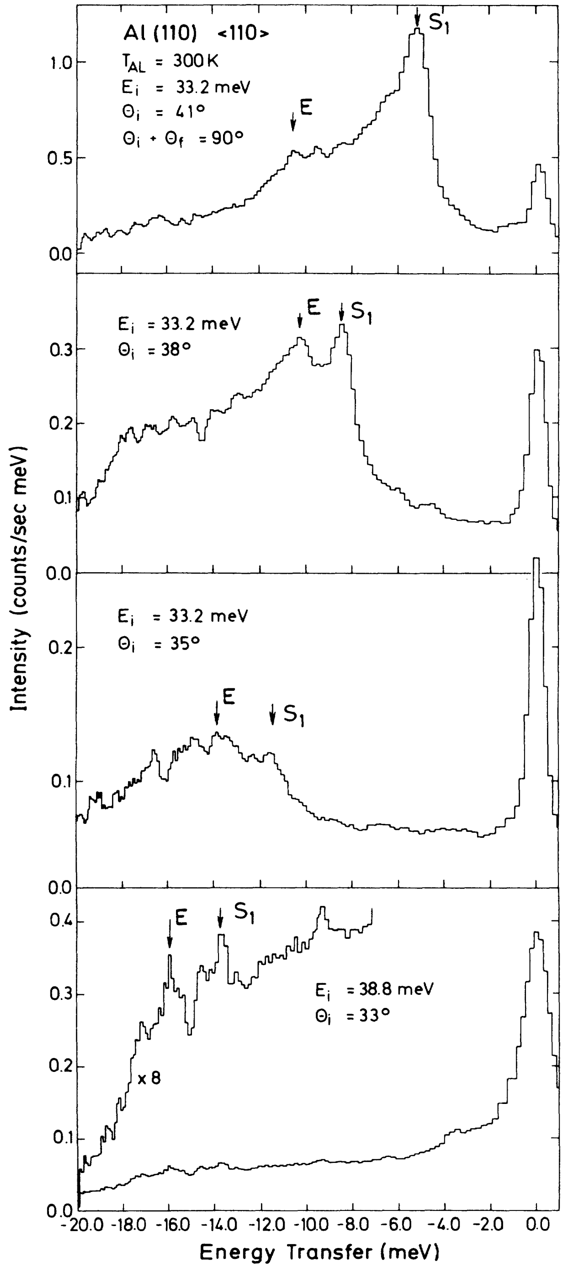

FIG. 1. Some typical time-of-flight spectra transformed to an energy abscissa for the $\bar{\Gamma}$-$\bar{X}$($\langle 110 \rangle$) direction. The measuring times were below 40 min for the upper three spectra and 4 h for the bottom spectrum. The peak at smaller energy transfer belongs to the S_1-Rayleigh mode along this direction; the second has not yet been identified.

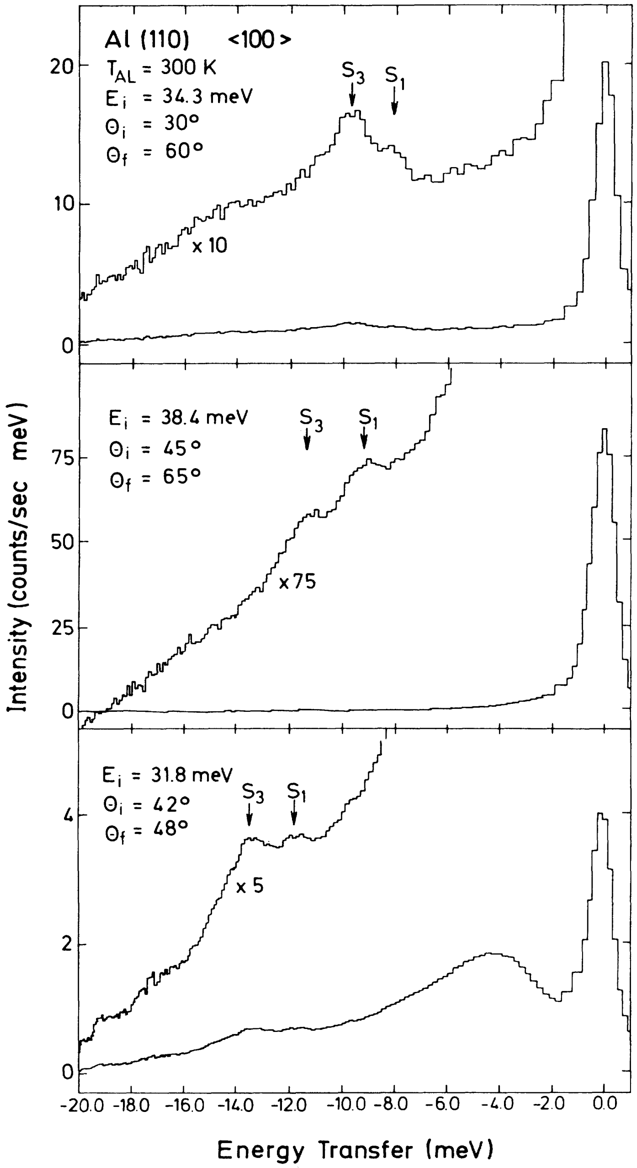

FIG. 2. Some typical time-of-flight spectra transformed to an energy abscissa for the $\bar{\Gamma}$-$\bar{Y}$($\langle 100 \rangle$) direction (measuring times below 40 min). The peak at smaller energy transfer belongs to the S_1 mode, which is mainly longitudinal along this direction. The second peak is attributed to the transversely polarized S_3 mode. Note the strong diffuse peak at zero-energy transfer which is indicative of a large amount of disorder (see text). The broad peak at ~4 meV is due to umklapp phonons from the second Brillouin zone.

mode S_1 is of longitudinal polarization.

In Fig. 3 we compare our experimental dispersion curves with the results of Ho and Bohnen.[10] The crosses indicate the results of their self-consistent pseudopotential calculations at $\bar{X}$ and $\bar{Y}$. Also given are the results of lattice dynamical calculations from Ref. 10. The bold lines are the surface phonon dispersion curves for the unrelaxed surface as obtained from bulk force constants, whereas the continuous lines represent the results with the surface force constants modified in order to reproduce the results of the pseudopotential calculations at the high-symmetry points (for further details, see Ref. 10).

At the $\bar{Y}$ point the experimental data and the theoretical results of Ho and Bohnen for the relaxed Al(110) crystal are in reasonable agreement. For the relaxed surface they predict a longitudinally polarized phonon mode

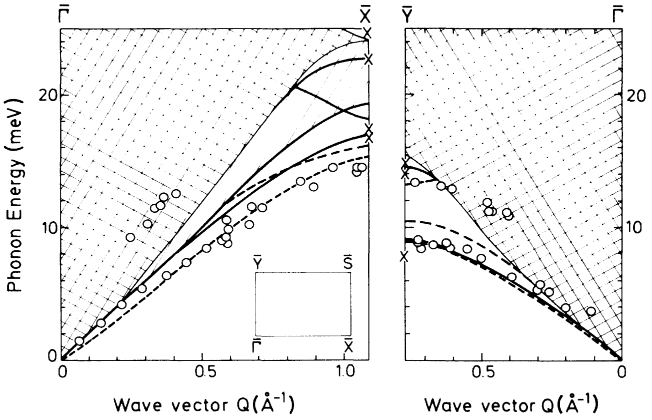

FIG. 3. Comparison of experimental data with the results of Ho and Bohnen (Ref. 10). The crosses indicate the results of their self-consistent pseudopotential calculations at $\bar{X}$ and $\bar{Y}$. The broken bold lines are their surface phonon dispersion curves for the unrelaxed surface as obtained from lattice dynamical calculations using bulk force constants, whereas, the continuous lines are their results of lattice dynamical calculations with the surface force constants modified in order to reproduce the results of the pseudopotential calculation at the high-symmetry points.

of about 7.9 meV and a transverse polarized mode at 14.1 meV. The experiment reveals a mode at 8.9 ± 0.3 and 13.5 ± 0.2 meV, respectively.

At the $\bar{X}$ point a qualitative agreement concerning the polarization of experimental and theoretical phonons is also present. However, here the experimental frequency at the zone boundary is 14.6 ± 0.2 meV compared to 17.0 and 17.4 meV for a longitudinally and transversely polarized mode, respectively. The agreement with Ho and Bohnen's calculations for the unrelaxed surface with a transverse mode at 15.3 meV is, in fact, much better. The experimental phonons with smaller Q vector, which appear as well-defined sharp peaks in the time-of-flight spectra, also very nicely reproduce the dispersion curves for the unrelaxed surface and lie significantly below the dispersion curves predicted for the relaxed surface.

This discrepancy of ~2.5 meV and $\bar{X}$ is considerably greater than the peak half width of about 1 meV, and is also greater than the $\bar{X}$-point frequency obtained from an extrapolation of the sharper peaks observed at smaller Q. Moreover, since it is also greater than the estimated errors of the *ab initio* calculation of about 1 meV, we feel that the discrepancy is significant. We do not think that the poor quality of the surface has an appreciable effect on the measured frequencies for several reasons. First we note that lattice dynamical calculations[16] show that at $\bar{X}$ the transverse S_1 frequency is mainly determined by the interaction of the surface atom with its four nearest neighbors in the second plane, and an additional single nearest neighbor directly below it in the third plane, and is less effected by its two nearest neighbors in the same row of the surface plane. Thus, any disorder which would lead to the removal of atoms from the rows will have only a minor effect on the S_1 frequency. Since steps are expected to lie parallel to the rows, they will most likely lead to the partial removal of an adjacent row but not of any of the seven nearest neighbors in the first, second, and third layer. Thus, we do not expect the high density of defects to directly effect the frequency at the zone boundary. Further away from the zone boundary the increased sharpness of the peaks is consistent with the greater phonon penetration and an even lesser sensitivity to the short-range disorder.

Both the experiment and theory seem to suggest that the longitudinal anomaly seen in the noble and transition metals is not present in aluminum. That the discrepancy at $\bar{X}$ is due to such an effect appears unlikely since we have found very good agreement between extensive measurements on the very slightly relaxed (~0.8%) Al(111) high-quality surface and highly accurate lattice dynamical calculations based on a 10 nearest-neighbor interaction model of the bulk phonons.[17] A similar lattice dynamical study for Al(110) is in progress and is expected to provide a more thorough understanding of the dynamics at this surface.

In summary then we are led to consider the possibility of a systematic error in the theory. This might appear to be unlikely since the theory is able to satisfactorily explain the observed large static structural relaxation of the surface interplanar distances.[18] But it must be kept in mind that the determination of phonon frequencies is much more delicate than the calculation of geometries. In the latter case, only the position of the minimum needs to be determined, whereas, the phonons depend additionally on the local curvature of the potential. Although certainly further work is called for there could be problems in using pseudopotentials at surfaces and we might also have to question the validity of approximations commonly used in pseudopotential calculations, especially the local density approximation when applied to metal surfaces.

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