RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 40, NUMBER 2 15 JULY 1989-I

Evidence for a soft-phonon mechanism in the reconstruction of the Mo(001) surface

E. Hulpke and D.-M. Smilgies
Max-Planck-Institut für Strömungsforschung, 3400 Göttingen, Federal Republic of Germany
(Received 15 February 1989)

Surface-phonon dispersion curves of Mo(001) have been measured with high-resolution helium-atom scattering at three different surface temperatures, 1000, 750, and 400 K, respectively. Time-of-flight spectra in the ⟨100⟩ and ⟨110⟩ directions reveal two distinct phonon modes. The mode at higher energies can only be observed in the first third of the Brillouin zone and disappears for larger phonon wave vectors. The low-energy mode shows a remarkable softening in the ⟨110⟩ direction from about 8 meV at 1000 K to about 2 meV at 400 K at the wave vector $Q=1.1$ Å^{-1}, whereas, within experimental accuracy, no softening occurs in the ⟨100⟩ direction.

The reconstruction of the clean Mo(001) surface was observed by Felter, Barker, and Estrup[1] in low-energy electron diffraction (LEED) experiments. At the same time the study of the by now well-known reconstruction of the W(001) surface was revitalized.[1,2] In fact, Mo and W have very similar properties: Both are VI*B* transition metals and both crystallize in a bcc lattice with nearly identical lattice constants, 3.14 and 3.16 Å, respectively. However, already in the early experiments surprising differences were found in the LEED patterns of the (001) surfaces upon cooling: The high-temperature (HT) phases of both metals display the usual (1×1) pattern, but, whereas the clean W(001) surface reconstructs upon cooling below 300 K giving rise to a $c(2\times2)$ diffraction pattern, the LEED pattern of the clean Mo(001) surface cooled below 220 K consists of a quartet of spots surrounding the $(\frac{1}{2}\ \frac{1}{2})$ positions which are split in the ⟨110⟩ directions. Felter, Barker, and Estrup[1] have denoted this pattern as $Ic(2\times2)$. The reciprocal lattice vector Q_S of this "modulated" superstructure corresponds to about $0.45G_{11}$, where G_{11} is the reciprocal lattice vector of the HT phase in the ⟨110⟩ direction. Thus the low-temperature (LT) phase of Mo(001) is one of the rare cases of an incommensurate (IC) superstructure on a clean metal surface. Recently several He-atom scattering groups also reported evidence for an intermediate IC phase on the W(001) surface in the temperature range of about 250 to 500 K.[3-5] But, whereas the reconstructed W(001) surface becomes commensurate upon further cooling,[4] the Mo(001) surface is believed to remain IC even at zero temperature, as indicated by the fact that upon cooling down to 30 K no change in the diffraction pattern could be observed.[6]

At about the same time that the reconstruction of the Mo(001) and W(001) surfaces was discovered a number of photoemission and field-emission experiments indicated the existence of occupied electronic surface states in the HT phase of both surfaces.[7] Although the role of these electronic surface states in the reconstruction is still disputed,[8,9] recent work[10] shows that these states should at least contribute to the reconstruction in terms of a surface charge-density wave (CDW) as originally proposed by Tosatti and Anderson[11] for semiconductor surfaces. In this case the reconstruction should be a structural phase transition of the displacive type resulting in a soft surface phonon.[8] Such behavior has recently been observed for the W(001) surface.[3] The CDW model would also provide a natural explanation for the incommensurability of the low-temperature phase of the Mo(001) surface since Q_S would then be determined by properties of the Fermi surface.

In continuation of the work of our group on the W reconstruction we have investigated the Mo(001) surface with He-atom scattering. The high-resolution He time-of-flight spectrometer, similar to that described previously,[12] has a fixed angle between incoming and outgoing beams of 101°. The sample can be rotated with respect to its polar and azimuthal axis. Beam energies of 37 and 42 meV were used at an energy resolution of about 2% and an angular resolution of 0.2°. The $13\times6\times1.5$ mm^3 oriented ($\pm0.5°$) molybdenum single crystal (Materials Research Corporation) was mechanically polished and cleaned in UHV (2×10^{-10} mbar) by numerous cycles of oxygen etching (5×10^{-7} mbar O_2 at about 1200 K), flashing to 2000 K and annealing at 1500 K. The prepared crystal was characterized by LEED and Auger-electron spectroscopy, revealing C and O contaminations of less than 3% and a S contamination below the detection limit. In addition the crystal was flashed to 2000 K and then allowed to cool for 2 min before starting each time-of-flight measurement. The different final temperatures (1000, 750, and 400 K) were obtained by radiative heating of the back side of the crystal during cooling. The measuring time was limited to only 3 to 5 min. During that time the crystal temperature drifted further down by about 10, 30, and 50 K, respectively, as later confirmed in a separate experiment in which a WRe 3%-WRe25% thermocouple had been spot welded to the crystal surface. The total measuring time is restricted by the onset of hydrogen adsorption below 500 K which after 5 min leads to a drastic decrease in the inelastic signal.

Figure 1 shows the phonon dispersion curves of the clean Mo(001) surface in the ⟨100⟩ direction at two surface temperatures, 750 and 400 K. Since the "modulation" wave vector Q_S is expected to be oriented in the ⟨110⟩ direction, the dispersion in the ⟨100⟩ azimuth should not be affected by the reconstruction. Two phonon modes are clearly observed and do not show any temperature

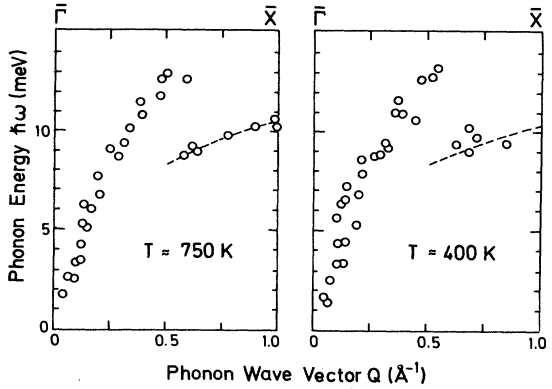

FIG. 1. Surface-phonon dispersion curves of Mo(001) in the ⟨100⟩ azimuth for two different temperatures, 750 and 400 K. Note that the two observed phonon modes do not display any temperature dependence within the experimental accuracy. The dashed curves provide a guideline to the eye.

dependence within experimental accuracy. In the present experimental setup 350 to 400 K was the lowest temperature that could be reached after the 2 min of cooling following the flash. Note that the occurrence of the extra spots in LEED is observed at 220 K.[1,13] The surprising feature in the dispersion curves in the ⟨110⟩ azimuth, shown in Fig. 2, is the strong temperature dependence of the lower-energy mode: The energy of this mode at $Q=1.1$ Å^{-1} is lowered from about 8 meV at 1000 K to 2 meV at 400 K. An energy of 2 meV corresponds to our resolution for low-energy phonons, since smaller energy transfers are obscured by the diffuse elastic peak due to scattering from defects. Note that, if the large Q end of the dispersion curve at 400 K is extrapolated to zero energy, the intersection with the Q axis would correspond roughly to the CDW wave vector Q_S. In order to illustrate the quality of our measurements a series of time-of-flight spectra is shown in Fig. 3. The inset shows the kinematical constraints (scan curves[12]) at each incident angle. The largest feature in all spectra is the partially suppressed diffuse elastic peak; the inelastic peak at the left-hand side of the elastic peak corresponds to phonon creation in the higher-energy mode, whereas the peak at the right-hand side corresponds to phonon annihilation in the soft low-energy mode. At an incident angle of 56° the latter peak coalesces with the diffuse elastic contribution which makes it impossible to decide whether there exists a phonon of even lower energy or a central peak due to overdamping of the soft mode. The experiments show that the rate of diffuse elastic scattering increases, while that of the inelastic processes decreases with measuring time which indicates that hydrogen adsorption from the residual gas is responsible for the amount of diffuse elastic scattering. The size of this peak reported in Fig. 3 is thus a result of the trade off between statistical error in the inelastic scattering and beginning surface contamination discussed above which apparently has little influence on the positions of the inelastic peaks.

If the reconstruction on Mo(001) is driven by the onset of a CDW, the lower-energy mode should have longitudinal polarization, since in this case the electrons are expected to couple strongest to a longitudinal phonon.[14] Experimental indication that the periodic lattice distortion induced by the CDW is longitudinal, i.e., the displacements are parallel to Q_S, was provided by the LEED work of Barker, Semancik, and Estrup.[15] Since shear horizontal modes cannot be observed in our scattering geometry we expect that the higher-energy mode is polarized predominantly normal to the surface and is the Rayleigh mode. This mode has been the subject for a recent controversy among theoretical groups: In their molecular dynamics model of the Mo(001) reconstruction, Wang, Tosatti, and Fasolino[16] have come to the conclusion that there has to be a coupling between the Rayleigh mode and the longitudinal mode resulting in a softening of both modes. This hypothesis is confirmed by symmetry arguments of Heine and Shaw.[17] In contrast, Ho and coworkers[10] predict only a softening of the longitudinal mode using an approach based on first-principles calculations of the surface electronic band structure and taking into account the electronic response in the dynamical matrix. In our experiment the higher-energy mode vanishes for wave vectors greater than 0.5 Å^{-1}, a behavior also ob-

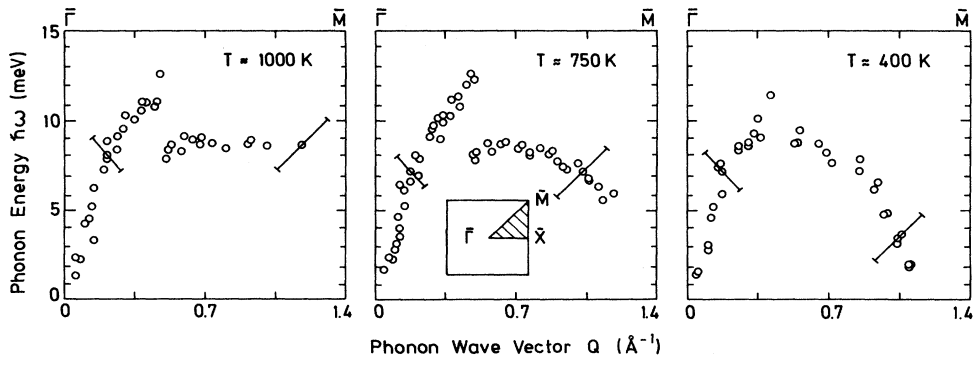

FIG. 2. Surface-phonon dispersion curves of Mo(001) in the ⟨110⟩ direction for temperatures of about 1000, 750, and 400 K (from left to right). Note that the CDW wave vector Q_S corresponds to 1.27 Å^{-1}. The bars show the FWHM of the measured inelastic peaks along the scan curve. The inset in the middle panel shows the surface Brillouin zone of the unreconstructed high-temperature phase.

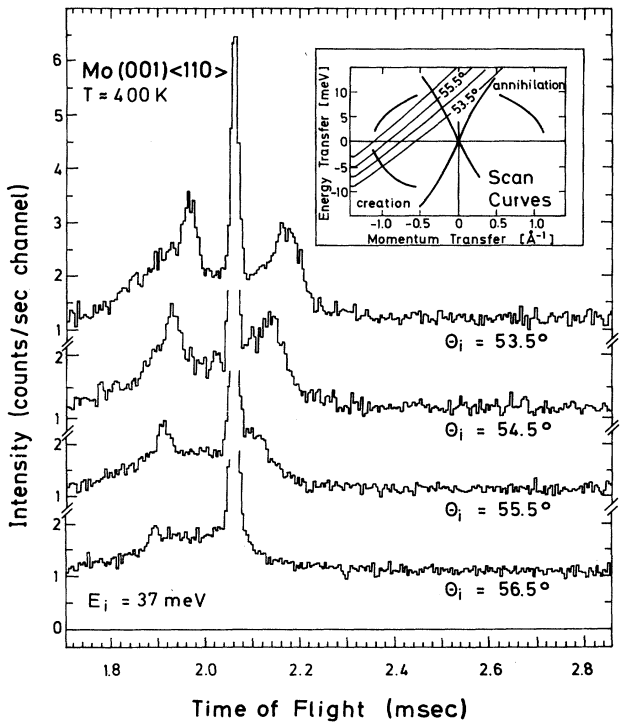

FIG. 3. Series of time-of-flight spectra taken in the ⟨110⟩ direction at a surface temperature of about 400 K. The largest feature, partly suppressed, is due to diffuse elastic scattering from defects. The inelastic peak at the left-hand side of the elastic one refers to phonon annihilation in the upper energy mode, the peak at the right-hand side refers to phonon creation in the lower-energy mode. The inset shows the scan curves corresponding to a beam energy of 37 meV and incident angles θ_i as indicated. Analogous spectra for incident angles between 45.5° and 48.5° have also been measured which show the low-energy mode in the light of annihilation events (flight path chopper detector, 2.741 m; target detector, 1.940 m; chopper opening time, 10 μsec).

served for the W(001) surface.[3] Within a CDW model of the reconstruction, Benedek[18] has explained the vanishing of the Rayleigh mode for large wave vectors by the coupling of the Rayleigh mode to the bulk phonon band via the CDW wave vector. As a result this mode disappears as soon as Q_S connects a point along the dispersion curve of the Rayleigh mode with one on the bulk band edge.

In this Rapid Communication we present evidence that the phase transition of the clean Mo(001) surface occurs via a soft-phonon mechanism. The amount of the softening at 400 K implies that the transition temperature T_c should be higher than the value of 220 K,[13] reported in most recent LEED work. A rough extrapolation of our phonon data assuming mean-field behavior [$\omega^2(Q_s) \propto T - T_c$] favors a value of $T_c = 350\ \text{K} \pm 50\ \text{K}$. It should be noted that Felter[6] found an indication that there could be two phases on the clean Mo(001) surface. LEED intensity measurements of the $Ic(2\times2)$ spots for a temperature range from 100 to 300 K yield two slopes of the intensity versus temperature curve, the first favoring a phase transition at about 150 K and a second, very slow falloff extending to about 300 K. In the latter temperature region the $Ic(2\times2)$ spots appear diffuse and broadened. Future work of our group will be devoted to the study of the LT phase of Mo(001). The question of whether it is possible to see the split $Ic(2\times2)$ diffraction spots by He scattering is still open, since in the intermediate IC phase of W(001) only the satellite of the specular peak is observed.[4] Another intriguing problem is the study of the excitations in the IC phase: The observation of "phasons" and "amplitudons"[19] would provide further evidence of the incommensurability of this reconstructed surface.

We would like to thank J. P. Toennies, W. Weber, K.-M. Ho, R. Currat, and G. Benedek for stimulating discussions and J. A. Prybyla and P. J. Estrup for sending us recent experimental results on Mo(001) prior to publication.

[1]T. E. Felter, R. A. Barker, and P. J. Estrup, Phys. Rev. Lett. **38**, 1138 (1977).

[2]M. K. Debe and D. A. King, J. Phys. C **10**, L303 (1977); the occurrence of the extra spots on W(001) was observed for the first time by K. Yonehara and L. D. Schmidt, Surf. Sci. **25**, 238 (1971).

[3]H.-J. Ernst, E. Hulpke, and J. P. Toennies, Phys. Rev. Lett. **58**, 1941 (1987).

[4]H.-J. Ernst, E. Hulpke, and J. P. Toennies (unpublished).

[5]B. Salanon and J. Lapujoulade, Surf. Sci. **173**, L613 (1983); E. K. Schweizer and C. T. Rettner, *ibid.* **208**, L29 (1989).

[6]T. E. Felter, J. Vac. Sci. Technol. A **2**, 1008 (1984).

[7]S.-L. Weng, E. W. Plummer, and T. Gustafsson, Phys. Rev. B **18**, 1718 (1978), and references therein.

[8]E. Tosatti, Solid State Commun. **25**, 637 (1978).

[9]J. E. Inglesfield, J. Phys. C **12**, 149 (1979); I. Terakura, K. Terakura, and N. Hamada, Surf. Sci. **111**, 479 (1981).

[10]X. W. Wang, C. T. Chan, K.-M. Ho, and W. Weber, Phys. Rev. Lett. **60**, 2066 (1988).

[11]E. Tosatti and P. W. Anderson, Jpn. J. Appl. Phys. Suppl. **2**, 381 (1974).

[12]J. P. Toennies, J. Vac. Sci. Technol. A **2**, 1055 (1984).

[13]J. A. Prybyla, P. J. Estrup, and Y. J. Chabal, J. Vac. Sci. Technol. A **5**, 791 (1987); J. A. Prybyla, P. J. Estrup, S. C. Ying, Y. J. Chabal, and S. B. Christman, Phys. Rev. Lett. **58**, 1877 (1987).

[14]D. E. Moncton, J. D. Axe, and F. J. DiSalvo, Phys. Rev. B **16**, 801 (1977).

[15]R. A. Barker, S. Semancik, and P. J. Estrup, Surf. Sci. **94**, L162 (1980).

[16]C. Z. Wang, E. Tosatti, and A. Fasolino, Phys. Rev. Lett. **60**, 2661 (1988).

[17]V. Heine and J. J. A. Shaw, Surf. Sci. **193**, 153 (1988).

[18]G. Benedek (private communication).

[19]A. W. Overhauser, Phys. Rev. B **3**, 3173 (1971); J. D. Axe, in *Proceedings of the Conference on Neutron Scattering, Gatlinburg, 1976,* CONF-760601-P1 (National Technical Information Service, Springfield, VA, 1976), p. 353.