tending from about $3v_e$ to 6 or $7v_e$. If 10^{15} W/cm^2 is conducted by the electrons and $Q/nmv_e^3 \sim 0.2$ as indicated in Ref. 4, then the temperature is about 6 keV. Thus the nonthermal tail would extend from about 60 keV to about 300 keV. The layered-target experiments and others[6] show very few hard x rays above 100 keV. Thus, there appears to be no indication of a strong superthermal tail to the electron distribution function.

In summary then, there are good theoretical and experimental indications that light absorption by enhanced ion-density fluctuations is a very important process for laser fusion.

---

*This work was sponsored by the Office of Naval Research.

[1] W. Manheimer, Phys. Fluids 20, 265 (1977).

[2] R. C. Malone, R. L. McCrory, and R. L. Morse, Phys. Rev. Lett. 12, 721 (1975).

[3] S. Bodner *et al.*, in Proceedings of the Sixth International Conference on Physics and Controlled Nuclear Fusion Research, Berchtesgaden, West Germany, October 1976 (International Atomic Energy Agency, Vienna, to be published).

[4] F. C. Young *et al.*, Appl. Phys. Lett. 30, 45 (1977).

[5] B. H. Ripin, Appl. Phys. Lett. 30, 134 (1977).

[6] B. H. Ripin *et al.*, Phys. Rev. Lett. 34, 1313 (1975).

[7] B. H. Ripin, Bull. Am. Phys. Soc. 21, 1083 (1976), and to be published.

[8] J. P. Friedberg *et al.*, Phys. Rev. Lett. 28, 795 (1972); K. G. Estabrook *et al.*, Phys. Fluids 18, 1151 (1975).

[9] M. Lampe *et al.*, Phys. Fluids 17, 428 (1974); D. Biskamp and R. Chodura, Phys. Rev. Lett. 27, 1553 (1971).

[10] J. A. Stamper and B. H. Ripin, Phys. Rev. Lett. 34, 138 (1975).

[11] W. Manheimer and C. Max, to be published.

[12] K. Lee, D. Forslund, J. Kindel, and E. Lindeman, Phys. Fluids 20, 51 (1977).

[13] R. Faehl and W. L. Kruer, Phys. Fluids 20, 55 (1977); J. M. Dawson and C. Oberman, Phys. Fluids 6, 394 (1963).

[14] D. G. Colombant *et al.*, Phys. Fluids 18, 1687 (1975).

[15] R. L. Morse and R. C. Malone, Bull. Am. Phys. Soc. 21, 1028 (1976), and to be published.

[16] W. Manheimer and H. Klein, Phys. Fluids 18, 1299 (1975).

Phase Transition on Mo(100) and W(100) Surfaces

T. E. Felter, R. A. Barker, and P. J. Estrup*
Brown University, Providence, Rhode Island 02912

(Received 2 March 1977)

Low-energy-electron-diffraction studies of carefully cleaned and annealed surfaces of molybdenum (100) and tungsten (100) show that a phase transition can be induced by lowering the temperature below 300 K. The periodicity of the "reconstructed" surface is believed to be due to the formation of a displacement wave with a wavelength which is $2a$ (a is the lattice parameter) for W(100) and $\sim 2.2a$ for Mo(100). The phase transition is reversible and seemingly second order. It appears possible that displacements of this type also occur in chemisorption on these surfaces.

In recent low-energy-electron-diffraction (LEED) studies we have observed a temperature-dependent structural transformation occurring on the molybdenum (100) surface. The transformation is completely reversible and appears to be characteristic of the clean surface. This discovery has led us to re-examine the behavior of the tungsten (100) surface which is one of the most widely studied substrates and which in many respects is similar to Mo(100). As discussed below, the results indicate that a "reconstruction" of the clean surface takes place also in the case of W(100) as the temperature is lowered.

The relevant LEED patterns are shown in Fig. 1. Above room temperature the pattern from either Mo(100) or W(100) shows only the "normal" spots [Fig. 1(a)], but as the crystal is cooled in vacuum the pattern changes. On Mo(100) the change consists of the appearance of a quartet of spots around the $(\frac{1}{2}\frac{1}{2})$ positions [Fig. 1(b)]; on W(100) single $(\frac{1}{2}\frac{1}{2})$ spots appear [Fig. 1(c)]. The variation of the intensity of the extra diffraction spots with temperature is shown in Fig. 2. As seen, the intensity changes gradually, suggesting a second-order transition. No hysteresis was seen for either sample as the temperature was raised or lowered. For both surfaces, as the intensity decreases with increasing temperature, the extra diffraction spots become larger, more diffuse, and streaky, presumably because of critical scattering. On the basis of these observations and data obtained by other techniques we

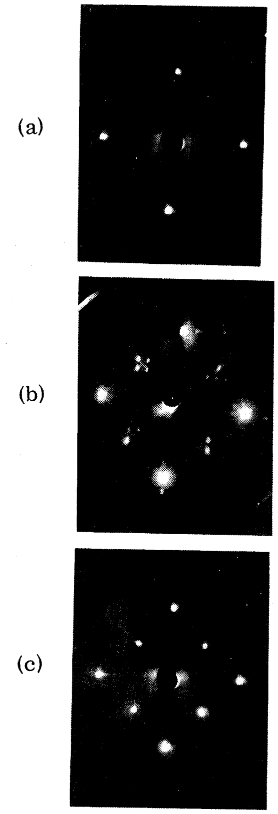

FIG. 1. (a) LEED pattern from clean W(100) above room temperature. Beam voltage 42 V. The pattern contains only the expected "normal" diffraction spots. Mo(100) gives an identical spot pattern. (b) LEED pattern from clean Mo(100) cooled to ~160 K. "Extra" beams are present, consisting of a quartet of spots surrounding the $(\frac{1}{2}\frac{1}{2})$ positions. The separation between the spots does not vary with temperature and is $\frac{1}{8}-\frac{1}{9}$ of the separation between the normal spots. (c) LEED pattern from clean W(100) cooled to ~160 K. The extra beams appear in the $(\frac{1}{2}\frac{1}{2})$ positions.

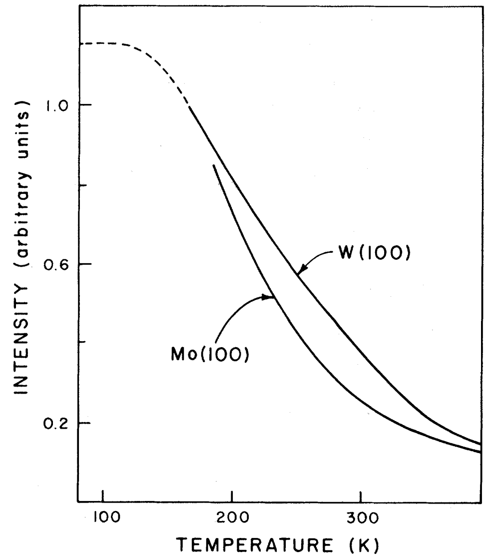

FIG. 2. Temperature dependence of the intensity of the "extra" diffraction spots shown in Figs. 1(b) and 1(c). In the case of W(100) the intensity has been normalized to the value at 160 K. Accurate data were not obtained below this temperature but the dependence indicated by the broken line agrees qualitatively with the data of Yonehara and Schmidt (Ref. 1).

conclude that the nature of the transition is the same for the two surfaces.

While the Mo(100) transformation has not been reported previously, the changes described here for W(100) were observed a few years ago by Yonehara and Schmidt,[1] who speculated that the low-temperature structure was due to either a rearrangement of the tungsten atoms or to the migration of hydrogen to the surface. The $c(2\times2)$ structure inferred from the LEED pattern in Fig. 1(c) might be produced by half a monolayer of adatoms; however, by means of Auger electron spectroscopy (AES) the presence of foreign atoms in such amounts has been ruled out. The exception is hydrogen—which is known to produce a $c(2\times2)$ structure[2]—and it was therefore proposed that some hydrogen segregates to the surface at low temperature but dissolves in the bulk at higher temperatures so that it is not observed in flash desorption experiments.[1] However, it seems possible to exclude this mechanism for both Mo(100) and W(100), considering the evidence now available from LEED, AES, and work-function measurements.[3]

Detailed studies[4,5] have been made of hydrogen overlayers on Mo(100), as a function of the temperature T and coverage θ. Hydrogen produces a number of different surface structures but none corresponding to the pattern in Fig. 1(b). We have also observed[4] that hydrogen adsorption leads to appreciable work-function changes, $\Delta\varphi$ (~0.5 eV at $\theta\sim0.5$ and ~1.2 eV at saturation) but no detectable change accompanies the phase transition shown in Fig. 1. Furthermore, the magnitude of two of the NNN peaks in the molybdenum Auger spectrum has been found to be sensitive to hydrogen adsorption[4] but is unaffected by the phase transformation. In the case of W(100) a work function change of ~0.2 eV is characteristic of the $c(2\times2)H$ structure[2] but, again, cooling of the clean surface gives $\Delta\varphi\simeq0$. In addition, for each surface, the $I(V)$ curve (the diffracted intensity versus electron energy) for the (00) beam shows distinct—if relatively small—changes upon hydrogen adsorption, also at low temperature, and these changes were absent for the phase transition described here. For both Mo(100) and W(100) the transformation at low temperature tends to disappear if adsorbates (including hydrogen) are present[6]; on the other hand, careful annealing and cleaning makes the transformation more pronounced.

In earlier experiments[7] it has been demonstrated that a LEED system may be adapted to studies of electron-stimulated desorption (ESD) and attempts were made to use this method to obtain additional evidence for the absence of hydrogen on the W(100) surface. However, the sensitivity required in this case[8] could not be achieved. Other techniques, such as secondary-ion mass spectroscopy (SIMS),[9] which would be well suited for further tests, were not available.

The possibility that the observations are due to a *bulk* phase transition was investigated by means of x-ray diffraction from single crystals of W and Mo at a temperature of ~ 100 K. Special attention was given to those regions of reciprocal space where, according to the LEED patterns, the extra reflections should occur but no indications of changes in the bulk structure were seen. We therefore believe that the transition is specific to the surface. So far there is no experimental evidence that it occurs on any face other than the (100).

Although the details of the low-temperature structure cannot be determined at this time, there appears to be only one type of arrangement of the surface atoms which is consistent with the observations. Because of the rapid kinetics of the transformation we exclude models which require the migration of metal atoms, and since the LEED pattern persists at high electron energy it is improbable that a magnetic superstructure is the origin of the extra spots.[10] We propose instead that the reconstruction consists of a *periodic displacement* of the atoms. The closely spaced "split" spots in Fig. 1(b)—and the absence of any other extra spots—suggest that the effective scattering power of the surface atoms varies approximately sinusoidally across the surface, an effect which may be produced by a displacement wave. As a specific illustration we consider a surface in which the x and y coordinates of the atoms in the top layer are unchanged—i.e., $(x,y) = (ma, na)$ where a is the lattice parameter, and m and n are integers—but the z coordinate is changed by a displacement perpendicular to the surface. The sign of the displacement alternates along a row of atoms and its magnitude is modulated to give a scattering amplitude of the form

$$\begin{aligned} f'(m,n) &\simeq f\{1+(-1)^{m+n}\alpha\cos[2\pi\Delta(m+n)]\} \\ &= f\{1+\alpha\cos[\pi(m+n)(1-2\Delta)]\}, \end{aligned}$$

where f is the atomic scattering factor and α is proportional to the amplitude of the displacement. The wavelength of the displacement wave is thus $\Lambda = 2a/(1-2\Delta)$. The LEED pattern from this structure will contain a pair of extra spots in the positions $(\frac{1}{2}\pm\Delta, \frac{1}{2}\mp\Delta)$. An equivalent domain, rotated 90°, will produce the other pair of spots in the quartet [Fig. 1(b)], in the positions $(\frac{1}{2}\mp\Delta, \frac{1}{2}\mp\Delta)$. Alternatively, by superimposing two displacement waves a model can be constructed to give all four spots from a single domain.

The extra spots in Fig. 1(b) appear slightly elongated even at the lowest temperatures; this property, as well as the experimental resolution, limit the precision with which Δ can be determined. For the Mo(100) surface Δ is between $\frac{1}{16}$ and $\frac{1}{18}$, and for W(100) $\Delta \simeq 0$. The corresponding wavelength of the displacement wave is $\Lambda(\text{Mo}) \simeq 2.2a$ and $\Lambda(\text{W}) \simeq 2.0a$. In the analysis it has been assumed that Δ is a rational number, i.e., that the displacement wave is commensurate with the lattice parameter but it is evident that a distinction between commensurate and incommensurate structures cannot be made here by measuring the splitting.

The discussion given above relies on a kinematical treatment of the diffraction; to verify the model and to determine the magnitude of the displacements[11] a dynamical calculation of the LEED intensity will be necessary. Such calculations may be feasible before long, since considerable success has been achieved recently in the analysis of the normal (high-temperature) phase of Mo(100)[12] and W(100),[13] for which a contraction of the interlayer spacing by ~ 10% at the surface is indicated.

Reconstruction to produce a new surface periodicity has been observed on many semiconductors and on a few metals (Au, Pt, and Ir).[14] The semiconductor (111) surfaces have been of particular interest in theoretical studies and for these the reconstruction appears to be associated with a Fermi surface instability, the formation of a charge density wave, and surface phonon softening.[15] It is possible that the reconstruction on Mo(100) and W(100) has the same origin; the similarity of the transition to that of a layer compound, such as TaSe_2,[16] argues in favor of this hypothesis. In any case, the Mo(100) and W(100) should prove useful in studying the nature of the phenomenon. Unlike the other surfaces on which reconstruction has been seen, the transition on Mo(100) and W(100) can be controlled completely and reversibly by varying only the temperature. Furthermore, practically all the available surface spectroscopic techniques are applicable to these substrates; it should therefore be possible to explore the relationship of the phase transition to the surface electronic structure (and to surface states) by means of techniques such as ion-neutralization spectroscopy,[17] field-emission spectroscopy[18] and photoemission,[18] and electron reflectance.[19]

Besides being of interest in itself, the reconstruction of W(100) and Mo(100) is likely to have consequences for the interpretation of chemisorption data. For example, we have found that the $I(V)$ curve for the $(\frac{1}{2}\frac{1}{2})$ beam from the reconstructed W(100) is almost identical to the corresponding curve from the $c(2\times2)H$ structure. The reason may be that a displacement of metal atoms also occurs in hydrogen adsorption and that the H atoms contribute little to the LEED intensity, as was assumed in the early LEED literature. Using this interpretation it may be possible to understand some of the surface structures[2-4] in terms of displacement waves; the wavelength depends on the electron density which in turn is altered by the presence of an adsorbate. Thus, an explanation may be found for the peak in the $(\frac{1}{2}\frac{1}{2})$ intensity from the W(100) $c(2\times2)H$ at a coverage significantly below $\theta = 0.5$, and for the subsequent splitting of the $(\frac{1}{2}\frac{1}{2})$ spots. Preliminary results suggest that the inconsistencies which exist in the extensive literature on hydrogen adsorption on W(100)[18,20] may be removed in this way. Finally it should be noted that metal atom displacements might be a general phenomenon in adsorption on these surfaces and this possibility should be considered in the construction of overlayer models.

We are indebted to Dr. G. Carpenter for his help with the x-ray diffraction experiments. The support of the Brown University Materials Research Program, funded by the National Science Foundation, is gratefully acknowledged.

---

*Correspondence should be addressed to P. J. Estrup, Department of Physics, Brown University, Providence, Rhode Island 02912.

[1] K. Yonehara and L. D. Schmidt, Surf. Sci. 25, 238 (1971); J. C. Tracy, private communication, also observed the appearance of $(\frac{1}{2}\frac{1}{2})$ spots in the LEED pattern from W(100).

[2] P. J. Estrup and J. Anderson, J. Chem. Phys. 45, 2254 (1966).

[3] After this Letter had been submitted for publication it was learned that for tungsten the same conclusion has been reached independently by M. K. Debe and D. A. King (D. A. King, private communication).

[4] C. H. Huang and P. J. Estrup, to be published.

[5] P. J. Estrup, Phys. Today 28, No. 4, 33 (1975).

[6] This may explain why the transformation has been overlooked in almost all of the many LEED studies of W(100). Weak and diffuse $(\frac{1}{2}\frac{1}{2})$ spots observed near room temperature might be due to impurities and would suggest the need for cleaning by heating in oxygen. The cleaning procedure tends to leave the surface at a higher temperature and with small amounts of oxygen; both will impede the transformation.

[7] T. E. Felter and P. J. Estrup, Bull. Am. Phys. Soc. 21, 939 (1976).

[8] T. E. Madey, Surf. Sci. 36, 281 (1973); D. Menzel, Surf. Sci. 40, 295 (1973).

[9] A. Benninghoven, Appl. Phys. 1, 3 (1973).

[10] P. W. Palmberg, R. E. DeWames, L. A. Vredevoe, and T. Wolfram, J. Appl. Phys. 40, 1158 (1969).

[11] The magnitude of the displacement may be temperature dependent; this would be one way to account for the intensity variation shown in Fig. 2.

[12] A. Ignatiev, F. Jona, H. D. Shih, D. W. Jepsen, and P. M. Marcus, Phys. Rev. B 11, 4787 (1975).

[13] M. A. Van Hove and S. Y. Tong, Surf. Sci. 54, 91: (1976); B. W. Lee, A. Ignatiev, S. Y. Tong, and M. A. Van Hove, J. Vac. Sci. Technol. 14, 291 (1977).

[14] A summary may be found in, for example, G. A. Somorjai and L. L. Kesmodel, MTP Int. Rev. Sci. 7, 1 (1975).

[15] E. Tosatti and P. W. anderson, Jpn. J. Appl. Phys. Suppl. 2, Pt. 2, 381 (1974).

[16] J. A. Wilson, F. J. DiSalvo, and S. Mahajan, Advan. Phys. 24, 117 (1975).

[17] H. D. Hagstrum, Science 178, 275 (1972).

[18] E. W. Plummer, in *Interactions on Metal Surfaces*, edited by R. Gomer (Springer, New York, 1975), p. 143.

[19] E. G. McRae and C. W. Caldwell, Surf. Sci. 57, 63 (1976).

[20] L. D. Schmidt, in *Interactions on Metal Surfaces*, edited by R. Gomer (Springer, New York, 1975), p. 63.

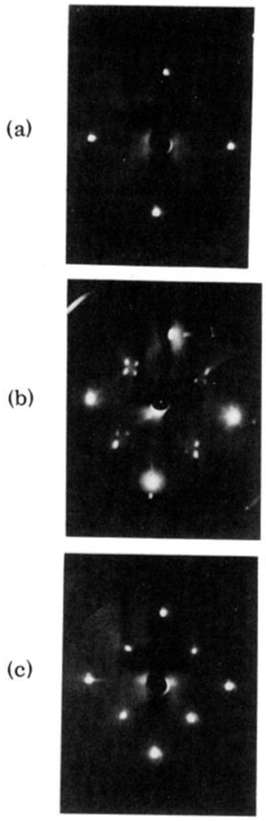

FIG. 1. (a) LEED pattern from clean W(100) above room temperature. Beam voltage 42 V. The pattern contains only the expected "normal" diffraction spots. Mo(100) gives an identical spot pattern. (b) LEED pattern from clean Mo(100) cooled to ~160 K. "Extra" beams are present, consisting of a quartet of spots surrounding the $(\frac{1}{2}\frac{1}{2})$ positions. The separation between the spots does not vary with temperature and is $\frac{1}{8}-\frac{1}{9}$ of the separation between the normal spots. (c) LEED pattern from clean W(100) cooled to ~160 K. The extra beams appear in the $(\frac{1}{2}\frac{1}{2})$ positions.