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Diffraction of helium from an ordered adsorbed layer: Oxygen on copper (110)

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The diffraction of a helium nozzle beam from an ordered adsorbed layer of oxygen on copper Cu (110)-O(2×1) has been experimentally observed. The amplitudes of diffraction peaks were determined under various incidence conditions. This system is found to be very strongly corrugated in contrast with the clean surface. An analysis within the frame of the corrugated hardwall model gives a position for the oxygen atoms 0.7±0.1 Å below the copper surface. Resonances with bound states are also observed from which information about the He–surface-potential curves was deduced.

The diffraction of helium has been proven to be a powerful tool to study surface crystallography.[1] Recently it has been shown that helium readily diffracts from an ordered adsorbed layer [H on Ni (110)](Ref. 2), opening a new approach for chemisorption investigations. Following our previous work about the reflection of helium from copper surfaces, Cu (100) (Ref. 3) and Cu (117) (Ref. 4), we describe here the results we have obtained for the diffraction of helium from an ordered adsorbed layer of oxygen on Cu (110).

It is known from low-energy electron diffraction (LEED) measurements[5-9] that oxygen on Cu (110) forms an ordered (2 ×1) layer which is stable under a wide range of pressures and temperatures. From ion-scattering experiments[10] it has been inferred that the center of the adsorbed oxygen atom lies 0.6 ± 0.1 Å below the midpoint between two neighboring Cu atoms in a [100] row as shown on Fig. 1(a).

The nozzle beam scattering experiment is identical to that used for He-Cu (117) (Ref. 4) except that the detector sensitivity has been improved by using a stagnation detector in connection with a low-frequency chopper (2 Hz) which allows a lock-in detector to be used.[11] With these conditions, scattered fluxes as low as 5×10^{-5} times the incident flux can be readily detected.

The surface is cleaned *in situ* in the usual way by alternate cycles of ion bombardment and annealing. The cleanliness is monitored by Auger-electron spectrometry. Oxygen is deposited onto the surface through a capillary tube (diameter 0.028 cm, length 50 cm), the end of which is located 3 cm in front of the surface. Such a disposition has the advantage of delivering a relatively large gas flux onto the surface without raising the isotropic pressure in the chamber and thus avoiding an increase of the background oxygen partial pressure after the adsorption procedure. The same injection device has been used in an auxiliary experiment in which an LEED facility was available. We found that exposing the surface during 5 min with an upstream pressure of 5 Torr was sufficient to get a very-well-defined (2 ×1) LEED structure while the Auger oxygen peak reaches a characteristic plateau. We have reproduced these conditions in the scattering experiment and we have checked that the Auger oxygen signal was the same as in the auxiliary experiment.

The helium beam impinges on the surface parallel to the [110] direction, i.e., parallel to the rows of copper atoms (Fig. 1). Only in-plane scattering can be recorded in our experiment. For scattering on the clean surface only a strong specular peak appears. No higher-order diffraction peaks have been detected, indicating that the (110) copper surface is very smooth in the [110] direction. This is in good agreement with the result of Rieder and Engel for Ni (110) (Ref. 2). The adsorption of oxygen brings about a dramatic change. Figure 1(b) shows the scattering with an oxygen coverage corresponding to the (2 ×1) LEED pattern. The specular peak has decreased by two orders of magnitude and many diffraction peaks appear. Peaks are indexed with respect to the copper reciprocal-lattice vectors so that half-order peaks are present which characterize the double-unit mesh lattice of oxygen in the [110] direction. A measurable peak corresponds to each open channel. The rainbow pattern is very extended so that high-index peaks such as the $\bar{4}$ remain quite large. This is in contrast to the Ni (110)-H system where the specular peak remains predominant, indicating a moderate corrugation (Rieder and Engel found 0.23 Å). Thus in our case a much larger corrugation is expected. We have checked, using a method previously described,[4] that the peak shapes do correspond to the instrumental broadening due to beam and detector apertures and the velocity distribution. No additional broadening due to incoherence effects oc-

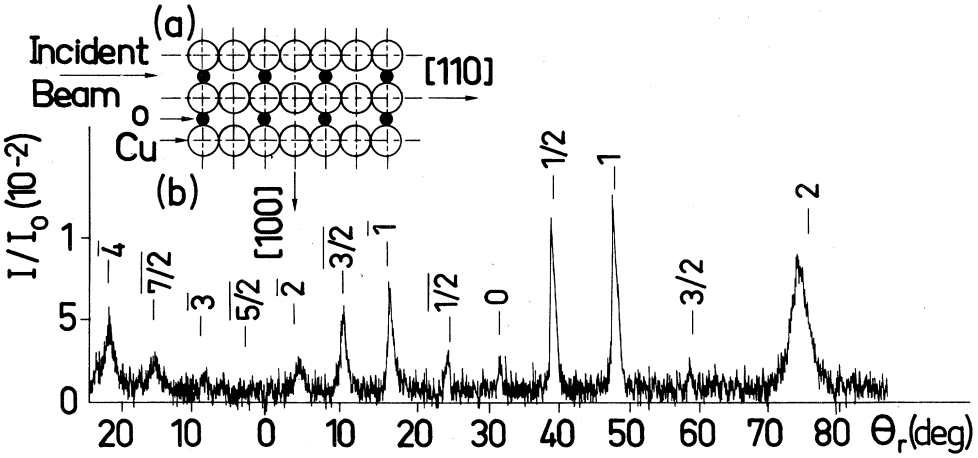

FIG. 1. (a) Structure of Cu (110)-O (2×1); Oxygen adlayer. (b) In-plane scattering of helium on this oxygen structure; $\Theta_i = 31.5°$, $E_i = 63$ meV.

curs, which is evidence that the adsorbed layer is very well ordered.

Additional measurements were done on the (2 ×1) structure for different values of the incidence angle Θ_i. The intensities of the observed diffraction peaks are summarized on Fig. 3. The peak intensities were corrected for two effects: (1) The instrumental peak broadening has been taken into account as mentioned above. (2) The peak intensities were divided by the Debye-Waller factor in order to get the peak intensities corresponding to an immobile lattice which are more suitable to comparison with theoretical calculations.

The Debye-Waller factor was experimentally measured by following the thermal dependence of every diffraction peak between 70 and 473 K. The oxygen structure was found to be stable throughout this temperature range. The Debye-Waller factor for the oxygen structure is definitely smaller than for the clean metal by at least a factor of 3. For the specular peak it has been shown[3,12] that the exponent of the Debye-Waller (e^{-2W}) factor can be approximately expressed as

$$2W \simeq (8m/\hbar^2)E_i\langle u^2_{\text{eff}}\rangle(\cos^2\Theta_i + D/E_i),$$

where m is the mass of the incident atom, D is the well depth, and $\langle u^2_{\text{eff}}\rangle$ are the effective mean-square displacements which take into account multiple interactions due to the finite size of the incident atom. The lowering of the D-W factor by oxygen means either a larger $\langle u^2_{\text{eff}}\rangle$ or a larger D (or both).

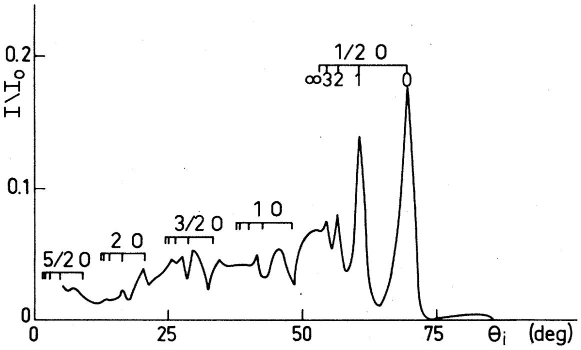

FIG. 2. Variation of the specular peak intensity with respect to incidence angle Θ_i. The position of the resonances corresponding to the four deeper levels and the threshold (∞) are indicated for the various reciprocal-lattice vectors involved.

An independent evaluation of D can be obtained by looking at the resonances with bound states. Figure 2 shows a plot of the intensity of the specular peak versus incidence angle. Very sharp maxima are readily seen, especially near grazing incidence, which are typical of such resonances. The intensity of the other diffraction peaks behaves in the same way, displaying sharp maxima and minima for the same incidence angles. By comparing the location of these extremes for two incidence energies (63 and 21 meV) we are led to deduce that the observed resonances are only due to transitions with in-plane reciprocal-lattice vectors as labeled on Fig. 2. Four energy levels are then identified:

$$\epsilon_0 = -17.6,\quad \epsilon_1 = -8.5,$$

$$\epsilon_2 = -3.8,\quad \epsilon_3 = -1.25\ \text{meV}.$$

A fitting of the two deepest levels by a 9-3 potential,

$$v(z) = (3^{3/2}D/2)[(\sigma/z)^9 - (\sigma/z)^3],$$

gives $D = 24.6$ meV, $\sigma = 1.33$ Å, $\epsilon_2 = -3.7$, and $\epsilon_3 = -1.4$ meV. The agreement with the observed upper levels falls within the experimental accura-

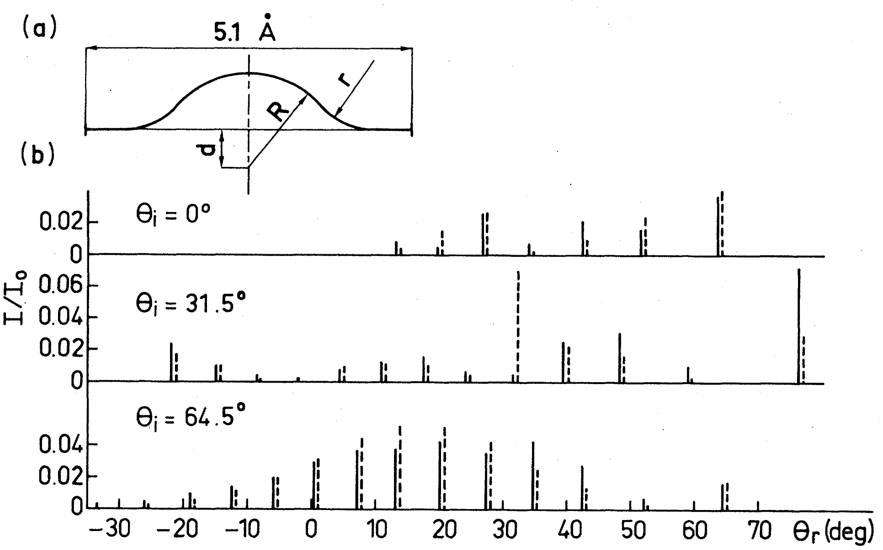

FIG. 3. (a) CHW profile. (b) Intensity of diffraction peaks for various incidence angles ($E_i = 63$ meV). Solid lines: experimental results; dashed lines: CHW calculations.

cy. The well depth is much larger than the well depth expected for the clean metal ($D \sim 6$ meV as obtained from the D-W factor). This difference in well depths is almost sufficient by itself to explain the D-W factor differences between the oxygen structure and the clean metal so that the $\langle u_{\mathrm{eff}}^2 \rangle$ are likely very similar in the two cases.

The interpretation of the diffraction-peak intensities in terms of the corrugated hard-wall model (CHW) (Ref. 13) is not straightforward for two reasons: (1) As already pointed out, the corrugation amplitude is fairly high, thus the eikonal approximation which leads to analytic calculations cannot be used. One must use a numerical method as in the case of He-LiF (Ref. 14). But here the number of open channels is much higher (177 for $E_1 = 63$ meV) which makes this computation more tedious. (2) Resonance effects are very important (especially at low energy) and in some places completely modify the shape of the rainbow pattern.

However, we can take advantage of the fact that the corrugation seems to be larger in plane than out of plane. This is supported by two observations: (a) Only resonances with in-plane G vectors are detected, indicating that the out-of-plane Fourier components of the potential are weaker than in-plane ones. (b) The total in-plane scattering is more important than it would be if the scattering were equally distributed among every open channel. For instance, at $\Theta_i = 64.5°$ the total in-plane measured scattering is 0.32 for 14 channels. There are 177 open channels so that we would expect only $\frac{14}{177} = 0.079$ for homogeneous distribution.

Thus in order to get a very qualitative view of the scattering, we may tentatively assume that the in-plane rainbow pattern is dominated by the in-plane corrugation. We have therefore done a CHW calculation with the Garcia-Cabrera[15] method, neglecting the out-of-plane corrugation. The corrugation used is shown on Fig. 3. The radius R is chosen to be the van der Waals radius of the oxygen atom (1.40 Å) (Ref. 16), and r is assumed to be the radius of the helium atom deduced from the second virial coefficient (1.44 Å) (Ref. 17). The distance d is taken to be an adjustable parameter. The best fit is obtained for $d = 0.7$ Å, which compares well with the value deduced from ion-scattering experiment (0.6 Å). The results of the calculation are shown on Fig. 3. Of course only the relative amplitudes between the various peaks can be compared since in the calculation all the scattering is in plane. The agreement is quite good for $\Theta_i = 64.5°$. The position of the rainbow maximum is very sensitive to the choice of d: it is shifted by ± 10° for a variation of ± 0.1 Å. The agreement is not so good for the two other incidence angles, especially for the specular peak at $\Theta_i = 31.5°$. The corrugation amplitude ($R - d$) is 0.7 Å, which is more than twice the corrugation found for N (110) − H(2 × 1). This is not surprising since the size of the oxygen atom does not allow it to penetrate so deeply into the lattice as hydrogen does. This very large corrugation makes helium diffraction very sensitive to the position and structure of the adsorbate. Even with the very rough model used here we are able to make quantitative predictions about the oxygen position with respect to copper lattice.

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