

## Attractive Interaction between Steps

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By using the scanning tunneling microscope we have determined the probability distribution for the distances between steps on the Cu(100) surface and the vicinal surfaces (11 $n$ ) with  $n=7$  and 19. The results indicate a repulsive short-range step-step interaction, however, unexpectedly, an attractive interaction at intermediate distances of 3–5 atoms.

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The interaction potential between steps on low index surfaces is of central importance for the equilibrium shape of crystals, step roughening on vicinal surfaces, and the dynamics of crystal growth. The equilibrium shape of crystals, e.g., is determined by the dependence of the surface free energy on the orientation of the surface [1]. Step-step interactions enter third- and higher-order terms in the expansion of the free energy with respect to the step concentration [2] and thus determine crystal-shape profiles between facets of low index faces. Likewise they control the steady-state shape of periodic profiles etched into a surface [3]. On surfaces vicinal to a low index face steps frequently order into a superlattice of equally spaced steps [4]. Such ordering is effected by repulsive step-step interactions, whereas with attractive interactions steps would accumulate in some areas, leaving the rest of the surface free of steps. At temperature  $T > 0$  thermal disorder through the production of kinks competes with the order established by the repulsive step-step interaction, which gives rise to the interesting phenomenon of a step roughening transition. This roughening transition has been studied experimentally [5] and theoretically [6,7] in great detail on the Cu(11 $n$ ) vicinal surfaces with  $n$  varying between 3 and 11 and also for some related Ni and Ag surfaces [8,9]. Whereas the theoretical models used different model Hamiltonians which were solved either analytically or numerically, the models agreed in their assumption of an entirely repulsive step-step interaction, although the possibility of an attractive dipole interaction was mentioned [2,6]. Evidence for a repulsive interaction was also obtained recently for silicon surfaces vicinal to (111) by observing the terrace-width distribution directly in tunneling microscopy [10].

In this Letter we report on an investigation of the terrace-width distribution for the nominally flat Cu(100) surface and for vicinal surfaces of the (11 $n$ ) type, a surface which consists of (100) terraces and (111)-oriented steps along the [110] direction. Our observations are incompatible with a purely repulsive step-step interaction. The interaction is repulsive for short distances, however, is attractive for intermediate distances and possibly also in the limit of large distances.

The single-crystal copper surfaces were cut by spark erosion and polished to the desired orientation to within

0.2°. The surfaces displayed a perfect mirrorlike finish. The roughness was less than 60 Å and the variation of the surface angle of the surface normal was less than 1'. No mosaic structure was observable by x-ray diffraction to within 1'. Standard procedures to produce "Auger-clean" surfaces in ultrahigh vacuum by sputter erosion and annealing were found insufficient, as residual small amounts of sulfur or oxygen tend to segregate to the steps, where these impurities hinder the motion of kinks along the steps. Good results with regard to cleanliness were obtained after leaching the crystals of their oxygen and sulfur content by heating them in a 1-bar hydrogen-argon (1:25) atmosphere at 800°C for 2 h, prior to the UHV-cleaning procedures. UHV cleaning involved more than 100 cycles of neon sputtering followed by annealing to 900 K. The final anneal was to 800 K with a slow cooldown (~1 h). Experimental observations on the steps were made using a tunneling microscope as described by Frohn *et al.* [11]. The instrument achieved atomic resolution.

As an introduction the appearance of steps on the Cu(100) and Cu(117) surfaces are shown in Figs. 1(a) and 1(b), respectively. Despite the fact that the two steps on the (100) and the steps on the (117) surface have about the same distance, their appearance in a tunnel microscope picture is quite different. On the (117) surface steps are essentially at their expected atomic distances of 3.5 atoms, and kinks are clearly visible, although they are found in different positions in pictures taken immediately after each other. Figure 1(b) therefore does not represent a true instantaneous picture of the surface. This is even more so for steps on flat (100) surfaces, where the kinks move so rapidly that their residence time is small compared to the time the tunneling tip needs to move by one atomic distance, e.g., across the step from one terrace to the next [12]. Consequently, the step-step distance distribution measured on a flat (100) surface is not peaked at the possible atomic distances, but is rather a continuous Gaussian distribution. Observations as reported here are typical for soft metals (compare also [9]). The frizzed appearance of steps disappears at low temperatures [12]. A quantitative study of the frizziness together with a theoretical modeling was also performed and will be published elsewhere [13]. Here we merely

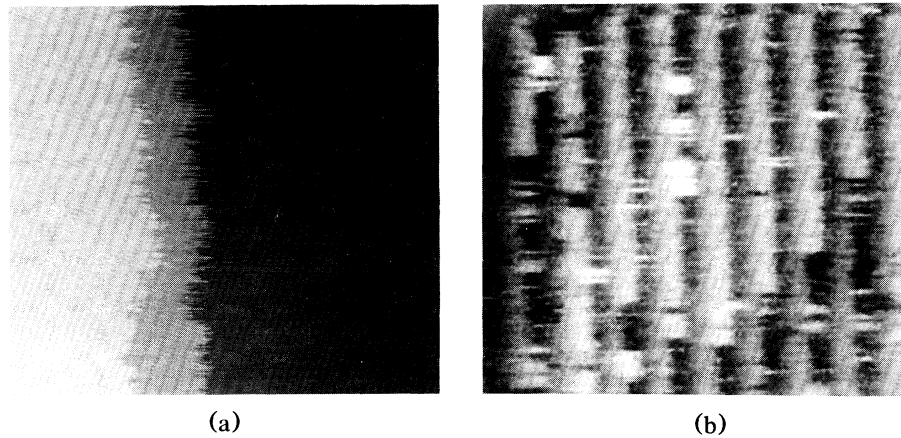


FIG. 1. Tunneling image of steps on copper surfaces ( $88 \times 88 \text{ \AA}$ ). (a) On Cu(100) steps appear frizzed because the motion of kinks along the steps is so rapid that the residence time for a step is shorter than the time needed to scan across one atomic distance. As a consequence the step is in a different position in each scan. Note that the grey scale in each scan line changes abruptly to the value of the next terrace. (b) On Cu(117) kinks move less rapidly due to the repulsive interaction between steps. The residence time of a kink is now larger than the scan time for one atomic distance, however, still smaller than the scan time for the entire picture. Consequently, each tunneling image looks different and occasionally one still finds a particular step position to appear only in one or two scan lines.

make use of the fact that the frizzed appearance of steps does not prevent the determination of the thermodynamic averages. Even the kink concentration can be determined by measuring the mean-square deviation of the step position  $x$  as a function of the coordinate  $y$  running along the step in the densely packed [110] direction [14]. If the coordinates  $x$  and  $y$  are measured in units of their respective atomic distances, then one obtains from random walk

$$\langle [x(0) - x(y)]^2 \rangle = b^2 y, \quad (1)$$

with  $b$  the diffusivity of the step which is equal to the concentration  $P_k$  of kinks, if kinks of more than a single atom height can be neglected. This is a reasonable assumption as long as  $P_k \ll 1$  [14,15]. Since the [110] direction may not be known exactly, it is better to use the double-step correlation

$$\langle [\Delta x(0) - \Delta x(y)]^2 \rangle = 2P_k y, \quad (2)$$

where  $\Delta x$  is the distance of two noninteracting, i.e., well separated steps. By evaluating (2) for about 5000  $\text{\AA}$  of the total length of steps we found  $P_k = 0.040$  [13], from which the energy of kink formation  $W_0$  is calculated to be  $\sim 1140 \text{ K}$  [14,16].

We now turn to the central issue of this paper which is the step distance distribution. We begin with a qualitative, yet important, observation on the distribution of steps on the nominally flat (100) surface. There, steps are generated by the process of sputter annealing. For a well-annealed and slowly cooled surface one would expect steps to lie essentially at random positions, with occasional local pinning by dislocations. However, wide-range ( $\sim 1 \mu\text{m}$ ) tunneling pictures show a surface where steps

are clustered in certain areas to have an average separation of a few atoms, while other large areas of  $\sim 1000 \text{ \AA}$  are step free [17]. In order to obtain more quantitative data, we have observed the two steps in Fig. 1(a) over a long period of several hours. Each picture (taken in 30–120 s) showed a different position and structure of the two steps [Fig. 1(a)] which indicates a rapid step motion. The steps were also not pinned by dislocations over a distance of at least a few thousand  $\text{\AA}$ . Furthermore, the mean distance between the steps was fluctuating from frame to frame, but did not increase (or decrease). We can therefore assume that the observed probability distribution represents the equilibrium and that the observed fluctuations are equilibrium fluctuations. The step distance distribution taken from twelve pictures of 100–400- $\text{\AA}$  scan width is shown in Fig. 2. It is obvious from the distribution that the steps avoid close contact to form a (111) microfacet. Since the surface energy of a (111) face is smaller than the energy of the (100) face, the formation of (111) facets must be prevented by a repulsive potential barrier, the well-known barrier which stabilizes the vicinal surfaces of high step density. On the other hand, the steps would not stay together as they do, if it was not for an attractive potential at larger distances; instead they would drift apart with time. An example of a vicinal surface (117) stabilized by repulsive interaction between steps was already shown in Fig. 1(b). The corresponding step distance distribution [Fig. 3(a)] indicates again that close contact of steps does not occur. The distribution is symmetrical about the mean distance of 3.5 atoms, with more than 50% weight on the mean distance. This result is in remarkable contrast to the (1119) surface, where the average terrace width is 9.5 atoms [Fig.

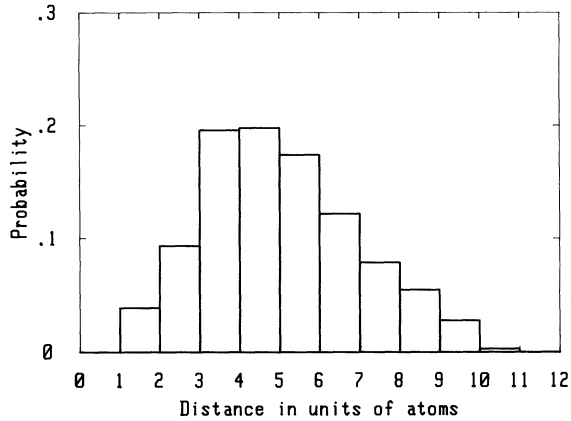


FIG. 2. Histogram of the distance distribution of two steps on a Cu(100) surface observed over a time period long in relation to the step mobility. Because of the high kink mobility, one has a frizzed appearance of steps and therefore a finite probability for any distance, not only for the distances allowed by the lattice structure. In the histogram we have assembled all data within  $\pm 0.5$  atom about the possible lattice distances 1.5, 2.5, 3.5, etc.

3(b)]. Here only 6% weight is on the nominal mean distance and the distribution shows clearly an extra hump at a distance corresponding to about 4 atoms, i.e., at a distance where also the distribution for the two-step peaks. The data on Cu(1119) were taken from 18000 individual measurements in 29 tunneling images, taken at random in a larger surface area of a few hundred microns. The mean terrace width was 9.53 atoms, in close agreement to the nominal mean width of 9.50 atoms. Even without further theoretical analysis it is obvious that the probability distributions in Figs. 2 and 3 are incompatible with a purely repulsive potential between steps. Because of the preparation procedures described above we can also exclude that the distribution for the Cu(1119) surface is due to insufficient annealing of a corrugated surface.

In general the problem of interacting noncrossing steps can be mapped onto the problem of interacting, spinless fermions [2]. Solutions for arbitrary potentials can, however, only be obtained in simulations. Here we discuss our results on the step distance distribution in the context of a simple model which is effectively a mean-field model [14]. In this model steps are allowed to move about in a local coarse-grained potential  $V(x(y))$  set up by all other steps which are assumed to be kinkless and placed at their mean position with a distance  $l$ . Obviously this model produces a necessarily symmetric distribution function. Aside from the asymmetric tail the model accounts well for the observed terrace-width distribution on Si(111) [10]. With these assumptions the problem of finding the step distance distribution  $P(x)$  can be mapped onto the solution of a one-dimensional Schrödinger equation [2,14]. For the case of only repulsive interactions it

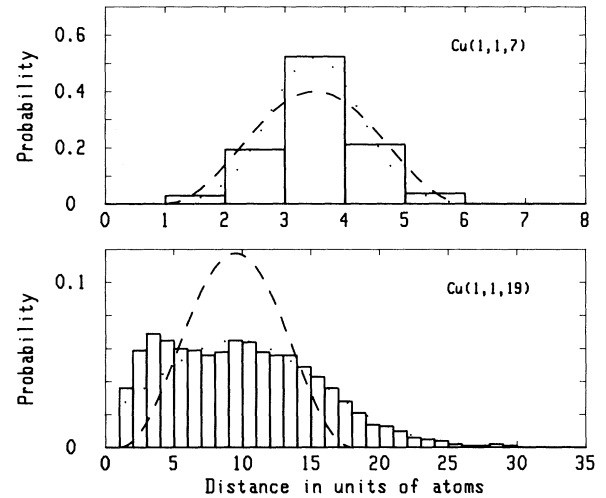


FIG. 3. Distance distribution on the Cu(117) and the Cu(1119) surface. The dotted and dashed lines result from simple models with repulsive step-step interactions and represent Eqs. (3) and (4), respectively. The double-peak distribution for Cu(1119) clearly shows the propensity of the surface to faceting mediated by attractive step-step interactions.

is straightforward to show that the shape of the distribution function should be somewhere between two limits. The first limit is obtained if the repulsive potential  $V(x)$  is expanded into a power series around the equilibrium position at  $x=0$  and only the first, quadratic term is retained. The Schrödinger equation is then the equation for the harmonic oscillator and the probability distribution is

$$P(x) = P_0 e^{-\pi P_0^2 x^2} \quad (3)$$

The quadratic term in the expansion is determined by the single parameter in the distribution  $P_0$ , which is the probability of occurrence of the mean distance. The second limit takes into account that steps cannot completely coalesce to form (111) facets by assuming a hard wall potential, which should be placed somewhere between 0.5 and 1.5 atomic distances from a step. With  $l_0$  the hard wall distance, the probability distribution is then obtained from the Schrödinger equation of a free particle in a one-dimensional box,

$$P(x) = \frac{1}{l-l_0} \cos^2[\pi x/2(l-l_0)]. \quad (4)$$

The distributions for the two model potentials are plotted in Fig. 3 as dotted and dashed lines, respectively. For the harmonic oscillator model  $P_0$  is matched to the probability of the mean distance. The hard wall distance  $l_0$  was taken as one atomic distance. For the (117) surface the harmonic oscillator model matches the experimental result quite well. As expected, in the hard wall model the

probabilities are more evenly distributed among the center positions. For the (1119) surface neither distribution is anywhere near the experimental result. The hard wall model, e.g., would predict much higher probabilities near the mean value and much lower values for the smaller distances. Obviously this discrepancy is not diminished by changing the position of the hard wall within the constraints discussed above. The harmonic oscillator model also does not account for the experimentally found higher probabilities at low distances.

Even without further quantitative analysis it is obvious that only a potential which is repulsive at small distances of 1–2 atoms and attractive at higher distances can account for the experimentally observed distance distribution in Figs. 2 and 3. While a quantitative analysis—be it in the framework of the simple model outlined above or in a many-body approach—is left to future work, we want to comment briefly on the possible nature of the attractive forces between steps. As mentioned earlier, dipolar forces between steps can be attractive, if the component of the dipole moment parallel to the surface prevails [2,6]. Because of the change in the effective angle between the dipole moments of two steps when these steps move closer and closer, even a repulsive interaction at large distance can turn into an attractive one within the dipole approximation. While those dipolar forces cannot be excluded as a possible source for an attractive potential, we wish to point out also the analogy to the interaction between adsorbate atoms. There the interaction is always repulsive at sufficiently short distance, however frequently attractive at intermediate distances. The latter interaction is mediated through the substrate [18], and this is, e.g., the reason for the formation of the well known  $2 \times 2$  and  $c(2 \times 2)$  adsorbate lattices on the (100) surfaces of fcc and bcc metals and a large variety of other structures on other surfaces. It is conceivable that similar oscillatory interactions with an attractive potential at medium distances can also occur for monatomic steps.

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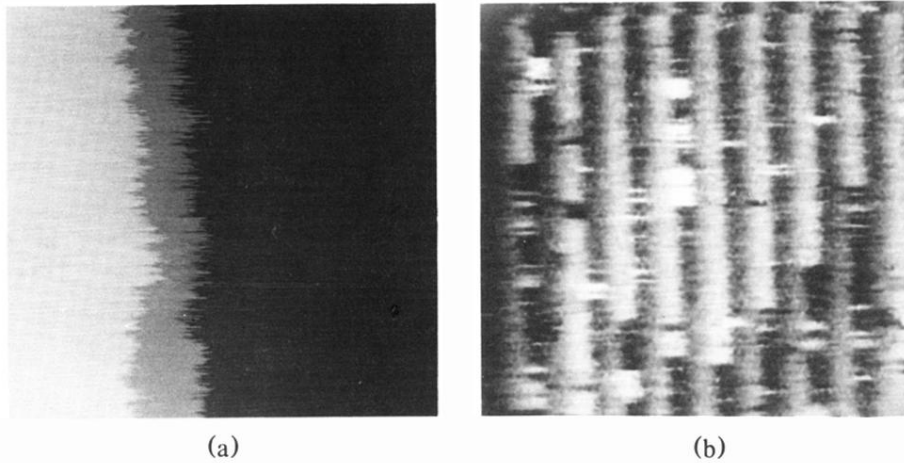


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