

No Thermal Roughening on Cu(110) up to 900 K

Peter Zeppenfeld, Klaus Kern, Rudolf David, and George Comsa

Institut für Grenzflächenforschung und Vakuumphysik, Kernforschungsanlage Jülich, 5170 Jülich, West Germany

(Received 19 April 1988)

We present energy-resolved He-scattering data on the thermal behavior of the clean Cu(110) surface. At variance with a recent x-ray study we have observed no evidence for a proliferation of steps, i.e., for thermal roughening, up to $T=900$ K. The analysis points to an anomalous increase of the mean-square displacement of the surface atoms at temperatures $T \geq 550$ K which might be ascribed to an enhanced surface anharmonicity.

PACS numbers: 64.60.Cn, 68.35.Bs, 68.35.Rh, 79.20.Rf

The concept of a roughening transition has been developed by Burton, Cabrera, and Frank.¹ It plays a crucial role in the understanding of the crystal growth and the equilibrium shape of crystal surfaces. On an atomic scale the roughening of a clean smooth surface is defined as the proliferation of atomic steps by thermal generation at a roughening temperature T_R at which the free energy for creation of a step becomes zero. The basic question, whether the roughening transition temperature of a low-indexed surface is lower than the crystal melting temperature or not, is still a matter of dispute.

More recently, a less stringent definition of the roughening—this time of nominally stepped high-Miller-index surfaces—has been given: the proliferation of the kinks on the already present step rows, which thus meander dramatically. At the corresponding roughening temperature T_R , the free energy for the creation of a kink within a step becomes zero. Since the energy for creation of such a kink atom is lower than that necessary for the generation of a step atom, roughening is expected to occur at lower temperatures on the nominally stepped surface than on low-indexed surfaces. Theoretical^{2,3} and experimental⁴⁻⁶ investigations have been mainly focused on nominally stepped, high-indexed surfaces. With He-atom diffraction^{4,5} and x-ray scattering,⁶ the high-indexed (1,1, n) surfaces (with $n \geq 3$) of Cu^{4,6} and Ni⁵ were indeed shown to undergo a roughening transition well below the melting temperature.

The low-index Cu(110) face is known to show an anomalous thermal behavior. Various surface probe techniques^{7,8} such as thermal He scattering, low-energy ion scattering, photoemission, and inverse photoemission, reveal a dramatic decrease in the measured signal upon increasing the surface temperature above ~ 500 K. Thermal roughening has been considered as one possible explanation. Very recently, however, it was definitely inferred from x-ray scattering data that the (110) surfaces of Cu⁹ and Ag¹⁰ undergo a roughening transition. Mochrie⁹ has fitted his x-ray scattering data on Cu(110) as a function of temperature by assuming an increase of the mean-square displacement of the surface atoms ($\langle u^2 \rangle$).

Then he ascribed this increase to thermally generated steps, i.e., to thermal roughening: "This behavior corresponds to $\langle u^2 \rangle$ rapidly becoming larger. The most reasonable interpretation is that the thermally generated steps give rise to the extra interfacial width. By $T=600^\circ\text{C}$ there are numerous steps at the surface. This is precisely the requirement for a roughening transition."⁹

In the following we will confirm that there is indeed a strongly enhanced mean square displacement ($\langle u^2 \rangle$) of the Cu(110) surface atoms for temperatures $T \geq 550$ K. However, we will demonstrate that there is no increase in step density up to $T=900$ K. This shows that an anomalous thermal behavior of the coherent intensity is not a sufficient proof for the occurrence of thermal roughening.

The experimental data reported here have been obtained with the UHV high-resolution He-scattering apparatus described in detail elsewhere.¹¹ The He-beam generator and detector being immobile, the total scattering angle is fixed: $\vartheta_i + \vartheta_f = 90^\circ$. The angular divergence of the incident beam and the angle subtended by the detector are both 0.2° . The energy of the incident beam in the experiments reported below is 18.3 meV at an energy spread of 0.25 meV. Using a pseudorandom chopper, we are able to perform a time-of-flight analysis of the scattered He atoms, by which we can discriminate between purely elastic-scattered atoms and those which have undergone one-phonon or multiphonon interactions with the surface. The base pressure in the scattering chamber is in the low 10^{-11} -mbar range. The Cu sample was cut by spark erosion and carefully polished. The miscut angle was checked by Laue back reflection to be $< 0.2^\circ$. The Cu(110) surface was cleaned by successive cycles of sputtering with Ar ions and heating. The quality of the surface was controlled by LEED and Auger-electron spectroscopy and finally by He diffraction and diffuse He scattering.

As a first step of our investigation, the peak height I of the specular beam ($\vartheta_i = \vartheta_f = 45^\circ$) was recorded as a function of temperature. Figure 1 shows, for temperatures $T \leq 550$ K, an almost linear decrease of $\log I$ which

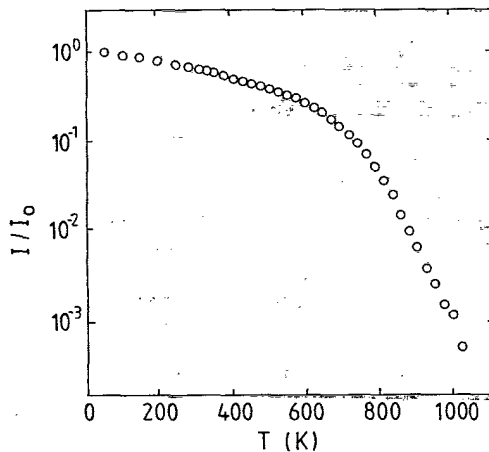


FIG. 1. Normalized specularly reflected He-beam intensity as a function of surface temperature $\vartheta_i = \vartheta_f = 45^\circ$ and beam energy $E_i = 18.3$ meV.

corresponds to the usual thermal Debye-Waller behavior. For temperatures $T \geq 550$ K, however, the intensity decreases much more rapidly [$I(1000 \text{ K})/I(550 \text{ K}) \sim 5 \times 10^{-3}$]. A similar behavior has been observed earlier on Cu(110)⁷ and Cu(100).¹²

The anomalous peak-height decrease above 550 K may have different causes: the proliferation of steps (i.e., thermal roughening as conjectured by Mochrie⁹), the proliferation of other type of defects such as vacancies or adatoms, and/or an anomalous increase of $\langle u_z^2 \rangle$ (anomalous Debye-Waller effect) due to an increase of the anharmonicity of the surface atom vibrations with increasing temperature. In the following we will show how the various capabilities of high-resolution He scattering allow us to discriminate between these causes.

The creation of steps on a low-index surface leads obviously to the appearance of low-index terraces separated by these steps, i.e., by a height difference $h = 1.27 \text{ \AA}$ in the case of Cu(110). Under appropriate scattering conditions the widths of the diffracted beams (in particular the specular beam) increase substantially as soon as the average terrace width becomes of the order of the transfer width of the instrument or smaller.^{13,14} The scattering conditions have to be chosen so that the amplitudes scattered from adjacent terraces do not interfere constructively in the specular direction. This leads to the broadening; the situation is named "out of phase" in contrast to the "in-phase" situation, where the interference is constructive exactly in the specular direction. In the present experiment the transfer width associated with the specular beam is about 350 \AA . Thus a step density even below 1% leads to an easily observable broadening. This also holds for scattering conditions which are not exactly antiphase (in the following called the "out-of-phase" regime), as long as the interference is not purely constructive.^{5,13} Consequently, if no peak broadening is observed, a proliferation of steps and thus a roughening of

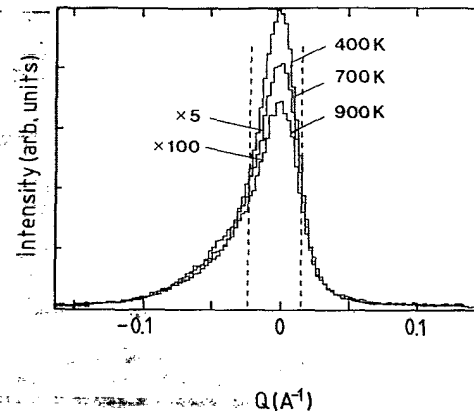


FIG. 2. Polar peak profile of the specular beam along the [001] direction for three surface temperatures. (A constant background has been subtracted.) Q denotes the momentum transfer parallel to the surface: $Q = k_i(\sin\vartheta_f - \sin\vartheta_i)$.

the low-indexed surface can be excluded. The application of this straightforward criterion is not hampered by the interference with the other effects. Indeed, vacancies and adatoms as well as Debye-Waller-type effects lead mainly to large-angle scattering and thus contribute only marginally to diffraction-peak broadening. Even if vacancies and adatoms were to broaden the peaks, the following statement—which is important here—rigorously holds: If there is no peak broadening in the "out-of-phase" regime, there are no terraces of average width between the size of the transfer width ($\sim 350 \text{ \AA}$) and 10 \AA .

In Fig. 2 the specular peak profiles monitored at three temperatures of the Cu(110) surface are shown [the asymmetry of the peak profile is due to the small residual mosaic structure ($< 0.2^\circ$) of the Cu(110) surface]. The scattering conditions $E_{\text{He}} = 18.3$ meV, $\vartheta_i = \vartheta_f = 45^\circ$ were, in view of the interplane distance of Cu(110), well inside the "out-of-phase" regime [the phase difference between beams scattered from adjacent terraces is $hk_i(\cos\vartheta_i + \cos\vartheta_f) = 1.68 \times 2\pi$]. The peak heights differ by more than 2 orders of magnitude in accordance with Fig. 1. In spite of this, the FWHM are identical within the experimental uncertainty (0.018° , the width of one channel corresponding to $\Delta Q = 0.0026 \text{ \AA}^{-1}$). This demonstrates that up to 900 K, the step density is substantially less than 1%, i.e., there is no sign of step proliferation. Thus, up to this temperature there is not even the slightest indication for roughening.

In the case of nominally stepped surfaces, starting from more sophisticated theoretical considerations, a roughening criterion based on the profile analysis of the wings of the diffraction peaks has been developed.^{2,3} As Conrad *et al.* have pointed out,¹⁵ only the elastic component of the profile has to be considered. Therefore, we recorded the purely elastic-scattered intensity only, by discriminating all inelastic contributions by means of a time-of-flight analysis. The time-of-flight spectra were

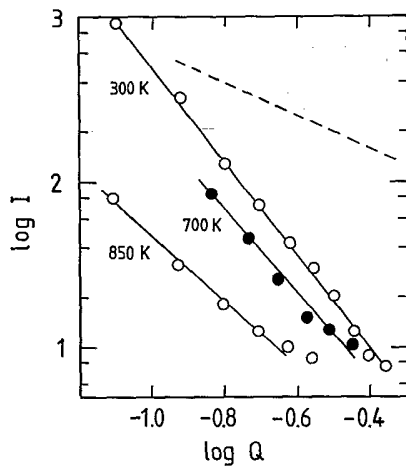


FIG. 3. Log-log plot of the elastic contribution to the polar peak profiles in an extended region of the first Brillouin zone for different temperatures. A slope of -1 (dashed line) is expected for a surface at its roughening temperature (Refs. 2 and 3).

taken for polar angles $\vartheta_i < 45^\circ$, corresponding to the steeper right side of the peak profiles in Fig. 2, where the effect of the crystal mosaic structure is minimized. The result is shown in Fig. 3. The momentum transfer parallel to the surface, given by $Q = k_i(\sin\vartheta_f - \sin\vartheta_i)$, extends from close to the peak maximum up to the middle of the first Brillouin zone along the $\bar{\Gamma}\bar{Y}$ direction ($44.5^\circ \geq \vartheta_i \geq 42^\circ$). The log-log representation was chosen in order to make the comparison to the theoretically predicted power-law line shape.^{2,3} Although the slope in Fig. 3 is slightly varying with temperature (-2.8 for $T=300$ K, -2.5 for $T=700$ K, and -2.0 for $T=850$ K), it is still far beneath the value of -1 expected for a surface at the roughening temperature.^{2,3}

This result shows that there is no significant contribution of step scattering in the wings of the specular beam, i.e., the density of steps is negligible. Indeed, theory and experiment⁴ have shown that steps become rough (meander) at relatively low temperatures [720 and 380 K on Cu(113) and Cu(115), respectively]. Thus, if present on the Cu(110) surface, the steps should be fully roughened by 850 K, and if their density were high enough they should lead to a slope of -1 in Fig. 3.

We have demonstrated so far that up to 900 K there is no indication whatsoever for a roughening of the Cu(110) surface, not even for a "preroughening."¹⁶ This is the main result of this Letter. In addition, we are able to explore another possible cause of the dramatic decrease of the intensity of the coherent beams above $T=550$ K: the proliferation of vacancies and adatoms (either Cu or segregated impurity atoms). This can also be done in a direct experiment. High-resolution He scattering is particularly suited also for this type of investigation, because of the very large total cross section for diffuse thermal He scattering for both adatoms and

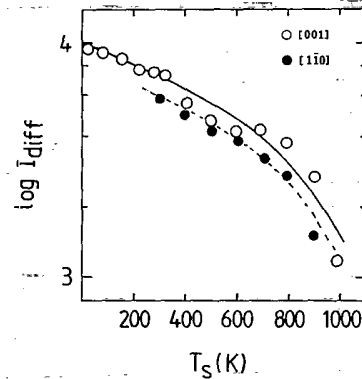


FIG. 4. Diffuse elastic-scattered intensity as a function of surface temperature, $Q=0.73 \text{ \AA}^{-1}$ ($\vartheta_i=40^\circ$), measured along the [001] direction (○) and along the [110] direction (●).

vacancies ($\approx 100 \text{ \AA}^2$).¹⁷ The He atoms are thought to be scattered mainly elastically and rather uniformly in a wide solid angle by adatoms and vacancies. The diffuse elastic peak has become a standard measure for the estimation of the density (and even of the detailed structure) of these scatterers.^{18,19} The effectiveness of this criterion for the appearance of the roughening itself has recently been demonstrated in the case of the Ni(113) surface which does roughen around 750 K: the diffuse elastic peak increases dramatically with temperature, because of the increase of the total step length, as a consequence of the meandering of the step rows.¹⁹ We have thus monitored the diffuse elastic peak as a function of the Cu(110) temperature at various scattering geometries. Under all conditions the diffuse elastic intensity does not increase but decreases with increasing temperature. In Fig. 4 a typical plot taken at a parallel wave-vector transfer $Q=0.73 \text{ \AA}^{-1}$ along the [001] direction is shown. The experimental data presented so far have been measured in the [001] direction, i.e., probing primarily the existence of steps running along the [110] direction. We have emphasized this direction because, if steps were to appear their edge should be parallel to the [110] and not to the [001] direction. Indeed, measurements on various (110) surfaces performed with scanning tunneling microscopy and ion scattering (see, e.g., Ref. 20) have shown that disorder on these surfaces is due to long segments of close-packed [110] rows moving rather freely along [110] channels. In spite of this obvious argument, we have still performed control measurements in the [110] direction. Again, no sign of roughening has been found. An example is given in Fig. 4 (filled circles). The diffuse elastic peak has the same decreasing behavior independent of direction.

Since there is no increase in diffuse elastic intensity above $T=550$ K as in the case of truly rough surfaces¹⁹ (but instead an enhanced decrease), we can also rule out the increase of adatom or vacancy density as the main cause for the observed anomalous thermal behavior for $T \geq 550$ K evidenced in Fig. 1.

The fact that, in contrast to the true roughening case,¹⁹ the diffuse elastic scattering *decreases* more rapidly than by the "normal" Debye-Waller factor above 550 K when the surface temperature *increases* indicates that the main cause for the dramatic specular intensity decrease above 550 K may be ascribed to inelastic effects. An anomalous increase of the mean-square displacement of the surface atoms $\langle u^2 \rangle$ (anomalous Debye-Waller effect) due to an increase in anharmonicity could certainly be a realistic cause.¹² Indeed, an enhanced surface anharmonicity has also been proposed as the cause of the dramatic increase of the thermal expansion coefficient of Pb(110) at temperatures above $0.5T_M$, with T_M being the melting temperature.²¹ We have measured by time-of-flight spectroscopy the energy distribution of the He atoms scattered under different geometries and noticed a strong enhancement of the multiphonon events above 500–600 K; a theoretical investigation is currently underway.²² A real experimental exploration of the contribution of these inelastic events to the loss of specular intensity is, however, only possible by inelastic measurements in the whole 2π solid angle. The present experimental capabilities (only in-plane scattering and $\vartheta_i + \vartheta_f = 90^\circ$) do not allow for such measurements yet. However, a theoretical modeling of the scattering in the presence, for instance, of an enhanced anharmonicity might lead to predictions of a certain characteristic behavior in the scattering plane which could then be looked for with one of the present time-of-flight machines.

We gratefully acknowledge fruitful discussions with Georges Armand, Dick Manson, Bene Poelsema, Laurens Verheij, and Jacques Villain.

¹W. K. Burton, N. Cabrera, and F. C. Frank, *Philos. Trans. Roy. Soc. London A* **243**, 299 (1951).

²J. Villain, D. R. Grempel, and J. Lapujoulade, *J. Phys. F* **15**, 809 (1985).

³M. den Nijs, E. K. Riedel, E. H. Conrad, and T. Engel, *Phys. Rev. Lett.* **55**, 1689 (1985), and **57**, 1279(E) (1986).

⁴F. Fabre, D. Gorse, B. Salanon, and J. Lapujoulade, *J. Phys. (Paris)* **48**, 1017 (1987); F. Fabre, B. Salanon, and J. Lapujoulade, in *The Structure of Surfaces II*, edited by J. F. van der Veen and M. A. van Hove (Springer-Verlag, Berlin, 1988), p. 520.

⁵E. H. Conrad, R. M. Aten, D. S. Kaufman, L. R. Allen, and T. Engel, *J. Chem. Phys.* **84**, 1015 (1986); E. H. Conrad, L. R. Allen, D. L. Blanchard, and T. Engel, *Surf. Sci.* **187**, 265 (1987).

⁶K. S. Liang, E. B. Sirota, K. L. D'Amico, G. J. Hughes, and S. K. Sinha, *Phys. Rev. Lett.* **59**, 2447 (1987).

⁷D. Gorse and J. Lapujoulade, *Surf. Sci.* **162**, 847 (1985).

⁸Th. Fauster, R. Schneider, H. Dürr, G. Engelmann, and E. Taglauer, *Surf. Sci.* **189/190**, 610 (1987); R. S. Williams, P. S. Wehner, J. Stöhr, and D. A. Shirley, *Phys. Rev. Lett.* **39**, 302 (1977).

⁹S. G. J. Mochrie, *Phys. Rev. Lett.* **59**, 304 (1987).

¹⁰G. A. Held, J. L. Jordan-Sweet, P. M. Horn, A. Mak, and R. Birgeneau, *Phys. Rev. Lett.* **59**, 2075 (1987).

¹¹R. David, K. Kern, P. Zeppenfeld, and G. Comsa, *Rev. Sci. Instrum.* **57**, 2771 (1986).

¹²G. Armand, D. Gorse, J. Lapujoulade, and J. R. Manson, *Europhys. Lett* **3**, 1113 (1987).

¹³T. M. Lu and M. G. Lagally, *Surf. Sci.* **120**, 47 (1982); G. Blatter and T. M. Rice, *Phys. Rev. B* **27**, 7050 (1983).

¹⁴L. K. Verheij, B. Poelsema, and G. Comsa, *Surf. Sci.* **162**, 858 (1985).

¹⁵E. H. Conrad, L. R. Allen, D. L. Blanchard, and T. Engel, *Surf. Sci.* **184**, 227 (1987).

¹⁶K. Rommelse and M. den Nijs, *Phys. Rev. Lett.* **59**, 2578 (1987).

¹⁷G. Comsa and B. Poelsema, *Appl. Phys. A* **38**, 153 (1985).

¹⁸A. M. Lahee, J. R. Manson, J. P. Toennies, and Ch. Wöll, *Phys. Rev. Lett.* **57**, 471, 2331(E) (1986); A. M. Lahee, J. R. Manson, J. P. Toennies, and Ch. Wöll, *J. Chem. Phys.* **86**, 7194 (1987); J. R. Manson, *Phys. Rev. B* **37**, 6750 (1988).

¹⁹E. H. Conrad, L. R. Allen, D. L. Blanchard, and T. Engel, in *The Structure of Surfaces II*, edited by J. F. van der Veen and M. A. van Hove (Springer-Verlag, Berlin, 1988), p. 514, and *Surf. Sci.* **198**, 207 (1988).

²⁰H. Niehus, *Surf. Sci.* **145**, 407 (1984).

²¹J. W. M. Frenken, F. Huussen, and J. F. van der Veen, *Phys. Rev. Lett.* **58**, 401 (1987).

²²G. Armand, private communication.