Structure of the hydrogen covered Cu(110) surface studied with thermal energy helium scattering

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The adsorption of atomic hydrogen on the Cu(110) surface has been studied with thermal energy helium scattering. Upon hydrogen adsorption the structure exhibits a variety of structures: At temperatures above 140 K the helium diffraction spectra show a clear (1×2) structure even at very low H coverages. This phase is the well known (1×2) Cu(110)–H "missing row" reconstructed phase. Based on an analysis of the specularly reflected He-intensity as a function of hydrogen coverage we have characterized the nucleation and growth of this phase. After the formation of small reconstructed areas the development of the reconstructed phase proceeds via the growth of these nuclei into large (1×2) Cu(110)–H islands indicating an *attractive* interaction between adsorbed H atoms within the reconstructed unit cells. Adsorption at temperatures below 80 K yields a sequence of adsorbate phases as a function of hydrogen exposure: at low exposures a (1×4) phase is observed. With increasing hydrogen exposure the (1×4) structure changes continuously into a well ordered (1×3) phase, which then evolves into a (1×2) phase at higher exposures. This (1×2) structure is only poorly ordered and transforms upon further hydrogen exposure into a (1×1) structure. This sequence of adsorbate phases, as well as the continuous transition between them, suggests a *repulsive* interaction between the adsorbed H atoms. All adsorbate phases formed at surface temperatures T_s below 120 K undergo an irreversible transition into a disordered phase upon heating to $120 \text{ K} < T_s < 140 \text{ K}$. Heating above $T_s = 140$ K irreversibly yields the (1×2) "missing row" phase.

1. Introduction

The structures of hydrogen adsorbed on the Cu(110) surface have been studied previously by many other groups using a variety of experimental techniques [1–6,11–13]. Rieder and Stocker [1] investigated this system by He scattering, low energy electron diffraction (LEED) and thermal desorption spectroscopy (TDS). To motivate our (re)investigation, their results will be briefly reviewed first: Adsorption of small amounts of hydrogen at room temperature was found to yield a LEED pattern characteristic of a (1×2) superstructure which, however, could not be observed by He atom diffraction. Only after much larger exposures a (1×2) superstructure could be seen with He diffraction. Contrary to low energy electrons, which penetrate some layers deep into the crystal, thermal energy helium atoms are scattered 3–4 Å in front of the surface. Thus the information provided by helium atom scattering

is of the topmost layer exclusively, whereas LEED is sensitive to the structural properties underneath the first layer, too. Thus, Rieder and Stocker concluded that the hydrogen induced restructuring of the Cu(110) surface, initially, would not affect the atoms of the topmost surface layer but only Cu atoms underneath the surface. Only with increasing hydrogen exposure the reconstruction would also include the top layer and become visible in helium scattering. Theoretical investigations [2] do not support the presence of a subsurface state of hydrogen, but predict the hydrogen induced reconstruction at room temperature to be of the missing row type and hence involving a structural change of the first layer Cu atoms. The subsurface reconstruction was also refuted by experiments using HREELS [3] and ion scattering [4], both reporting a hydrogen induced (1×2) missing row reconstruction at room temperature, even at lowest hydrogen coverage.

Hydrogen adsorption at lower surface temper-

ature (100 K) leads to clear (1 × 3) helium diffraction spectra but only weak LEED patterns [1]. Therefore, this structure has been suggested to be an adsorbate phase of hydrogen rather than a reconstruction of the copper substrate. Upon heating to $T_s \approx 220$–250 K the (1 × 3) phase transformes into the (1 × 2) reconstructed phase [1]. Obviously, this (1 × 2) reconstruction is thermally activated, whereas the (1 × 3) phase is formed instantly even at low temperature. With increasing H coverage this (1 × 3) phase ($\Theta_H = 0.33$) turns into a rather poorly ordered (1 × 2) phase [3,5]. In contrast to Stocker and Rieder [1] the (1 × 3) phase was assigned by Hayden et al. [3] to a displacive reconstruction lifting the inward relaxation of every third close packed copper row. This interpretation was motivated by LEED I-V investigations [6] showing that adsorption of atomic hydrogen at $T_s \approx 90$ K removes the inward relaxation of the interlayer spacing between the topmost two layers of the clean copper surface. This removal of the relaxation upon hydrogen adsorption was also confirmed by effective medium calculations [2].

As shown below, our He diffraction data clearly demonstrate that at surface temperatures above 140 K a (1 × 2) structure can be observed even at coverages as low as a few percent of the H saturation coverage. There is no evidence for an anomaly of the hydrogen induced (1 × 2) missing row reconstruction. The lifting of reconstruction due to hydrogen desorption appears to take place at a significant rate already at temperatures around 250 K, i.e. well below room temperature.

At low temperature ($T_s < 80$ K) and low hydrogen exposure we have observed a hitherto unreported (1 × 4) structure. With increasing H exposure the (1 × 4) phase continuously transformes into phases whose periodicities along the [001] direction decrease. By increasing the H exposure the complete succession of a (1 × 4), (1 × 3), (1 × 2), and (1 × 1) phase can be observed. From our He scattering data it is evident, that the "low temperature" (1 × 2) phase is of entirely different nature than the (1 × 2) "missing row" reconstructed phase at temperatures above $T_s \geq 140$ K.

In brief, our results show that the H induced structures at low temperature can be described by

repulsive H–H interaction, while the (1 × 2) "missing row" phase is governed by an effective attractive interaction between the H–Cu(1 × 2) unit cells.

Following an outline of the experimental procedures, we will present the details of the nucleation and growth of the (1 × 2) "missing row" reconstructed phase and then give a characterization of the series of hydrogen phases at low surface temperature as well as their stability with respect to temperature and coverage.

2. Experimental

The experiments were performed using the UHV high resolution He scattering spectrometer described in detail in ref. [7]. The in situ temperature calibration outlined in ref. [7] was not performed for the Cu(110) crystal. Consequently there may be a systematic error in the temperature reading of about ±5 K in the low temperature range (40 K). At room temperature the measured temperatures are correct to within ±1 K. These uncertainties in the temperature reading, however, are of minor importance to the results reported here.

In order for the hydrogen to stick on the Cu(110) surface, the H_2 molecules have to be excited or dissociated before hitting the surface. This is achieved by placing a hot tungsten ring filament (1450°C) between a H_2 gas doser and the sample.

In all scattering experiments reported here the wavelength of the incident He beam was 1.06 Å (which corresponds to a He beam energy $E_{He} = 18.3$ meV) with a monochromaticity of $\Delta\lambda/\lambda = 0.007$.

The Cu sample was cut by sparc erosion and carefully polished. The surface orientation was checked by Laue backreflection to match a (110) plane within 0.2°. The sample was cleaned by repeated cycles of sputtering with Ar ions and annealing until no contamination could be detected by Auger electron spectroscopy and LEED. The daily cleaning procedure consists of sputtering with Ar ions followed by annealing to 900 K.

The possibility of sample contamination caused by the hot tungsten filament was examined by monitoring the specularily reflected He beam, whose intensity is a very sensitive probe for isolated defects such as impurity adatoms [8]. In the entire temperature range between 50 K and room temperature no contamination could be detected over a typical time scale of about one hour. Furthermore, the influence of dosing H_2 molecules only (i.e. the filament being off) was checked by measuring the specular He reflectivity: No intensity decrease was observed even at large exposures, indicating that the thermal H_2 molecules do not adsorb dissociatively on the Cu(110) surface and that no measurable amount of contaminants is carried along with the H_2 gas. In contrast, if the filament is turned on in the presence of H_2 gas, the specular intensity decreases rapidly, indicating the adsorption of atomic hydrogen on the Cu surface.

The hydrogen exposures quoted below are given in terms of the H_2 background pressure as measured at the wall of the UHV chamber. The actual hydrogen pressure in front of the sample is significantly higher, because a gas doser was used and directed towards the sample. Anyhow, we have to keep in mind, that the quoted exposures can only serve as a relative measure for the exposure of *atomic* hydrogen.

In order to investigate the surface structures we performed two different types of diffraction experiments, which are described here briefly: in the so-called *polar scans* we have measured the scattered He intensity as a function of the parallel wavevector transfer Q. These measurements yield the familiar diffraction spectra (as shown for instance in fig. 3) from which information about the surface structure at fixed coverage and temperature can be obtained. In the second type of experiments, the so-called *exposure curves*, the scattering geometry is set to a fixed point in the reciprocal space (fig. 1 sketches out the structure of the clean Cu(110) surface in real and reciprocal space) and the He intensity is measured at this fixed wave vector transfer as a function of exposure (as e.g. in fig. 2 for $Q = 0.87$ Å^{-1}, corresponding to the position of the (0, 1/2) diffraction peak). These exposure curves show
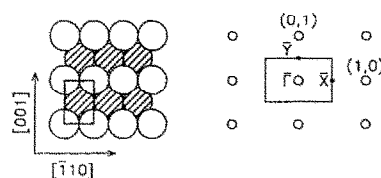

Fig. 1. Sketch of the clean Cu(110) surface in real space (left) and in reciprocal space (right). The rectangle in the right panel is the first Brillouin zone with the symmetry points $\bar{\Gamma}$, $\bar{X}$ and $\bar{Y}$.

the evolution of the hydrogen induced phases with coverage in "real time".

3. Results and discussion

In fig. 2 the He intensity of the (0, 1/2) half order diffraction peak ($Q = 0.87$ Å^{-1}) along the [001] azimuth is plotted as a function of hydrogen exposure for two different surface temperatures. During the measurement the H_2 partial pressure was held constant at $p = 1 \times 10^{-7}$ Torr with the filament being turned on. The data in fig. 2 evidence the dramatically different shape of the intensity curves at surface temperatures $T_s = 50$ K (a) and $T_s = 200$ K (b), respectively. Obviously
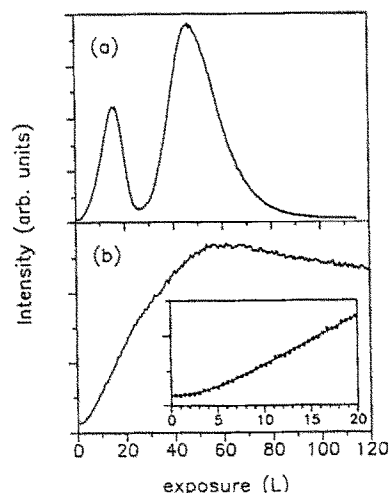

Fig. 2. Exposure curves at a wavevector transfer $Q = 0.87$ Å^{-1} along the [001] direction, corresponding to the position of the (0, 1/2) diffraction peak, at surface temperatures (a) $T_s = 50$ K and (b) $T_s = 200$ K. The inset gives a magnified view of the initial variations of the scattered intensity.

different mechanisms and structures are responsible for the (0, 1/2) diffraction signatures observed. Therefore, we will discuss the results obtained for the different temperature regimes in separate paragraphs.

3.1. The Cu(110)–(1 × 2)H "missing row" reconstruction ($T_s > 140$ K)

In this temperature range the hydrogen induced structure was found to be of the "missing row" type even at very low hydrogen coverages of about 5% of the saturation coverage [3,4]. However, earlier He scattering experiments [1] were not sensitive to this phase at these low coverages. Our He scattering data now clearly demonstrate the sensitivity of He scattering to the hydrogen induced (1 × 2) "missing row" phase even at the early stage of growth on the basis of two different expriments:

(i) In the exposure curve (cf. fig. 2b) the intensity of the (0, 1/2) diffraction peak, characteristic of the (1 × 2) structure, increases steadily right from the onset of hydrogen exposure until saturation is reached at about 50 L.

(ii) The He diffraction profile (fig. 3a) taken along the $\overline{\Gamma Y}$ azimuth (i.e. perpendicular to the close packed Cu-rows in real space) at 220 K after a H exposure of 5 L, corresponding to about 10% of the saturation exposure, clearly features a (0, 1/2) diffraction signature originating from the hydrogen induced (1 × 2) "missing row" reconstruction. Though the intensity of the (0, 1/2) diffraction peak at low coverages (fig. 3a) is small, it is only slightly broadened with respect to the peak obtained at H saturation (fig. 3b). This implies that the (1 × 2) reconstructed areas are well ordered with an average domain size of several hundred ångström even at this very low coverage. The early formation of such large islands at low coverage is indicative of an *attractive* effective interaction between the reconstructed unit cells. The slow initial rise of the intensity curve in fig. 2b is caused by the increase of the coherently scattering (1 × 2) reconstructed areas, rather than by an increase of the He background intensity due to diffuse scattering. This slow rise of intensity is in accordance with the scattering
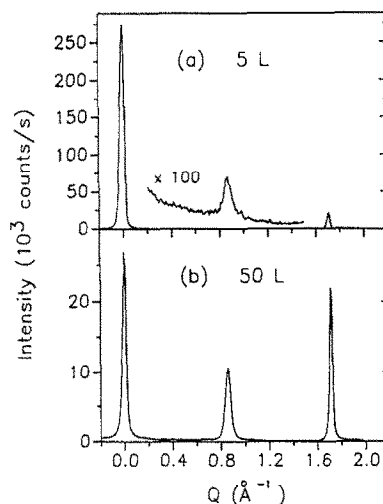

Fig. 3. Polar scan along the $\overline{\Gamma Y}$ direction at a surface temperature $T_s = 220$ K after hydrogen exposure of (a) 5 L and (b) 50 L, respectively.

theory, since the intensity of any diffraction peak increases proportional to the square of the number of scattering unit cells until the size of the scattering domains gets comparable to the transfer-width of the instrument (in the present case about 250 Å). When the domain size exceeds the transfer-width, the intensity rises almost linearly with the number of unit cells. In our experiments the regime of linear rise of intensity of the (0, 1/2) peak with H exposure is reached at about 5 L exposure of hydrogen. Therefore, we can conclude from this experiment, too, that for a H exposure of about 5 L the (1 × 2) reconstructed domains reach a size of about 250 Å. Furthermore, the linear rise of intensity with exposure requires the sticking coefficient to be constant until the surface is nearly saturated with hydrogen. Close to saturation the intensity of the exposure curve reaches a maximum and slowly decays with further hydrogen adsorption most likely due to a disordering of the structure at hydrogen supersaturation.

In contrast, except for the very low exposures, the intensity of the specularly reflected He beam *decreases* almost linearly with H exposure until saturation (fig. 4). The drastically reduced specular intensity at saturation indicates that the He reflectivity of the (1 × 2) reconstructed Cu(110)–
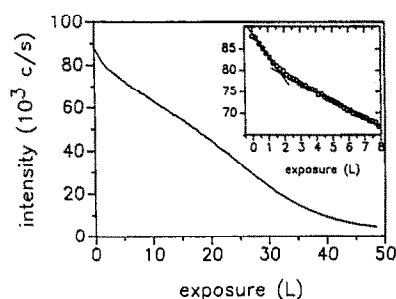
Fig. 4. Exposure curve of the (0, 0) (specular) diffraction peak at $T_s = 210$ K. The inset shows the behavior at the early stage of exposure.
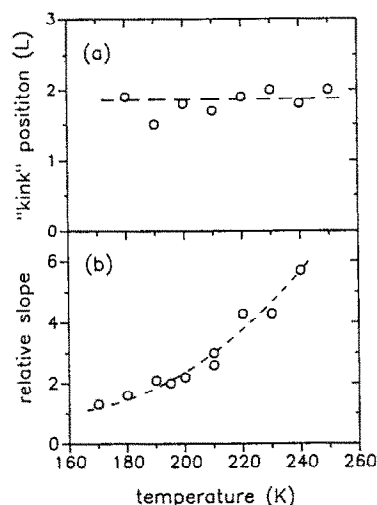

Fig. 5. Evaluation of the initial intensity decrease of the specular beam as a function of surface temperature: (a) Position of the "kink". (b) Ratio of the slopes before and after the "kink".

H surface is much lower than that of the clean Cu(110) surface. The steeper slope at the very beginning of the intensity curve is due to diffuse scattering from small structures in the early stage of nucleation and growth of the reconstructed phase. Once the reconstructed domains have reached a size of some hundred ångström in diameter after exposure to a few langmuir of hydrogen, both the intensity of the (0, 1/2) diffraction peak and the specular intensity indicate the linear increase of hydrogen coverage with exposure almost until saturation.

From an analysis of the specularly scattered He intensity in the low exposure regime ($\lesssim 5$ L) we have obtained information about the nucleation of the hydrogen induced (1 × 2) Cu(110) reconstructed phase. Adsorption of hydrogen at a constant rate causes the intensity of the specularly reflected He beam to decrease as shown in fig. 4. The curve is characterized by a steep decay for very small exposure followed by the more gradual linear intensity decrease discussed above. The two regimes are separated by a kink as seen in the inset in fig. 4. We have studied the shape of the specular intensity curves for various temperatures between 170 and 240 K. The position of the kink always occurs at about the same exposure of 2 L regardless of adsorption temperature (fig. 5a). However, the ratio of the slopes before and after the kink increases with temperature (fig. 5b).

Since the rate of adsorption is constant, the different slopes before and after the kink indicate that for exposures below 2 L the effective cross

section for diffuse scattering per adsorbed hydrogen atom is larger than for higher exposures. It is known [8], that the diffuse cross section of an isolated defect (such as an individual adatom) on the surface can be about ten times larger than the actual geometric size of the defect. If the defects coalesce to form a condensed phase, the partial overlap of the individual cross sections leads to a decrease of the effective cross section per defect. This is illustrated schematically in fig. 6. At the same total coverage the diffuse scattered intensity will therefore depend strongly on the relative arrangement of the defects and thus on the growth mode of the hydrogen induced reconstruction.
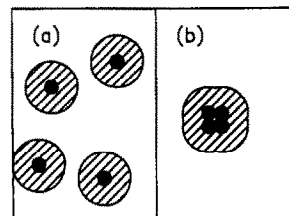

Fig. 6. Sketch illustrating the dependence of the total cross section for diffuse scattering (hatched area) on the relative arrangement of defects: (a) Isolated defects or adatoms. (b) Defects or adatoms forming small islands.

Depending on whether many small islands are created or a few large ones, the intensity will decrease faster or slower, respectively. Applying this to the present case, it is obvious that in the low coverage regime relatively small nuclei are created, whose cross sections only marginally overlap. Then, at exposures beyond 2 L no more nuclei will be created but instead the incoming hydrogen atoms are incorporated in the already existing nuclei. Therefore, each newly adsorbed hydrogen atom only contributes with the size of a single reconstructed unit cell to the total diffuse cross section [9]. Thus, the ratio between the slopes before and after the kink reported in fig. 5b is a measure of the size of the nuclei, while the position of the kink marks the "critical" coverage where the transition from nucleation to growth occurs. The most remarkable observation is the *increase* of the relative slope with temperature corresponding to a *decrease* of the average nuclei size. This is exactly the opposite behavior of what is expected from classical nucleation theory. Thus the classical nucleation theory is not able to describe this (1×2) "missing row" reconstruction.

We propose an explanation based on the fact that the hydrogen induced reconstruction is thermally activated (a fact that will become more evident in the forthcoming sections of this paper). Since hydrogen as well as thermal energy is necessary to induce the (1×2) "missing row" reconstruction it is conceivable that at relatively low temperatures it would take several hydrogen atoms to drive the reconstruction. The hydrogen atoms would have to diffuse in a highly mobile precursor state across the surface until they eventually form a sufficiently large cluster (nucleus) which then locally induces the reconstruction. In contrast, at elevated temperatures, where more thermal energy is available, the reconstruction can be induced by only a few or even a single hydrogen atom. Assuming that the hydrogen in the reconstructed Cu(110)–(1×2)H unit cell has a much lower mobility than the adsorbate hydrogen, the so formed nuclei would also be stable. Thus the role of the thermal activation energy could explain the decreasing size of the nuclei with increasing temperature. For the same reason, it is also possible, that at elevated surface temperature the size of the reconstructed area around a single H atom is larger than at lower temperature. This effect could also explain the larger relative slope of the reflectivity curve with increasing temperature. Indeed, the cross section for diffuse scattering per H atom would truely become larger, as more unit cells are affected. At this point a precise microscopic picture of the nucleation process cannot be given although it appears that the energetics of the reconstruction plays the key role. It is also not clear why the position of the "kink" is independent of the surface temperature and whether it depends on the adsorption kinetics. Measurements at different hydrogen adsorption rates are currently underway to elucidate the nucleation process in more detail.

To investigate the thermal stability of the (1×2) "missing row" reconstructed phase we have studied the lifting of the reconstruction due to desorption of the hydrogen at sample temperatures between 250 and 285 K. After exposure of 50 L hydrogen at 130 K the sample was annealed at 245 K for ten minutes in order to establish a well ordered (1×2) structure without significant loss of hydrogen due to desorption. The ordering was checked by monitoring the intensity of the $(0, 1/2)$ diffraction peak. After this annealing procedure, keeping the temperature at 245 K, the intensity remains constant over a time scale of about twenty minutes. After extended periods, however, a slight decrease of the intensity could be observed due to the very slow onset of desorption.

In order to measure the desorption, after the annealing process the sample temperature was quickly raised to a value between 250 and 285 K and kept constant. As a result, the intensity of the $(0, 1/2)$ diffraction peak decreases with time, indicating the lifting of the reconstruction due to the desorption of hydrogen (fig. 7a). Because the He diffraction peak intensity is sensitive not only to the size of the reconstructed area but also to the degree of order of the surface structure, the shape of the curve has to be interpreted with caution. Consequently, the intensity is not directly proportional to the number of desorbed hydrogen molecules; it is therefore not surprising
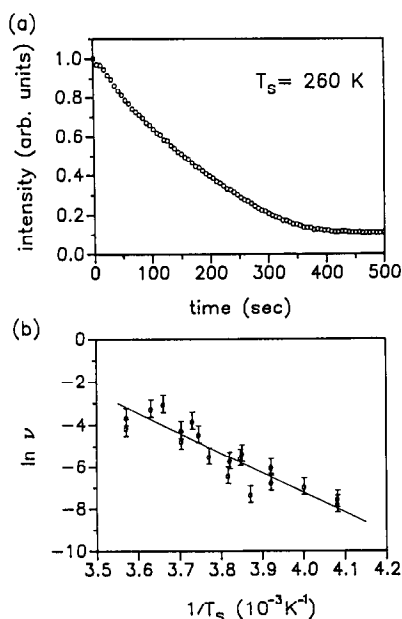
Fig. 7. (a) Intensity of the (0, 1/2) diffraction peak as a function of time for a surface temperature of 260 K. (b) Desorption (deconstruction) rates ν plotted in an Arrhenius plot.

that the shape of the curve deviates from the simple exponential form characteristic for first-order kinetics as observed by Spitzl et al. [4]. Nevertheless, the initial slope of the curve should be proportional to the desorption rate ν. Since desorption is a thermally activated process ν should be related to an activation energy E_a by $\nu = \nu_0 \exp(-E_a/k_B T_s)$. Indeed, reporting the initial slopes for various surface temperatures in an Arrhenius plot (fig. 7b), an activation energy $E_a = 0.8 \pm 0.1$ eV and a preexponential factor of $\nu_0 = 1.6 \times 10^{13 \pm 1}$ s^{-1} is obtained. The value of E_a is in good agreement with the value of 0.88 ± 0.07 eV obtained by Spitzl et al. [4]; the preexponential factor is higher by two orders of magnitude. However, due to the strong influence of the order parameter on the diffraction intensity, as mentioned before, the magnitude of this difference should not be overestimated. Indeed, while the initial slope is *proportional* to the desorption rate, the proportionality factor will be much larger than 1, depending on how much He diffraction

from the defected reconstructed domains is affected.

The main result of this measurement is that hydrogen desorption takes place at a significant rate even at temperatures as low as 250 K. At 275 K the (0, 1/2) peak vanishes completely within two minutes. This is in close agreement with results obtained by Bertel et al. [11]. Indeed, the desorption of H might have been one reason for the difficulties in observing He diffraction patterns at low hydrogen coverage at $T_s = 300$ K as reported in ref. [1].

3.2. The adsorbate phases at low surface temperatures ($T_s < 140$ K)

As mentioned before, the hydrogen induced phases at temperatures below $T_s = 120$ K are of different nature than the "missing row" reconstructed phase. This is most evident from the fact that, instead of one single phase stable in the entire coverage regime, a series of phases with different periodicities along the [001] direction is observed, each phase being stable within a limited coverage range only. Fig. 8 depicts characteristic polar profiles taken below 80 K: a (1×4) structure after exposure to about 16 L of hydrogen (fig. 8a), a (1×3) structure after 33 L (fig. 8b), and a (1×2) structure after 50 L (fig. 8c).

By means of exposure curves (as shown in fig. 9), taken at various surface temperatures and fixed wave vectors of $Q = 0$, 0.87, and 1.17 Å^{-1} (corresponding to the specular, (0, 1/2) and (0, 2/3) diffraction peaks, respectively) the growth of each phase can be characterized in detail.

For small hydrogen exposures and surface temperature $T_s < 80$ K at first a (1×4) structure develops. Hence, the initial rise of the diffraction intensity at $Q = 0.87$ Å^{-1} in fig. 9 (left panel) is due to the (0, 2/4) peak of the (1×4) structure and not due to a (0, 1/2) peak of a (1×2) structure. At 16 L the intensity reaches a maximum. Adding more hydrogen changes the (1×4) structure continuously into the (1×3) phase. The transition is characterized by the decline of the (0, 2/4) intensity and the simultaneous appearance of the (0, 2/3) diffraction peak. The (1×4) structure and the transition to the (1×3) phase is
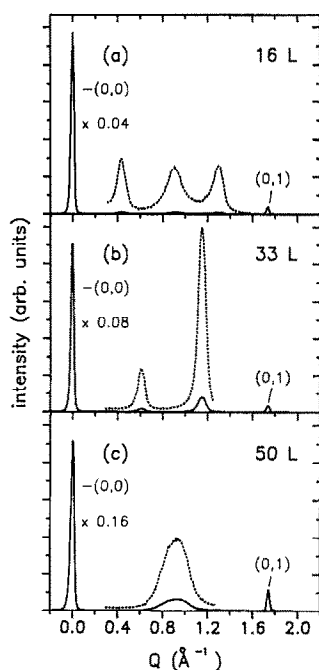
Fig. 8. Polar diffraction scans of the Cu(110) surface after hydrogen exposures of 16, 33 and 50 L at $T_s = 80$ K. The peaks are drawn in all panels with the same scale.

only observable for $T_s < 80$ K, whereas for $T_s > 80$ K the (1×3) structure is the first visible structure, even at low coverage. Indeed, at 80 K the first maximum of the intensity at the $(0, 1/2)$
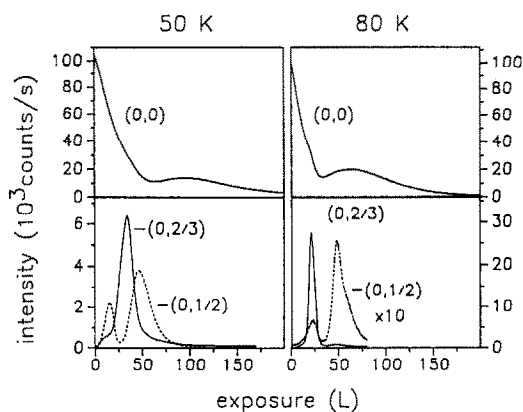

Fig. 9. H exposure curve measured at a wave vector transfer $Q = 0$ Å^{-1} (upper panels), $Q = 0.87$ Å^{-1} (lower panels, dotted line), and $Q = 1.17$ Å^{-1} (lower panels, solid line). The surface temperatures are 50 K (left panel) and 80 K (right panel).

peak position in fig. 9 (right panel) at about 20 L is an artefact: it is caused by an enhanced background due to the intense neighboring $(0, 2/3)$ diffraction peak of the (1×3) structure. Indeed, the $(0, 2/3)$ diffraction peak has about 40 times the intensity of the diffraction feature at the $(0, 1/2)$ position and has its maximum at exactly the same H exposure.

The (1×3) structure is the best ordered of all low temperature structures as evident from the intense and narrow diffraction peaks in the polar profile of fig. 8 (b). The intensity of the $(0, n/3)$ peaks and therefore the order of the (1×3) structure increases with annealing or adsorption temperature up to 120 K. At all temperatures below 120 K the (1×3) structure transforms into a weakly ordered (1×2) structure upon further hydrogen exposure (fig. 8c). At even higher hydrogen exposure the (1×2) structure slowly degrades and only a (1×1) diffraction pattern remains (fig. 10j). The formation of the (1×1) structure is accompanied by a slight, but noticeable increase of the specularly reflected intensity (see top panels in fig. 9) as well as by an increase of the $(0, 1)$ diffraction peak intensity (fig. 10h–10j).

The series of polar profiles in fig. 10 illustrates the evolution of the different phases at 70 K. This series of diffraction patterns and the diagram of the peak positions as a function of exposure (fig. 11), extracted from these polar profiles, demonstrate the continuous shift of the diffraction peaks and thus the continuous transitions between the individual phases. The transition from the (1×4) into the (1×3) phase proceeds via a rapid decline of the $(0, 2/4)$ peak and a shift of the $(0, 1/4)$ and $(0, 3/4)$ peak towards the $(0, 1/3)$ and $(0, 2/3)$ positions, respectively (fig. 10a–10d and fig. 11). The (1×3) structure then transforms into the (1×2) phase by the shifting of the $(0, n/3)$ peaks towards each other onto the half order position. The last transition from the (1×2) to the (1×1) phase takes place via an intensity decrease and broadening of the $(0, 1/2)$ peak. In fig. 10i traces of additional diffraction signatures are also observed. As mentioned before, the $(0, 0)$ and the $(0, 1)$ peaks gain some intensity as the (1×1) structure is formed (fig. 10h–10g).
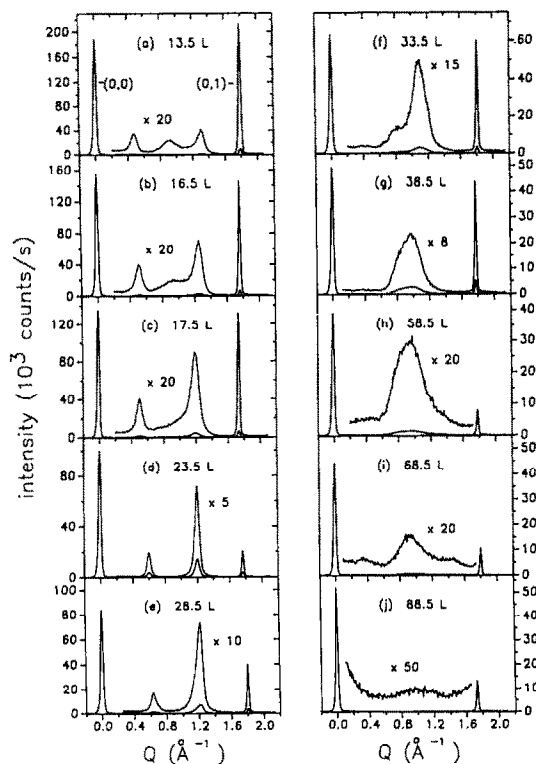
Fig. 10. Series of polar scans as a function of exposure (surface temperature $T_s = 70$ K) illustrating the continuous shifting of the diffraction peaks between the different phases.

The existence of these distinct phases and their stability within narrow coverage regions suggests a lattice gas model with *repulsive* interactions along the [001] direction between the adsorbed atoms. In such a system the atoms will occupy sites at the largest possible distances from each
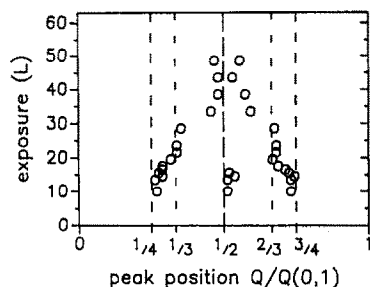

Fig. 11. The positions of the diffraction peaks as a function of H exposure, as obtained from the diffraction spectra shown in fig. 10.

other. Accordingly, at a coverage of 0.25 the adsorbed hydrogen atoms would arrange themselves at a distance of four Cu lattice spacings along the [001] direction, giving rise to a (1×4) structure. Similarly a (1×3) and a (1×2) structure would be stabilized at a hydrogen coverage of 0.33 and 0.5, respectively, while a (1×1) structure would correspond to the fully covered surface, i.e. $\Theta_H = 1$. At the lowest coverage structures of even larger periodicities might be expected but one has to keep in mind, that the interaction between the hydrogen atoms is likely to become weaker at larger separation. Thus, for instance, thermal disorder might be a reason why structures such as the (1×5), (1×6) etc. are not readily observed in our experiment. It should also be noted that even the (1×4) structure is thermally stable only below $T_s = 80$ K.

The lattice gas model with mainly repulsive interaction can also explain the observed continuous peak shift. The peak shift is not caused by a new structure but is due to a (random) mixture of $(1 \times n)$ H/Cu(110) unit cells [12]. If, for instance, the (1×4) structure is exposed to hydrogen, the average distance between neighboring adsorbed atoms has to decrease, in order to accommodate the new H atoms. Consequently, more and more interatomic distances will change from four to three lattice spacings yielding a mixture of unit cells with the periodicities (1×4) and (1×3) in the coverage range between 0.25 and 0.33. Computer simulations in that coverage regime show, in accordance with the experiment, the rapid decline of the $(0, 2/4)$ peak and the shift of the $(0, 1/4)$ and $(0, 3/4)$ peaks towards the $(0, 1/3)$ and $(0, 2/3)$ position, respectively. When the coverage has reached 0.33, all hydrogen atoms can be accommodated in the (1×3) structure, in which the separation between neighboring H atoms is three Cu lattice spacings. Upon further increase of the coverage, more and more distances change from three to two lattice spacings, again resulting in a peak shift of the $(0, n/3)$ diffraction peaks towards the $(0, 1/2)$ peak position. At $\Theta_H = 0.5$ the (1×2) structure is completed. Adsorbing more hydrogen results in a filling of the remaining "holes" between the adatoms of the (1×2) structure. This creates

domains of (1×1) periodicity. Therefore the number of (1×2) unit cells steadily decreases resulting in a decrease and a broadening of the $(0, 1/2)$ diffraction peak until only the peaks of the (1×1) structure remain. Our one-dimensional simulations mentioned above only allow for repulsive interactions at zero temperature and are based on the kinematic diffraction theory. Consequently, they can describe the observed peak shifts only qualitatively. As already mentioned above, no structures with larger periodicities than in the (1×4) structure are observed in the experiment (probably due to thermal instability). More important, the measured peaks are "locked" onto the $(0, n/3)$ positions over a wide range of exposure (fig. 11), whereas the simulations predict a linear shift of the peaks with exposure. These discrepancies are due to the simplification of an overall repulsive interaction between atoms used in our simulations. There must be more complex components to the H interatomic interaction, which, for instance, would stabilize the (1×3) phase over a relatively large coverage regime. By using a more refined Monte Carlo simulation, in order to reproduce the measured peak shifts as a function of coverage, it should be possible to determine the relative interaction strengths between the adsorbed hydrogen atoms as a function of lattice separation.

It should be pointed out here, that the appearance of the sequence of the adsorbate phases with structures (1×4), (1×3), and (1×2) at 16, 33 and 50 L, respectively (see e.g. fig. 8) matches rather nicely the expected stoichiometric coverages of 0.25, 0.33, and 0.5 in the repulsive lattice gas model, assuming constant sticking probability. Furthermore, comparison of the saturation coverage of ~ 50 L in the case of the hydrogen induced reconstructed phase with that of the (1×2) phase at low temperature, provides strong evidence that the saturation coverage of the "missing row" Cu(110)–(1×2)H structure also corresponds to $\Theta_H = 0.5$. This is in agreement with recent results based on thermal desorption spectroscopy [13,14]. Earlier investigators [1] have reported values for Θ_H ranging from $\Theta_H = 0.5$ up to $\Theta_H = 1.5$.

Another important feature of the low temperature phases is the development of well ordered structures even at very low temperatures. The missing row reconstruction is thermally activated and temperatures well above 140 K are necessary in order to form a properly ordered (1×2) reconstructed phase. This is mainly due to the long-range mass transport of copper atoms involved in the formation of the "missing row" reconstructed phase, which is slowed down by the reduced mobility of the copper atoms at lower temperature. It is therefore very unlikely that a long-range mass transport is involved in the formation of the structures observed below 120 K. More likely, the low temperature structures are due to adsorbate phases of the hydrogen, possibly connected with a small displacive reconstruction of the substrate. This is in close agreement with the results of other groups [1,3,5,6].

Adsorption of hydrogen in the temperature range between 120 and 140 K results just in a broad and structureless diffraction feature located in between the $(0, 1/2)$ and the $(0, 2/3)$ position. With increasing exposure the shape of this peak remains unchanged, whereas its intensity increases linearly with exposure up to 70 L.

Similarly, heating the adsorbate phases created below 120 K up to a temperature $120 \text{ K} < T_s < 140 \text{ K}$ these phases undergo an irreversible transition into a disordered phase. In that temperature regime and for all hydrogen exposures the diffraction spectra only show a (1×1) periodicity. Further heating of the disordered phase to temperatures above 140 K irreversibly yields the hydrogen induced (1×2) "missing row" reconstructed phase, in agreement with ref. [5]. At temperatures below 120 K the various $(1 \times n)$-H phases show different thermal behavior:

The diffraction peaks of a (1×4) structure created at 50 K shift upon heating towards the $(0, n/3)$ positions (figs. 12 and 13); cooling down again, restores the (1×4) diffraction pattern. This behavior is somewhat surprising since the hydrogen coverage remains constant. If, however, the sample is exposed to the same amount of hydrogen at a sample temperature of 110 K a well ordered (1×3) structure is formed; cooling down this phase to 50 K only freezes out the (1×3) diffraction pattern without any change of the
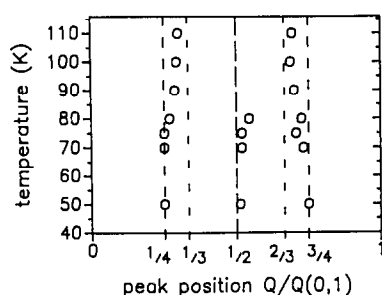
Fig. 12. The thermal behavior of the (1×4) structure: Position of the diffraction peaks as a function of temperature.

positions of the diffraction peaks. This demonstrates that kinetic effects play an important role in the growth and the phase transitions of the hydrogen adsorbate phases.

The (1 × 3) structure is thermally stable up to 120 K and is observed over a wide range of exposures. Therefore this structure seems to be the most stable of the hydrogen adsorbate phases on Cu(110). An improved ordering of the (1 × 3) phase is achieved by careful annealing up to $T_s = 120$ K.

The (1 × 2) structure is the least stable of the adsorbate phases. Adsorption at 50 K leads to a rather poorly ordered structure, whereas warming up to just 70 K slowly and irreversibly further
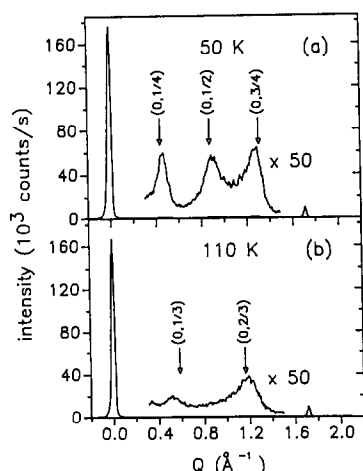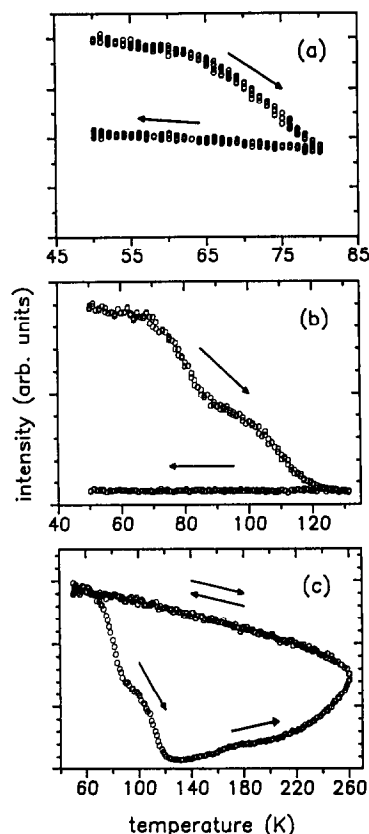

Fig. 14. Temperature dependence of the (1×2) structure, probed by the intensity of the (0, 1/2) diffraction peak. The heating/cooling rate was 0.25 K per second. At 80 K the structure disorders irreversibly (a); at 120 K the (0, 1/2) diffraction peak completely disappears; the disordering takes place without the loss of hydrogen and can be "frozen" in by cooling the sample (b). Heating the "frozen" disordered structure obtained after the treatment in (b) beyond 140 K shows the building up of the (1×2) "missing row" reconstructed phase (c).

Fig. 13. Polar profile of the (1×4) structure at (a) 50 K and (b) during annealing at 110 K.

disorders this (1 × 2) structure (fig. 14a). Adsorbing hydrogen at temperatures above 70 K produces a metastable (1 × 2) structure which vanishes with time. At a temperature of about 120 K the (0, 1/2) peak has completely disappeared. This state of disorder can be frozen in by cooling the sample as illustrated in fig. 14b. However, heating this disordered structure to temperatures above 140 K leads to the growth of the (1 × 2) "missing row" reconstructed phase, and the (0, 1/2) diffraction peak reappears (fig. 14c).

Again, this transition is irreversible; lowering the temperature leads to an increase of the (0, 1/2) diffraction intensity (fig. 14c) which can be explained by the Debye–Waller effect. On one hand this indicates that the hydrogen is still present on the surface at 120 K albeit there is no structure visible by diffraction. On the other hand this result again demonstrates, that the low temperature phases, in particular the (1 × 2) phase, are qualitatively different from the "missing row" reconstructed phase. Only via a complete disordering of the adsorbate structures they can be transformed into the "missing row" reconstructed phase.

4. Summary

The results reported are summarized in the schematic phase diagram shown in fig. 15. Since the transitions between the individual phases are continuous, it is hardly possible to establish exact phase boundaries between them. The phase diagram was constructed from exposure curves (as shown in fig. 9) taken at various surface tempera-

tures. The phase boundaries in fig. 15 correspond to the exposures at which the peak intensity reaches half its maximum value. This procedure is at least consistent in so far as the "end" of the vanishing and the "beginning" of the newly appearing phase match quite well.

At temperatures below 80 K the entire sequence of adsorbate phases, as a function of exposure is observed. The succession of a (1 × 4), (1 × 3), (1 × 2), and (1 × 1) structure suggests *repulsive* interaction along the [001] direction between the adsorbed hydrogen atoms to dominate. At slightly higher temperatures (80 K < T_s < 120 K) the stability region of the (1 × 3) phase shifts to lower exposures and the (1 × 4) structure does not develop. Heating the adsorbate phases to temperatures between 120 K < T_s < 140 K transforms the phases into a highly disordered phase. After heating above T_s = 140 K the hydrogen induced (1 × 2) "missing row" reconstructed phase develops. The different quality and growth mode of the (1 × 2) phase below and above T_s = 120–140 K, as well as the phase transformation via the complete disordering of the low temperature phase, indicate, that the low temperature (1 × 2) and the (1 × 2) "missing row" structure at temperatures above 140 K are of entirely different nature. Our investigation of the system H/Cu(110) by He scattering at temperatures above 140 K shows that the (1 × 2) "missing row" structure develops by forming relatively large coherent (1 × 2) reconstructed domains even at the lowest hydrogen exposures. This is indicative of *attractive* interactions between the H atoms once incorporated in the reconstructed unit cell. By monitoring the specularly reflected He intensity the nucleation of the (1 × 2) "missing row" reconstruction has been analyzed and discussed in terms of the formation of small nuclei, whose size depends upon temperature. Above a "critical" hydrogen coverage the nuclei grow by forming large well ordered (1 × 2) domains until saturation is reached around 50 L. In order to characterize the nucleation process in more detail and to unravel the role of the kinetics and of the activation barrier for reconstruction further measurements at different adsorption rates and temperatures are currently underway.
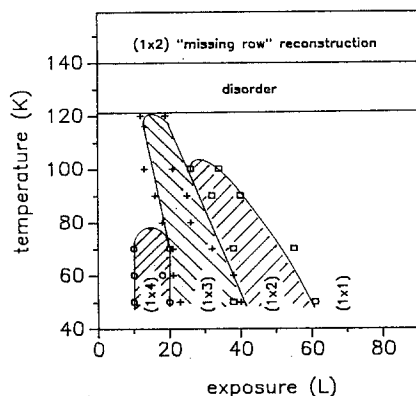

Fig. 15. Schematic phase diagram of H/Cu(110). The phase boundaries are obtained from the exposure curves as described in the text. These boundaries are not "sharp" as in a traditional phase diagram since the phase transitions occur via the continuous mixture of the corresponding phases. Also, most of the "phase transitions" are not reversible, in particular the transition from the low temperature phases to the "missing row" reconstructed phase above T_s = 140 K.

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