

## Hydrogen-Induced Subsurface Reconstruction of Cu(110)

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Room-temperature adsorption of atomic hydrogen on Cu(110) initially yields a  $(1 \times 2)^*$  phase visible with low-energy electron diffraction but not with atom diffraction; this surprising observation suggests that H moves below the surface and induces a reconstruction in deeper layers. Upon further H uptake the  $(1 \times 2)$  periodicity extends to the surface and also becomes visible with atom diffraction. Low-temperature phases, in which H adsorbs above the surface, transform at  $\sim 240$  K into the  $(1 \times 2)$  reconstructed phases, proving that H subsurface movement requires thermal activation.

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The existence of subsurface hydrogen on transition-metal surfaces was postulated on the basis of photoemission data,<sup>1-4</sup> and to explain the puzzling results on the distribution of translational<sup>5</sup> as well as rotational and vibrational states<sup>6</sup> upon molecular desorption of permeated hydrogen. Indirect support came from theoretical calculations,<sup>7,8</sup> but direct evidence based on structural investigations has remained rather scarce up to now.<sup>9,10</sup>

Here, we report adsorption studies of atomic hydrogen on Cu(110) with low-energy electron diffraction (LEED), atom diffraction and thermal desorption spectroscopy (TDS). Most strikingly, at room temperature, H adsorption induces a  $(1 \times 2)$  reconstruction which at low coverages only affects layers below the topmost layer; this follows from the finding that LEED (sensitive to the first few layers) starts seeing the  $(1 \times 2)$  periodicity, whereas He and Ne diffraction (sensitive to the topmost layer only) still observes the structure of the clean surface. Uptake of more H causes the  $(1 \times 2)$  structure to extend from the interior to the surface, since the  $(1 \times 2)$  periodicity also becomes visible with atom diffraction and the LEED intensities change. Ordered and disordered H-chemisorption phases forming upon low-temperature adsorption transform (without loss of hydrogen into the gas phase) into the  $(1 \times 2)$  reconstructed phases upon heating to 240 K.

The Cu (110) sample was the one used in our previous atomic- and molecular-beam diffraction studies of the clean surface.<sup>11</sup> As low-index Cu surfaces do not dissociate thermal energy hydrogen molecules,<sup>2,12</sup> atomic hydrogen was produced in the scattering chamber with a hot tungsten filament glowing in the vicinity of the sample. Rather long H<sub>2</sub> exposures between 200 and 2000 L (1 L =  $10^{-6}$  Torr sec) were necessary to obtain the H phases reported here.

We first describe our results obtained upon H adsorption at room temperature. Figure 1(a) shows a typical He-diffraction scan of the clean surface. The solid line in Fig. 1(b) exhibits a scan after exposure to 250 L. This spectrum shows an overall decrease of intensity of 25%–30% as compared to the clean surface, but the rela-

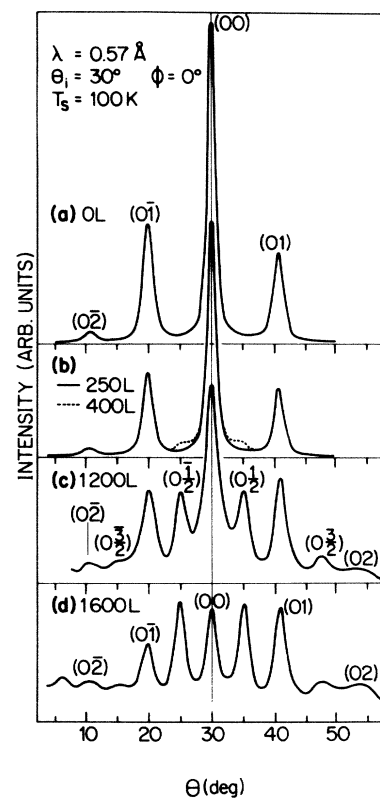


FIG. 1. In-plane He-diffraction scans with room-temperature beam along the [001] azimuth, i.e., perpendicular to the close-packed rows. Exposure to H<sub>2</sub> is performed with a W filament on. Adsorption temperature is 300 K. (a) Clean Cu(110) surface. (b) After exposure to 200 L. The spectrum shows the same distribution of diffraction intensities as the clean surface; the corresponding LEED pattern, however, shows the  $(1 \times 2)$  superstructure of Fig. 2(a). After exposure to 300 L, shoulders form near the specular direction as indicated by the dashed lines. (c) After exposure to 1200 L; half-order beams are now also visible with He diffraction. (d) After exposure to 1600 L. The LEED intensities of Fig. 2(b), obtained after large exposures, are different from those of Fig. 2(a).

tive intensities of all beams are the same as on the clean surface (within an experimental error of a few percent). Thus, the corrugation is identical to that of the clean surface both in shape and amplitude. The striking observation is, however, that the LEED picture displays a clear  $(1 \times 2)$  structure with rather intense half-order spots [Fig. 2(a)]. Since such a situation has never been previously observed, we checked whether the  $(1 \times 2)$  periodicity would be observed with Ne; Ne penetrates to higher surface charge densities than He, and is therefore more sensitive to details of the corrugation. However, the relative intensities of the diffraction beams were again the same as for the clean surface. In order to distinguish this particular phase, we denote it in the following by  $(1 \times 2)^*$ . Its peculiarity is recognized by confronting of the two structural methods employed: (i) The result that He and Ne, which are very sensitive to H on top of the surface, are blind to the  $(1 \times 2)^*$  structure indicates that the H atoms move below the surface, and (ii) the fact that the LEED superspots are rather intense requires a Cu(110)-subsurface reconstruction since the H atoms scatter electrons only weakly. The following argu-

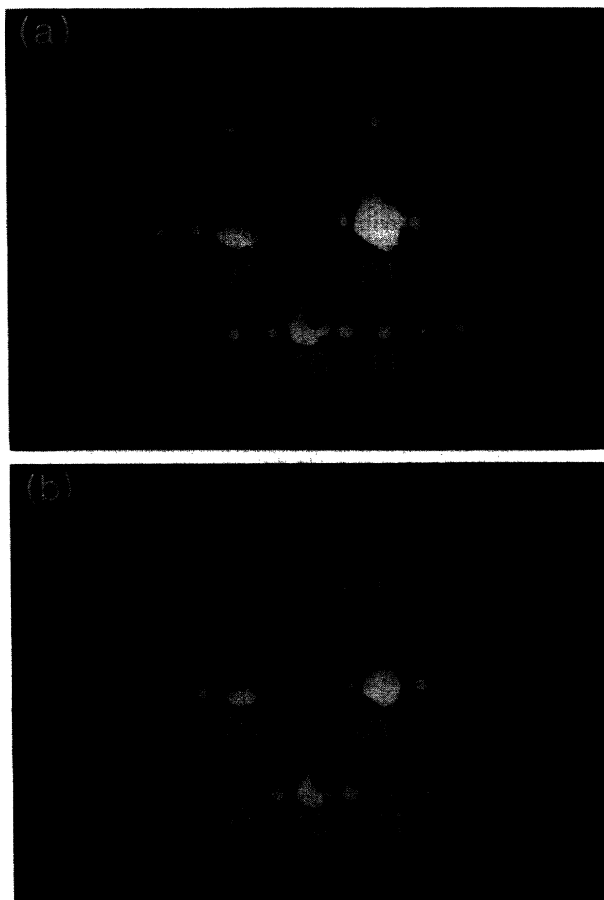


FIG. 2. LEED patterns with the electron beam impinging near surface normal at 130 eV. (a) After exposure to 200 L H<sub>2</sub> at 300 K. (b) After exposure to 1200 L.

ments support these conclusions: (i) Low-temperature adsorption yields a “ $(1 \times 3)$ ” phase which causes a pronounced change in the shape and amplitude of the surface corrugation showing that H chemisorbs above the surface. (ii) Surface-charge-density model calculations using overlapping atomic densities show that even “weak”  $(1 \times 2)$  surface reconstructions such as the pairing or buckled-row types<sup>13</sup> would produce half-order diffraction peaks measurable with He and Ne with metal atom displacements as small as 0.01 Å.

Upon further H adsorption at room temperature, the He diffraction pattern starts to develop shoulders near the specular direction [dashed line in Fig. 1(b)] and then develops half-order diffraction beams, whereby the relative intensities of the different beams change continuously [Figs. 1(c) and 1(d)]. Also the LEED intensities change, as seen by comparison of Figs. 2(a) and 2(b): Whereas the  $(\pm \frac{1}{2}, -1)$  and  $(\pm \frac{1}{2}, 1)$  spots in the  $(1 \times 2)^*$  phase are less intense than the  $(\pm 1, -1)$  and  $(\pm 1, 1)$  spots, respectively, the situation is reversed for the  $(1 \times 2)$  phase visible to both LEED and atom diffraction.

Further important information was obtained by adsorption experiments at 100-K surface temperature. TDS data showed that the effective sticking coefficient of atomic hydrogen at 100 K is about twice that at 300 K. A “ $(1 \times 3)$ ” structure forms after exposure to ~200 L as observed with He diffraction (Fig. 3), while with our visual LEED system no superstructure could be observed. We use quotation marks to denote this phase

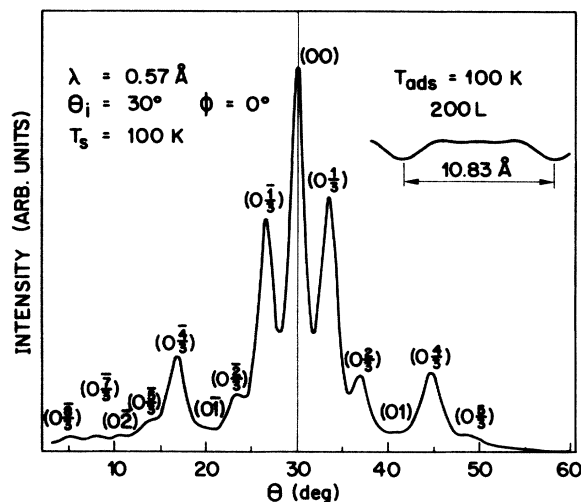


FIG. 3. In-plane He-diffraction scan for the “ $(1 \times 3)$ ”-H phase formed upon H adsorption on Cu(110) at 100 K. The scattering geometry is the same as in Fig. 1. The one-dimensional best-fit corrugation of the “ $(1 \times 3)$ ” is in shape and amplitude very similar to that of the  $c(2 \times 6)$  phase on Ni(110) corresponding to a  $\Theta = \frac{1}{3}$  ML. As no superspots are visible with LEED, there is no metal reconstruction and H must be adsorbed on top of the surface.

since only good in-plane He-diffraction patterns were observed and therefore the real unit cell could be different.<sup>14</sup> Analyses of the He-diffraction intensities do indeed yield an average corrugation perpendicular to the close-packed rows (Fig. 3) which is similar both in shape and amplitude to the corrugation of the  $c(2 \times 6)$  H phase on Ni(110) with coverage  $\Theta = \frac{2}{3}$  monolayer (ML) [Fig. 9(d) in Ref. 14]. This suggests for the Cu(110) + "(1  $\times$  3)" H phase the same coverage and a similar arrangement of adatoms above the surface although more disordered along the close-packed rows. Heating the sample to room temperature transforms the "(1  $\times$  3)" into the (1  $\times$  2)\* of Fig. 1(b) which displays small shoulders near the specular direction. A hydrogen exposure of  $\sim 150$  L and 100 K yields a "(1  $\times$  3)" whose diffraction pattern is not as well developed as the one of Fig. 3. Warming up the sample to 300 K yields the (1  $\times$  2)\* of Fig. 1(b) without the shoulders. We judge from the  $\sim 30\%$  smaller exposure that the coverage in this case is also smaller by 30% than that of the ideal "(1  $\times$  3)." This yields  $\Theta = \frac{1}{2}$  ML for the (1  $\times$  2)\*. The "(1  $\times$  3)" pattern degrades upon further H exposure at 100 K, and at very large exposures only a broad and rather structureless intensity distribution is observed. Since the LEED pattern retains the (1  $\times$  1) periodicity, we conclude that a strongly disordered H-chemisorption phase is formed, whose coverage corresponds to 1.5–2 ML according to our TDS data [Fig. 4(b)]. The full sequence of diffraction patterns indicated in Fig. 1 can be obtained by adsorption at 100 K and subsequent heating to 300 K. Since the sticking coefficient at 100 K is about twice that at 300 K, all patterns can be reached in this way with shorter exposure times. Visual LEED inspection upon heating shows that the transformations to the (1  $\times$  2) patterns occur between 220 and 250 K. These transformations are also seen with He diffraction, Fig. 4(a). The full line corresponds to exposure to  $\sim 400$  L at 300 K. A continuous intensity decrease due to Debye-Waller effects is observed up to  $\sim 320$  K; the following intensity increase and the merging of the curve into that of the clean surface correlates well with the desorption of molecular hydrogen as can be seen from the TDS data of Fig. 4(b). The dashed and dash-dotted curves in Fig. 4(a) correspond to two different exposures at 100 K. In these cases, the intensity behavior exhibits structure at  $\sim 240$  K, which is connected with the transition from the low-temperature chemisorption phases to the (1  $\times$  2)-reconstruction phases. These results are important since they prove that the H subsurface movement and the connected substrate reconstruction require thermal activation. A phonon-assisted mechanism as proposed by Lagos<sup>7</sup> appears possible.

It is interesting to speculate on the nature of the (1  $\times$  2) reconstructed phases. A plausible structure of the (1  $\times$  2)\* phase with  $\frac{1}{2}$  ML H is the following: The H atoms occupy all short bridge sites below every other

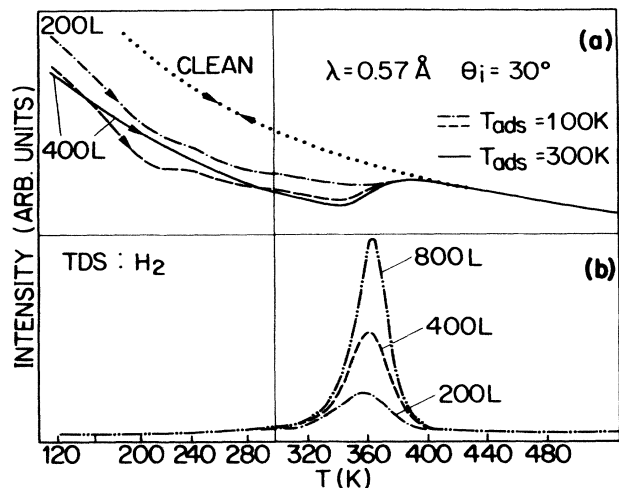


FIG. 4. (a) Temperature dependence of the He specular intensity for different H exposures as well as for the clean surface. The shoulders at  $\sim 240$  K obtained for adsorption at 100 K indicate the inward movement of the H atoms and the onset of reconstruction. The structure between 320 and 400 K correlates well with the desorption of molecular hydrogen as seen by comparison with the thermal desorption spectroscopy data of (b).

topmost close-packed Cu row; these correspond to the first available octahedral interstitial sites which are actually occupied in copper hydride.<sup>15</sup> The close-packed Cu rows in the second layer are pushed laterally away from the H atoms, forming a pairing-row reconstruction in the second layer and leaving the outermost layer unaffected (a small uniform outward relaxation of the topmost Cu layer would not affect the atomic beam diffraction intensities.)<sup>16</sup> The (1  $\times$  2) reconstruction at higher H concentrations probably involves further substrate atom displacements and very likely reconstruction of the topmost metal layer, whereby H is located above and below the surface. We did not attempt to distinguish between various possibilities using the He-diffraction data since both H and Cu atoms can contribute to the corrugation; LEED  $I$ - $V$  or ion-scattering analysis of the location of the Cu atoms will be a necessary prerequisite to determine the H locations in these phases.

The direct evidence of the existence of a subsurface reconstruction induced by subsurface H in the (1  $\times$  2)\* phase presented here is of importance for understanding the unusually large velocity and the high rotational excitation of H<sub>2</sub> permeating out of Cu(110).<sup>5,6</sup> It is likely that, although the H concentrations in these experiments are small, the (1  $\times$  2)\* reconstruction (and its lifting) is locally involved in the H<sub>2</sub> release.

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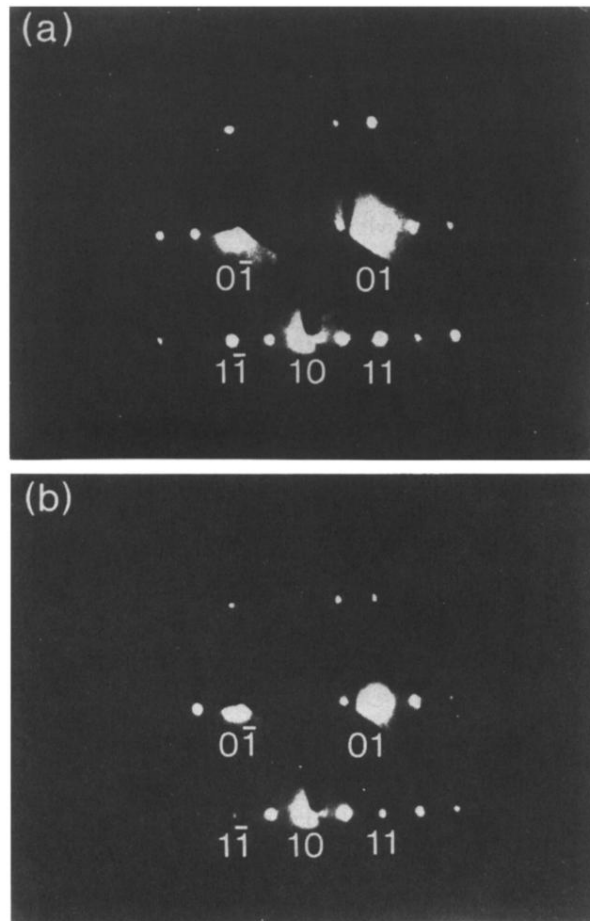


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