

Thermal roughness of the homogeneous and inhomogeneous Cu(311) surface studied by high-resolution low-energy electron diffraction

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The influence of temperature on the morphology of both the homogeneous and the inhomogeneous Cu(311) surfaces is investigated by high-resolution low-energy electron diffraction. Analyzing the spot profile of the diffracted electron beam under various scattering conditions provides information about both the surface roughness and inhomogeneities as a function of temperature. From the reversible spot broadening under the out-of-phase condition, it is concluded that atomic steps may be created reversibly on the Cu(311) surface by increasing the temperature. The critical temperature, at which the surface goes from the smooth, low-temperature phase into the rough, high-temperature phase, is obtained from the vanishing of the central spike of the (00) spot at $T_R = 750$ K. On the basis of a detailed analysis of the spot profile, we find that the height-height correlation of the Cu(311) surface cannot be described by the logarithmic behavior predicted for Kosterlitz-Thouless roughening. Instead of this behavior, in the low-temperature phase the height-height correlation saturates exponentially as the lateral distance goes to infinity, while it is characterized by a linear divergence for the high-temperature phase. Sulfur segregated at the surface has two effects: Large areas of the Cu(311) surface become amorphous and the step-atom density increases. The surface is still rough at room temperature even with small amounts of sulfur. With increasing sulfur coverage, the roughness due to inhomogeneities overwhelms the thermally induced surface roughness.

I. INTRODUCTION

Defects at surfaces are of great interest from both the technological and the physical points of view. For the technological application defects play an important role because they may be strongly involved in many physical and chemical processes occurring at surfaces: chemical reaction, catalysis, electronical conduction, and crystal growth. Since a surface is a drastic disturbance of the bulk structure, the physical properties of the surface may differ strongly from the bulk behavior.

The reduced dimensionality of the surface may lead to substantially different behavior of the crystalline material close to the surface, e.g., the surface may reconstruct or the distance of the topmost layers may relax.¹ Furthermore the surface may be a nucleus for the melting of the bulk material (surface premelting).²⁻⁴ Indeed, the critical temperature, at which the crystal starts to melt at the surface, is very close to the bulk melting temperature. On the other hand at lower temperatures there may exist thermally induced atomic steps at the surface (roughening transition). This concept was developed by Burton and Cabrera.⁵ It has been suggested that at low temperatures the growth mechanism for the smooth surface may be substantially different from the growth for the rough phase at high temperatures.⁶ However, the experimental evidence for the roughening transition has been very elusive for a long time. In 1980 it was observed at solid helium in equilibrium with its superfluid. Later the thermal roughening on high-index metal surfaces has been studied using helium atom diffraction,^{7,8} x-ray diffraction,^{9,10} and low-energy electron diffraction (LEED).^{11,12} Because of the weak interaction between the atoms of these surfaces the critical temperature, at

which the entropy contribution to the free energy enables any step production, is sufficiently low. Thus the roughening of these surfaces can be observed easily, although to date for close-packed surfaces no thermal roughness has been shown.

It is necessary to use an experimental technique with atomic resolution to characterize defects on surfaces in full detail. Some microscopic techniques, e.g., scanning tunnel microscopy (STM), transmission electron microscopy (TEM), or reflection electron microscopy (REM), can be applied with this resolution so that defects can be characterized qualitatively without any effort.¹³ On the other hand diffraction techniques using high-resolution instruments are better suited to obtain quantitative information about the kind and the distribution of defects due to superior averaging.^{14,15} For the study of structural phase transitions microscopic techniques fail in general, so thermally induced phenomena can only be measured with diffraction techniques. Because of the high sensitivity of low-energy electrons to surfaces and easy handling, LEED is one of the techniques used most often to study critical phenomena at and on surfaces.^{16,17}

After a description of experimental details (Sec. II) and some information on spot profile analysis of LEED (Sec. III), the experimental results (Sec. IV) will show the surface roughness for a wide temperature range and various surface conditions. The discussion reveals (Sec. V) that present day theory is not sufficient for a description of the results.

II. EXPERIMENTAL METHOD

The experiments were carried out in a standard ultrahigh-vacuum (UHV) chamber with a base pressure

below 10^{-8} Pa. The LEED data were taken with the SPA-LEED (spot profile analysis of low-energy electron diffraction) system described in detail in Ref. 18. Here only the main features of this high-resolution instrument shall be mentioned. The spots of the diffraction pattern are recorded by scanning electrostatically the electron beam over a fixed Channeltron. Using electrostatic lenses the instrument has a typical transfer width of 200 nm. Furthermore, the chamber is equipped with an Auger system with a cylindrical mirror analyzer (CMA) to check the cleanliness of the sample by Auger electron spectroscopy (AES) and an ion bombardment gun for Ar^+ sputtering.

The Cu(311) sample was spark erosion cut and chemomechanically polished.¹⁹ After removing the outer layers by etching it has a mosaic spread smaller than 0.01° as has been checked with an x-ray diffractometer. The final orientation of the sample was within 0.1° of the (311) plane. The UHV cleaning has been done by Ar^+ sputtering (600 eV, $1 \mu\text{A}$, 1 h) at a crystal temperature of 700–800 K. After each sputtering cycle the sample has been heated up to 900 K for 10 min. Even after heating the sample at this temperature no additional contamination of the surface can be observed by AES. Sulfur segregates at the surface not before heating the sample up to 950 K. The sample could be cooled down to 130 K by liquid nitrogen and was heated by radiation. The temperature of the sample was measured by a Ni-Cr/Ni thermocouple clamped on the backside of the sample.

III. ELECTRON DIFFRACTION AT SURFACES WITH DEFECTS

The surfaces of crystals may be described by the positions $\mathbf{r}(\mathbf{n})$ of the surface atoms. The wave function Ψ of an electron, which is scattered from the initial wave vector \mathbf{k}_i to the final wave vector \mathbf{k}_f by the crystal, is²⁰

$$\Psi = \sum_{\mathbf{n}} f(\mathbf{n}) e^{i\mathbf{K} \cdot \mathbf{r}(\mathbf{n})}, \quad (1)$$

where $\mathbf{K} = \mathbf{k}_f - \mathbf{k}_i$ is the scattering vector. The scattering amplitude $f(\mathbf{n})$ combines the wave coming from the n th surface atom and all underlying atoms and includes therefore all dynamical effects of electron diffraction.

For a perfectly periodic surface the intensity is given by

$$I = |\Psi|^2 = |f|^2 G_{\text{ideal}}(\mathbf{K}) \quad (2)$$

with

$$G_{\text{ideal}}(\mathbf{K}) = \sum_{\mathbf{n}} \delta(\mathbf{K}_{\parallel} - 2\pi\mathbf{n}/a). \quad (3)$$

The sharp spots may show a shoulder due to surface unit meshes with a different scattering factor f_b , as discussed in detail in Ref. 21. Here only the influence of steps is of interest.

We assume that all atoms are on perfect lattice sites. This means that only the vertical position $dh(\mathbf{n})$ of the n th atom can change its value by multiples $h(\mathbf{n})$ of the layer distance \mathbf{d} .

Then the lattice factor is given by

$$G(\mathbf{K}) = \sum_{\mathbf{n}} \langle e^{idK_{\perp}[h(\mathbf{n}+m)-h(\mathbf{m})]} \rangle e^{ia\mathbf{K}_{\parallel} \cdot \mathbf{n}}, \quad (3')$$

where K_{\perp} and \mathbf{K}_{\parallel} denote the components of the scattering vector perpendicular and parallel to the surface, respectively. The angular brackets $\langle \rangle$ denote averaging with respect to \mathbf{m} .

Two kinds of surface roughness may be distinguished: the nearly smooth surface and the rough surface. Depending on the finite or infinite number of levels contributing to the surface the asperity height Δ defined by

$$\Delta^2 = d^2 [\langle h^2(\mathbf{m}) \rangle - \langle h(\mathbf{m}) \rangle^2] \quad (4)$$

has a finite or an infinite value for the smooth and rough surfaces, respectively. Therefore it is also possible to denote the smooth and rough surfaces by finite and infinite roughness, respectively, indicating that also for the smooth surface there exist some atomic steps.

For a smooth surface the lattice factor splits into a central spike G_{ideal} and a broadening Φ_{step} caused by the interference from different levels of the stepped surface:

$$G(\mathbf{K}) = G_0(K_{\perp}) G_{\text{ideal}}(\mathbf{K}_{\parallel}) + [1 - G_0(K_{\perp})] \phi_{\text{step}}(\mathbf{K}_{\parallel}). \quad (5)$$

The amplitudes of both central spike and broadening vary with K_{\perp} periodically. From this variation one can extract the layer distribution.^{22,23} Close to an in-phase condition $dK_{\perp} = 2\pi h$ (h denotes an integer) the variation $G_0(K_{\perp})$ can be approximated by²¹

$$G_0(K_{\perp}) = \exp(-\Delta^2 k_{\perp}^2). \quad (6)$$

Here $k_{\perp} = K_{\perp} - 2\pi h/d$ denotes the deviation of the vertical scattering vector from the in-phase condition. The broadening due to steps Φ_{step} contains the information about the terrace-length distribution.^{24–28}

For a rough surface the whole spot profile broadens^{29,30} instead of splitting into central spike and shoulder as one observes for a smooth surface. The shape of the spot profile depends on the scattering condition, but it varies periodically. Especially under the in-phase condition the spot gets sharp with δ -function profile. The details of the spot profile depend on both the terrace-length and step-height distributions.^{30,31} Assuming a reversible surface (upward and downward steps have the same probability) with geometric terrace-length distribution, one can show that the profile has a Lorentzian shape with half-width³¹

$$\Delta K_{\parallel} = 2[1 - \beta_s(K_{\perp})] / \langle \Gamma \rangle. \quad (7)$$

Here $\beta_s(K_{\perp})$ is the Fourier transform of the step-height distribution. Therefore both the average terrace length and the step-height distribution can be obtained by analyzing the spot profile with respect to the scattering condition.

As described in Ref. 21 the height-height correlation $\Gamma(n)$ is also derived out of the spot profile, if it has been measured for several scattering conditions. Even for the rough surface the height-height correlation is available if Eq. (8) from Ref. 32 is used:

$$G(\mathbf{K}) = \sum_{\mathbf{n}} e^{-\Gamma(\mathbf{n})[1 - \cos(dK_{\perp})]} e^{ia\mathbf{K}_{\perp} \cdot \mathbf{n}}. \quad (8)$$

Therefore many details about roughness are available if the spot profiles are recorded for many scattering conditions with high precision, so that a separation of central spike and shoulder is possible.

IV. RESULTS

A. Nomenclature and characterization of the surface at low temperature: inhomogeneities

The Cu(311) surface (fcc lattice) consists of close-packed rows in the $[01\bar{1}]$ direction. The distance of the atoms within the row is $a=0.255$ nm; the distance in the $[2\bar{3}\bar{3}]$ direction of the rows $b=0.423$ nm. Figure 1 shows that the surface builds a centered rectangular bravais lattice with layer distance $d=0.109$ nm.

After the surface has been cleaned and annealed as outlined in Sec. II, the profile of the (00) spot has been measured as a function of the vertical scattering vector K_{\perp} . Under the in-phase condition $S=dK_{\perp}/2\pi=2.0$ ($E=125$ eV), where no spot broadening due to atomic steps can be observed, the profile consists of two parts: a central peak and a very broad shoulder with low peak intensity (see Fig. 2). From the halfwidth of the central peak one obtains a transferwidth of 130 nm. Since the instrumental transfer width is 200 nm,¹⁸ the spot is broadened by defects as, e.g., dislocations or mosaics.³³ Supposing that

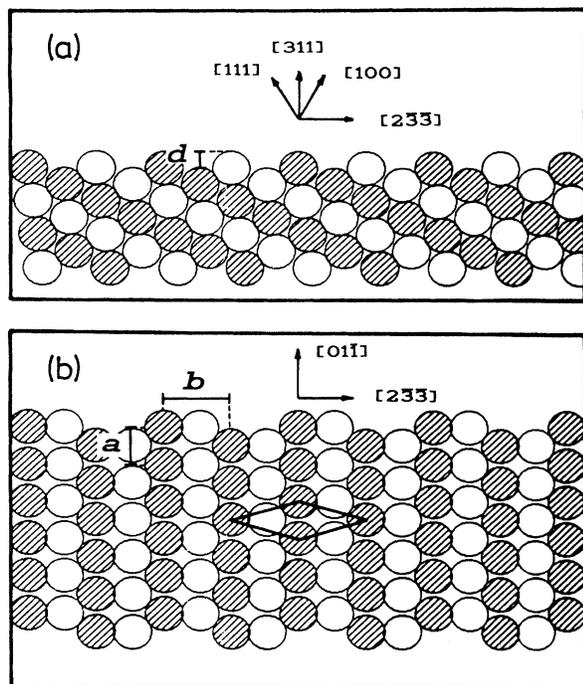


FIG. 1. Hard-sphere model of the Cu(311) surface. (a) Side view. The layer distance $d=0.109$ nm is shown. The (100) planes are marked by hatching. (b) Top view. The atomic distance $a=0.255$ nm in the $[01\bar{1}]$ direction and the row distance $b=0.423$ nm in the $[2\bar{3}\bar{3}]$ direction are shown. The hatched spheres mark the first layer, the open spheres the second layer. The solid line shows the primitive unit mesh.

this broadening is due to mosaics, the spread is less than 0.02° in accordance with the x -ray-diffraction measurements (see Sec. II).

The additional broadening of the spot at this scattering condition cannot be caused by steps. Therefore inhomogeneities of the surface are the origin of the weak shoulder shown in Fig. 2, curve *a*. Since for the almost clean surface the intensity of the shoulder is very small, there are very few inhomogeneities. This result is supported by AES. The ratio of the peak-to-peak intensity of the S(153 eV) Auger line to the peak-to-peak intensity of the Cu(63 eV) Auger line is less than 1%. This ratio is denoted by R in the following. Other contaminations cannot be observed. The profile of the broadening can be fitted very well by a Lorentzian-like profile

$$\Phi_{\text{inh}} \sim (1 + \xi_{\text{inh}}^2 K_{\parallel}^2)^{-3/2}. \quad (9)$$

Here ξ_{inh} denotes the correlation length of the inhomogeneities. This shape of the broadening implies that the inhomogeneities are distributed isotropically and that the domain sizes have a geometric distribution.³¹ Since the shoulder is very broad the average size of the domains due to inhomogeneities is also very small ($\xi_{\text{inh}} \approx 0.13$ nm).

To investigate the influence of sulfur on the morpholo-

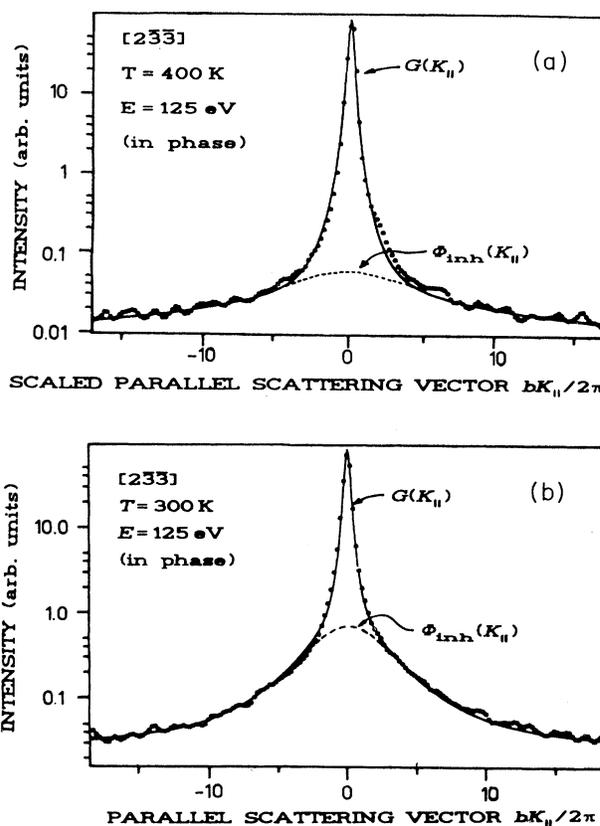


FIG. 2. Spot profile of the (00) spot under the in-phase condition $S=2.0$. The dashed line is the Lorentzian-like broadening due to residual inhomogeneities (sulfur contamination). The amount of segregated sulfur is characterized by AES: (a) $R = I(\text{S}(153 \text{ eV}))/I(\text{Cu}(63 \text{ eV})) = 1\%$; (b) $R = I(\text{S}(153 \text{ eV}))/I(\text{Cu}(63 \text{ eV})) = 9\%$. Notice the logarithmic scale of the ordinate.

gy of the Cu(311) surface the sulfur coverage has been increased stepwise by heating the sample at $T=970$ K for some time. At this temperature a satisfactory amount of sulfur segregates at the surface. For all studied sulfur coverages the profile of the additional broadening measured under the in-phase condition ($E=125$ eV, $S=2.0$) can be described by the Lorentzian-like profile of Eq. (11) (see Fig. 2, curve *b*). With increasing sulfur coverage characterized by the AES peak-to-peak ratio R the intensity of the central spike decreases while the correlation length ξ_{inh} does not change very much (see Fig. 3). From the AES data it is clear that the sulfur coverage Θ_s for the data shown in Fig. 3 is less than 0.03 ML. Nevertheless there is a very drastic decrease of the central spike intensity. Following Ref. 21 for this effect there are two possible reasons. First the scattering amplitude of the sulfur atoms f_s may be much larger than the scattering amplitude of the copper atoms f_{Cu} . A second reason may be that the segregated sulfur disturbs large areas of the Cu(311) surface. It seems to us that an unreasonable large scattering amplitude f_s is needed to explain this effect. On the other hand the distortion of the Cu(311) lattice by sulfur is emphasized by the observation that the central spike of the (00) spot also broadens if a large amount of sulfur is segregated at the surface ($R > 0.1$).

Besides the inhomogeneities discussed up to now there are also atomic steps at the Cu(311) surface. The surface roughness can be measured changing the scattering condition to the out-of-phase condition. The influence of both temperature and sulfur segregation on the surface roughness will be characterized in the following subsections.

B. Thermal behavior of the clean Cu(311) surface: atomic steps

To study the roughness of the Cu(311) surface as a function of the temperature the (00) spot has been measured at many scattering conditions ($E=90$ – 200 eV, $S=1.7$ – 2.5) for the temperature range $T=300$ – 800 K. When increasing the temperature the constant background intensity increases because of the thermal diffuse scattering due to thermal vibrations of the surface atoms (Debye-Waller factor).³⁴ Beyond this effect the shape of the spot also changes: above $T=600$ K there is a reversible increase of the spot half-width under the out-of-phase condition, while the half-width does not change for the in-phase condition (see Fig. 4). Therefore one can create

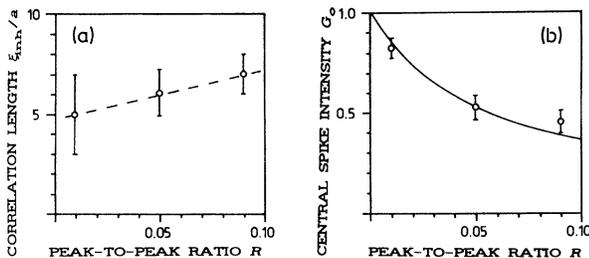


FIG. 3. Effects of the sulfur segregated at the surface (measured with the AES ratio R) for the spot profile under the in-phase condition $S=2.0$. (a) Correlation length of the broadening due to inhomogeneities. (b) Intensity of the central spike.

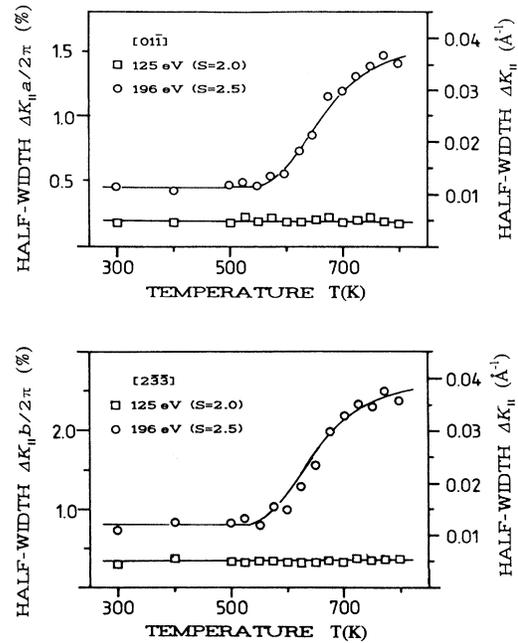


FIG. 4. Temperature dependence of the half-width of the (00) spot under the out-of-phase condition $S=2.5$ and at the in-phase condition $S=2.0$ for both directions $[01\bar{1}]$ and $[2\bar{3}\bar{3}]$.

and annihilate reversibly atomic steps by changing the surface temperature.

There exist several models to describe the roughening of a fcc(311) surface. A survey over these models is given in Ref. 35. When analyzing these models it is predicted that the roughening transition is of the Kosterlitz-Thouless type. That is, the height-height correlation $\Gamma(\rho)$ depends logarithmically on the two-dimensional distance ρ :

$$\Gamma(\rho) = A(T) \ln \rho + C, \quad (10)$$

where C denotes some constant and the coefficient $A(T)$ increases monotonously with temperature. This logarithmic behavior of the height-height correlation leads to a power law of the lattice factor³²

$$G(\mathbf{K}_{\parallel}) \sim |\mathbf{K}_{\parallel}|^{-2+\eta} \quad (11)$$

with

$$\eta = A(T) [1 - \cos(dK_{\perp})].$$

Figure 5 shows that the experimental data for the out-of-phase condition cannot be fitted well by a power law spot profile either for low or high surface temperature. To fit the spot profiles the power-law lattice factor Eq. (11) has been convoluted with the instrumental function.

As Fig. 6 illustrates a much better fit can be obtained if one splits the spot profile into a central spike and a Lorentzian-like broadening due to steps:

$$\Phi_{\text{step}}(\mathbf{K}_{\parallel}) \sim (1 + \xi^2 \mathbf{K}_{\parallel}^2)^{-3/2}, \quad (12)$$

where ξ denotes the correlation length of surface roughness. Under the out-of-phase condition, this broadening

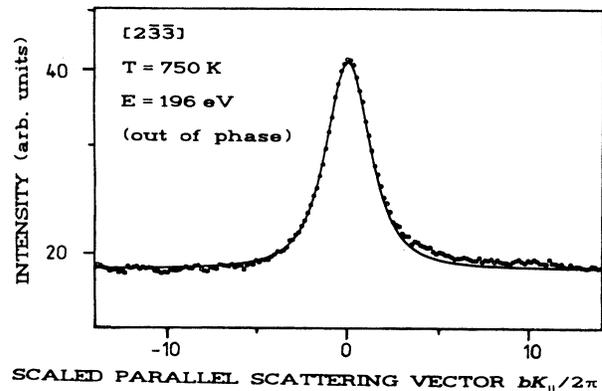
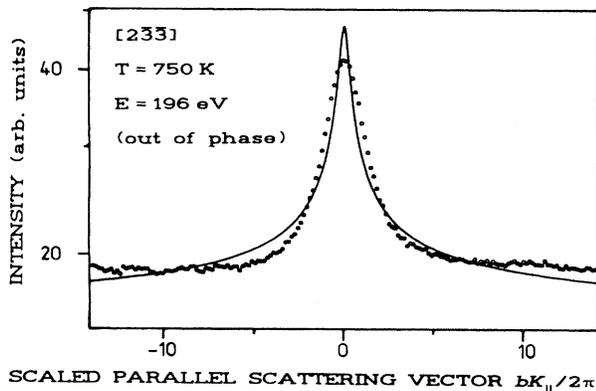
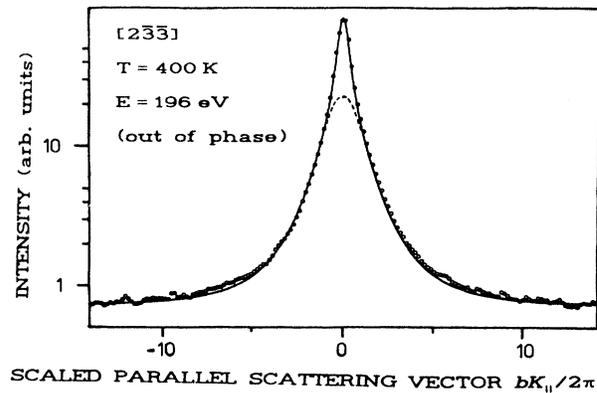
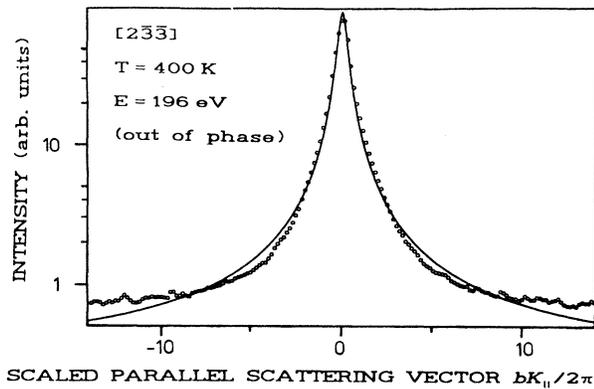


FIG. 5. Least-squares fits of the spot profiles recorded under the out-of-phase condition $S=2.5$ for several surface temperatures to the algebraic profile Eq. (11) after convolution with the instrumental broadening.

FIG. 6. The same experimental data as in Fig. 5 fitted to a profile consisting of central spike and Lorentzian-like broadening [Eq. (14)]. While for $T=400$ K there is a central spike (the shoulder is given by the dashed line), at $T_R=750$ K the central spike has vanished.

due to steps overwhelms the weak broadening due to inhomogeneities discussed in Sec. IV A. The Lorentzian-like profile of the broadening shows that the terrace-length distribution is geometric.³¹ The average terrace length $\langle \Gamma \rangle$ is twice the correlation length ξ .²⁵ The shoulder has some asymmetry for the two directions $[01\bar{1}]$ and $[2\bar{3}\bar{3}]$.

When increasing the temperature there are two effects on the spot profile: the intensity of the central spike decreases and the half-width of the broadening increases. The decrease of the central spike intensity G_0 with temperature T is shown in Fig. 7 for several scattering conditions. For all scattering conditions the central spike vanishes at the critical temperature $T_R=750$ K. Therefore at this critical temperature the surface goes from the smooth phase into the rough phase. Using the relation $\ln G_0 \sim \Delta^2$ of Eq. (6) the lines in Fig. 7 indicate that the asperity height Δ follows the behavior $\Delta \sim (T_R - T)^{-1/4}$ as has been predicted for the roughening transition.³⁶ The behavior of the correlation length ξ with increasing temperature is shown in Fig. 8. Within the observed temperature range it does not change very drastically. The asymmetry of the shoulder is nearly constant.

To extract the asperity height Δ from the LEED data

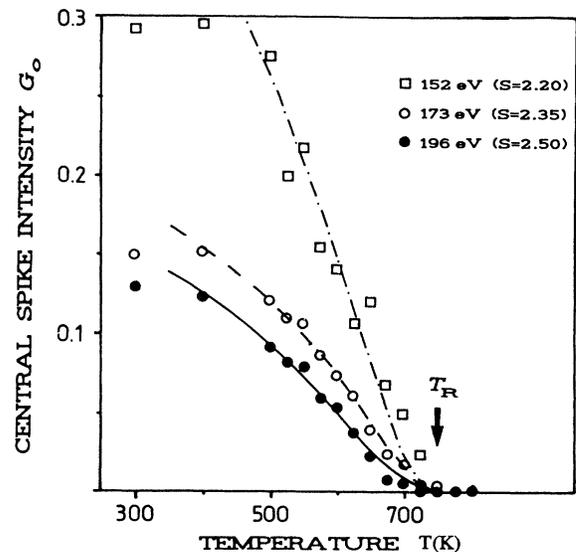


Fig. 7. Temperature dependence of the central spike intensity for several scattering conditions. At the critical temperature $T_R=750$ K (arrow) the central spike vanishes for all scattering conditions (except exact inphase): the surface goes from the smooth phase into the rough phase.

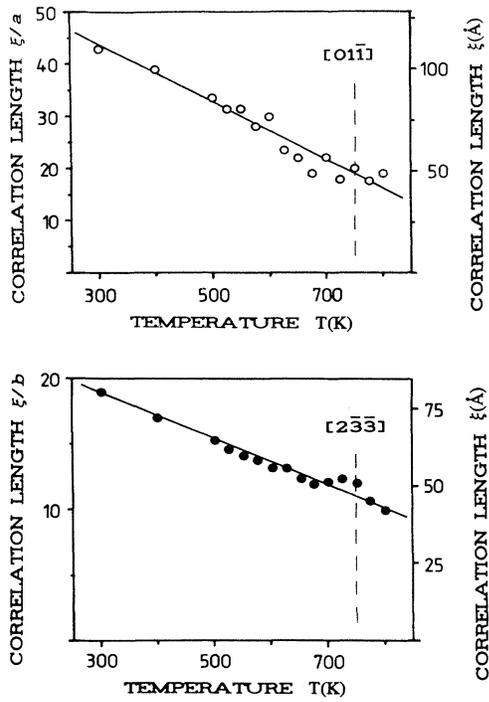


FIG. 8. Temperature dependence of the correlation length for both directions $[01\bar{1}]$ and $[2\bar{3}\bar{3}]$. The dashed line indicates the critical temperature $T_R = 750$ K.

one has to analyze spot profiles for many scattering conditions. Figure 9 shows the central spike intensity G_0 versus the vertical phase $S = dK_{\perp}/2\pi$ for two temperatures. The lines are fits of the Gaussian behavior Eq. (6) to the experimental data. From these fits one obtains the asperity height Δ as a function of the temperature T , which is shown in Fig. 10. The asperity height Δ is a more slowly changing function with the temperature T than the drastic decrease of the central spike intensity seems to indicate. The reason is that even a small increase of the asperity height decreases the central spike drastically because of the exponential dependency of the

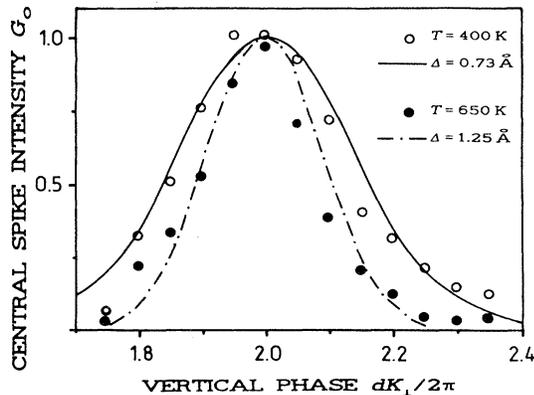


FIG. 9. Dependence of the relative central spike intensity on the vertical phase $S = dK_{\perp}/2\pi$ for two temperatures. The lines are fits of the experimental data to the Gaussian approximation Eq. (7) to obtain the asperity height Δ .

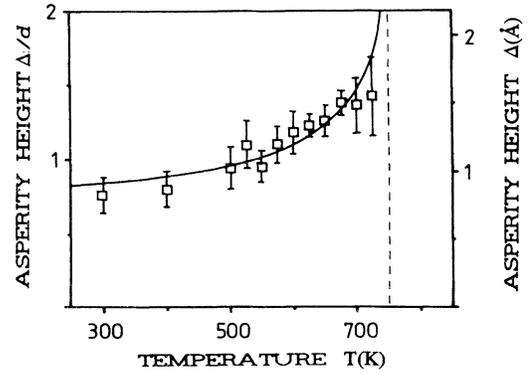


FIG. 10. Temperature dependence of the asperity height. The dashed line indicates the critical temperature T_R . The solid line is a fit of the experimental data to the theoretical predicted behavior $\Delta \sim (T_R - T)^{-1/4}$.

central spike on Δ^2 [see Eq. (6)]. This emphasizes that LEED is very sensitive to small changes of the surface roughness. Furthermore the solid line in Fig. 10 shows the dependency of the asperity height on the temperature $\Delta \sim (T_R - T)^{-1/4}$ predicted for the roughening transition (see also Fig. 6).

Finally we want to discuss what the consequences of the measured spot profile for the height-height correlation are. As has been mentioned above no evidence for a logarithmic behavior of the height-height correlation has been observed. Following the ideas presented at the end of Sec. III the dependency of the height-height correlation $\Gamma(\rho)$ on the lateral distance ρ can be obtained directly from the profile of the broadening due to steps $\Phi_{\text{step}}(K_{\parallel})$. For the smooth phase ($T \leq T_R$) the Lorentzian-like shape for the shoulder [see Eq. (12)] shows that the height-height correlation saturates with exponential dependency on the lateral distance. The function $\varphi(\rho)$ especially, which is involved in the height-height correlation (see Ref. 21), has the form $\varphi(\rho) = e^{-\rho/\xi}$, where ξ is the correlation length obtained from the shoulder via Eq. (14). On the other hand above the critical temperature T_R the spots do not have any central spike since the surface is rough. The height-height correlation does not saturate at any finite value but diverges as ρ goes to infinity. For this high-temperature range (rough phase) we have to consider Eq. (10) to calculate the height-height correlation. The Lorentzian-like shape of the spot profile indicates that the height-height correlation $\Gamma(\rho)$ depends linearly on the lateral distance ρ , namely, $\Gamma(\rho) = \rho/\xi$.³⁷ Here again ξ is the correlation length involved in the Lorentzian-like spot profile via Eq. (9). Summarizing these results for both the smooth and rough phases the height-height correlation can be described by

$$\Gamma(\rho) = \begin{cases} 2\Delta^2(1 - e^{-\rho/\xi}), & T \leq T_R \\ \rho/\xi, & T > T_R \end{cases}, \quad (13)$$

where both the asperity height Δ and the correlation length ξ depend on the surface temperature.

C. Influence of inhomogeneities on the thermal surface roughness

The surface roughness has also been studied by SPALEED for the sulfur covered Cu(311) surface. As was mentioned in Sec. IV A the half-width of the central spike at the in-phase condition does not increase whilst the sulfur coverage is not too large. On the contrary at the out-of-phase condition the half-width increases still with increasing sulfur coverage at low temperature. Therefore the step atom density also increases with respect to the sulfur coverage. This is shown in Fig. 11 for an almost out-of-phase condition ($S=2.35$, $E=173$ eV). This scattering condition has been chosen to study the thermal behavior of the sulfur covered Cu(311) surface because the intensity of the specular electron beam is much larger than for the exact out-of-phase condition. Nevertheless for this scattering condition the (00) spot is also very sensitive to atomic steps.

Figure 11 also shows that the half-width of the (00) spot at $S=2.35$ increases with increasing temperature, while it remains constant for the in-phase condition. Thus although the surface roughness is enhanced already at low temperatures by the segregated sulfur it is additionally increased by the surface temperature reversibly. Nevertheless there is a great difference from the thermal roughness of the clean surface reported in Sec. IV B. As Fig. 12 shows the spot profile at the out-of-phase condi-

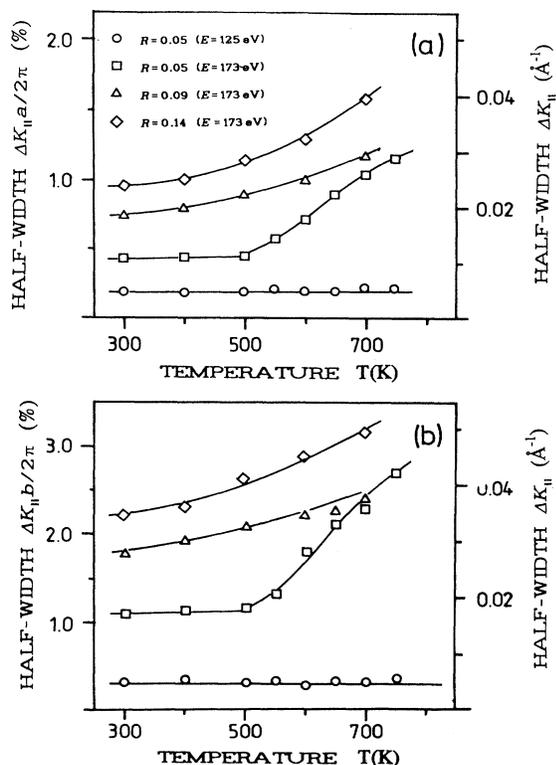


FIG. 11. Temperature dependence of the half-width of the (00) spot at the out-of-phase condition $S=2.5$ for several sulfur coverages. For comparison the half-width at the in-phase condition $S=2.0$ for $R=5\%$ is also shown.

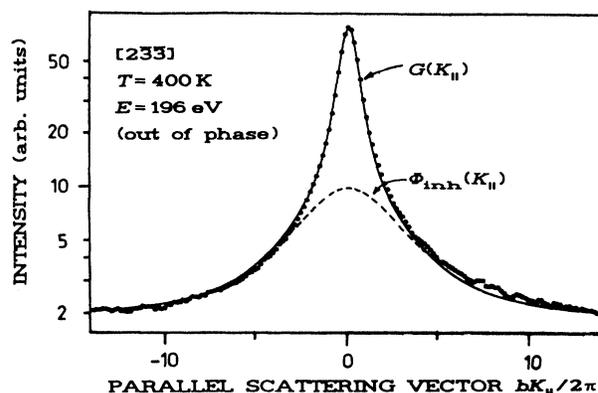


FIG. 12. Least-squares fit of the spot profile recorded at the out-of-phase condition $S=2.5$ to two Lorentzian-like broadenings due to steps and due to inhomogeneities (dashed line). A central spike cannot be determined.

tion is fitted well by only two parts, a broadened part due to steps and an additional broadening due to inhomogeneities as already measured at the in-phase condition. Contrary to the clean surface, a central spike cannot be determined. Therefore the surface is still rough at low temperatures.

The broadening due to steps can be described by a Lorentzian-like lattice factor

$$G(\mathbf{K}) \sim (K^2 + K_{\parallel}^2)^{-3/2}. \quad (14)$$

This implies a geometric terrace-length distribution. The parameter $K = K(K_{\perp})$ governing the half-width of the broadening due to steps is a function of the vertical scattering vector K_{\perp} . It is shown in Fig. 13 for two temperatures. Following Eq. (7) the dependence of the half-width on the scattering condition cannot be explained if only monoatomic steps exist. Especially that the half width does not change with K_{\perp} close to the out-of-phase condition points to a considerable amount of double steps contributing to the surface roughness. Denoting the density of double steps with respect to the total amount of steps by σ the Fourier transform of the step-height distribution involved in Eq. (7) is

$$\beta_s(K_{\perp}) = (1 - \sigma) \cos(dK_{\perp}) + \sigma \cos(2dK_{\perp}). \quad (15)$$

The solid lines in Fig. 13 are fits of the theoretically predicted behavior of the halfwidth to the experimental data if only monoatomic and double steps are taken into account.

From the Fourier analysis of the half-width dependency on the scattering conditions one obtains that the (relative) density of double steps σ decreases with increasing temperature. This is shown in Fig. 14 for a sulfur coverage characterized by $R=0.05$. Since the average terrace length decreases with increasing temperature (see Fig. 15) the total amount of steps also increases. Therefore the total amount of double steps does not decrease as drastically as Fig. 14 seems to demonstrate. Figure 15 shows the average terrace length as a function of the temperature. As the smoother variation of the half-width with

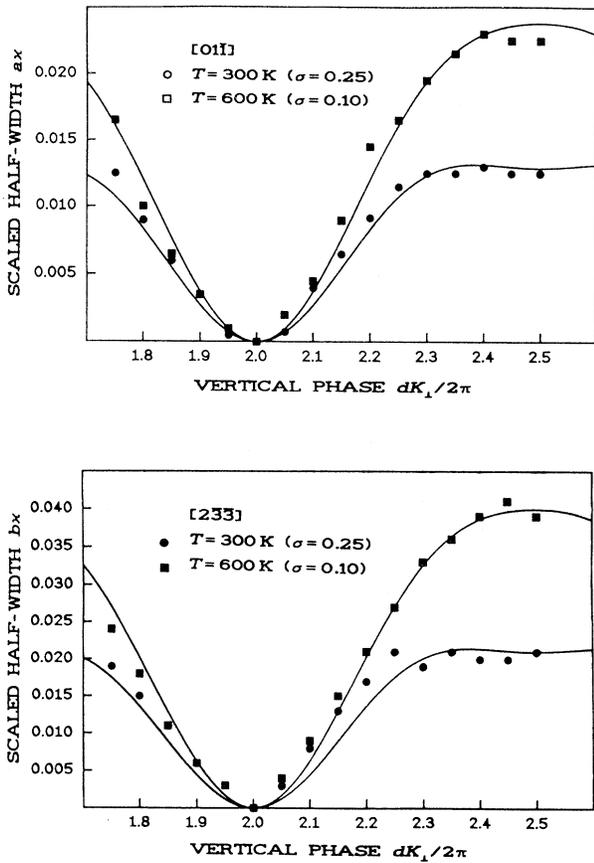


FIG. 13. Dependence of the half-width for the broadening due to steps on the vertical phase $S = dK_1/2\pi$ for two temperatures. The solid lines show the best fit assuming that only monoatomic and double steps are at the surface.

temperature for increasing sulfur coverage indicates (see Fig. 11) the average terrace length does not depend so strongly on the temperature if a larger amount of sulfur is segregated at the surface. Nevertheless the surface gets rougher with increasing temperature.

V. DISCUSSION AND CONCLUSION

In this report we have shown that atomic steps can be created on the Cu(311) surface by increasing the temperature. This has been concluded from the analysis of

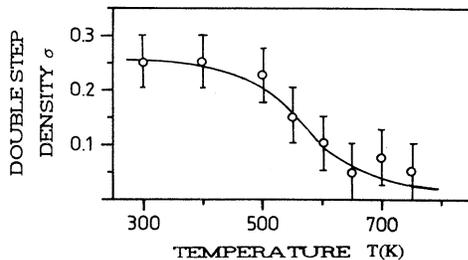


FIG. 14. Temperature dependence of the double step density for a segregated amount of sulfur characterized by the AES ratios $R = 5\%$.

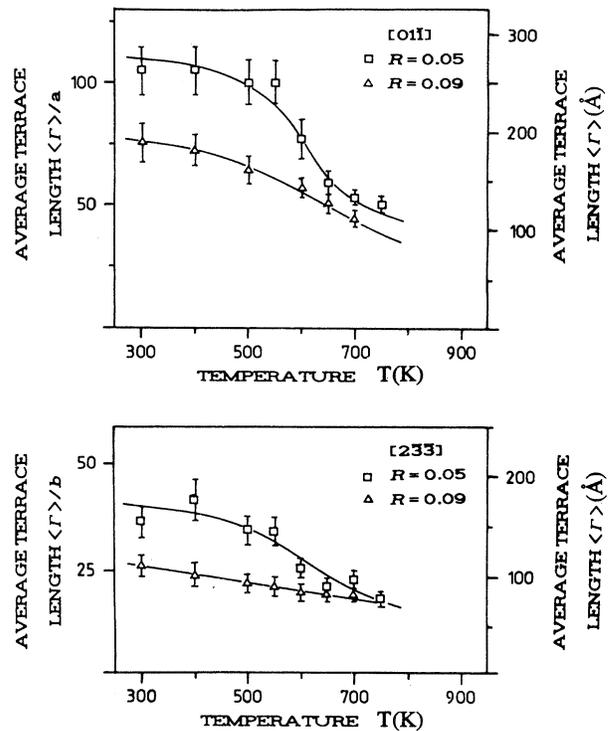


FIG. 15. Temperature dependence of the average terrace length for two sulfur coverages characterized by the AES ratio R . Increasing the amount of sulfur weakens the dependence of the surface roughness on the temperature.

diffraction spots recorded with a high-resolution instrument at different scattering conditions: the (00) spot broadens at the out-of-phase condition with increasing temperature, while the half-width of the spot remains constant for the in-phase condition. From this effect it can be concluded that the broadening of the spot is not caused by a quasielastic broadening due to phonons, since the broadening due to the one-phonon scattering should influence the spot profile at all scattering conditions in the same manner.³⁸ Thus no broadening periodically changing with the scattering condition can be produced by thermally activated phonons.

The roughening transition characterized in this work does not belong to the Kosterlitz-Thouless universality class since the recorded spot profiles cannot be fitted well with a power-law singularity. From the fit of the spot profile with a central spike and a Lorentzian-like shoulder, one deduces an exponentially saturating height-height correlation instead of the logarithmic behavior predicted for Kosterlitz-Thouless roughening. Nevertheless the asperity height Δ follows the critical behavior $\Delta \sim (T_R - T)^{-1/4}$ predicted for the Kosterlitz-Thouless phase transition. We have therefore directly observed the phase transition from the smooth into the rough phase by the vanishing of the central spike under various scattering conditions.

In contrast to these results are earlier investigations of the thermally induced surface roughness of Cu(311) analyzing the specular beam of a helium diffraction exper-

iment.³⁵ Taking the instrumental broadening into account the authors were able to fit the measured spot profiles with the power-law profile of Eq. (13). Similar results have been obtained in a helium diffraction investigation on Ni(311).⁸ However, in these experiments the transfer width of the instrument has not been very large (10–15 nm). Since still at the critical temperature T_R the step density is not very high, the spots are not broadened very drastically. Thus, because the instrumental broadening is very important, it is a difficult task to analyze the spot profile in full detail. A similar effect has even been observed in the high-resolution experiment presented here. For low temperature, if the spot profile is only broadened slightly by steps, the fit of the spot profile with an algebraic function convoluted with the instrumental broadening is nearly acceptable (see Fig. 5). If the experimental data presented here would be convoluted with the instrument response of a low-resolution instrument, the same degree of correspondence between experiment and theory would be obtained.

However, there may be a second reason for the discrepancy between both investigations on the thermal roughness of Cu(311). Both techniques, low-energy electron and helium diffraction, probe different properties of the surface. Especially, it is well known that for helium diffraction step atoms have an enhanced scattering cross section compared to terrace atoms due to diffuse scattering from areas around the step edges.^{39,40} This effect leads to a decrease in the diffracted intensity even under the in-phase condition. Therefore the kinematic approximation used to analyze the spot profiles may not work. On the other hand it is obvious from the profile under the in-phase condition that for a LEED experiment the scattering amplitudes of step and terrace atoms do not differ strongly, since in the case of large differences one should measure an increasing broadening of the spot profile under the in-phase condition with increasing step atom density. This effect has not been observed here.

Comparing the results obtained with helium diffraction³⁵ and electron diffraction presented here the profiles up to the roughening temperature agree with a Lorentzian profile, if the lower resolution of helium diffraction is considered. For a temperature above the roughening temperature, however, helium diffraction clearly shows a power-law profile beyond any uncertainty due to resolution limitations.⁴¹ Unfortunately no LEED profiles have been measured well beyond roughening temperature. As a result the transition should be Ising type up to T_R and Kosterlitz-Thouless type beyond T_R . A recent discussion with Tosatti and v. Beijeren revealed the possibility of a preroughening transition, where the roughening is restricted to two layers yielding an Ising transition. If the two transition temperatures are close to each other (within 50 K) the experiment will show a superposition of the two transitions with a clear distinction only well below and well above the measured transition temperature. Further detailed experiments could reveal such a twofold roughening transition.

Incongruous results have also been obtained with recent LEED investigations on the thermal roughness of fcc(110) surfaces. While for Pb(110) the spot profile

analysis has been done due to the algebraic profile,¹¹ for Ni(110) the splitting of the spot into central spike and shoulder has also been observed.¹² Indeed, in the work on Pb(110) only the wings of the spot profile have been analyzed; the central part of the spot has not been taken into account. It is decisive to fit a full profile, since by using different parts of a profile quite different fits may appear acceptable.

Although many studies done on the thermally induced surface roughening point to a roughening transition of the Kosterlitz-Thouless type, it is also discussed in the literature that this phase transition falls into another universality class.^{42,43} Thus the roughening transition seems to be a rather delicate phenomenon, because of the way a surface roughness depends on the details of the interaction between the surface atoms, e.g., for some theoretical models a sharp roughening transition is predicted, while for other models the roughening should occur very smoothly. Because of the asymmetry of the Cu(311) surface one may describe its structure by the rows in the $[01\bar{1}]$ direction (see Fig. 1). Steps lead to a displacement of the rows, since for different layers the rows have different phases. Therefore the rough surface can also be characterized by meandering rows. It has been shown that for a repulsive interaction between the rows the critical behavior switches from the Kosterlitz-Thouless to the Ising universality class. For a one-dimensional surface this means that the pair correlation decays exponentially, so that the shoulder has a Lorentzian profile.²⁷ Generalizing this case to an isotropic two-dimensional surface from the exponential dependency one gets the Lorentzian-like broadening of Eq. (14) obtained in this work.³¹

On the other hand it seems to be possible that residual defects (e.g., inhomogeneities, dislocations) at the surface due to preparation may substantially change the way a surface roughens. In this work the influence of inhomogeneities (here sulfur segregated at the surface) on the thermal roughness of the Cu(311) surface has been studied. It has been shown that still small amounts of sulfur ($\Theta_s \leq 1\%$) amorphousize large areas of the Cu(311) surface and increase the step atom density. Even at low temperatures the inhomogeneous surface is in the rough phase. Nevertheless, beyond the increasing roughness due to inhomogeneities it has been observed clearly that the surface roughness is a function of temperature. Indeed, its dependency on the temperature gets weaker due to the presence of sulfur. Up until now there have only been preliminary theoretical considerations about the influence of inhomogeneities (impurities) on the roughening transition.³⁶ This problem has been studied intensely for the Ising model with fixed impurities (random bonds for a two-dimensional Ising model).⁴⁴ Additionally these authors have shown with renormalization-group analysis that for three dimensions the character of the roughening transition also changes.

A very surprising result of these studies on the thermal behavior of the inhomogeneous surfaces is that the double step density decreases with increasing temperature. One reason for this phenomenon may be that double steps created by inhomogeneities at low temperatures de-

cay to monoatomic steps at high temperatures. A similar effect has been observed for vicinal surfaces studied by Monte Carlo simulations. Because of the small misorientation angle of a vicinal surface with respect to a low index plane there are still some straight steps on the surface at low temperature. These straight steps cannot be observed if the surface temperature is satisfactorily high, since the thermally created meandering steps overwhelm and hide and low-temperature steps. In recent STM investigations on the thermal roughness of Ag(511) this criterion of the vanishing of low-temperature steps has been used to estimate the critical temperature.⁴⁵

Summarizing the results of this report we have shown that LEED measurements using a high-resolution instrument are very useful tools for studying thermally induced effects at surfaces. Analyzing carefully the spot profiles recorded at many various scattering conditions provides a lot of information to characterize quantitatively both steps and inhomogeneities at the surface, as a function of temperature. In this investigation on the thermal rough-

ness of the Cu(311) surface we have shown that the clean surface goes from the smooth phase into the rough phase at the critical temperature $T_R = 750$ K. This has been calculated from the vanishing of the central spike at this critical temperature observed for what we believe to be the first time. Inhomogeneities at the surface lead to an increasing surface roughness even at low temperature. On the other hand they cause a weaker dependency of the surface roughness on the temperature. This influence of the inhomogeneities and the incompatibility of the measured profiles with currently available theories should stimulate both further theoretical and experimental studies.

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- ¹M. Prutton, *Surface Physics* (Clarendon, Oxford, 1975).
- ²J. F. van der Veen, B. Pluis, and A. W. Denier van der Gon, in *Chemistry and Physics of Solid Surfaces VII*, edited by R. Vanselow and R. F. Howe, Springer Series in Surface Science Vol. 14 (Springer, Berlin, 1982), p. 455.
- ³J. W. M. Frenken, J. P. Toennies, C. Wöll, B. Pluis, A. W. Denier van der Gon, and J. F. van der Veen, in *The Structure of Surfaces II*, edited by F. v. d. Veen and M. Van Howe, Springer Series in Surface Science Vol. 11 (Springer, Berlin, 1988), p. 545.
- ⁴J. G. Dash, *Contemp. Phys.* **30**, 89 (1989).
- ⁵W. K. Burton and N. Cabrera, *Discuss. Faraday Soc.* **5**, 33 (1949).
- ⁶H. Müller-Krumbhaar, in *Kinetics of Crystal Growth*, edited by E. Kaldis, Current Topics in Materials Sciences Vol. 1 (North-Holland, Amsterdam, 1978), p. 1.
- ⁷F. Fabre, D. Gorse, B. Salanon, and J. Lapujoulade, *J. Phys.* **48**, 1017 (1987).
- ⁸E. H. Conrad, L. R. Allen, D. L. Blanchard, and T. Engel *Surf. Sci.* **187**, 265 (1987).
- ⁹G. A. Held, J. L. Jordan-Sweet, P. M. Horn, A. Mak, and R. J. Birgeneau, *Phys. Rev. Lett.* **59**, 2075 (1987).
- ¹⁰K. S. Liang, E. B. Sirota, K. L. D'Amico, G. J. Hughes, and S. K. Sinha, *Phys. Rev. Lett.* **59**, 2447 (1987).
- ¹¹H. N. Yang, T. M. Lu, and G. C. Wang, *Phys. Rev. Lett.* **63**, 1621 (1989).
- ¹²Y. Cao and E. H. Conrad, *Phys. Rev. Lett.* **64**, 447 (1990).
- ¹³J. A. Venables, D. J. Smith and J. M. Cowley *Surf. Sci.* **181**, 235 (1987).
- ¹⁴M. Henzler, in *Dynamical Phenomena at Surfaces, Interfaces and Superlattices*, edited by F. Nizzoli, K. H. Rieder, and R. F. Willis, Springer Series in Surface Science Vol. 3 (Springer, Berlin, 1986), p. 14.
- ¹⁵M. G. Lagally, D. E. Savage, and M. C. Tringides, in *Reflection High-Energy Electron Diffraction and Reflection Electron Imaging of Surfaces*, edited by P. K. Larsen and P. J. Dobson (Plenum, New York, 1988), p. 163.
- ¹⁶W. N. Unertl, *Comments Condens. Mat. Phys.* **12**, 289 (1986).
- ¹⁷E. Bauer, in *Structure and Dynamics of Surfaces II*, edited by W. Schlommers and P. von Blankenhagen (Springer, Berlin, 1987), p. 115.
- ¹⁸U. Scheithauer, G. Meyer, and M. Henzler, *Surf. Sci.* **178**, 441 (1986).
- ¹⁹J. S. Ahearn, Jr., J. P. Monaghan, Jr., and J. W. Mitchell, *Rev. Sci. Instrum.* **41**, 1853 (1970).
- ²⁰J. M. Cowley, *Diffraction Physics* (North-Holland, Amsterdam, 1981).
- ²¹J. Wollschläger, J. Falta, and M. Henzler, *Appl. Phys.* **A50**, 57 (1990).
- ²²M. Horn, U. Gotter, and M. Henzler, *J. Vac. Sci. Technol.* **B6**, 727 (1988).
- ²³R. Altsinger, H. Busch, M. Horn, and M. Henzler, *Surf. Sci.* **200**, 235 (1988).
- ²⁴M. Henzler, *Surf. Sci.* **152/153**, 450 (1982).
- ²⁵H. Busch and M. Henzler, *Surf. Sci.* **167**, 534 (1986).
- ²⁶J. M. Pimbley and T. M. Lu, *J. Appl. Phys.* **55**, 182 (1984).
- ²⁷C. S. Lent and P. I. Cohen, *Surf. Sci.* **139**, 121 (1984).
- ²⁸M. Henzler, *Surf. Sci.* **73**, 240 (1978).
- ²⁹T. M. Lu and M. G. Lagally, *Surf. Sci.* **120**, 47 (1982).
- ³⁰P. R. Pukite, C. S. Lent, and P. I. Cohen, *Surf. Sci.* **161**, 39 (1985).
- ³¹J. Wollschläger and M. Henzler (unpublished).
- ³²J. Villain, D. R. Gempel, and J. Lapujoulade, *J. Phys. F* **15**, 809 (1985).
- ³³T. M. Lu and M. G. Lagally, *Surf. Sci.* **90**, 695 (1980).
- ³⁴M. G. Lagally, in *Solid State Physics: Surfaces*, edited by R. L. Park and M. G. Lagally, Methods of Experimental Physics Vol. 22 (Academic, London, 1985), p. 237.
- ³⁵B. Salanon, F. Fabre, J. Lapujoulade, and W. Selke, *Phys. Rev. B* **38**, 7385 (1988).
- ³⁶H. van Beijeren and I. Nolden, in *Structure and Dynamics of Surfaces II*, edited by W. Schlommers and P. von Blankenhagen (Springer, Berlin, 1987).
- ³⁷F. Fabre, B. Salanon, and J. Lapujoulade, *Solid State Commun.* **64**, 1125 (1987).
- ³⁸M. G. Lagally, in *Surface Physics*, edited by J. M. Blakely

(Academic, London, 1975), p. 419.

³⁹B. Poelsema, L. K. Verheij, and G. Comsa, *Phys. Rev. Lett.* **53**, 2500 (1984).

⁴⁰A. Sanchez and S. Ferrer, *Surf. Sci.* **187**, L587 (1987).

⁴¹J. Lapujoulade (private communication).

⁴²F. S. Rys, *Phys. Rev. Lett.* **56**, 624 (1986).

⁴³F. S. Rys, *Surf. Sci.* **178**, 419 (1986).

⁴⁴D. A. Huse and C. L. Henley, *Phys. Rev. Lett.* **54**, 2708 (1985).

⁴⁵J. W. M. Frenken, R. J. Hamers, and J. E. Demuth, *J. Vac. Sci. Technol. A* **8**, 293 (1990).