Observation of a Soft Surface-Phonon Mode in the Reconstruction of Clean W(100)

H.-J. Ernst, E. Hulpke, and J. P. Toennies
Max-Planck-Institut für Strömungsforschung, 3400 Göttingen, Federal Republic of Germany
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He-atom–beam scattering has been used to investigate the reconstruction of the W(001) surface. At low surface temperatures T_s a sharp $(\sqrt{2}\times\sqrt{2})R45°$ diffraction pattern is observed. When T_s is raised, the fractional-order beams broaden and shift towards the specular. At $T_s \approx 450$ K the time-of-flight spectra reveal two different surface phonons along the ⟨110⟩ direction, a normal Rayleigh mode and a strongly anomalous mode with a maximum at a wave vector Q at one-half of the zone boundary Q_{BZ} and an energy approaching zero at $Q \sim 0.8 Q_{BZ}$. This mode softens with decreasing temperature, identifying the structural transformation as a continuous displacive transition.

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The surface reconstruction of the (100) surfaces of the bcc metals, W and Mo, is one of the few examples of temperature-driven phase transitions between two structured phases which occur near room temperature. There is good evidence from LEED that the reconstruction is localized in the outermost layer so that these systems are prototypes for two-dimensional phase transitions.[1] Despite extensive experimental and theoretical studies of the W(100) system there is still no complete consensus concerning the structure of the high-temperature phase nor the detailed mechanism for driving the transition from a 1×1 structure at higher temperatures to a $(\sqrt{2}\times\sqrt{2})R45°$ structure at low temperatures ($T_s < 300$ K).

The character of the clean reconstructed phase (to be denoted by L for low temperatures) was first deduced by Debe and King[2] from a symmetry analysis of the LEED diffraction pattern and later verified by Barker *et al.*[3] using dynamical LEED calculations. According to this picture the surface atoms are displaced from their 1×1 locations in the high-temperature (H) phase by about 0.16 Å along diagonal ⟨11⟩ directions in the surface plane leading to zigzag chains in the $\langle 1\bar{1}\rangle$ directions consistent with a $(\sqrt{2}\times\sqrt{2})R45°$ diffraction pattern. These experiments have stimulated a large number of theoretical studies which have invoked either detailed electronic-structure calculations[4] or a lattice-dynamical approach,[5] which attributes the reconstruction to a lattice deformation on a potential-energy surface resulting from the changes in the electron density of states near the Fermi surface. Such models, pioneered by Tosatti and coworkers, have recently been placed on a quantitative basis by the "frozen phonon" total-energy calculations of Fu *et al.*[6] They predict a potential hypersurface with a local minimum of about 10 meV for displacements normal to the chain direction of $\delta = 0.18 \pm 0.01$ Å in reasonable agreement with the experimental evidence. Thus at low temperatures the atoms are vibrating with respect to the displaced minima corresponding to the $(\sqrt{2}\times\sqrt{2})R45°$ structure. At temperatures greater than about $T_s = 120$ K ($\simeq 10$ meV) the anharmonicity leads to large-amplitude oscillations of the $\bar{M}_5$ in-plane surface mode[7] along the direction of the displacements δ with a center of gravity of $\delta = 0$ at $T_s > 120$ K. This model suggests that the transition is driven by the softening of this surface-phonon mode. The observation of such a soft mode would thus provide compelling evidence for the displacive mechanism and also help clarify questions concerning the order of the transition.

Some indirect evidence for anomalous modes comes from an unexpected low value of the surface Debye temperature of 210 ± 40 K (bulk Debye temperature $\theta_D = 310$ K) from LEED measurements in the H phase.[8] In a recent electron-energy-loss spectroscopy study Woods and Erskine[9] reported a 36-meV mode at 78 K but saw no loss peaks below 45 meV at room temperature and thus argued against a soft-mode mechanism.

In the present paper we report on high-resolution He-atom diffraction and time-of-flight (TOF) energy-loss measurements on the clean W(001) surface at various temperatures. The diffraction patterns indicate that with increasing temperature the half-order peaks of the $(\sqrt{2}\times\sqrt{2})R45°$ structure are shifted towards the specular and gradually fade away. The measured dispersion curves reveal, in addition to a temperature-independent Rayleigh mode, the existence of an anomalous surface vibration mode with greatly lowered frequency near the Brillouin-zone boundary of the 1×1 lattice. The anomaly is observed both at elevated temperatures well within the H phase and at temperatures of about 280 K. Near the zone boundary the frequency of the anomalous mode and the extrapolated value Q for $\omega = 0$ (Q_0) both shift to lower values with decreasing temperatures. At $T_s \simeq 280$ K, $Q_0 = 0.82 Q_{BZ}$ (where $Q_{BZ} = 1.41$ Å^{-1}).

The high-resolution He-scattering apparatus is similar to those described previously[10] with the only major difference that the fixed angle between the incident and outgoing beams is $\theta_{SD} = 99°$. Beam energies between 17 and 25 meV were used and the velocity resolution was about 1%. The angular resolution was about 0.1°. The $15\times5\times0.2$-mm^3 oriented ($\pm0.5°$) polished tungsten

crystal was cleaned in vacuum by an annealing at 1800 K with intermittent flash cycles (2500 K) in a good vacuum. The prepared crystal was characterized by LEED, and a cylindrical-mirror-analyzer Auger analysis revealed a C and O contamination both of less than 2%.

To keep contamination from residual gas to a minimum the time-of-flight spectra were obtained in the following manner: The crystal was first flashed and, because of rapid cooling, measurements could be started within 2 min. The measuring time was never longer than 15 min. After this period the crystal was flashed again and the procedure repeated. With an H_2 partial pressure assumed to be equal to the total chamber pressure of 5×10^{-11} mbar (without He beam) and a sticking coefficient of $s=0.6$,[11] the H contamination after 15 min is estimated to be $\theta\leq 0.01$. This is an upper limit since in fact most of the data were taken within 8 min. The assumed cleanliness has been confirmed by comparison of selected time-of-flight spectra taken with measuring times between 5 and 15 min, which indicated no differences.

Figure 1 shows a series of angular distributions for various surface temperatures plotted as a function of the parallel momentum transfer. At the highest temperature

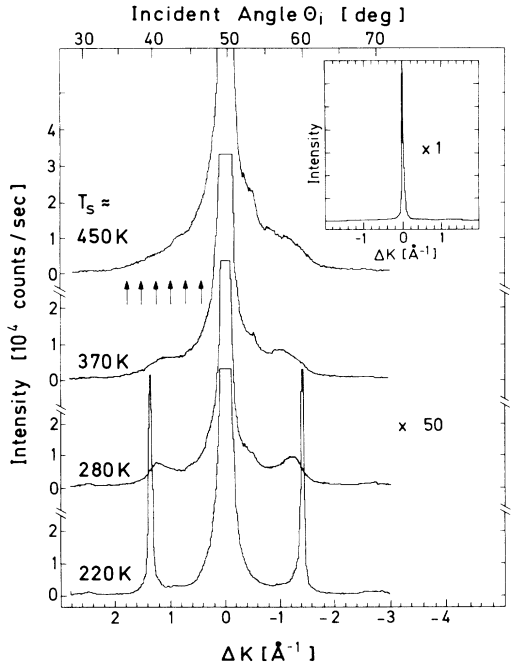

FIG. 1. Angular distributions along the ⟨110⟩ direction for four different surface temperatures measured for $k_i=5.66$ Å^{-1}. Note that the half-order superstructure peaks shift toward the specular with increasing surface temperature. The arrows mark angular positions at which TOF data shown in Fig. 2 have been taken. Inset: Full-scale angular distribution for $T_s\approx 450$ K, whereas the intensity in all the other traces has been magnified by a factor of 50.

the base of the specular peak is considerably broader than at lower temperatures. At both the highest and lowest temperatures the FWHM of the He specular peak was, however, less than 0.2°, indicating a surface with well defined terraces of at least 400-Å length. The small intensity ($<10^{-3}$ of I_0) of the first-order diffraction peaks (not visible in Fig. 1) suggests a smooth surface with a very weak corrugation (<0.03 Å). This is surprising in view of the open structure of the (001) face. With reduced temperature an additional peak appears which increases in intensity, sharpens, and shifts outwards towards the expected half-order location. This deviation from the exact half-order locations has never been observed in LEED, but was recently reported in similar, less well resolved He scattering diffraction experiments.[12]

Figure 2 shows a series of TOF spectra (converted into an energy-transfer scale) taken for the incident angles indicated by arrows in Fig. 1 at 450 K where no half-order peak is visible. The TOF spectra show well-defined maxima with a width somewhat broader than seen, for example, on the hydrogen-saturated W(001) H 1×1 surface. Note that the extraordinary width of the peak at $\Delta E=-5.5$ meV in the spectrum measured for $\theta_i=36°$ is, however, largely determined by kinematic focusing.[13] Phonon measurements were also performed at $T_s\approx 280$ K.

Figure 3 shows the dispersion curves determined from altogether forty time-of-flight measurements at these two temperatures. The bars indicate the widths (FWHM) of the peaks. The data provide evidence for two phonon modes, one with the expected behavior with an extrapolated maximum of 11.5 meV at the 1×1 Brillouin-zone boundary and the other with an anomalous shape with decreasing frequencies beyond a maximum of 7 meV at about $Q=0.5$ Å^{-1}. The width in the scatter of the points suggests that possibly several modes are present but not resolved. For $Q\geq 0.8$ Å^{-1}, the frequency of the anomalous mode decreases with decreasing temperature. A series of TOF measurements as a function of temperature at a fixed incident angle of $\theta_i=60°$ ($k_i=5.8$ Å^{-1}) shows clearly the temperature-dependent decrease in frequency of the anomalous mode.

There has been considerable discussion concerning the nature of the H phase. Whereas Barker and Estrup argue in favor of a disordered state, which is supported by ion backscattering experiments,[14] Debe and King have concluded that the state is ordered. Our results provide considerable evidence for order over larger distances. This comes from the observed sharpness of the specular peak which, in fact, is sharper than shown in Fig. 1 since the TOF spectra reveal that at the base of the peak most of the scattering is due to phonons. In addition, the diffuse elastic peaks in the TOF spectra are not excessively large. Even more convincing is the observation of well defined phonon dispersion curves for $Q<1.0$ Å^{-1}.

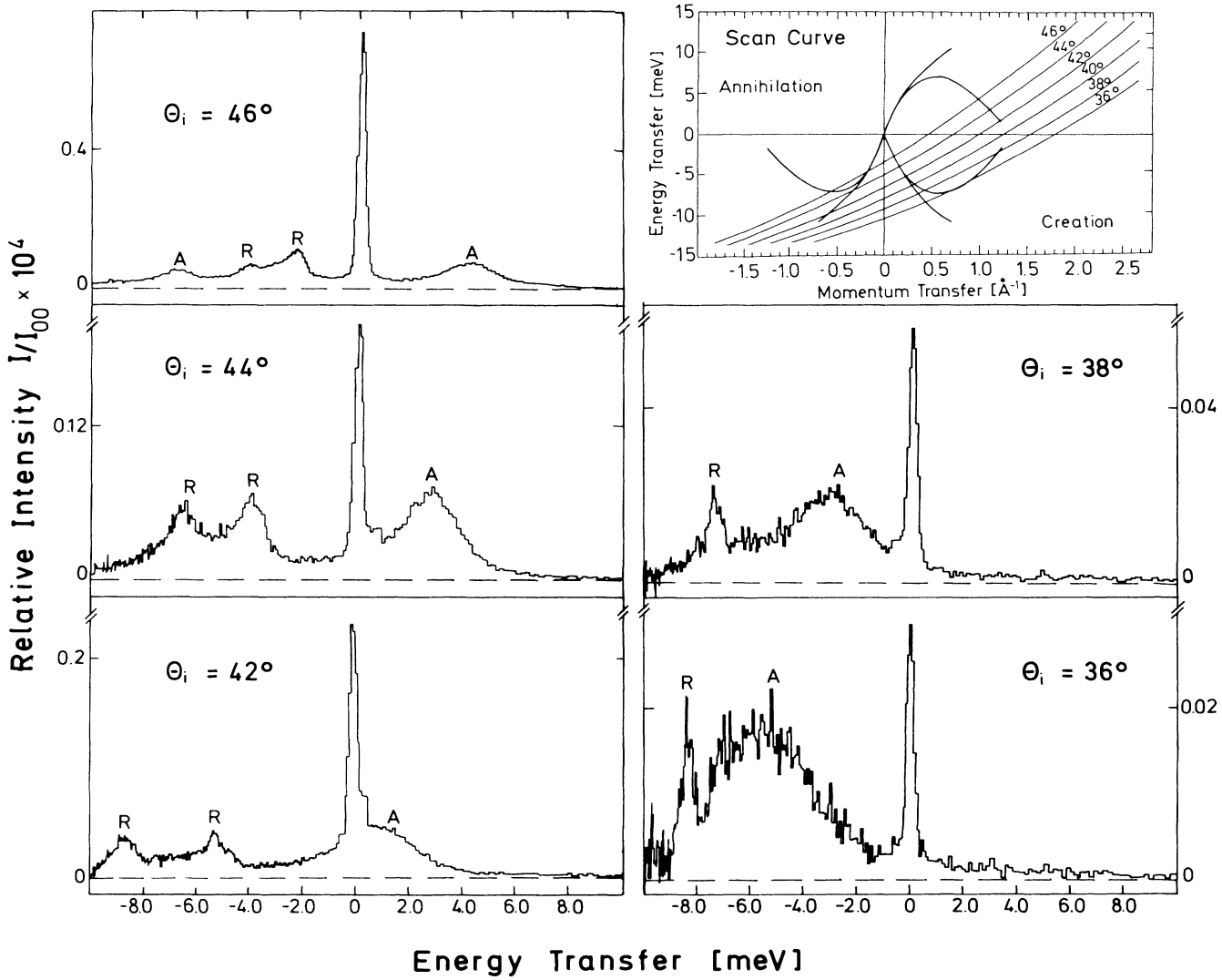

FIG. 2. Time-of-flight spectra (converted into an energy-transfer scale) at fixed surface temperature $T_s \approx 450$ K for various incident angles $\theta_i = 46°$ to $\theta_i = 36°$, $k_i = 5.66$ Å^{-1}. The peak at zero energy transfer is due to elastic incoherent scattering and the letters indicate inelastic peak positions corresponding to the Rayleigh mode (R) and the anomalous phonon mode (A). From the scan curves depicted in the upper right one can identify all the events seen in the time-of-flight spectra.

So far, however, we have not been able to observe sharp inelastic structures at larger Q, and this could be interpreted as indicating short-range disorder at the selvedge over short distances on a lattice-constant scale.

The dispersion curves indicate that in the high-temperature phase there is a strong softening of one of the surface-phonon modes. Our interpretation based on available calculations suggests that the upper mode is the Rayleigh mode.[15,16] The lack of any strong anomaly in this mode is consistent with the predictions[5,6] that transverse forces are not of importance in driving the transition. Thus the lower anomalous mode is likely to be polarized in the surface plane, i.e., either a shear horizontal or a longitudinal mode. Since helium scattering is only sensitive to saggital plane modes and not to the shear horizontal modes the observed mode is very likely longitudinal. However, since both the longitudinal and shear horizontal modes have to coalesce at the Brillouin-zone boundary by symmetry[7] we expect them to lie rather close to each other also for $Q < Q_{BZ}$. Thus, although the observed mode has longitudinal character, its behavior is closely linked with the shear horizontal mode driving the transition.

It is interesting to note that the observation that Q_0 is smaller than expected for the $(\sqrt{2}\times\sqrt{2})R45°$ reconstruction is in agreement with the shifted location of the

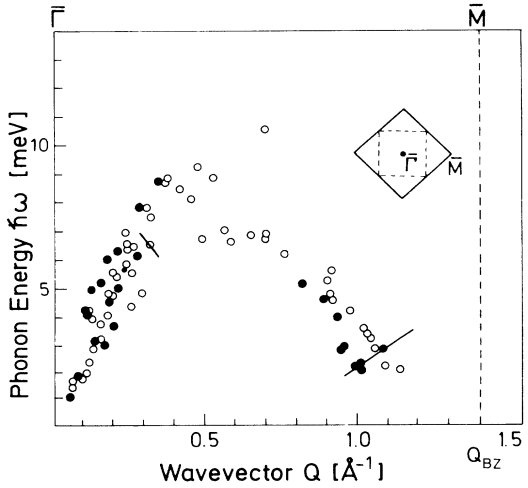

FIG. 3. Dispersion curves of clean W(001) for different surface temperatures $T_s \approx 450$ K (open circles) and $T_s \approx 280$ K (filled circles). Note that at $T_s \approx 280$ K superstructure peaks are seen at $Q = 1.24$ Å^{-1}, while the exact half-order location is at $Q = 1.41$ Å^{-1} in Q space (see Fig. 1). The bars indicate the widths (FWHM) of the peaks. The decrease in ω at $Q \approx 1.0$ Å^{-1} has been directly confirmed by measurements at a set geometry and varying temperatures. The data are taken at incident beam energies between 17 and 25 meV.

superstructure diffraction peaks. This shift in diffraction peaks in the transition region, also observed by Lapujoulade and Salanon,[12] was attributed by them to a new structural feature in which laterally expanded reconstructed domains of various sizes, separated by denser walls, appear along the zigzag chains. According to this picture this incommensurate modulation gradually disappears as the crystal locks into the ideal $(\sqrt{2}\times\sqrt{2})R45°$ structure at sufficiently low temperatures. Note, however, that the shift to smaller Q with decreasing temperatures seen in the anomalous dispersion curve is in fact in the opposite direction to what one would expect from the temperature-dependent shift in the "half-order" peaks.

These initial experimental results show the great potential of He scattering for the study of two-dimensional phase transitions. The observed temperature-dependent softening in W(100) provides the first direct confirmation of the soft-mode mechanism suggested by Tosatti and co-workers. The temperature-dependent shift in the half-order diffraction peaks as well as the broadened phonon peaks at $Q > 1.0$ Å^{-1} all suggest that the transition does not proceed in a simple way from the 1×1 to the $(\sqrt{2}\times\sqrt{2})R45°$ structure. This appears to indicate that strong longitudinal forces compete with the displacive forces as a result of a complicated anharmonic potential-energy surface in the x,y plane with a correspondingly complicated near "chaotic" dynamics leading possibly to a succession of complex intermediate incommensurate phases.

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