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Structure of the low-temperature phase of molybdenum (001) investigated by helium-atom scattering

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Using helium-atom scattering, we provide evidence that the low-temperature phase of the clean Mo(001) surface is a high-order commensurate structure. The reciprocal lattice vector $\mathbf{Q}_s$ of the superstructure is determined to be $\mathbf{Q}_s = \frac{3}{7}\mathbf{G}_{11}$, in accord with the Q value at which a longitudinal surface phonon becomes soft in the high-temperature phase giving rise to a periodic lattice distortion. Upon further cooling, extra satellites appear in the diffraction pattern, which cannot be observed with the *in situ* low-energy electron diffraction system. These extra features observed in He diffraction can be explained by a periodic lattice distortion involving normal as well as lateral displacements of the surface atoms.

The clean Mo(001) surface undergoes a reversible reconstruction below room temperature.[1] This behavior is similar to that of tungsten which has nearly identical lattice and electronic structure. The reconstruction of W(001) is now well known and represents the most thoroughly studied surface phase transition.[2] However, the structure of the low-temperature phase of the Mo(001) surface differs from that of W(001): whereas the low-energy electron diffraction (LEED) pattern of W(001) below T_c shows a $c(2\times2)$ structure, on Mo(001) a more complicated structure is found with the $c(2\times2)$ spot split into a quartet of spots in $\langle 110\rangle$ and the perpendicular direction. This structure was explained by Estrup[1,3] as arising from a periodic lattice distortion (PLD) modulating the positions of the surface atoms as

$$\mathbf{R}(l) = \mathbf{R}_0(l) + \mathbf{A}\sin[\mathbf{Q}_s \cdot \mathbf{R}_0(l)] , \qquad (1)$$

where $\mathbf{R}(l)$ is the actual position, $\mathbf{R}_0(l)$ the position in the (1×1) high-temperature phase. The vector $\mathbf{A}$ denotes amplitude and polarization of the PLD and $\mathbf{Q}_s$ is the wave vector of the PLD. Such structures are known from charge-density wave (CDW) systems like $TaSe_2$.[4] The PLD gives rise to satellite spots at $\mathbf{G}_{hk} \pm n\cdot\mathbf{Q}_s$, $n = 1,2,\ldots$ in the diffraction pattern, where $\mathbf{G}_{hk}$ are the reciprocal lattice vectors of the undistorted lattice. The intensity of the satellite spots depends on the PLD amplitude; since the amplitude is small compared to the lattice constant, usually only spots of first order ($n=1$) are observed.[4]

Recent helium-scattering experiments[5-8] have revealed that an intermediate incommensurate phase prevails on W(001) which is not observed in LEED (Refs. 2 and 9) and x-ray scattering.[10] The reason for these different findings is still a subject of debate.[11] Thus, one might ask what the Mo(001) surface would look like in the light of helium scattering. Therefore we have continued our previous work on the high-temperature phase of Mo(001) (Ref. 12) which had shown that the reconstruction of the clean Mo(001) is driven by the softening of a surface phonon—similar to the behavior of W(001) (Ref. 6)—with a study of the low-temperature phase. It should be noted that the PLD model is consistent with the condensation of such a soft surface phonon mode.

The scattering apparatus and the cleaning procedure of the surface have been described in a previous publication.[12] A new, oriented and polished single crystal (Metal Crystals and Oxides Ltd., Cambridge, UK) is connected to the holder by a number of thin tungsten wires to prevent damage due to thermal expansion during the flashes. The lowest temperatures that could be reached with this mounting are about 200 K for liquid-nitrogen cooling and about 100 K for liquid-helium cooling. The temperatures were determined with a NiCr-Ni thermocouple fixed to the holder. It took the crystal about 12 min to reach the lowest temperature at 5×10^{-11} mbar residual pressure. Under these conditions the superstructure of the reconstructed surface was visible in LEED for about $\frac{1}{2}$ h until it gradually vanished. Upon checking the orientation of this crystal it turned out to be accidentally misoriented, about 1° off plane in one of the $\langle 100\rangle$ directions corresponding to an average terrace width of 70 Å. Nevertheless, no split spots due to periodic step arrays were found in the LEED pattern and the previously observed soft phonon of the high-temperature phase could be reproduced with inelastic He atom scattering.

Figure 1(a) illustrates the helium diffraction pattern at 200 K, close to T_c which is about 250 K. Two superstructure peaks are observed in accord with the LEED pattern.[1] The peculiar shape and the width of the satellite peak of the specular beam (00) resembles that of the diffraction peak found on the W(001) surface close to T_c.[6,8] However, a corresponding satellite of the (11) peak is not observed for W(001).[5-8] Ernst, Hulpke, and Toennies[8] show that within the Eikonal approximation[13] this satellite is of very low intensity for the case of a small corrugation of both the surface and the CDW. Their corrugation model is consistent with a model used to calculate the He diffraction intensities from the CDW system $TaSe_2$.[14]

As shown in Fig. 1(b) for Mo(001) the situation changes dramatically upon further cooling of the surface to about 100 K. As in LEED (Refs. 1 and 15) the satellite peaks become more intense and sharpen as the phase

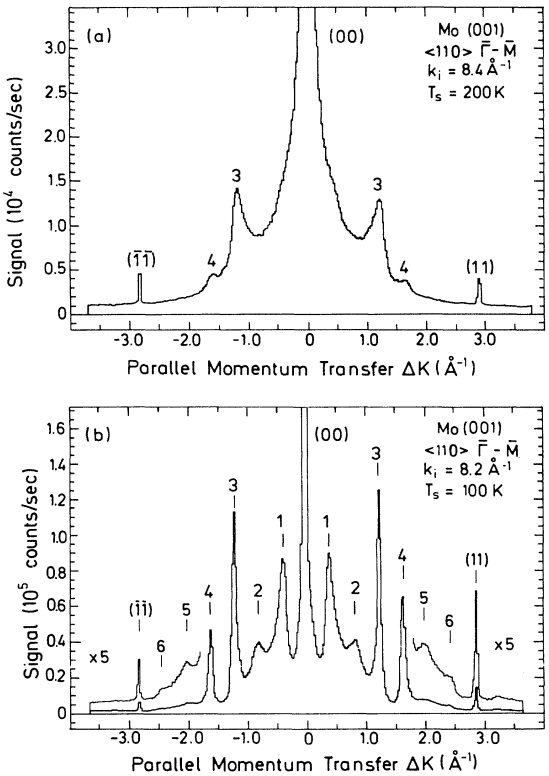

FIG. 1. Helium atom diffraction from the clean reconstructed Mo(001) surface in the ⟨110⟩ azimuth at (a) 200 K and (b) 100 K. The diffraction peaks of the parent structure are labeled by their Miller indices. The satellite peaks due to the superstructure are numbered, $n=1,2,3,\ldots$, and occur at the $(n/7, n/7)$ positions. The wave vector k_i of the incident He beam and the surface temperature T_s are denoted in each plot. Specular intensities are (a) 2.9×10^6 counts/sec and (b) 4.3×10^6 counts/sec, respectively. Note the different intensity scales.

transition proceeds to completion. However, additional satellite peaks are observed which do not appear in the LEED pattern which was measured afterwards by moving the crystal in front of the *in situ* LEED system. The extra features seen with He scattering were found to be very sensitive to contamination with H_2 and CO which are the main constituents of the residual gas. Deliberate dosing of some 0.01 L (1 L $=10^{-6}$ Torr s) of these gases causes a strong decrease of their intensities. Furthermore the intensities of the extra spots depend on the surface temperature. Unfortunately in the present setup intermediate temperatures between 100 and 200 K could not be achieved. The diffraction pattern shown in Fig. 1(b) corresponds to the lowest temperature we could reach.

The evaluation of the wave vectors of the superstructure at 100 K reveals that the ratio of the period of the superstructure to the one of the parent structure is seven:

$$G_{11}/\Delta K = 7.0 \pm 0.1 , \qquad (2)$$

where $\Delta\mathbf{K}$ is the distance between two neighboring satellites and $\mathbf{G}_{11}$ is the reciprocal lattice vector in the ⟨110⟩ direction. Therefore the structure of the reconstructed Mo(001) surface is rather a high-order commensurate structure than an incommensurate one as was speculated in early LEED work[16] from which this ratio was determined to be between eight and nine. However, the evaluation of the LEED pattern taken by us (cf. Fig. 2) is not at variance with the helium scattering results. From our LEED data we derive a value of $G_{11}/\Delta K = 7.0 \pm 0.5$. More recent LEED results[17] also give a value close to seven.

The positions of the helium diffraction peaks do not shift (cf. Fig. 1) in the range of surface temperatures between 100 and 200 K in accord with the LEED results.[1,15] This observation is in contrast to the helium scattering results for W(001),[6,8] even though the shape of the main satellite close to T_c looks similar in both systems. Furthermore the diffraction pattern of Mo(001) at low temperatures is in remarkable agreement with the observed dynamics of the high-temperature phase:[12] The wave vector at which the soft surface phonon would reach zero energy coincides almost perfectly with the observed satellite peak of the specular beam at 200 K [Fig. 1(a)]. Thus we can nicely verify that the phase transition is indeed of displacive nature. Concerning the periodicity of the PLD we therefore derive a value of

$$\mathbf{Q}_s = \tfrac{3}{7}\mathbf{G}_{11} . \qquad (3)$$

In order to explain the observed extra diffraction features in the He atom scattering we have performed Eikonal calculations. The essential ingredient of such a calculation is the corrugation function which corresponds to the electron-density contour at the classical turning points of the He atoms. The model corrugation proposed by Ernst *et al.*[8] for W(001) was found to be not appropriate for Mo(001) because no value of the adjustable parameters resulted in the proper He diffraction intensities. Recent theoretical models for Mo(001) suggest a different

FIG. 2. LEED pattern of the clean reconstructed Mo(001) surface at 100 K, obtained with the *in situ* LEED system at $\approx$ 250 eV electron energy and close to normal incidence. The LEED screen is partly obscured by the target holder. Diffraction from predominantly one of the two possible domains of the periodic lattice distortion is to be seen. The He diffraction of Fig. 1 was measured in the azimuth of the visible doublet of superstructure spots.

approach to construct a corrugation model: in molecular dynamics calculations[18] as well as from free energy considerations[19] it is found that the lateral displacements of the surface atoms are accompanied by normal displacements in the reconstructed phase. In order to obtain a smooth corrugation function which is capable of accounting for the local displacements of an individual surface atom we have chosen a superposition of Gaussians:

$$\zeta(\mathbf{R}) = \sum_l [h + z(l)] \exp\left[-\left(\frac{\mathbf{R} - \mathbf{R}(l)}{b} \right)^2 \right]. \quad (4)$$

In the low-temperature phase the lateral positions of the surface atoms $\mathbf{R}(l)$ are given by Eq. (1) whereas the normal displacements are predicted to be of the form

$$z(l) = a_z \cos[\mathbf{Q}_s \cdot \mathbf{R}_0(l)] \quad (5)$$

and the amplitude a_z should equal that of the lateral modulation A.[18] The parameters h and b were determined such that proper diffraction probabilities could be derived for the high-temperature phase resulting in the values of 1.6 Å for h and 2.4 Å for b. With this choice of parameters the corrugation given by Eq. (4) resembles closely the usual sine corrugation function (cf. Fig. 3) and, moreover, provides realistic classical turning points of the He atoms of about 3 Å above the positions of the ion cores in the surface layer. The diffraction intensities of the reconstructed phase can be qualitatively described by using the above values of h and b and assuming displacement amplitudes of $A = a_z = 0.2$ Å which are in accord with recent calculations.[18,20,21] The corresponding structural model and the corrugation function are shown in Fig. 3. The experimental and calculated relative intensities are listed in Table I.

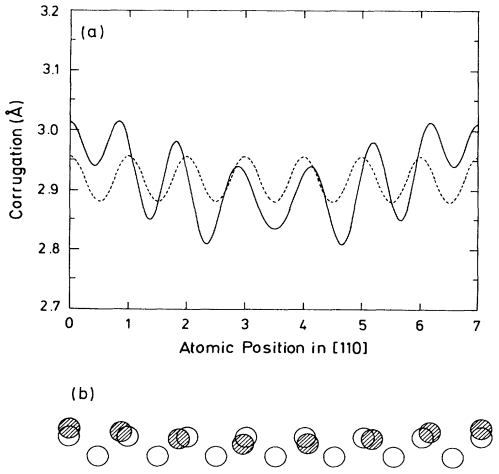

FIG. 3. Structural model and the corresponding corrugation function for Mo(001) in the low-temperature phase. Panel (b) shows a side view of the first and second layer surface atoms in a cut along the ⟨110⟩ direction displaying a circular PLD, panel (a) the corrugation function according to Eq. (4) (solid line). The dashed curve refers to the corrugation in the undistorted high-temperature phase.

Note that the period of the PLD corresponds to $\mathbf{Q}_s = \frac{3}{7}\mathbf{G}_{11}$; hence the first-order satellites at $\mathbf{G}_{hk} \pm \mathbf{Q}_s$ are predominant in the LEED pattern.[1,3,16,22] However, the corrugation function of the reconstructed surface with a circularly polarized PLD also contains appreciable Fourier components at $\frac{1}{7}\mathbf{G}_{11}$ and $\frac{4}{7}\mathbf{G}_{11}$ giving rise to the corresponding satellites in the He diffraction. Thus a PLD involving normal as well as lateral displacements of the surface atoms provides an explanation for both He atom and electron diffraction from the reconstructed Mo(001) surface. It should be further noted that the polarization vector of the longitudinal soft surface phonon also contains a normal component, since in general sagittal surface waves with wave vectors off the high symmetry points of the Brillouin zone have an elliptical polarization.

In addition we have measured the helium diffraction in the ⟨100⟩ azimuth at 100 K in order to determine whether extra spots could also be observed there. However, only the Bragg peaks of the parent structure are to be seen. This result is particularly interesting in the context of a question which had been raised by Bak.[23] From the Landau expansion of the free energy he predicted two possible low-temperature structures depending on the sign of the anisotropy parameter v. For $v > 0$ the minimum of the free energy corresponds to two domains, each modulated with a single wave vector, $\mathbf{Q}_{s1} = (Q_s, Q_s)/\sqrt{2}$ or $\mathbf{Q}_{s2} = (Q_s, -Q_s)/\sqrt{2}$. In case $v < 0$ both PLDs are superimposed. Such a "double-Q" domain would give rise to extra diffraction peaks occurring at $\mathbf{Q}_{s1} \pm \mathbf{Q}_{s2}$ and so forth. These features would show up the strongest at $\mathbf{Q}_{s1} \pm \mathbf{Q}_{s2}$, i.e., in the ⟨100⟩ direction. Since no extra satellite spots are observed in the ⟨100⟩ azimuth, we can state that in our system v must be positive, i.e., there are only single-Q domains.

In conclusion we find in our He atom scattering study that the low-temperature phase of Mo(001) has a high-order commensurate structure with a modulation wave vector $\mathbf{Q}_s = \frac{3}{7}\mathbf{G}_{11}$ yielding the same period of the PLD as with LEED. The intricate question arises concerning what kind of mechanism stabilizes this peculiar periodicity at a clean metal surface. Additional satellite peaks have been observed in He diffraction from the fully reconstructed surface which have not been found in previous

TABLE I. Relative intensities for the diffraction peaks $(n/7, n/7)$ with respect to the specular beam. Experimental intensity values are derived from Fig. 1(b). Parameters for the corrugation model given by Eqs. (1), (4), and (5): $h = 1.6$ Å, $b = 2.4$ Å, $A = a_z = 0.2$ Å.

Peak	Experiment	Calculated
1	1.4×10^{-2}	0.7×10^{-2}
2	2.4×10^{-3}	0.2×10^{-3}
3	2.6×10^{-2}	5.5×10^{-2}
4	1.2×10^{-2}	2.9×10^{-2}
5	4.7×10^{-4}	2.2×10^{-4}
6	1.2×10^{-4}	7.4×10^{-4}
7	2.4×10^{-3}	8.2×10^{-3}

LEED studies.[1,3,15,16] Eikonal calculations of their intensities indicate that in this phase the surface atoms are not only laterally displaced but are also displaced normal to the surface. Our findings are consistent with recently proposed theoretical models for the reconstructed Mo(001) surface. The presence of the extra satellites in the He diffraction is traced back to the differences between He atoms and electrons in the scattering process.

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