Microscopic Observation of Atomic Disorder near the Roughening Transition at Vicinal Copper Surfaces

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The appearance of a reversible order-disorder transition at Cu(115) and Cu(117) surfaces has been investigated using perturbed angular correlation spectroscopy. The local atomic arrangement at ^{111}In probes is detected via nuclear quadrupole hyperfine interaction. A broadening of the electric field gradient distribution is measured for elevated temperatures due to structural changes around the probes. The onset of disorder on the atomic scale is found to be well above the roughening transition temperatures measured by various scattering techniques.

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The occurrence of roughening transitions at metal surfaces and their relation to surface melting has stimulated a great number of experimental and theoretical efforts [1]. The concept of roughening has been developed by Burton and Cabrera [2] and is related to thermal formation of atomic steps at a surface. This effect, which was first discovered at surfaces of organic crystals [3], was found to be very distinct for $(11m)$ surfaces ($m=3,5,7$) of fcc metals, where a transition from an ordered surface characterized by straight steps to a phase with meandering steps occurs. The critical temperature in these cases is well below the bulk melting point [4].

For a direct observation of roughening experimental methods are needed permitting spatial resolution on atomic scales. In the past, various diffraction methods, for example high-resolution electron diffraction (HRLEED [5], spot profile analysis LEED [6]), high-resolution x-ray scattering [7], and helium beam diffraction [8] have been successfully applied. These methods are sensitive to atomic order on a length scale of about 50 Å. With the invention of the scanning tunneling microscope (STM) roughening has been studied on an even shorter length scale and first experiments on Ag(115) surfaces have proven the concept of meandering steps [9]. However, since data acquisition time in tunneling microscopy is long compared to the dwelling time of surface atoms, the full atomic resolution cannot be reached.

In this Letter we present first results on the investigation of order-disorder transitions at Cu(115) and Cu(117) surfaces by perturbed $\gamma\gamma$ angular correlation (PAC) spectroscopy, which has turned out to be very powerful for the study of surface properties on a microscopic scale [10]. The information is gained by measuring the electric field gradient tensor at the nuclear site of suitable probe atoms deposited onto the surfaces with concentrations of about 10^{-4} monolayers. The electric field gradient is described in its principal axis system by its largest component $|V_{zz}|$ and the asymmetry parameter $\eta=(V_{yy}-V_{xx})/V_{zz}$ reflecting the spatial charge symmetry around the z principal axis. Since this quantity is only sensitive to the local atomic surrounding around the probe one can distinguish different probe sites. A detailed description of the PAC method is given by Klas *et al.* [11].

In our experiments we use the isomeric state ($I=5/2$, $T_{1/2}=84$ ns) intermediate in the 172-247 keV $\gamma\gamma$ cascade in ^{111}Cd, which is populated through the decay of ^{111}In ($T_{1/2}=2.8$ d). The interaction of the nuclear quadrupole moment Q with the electric field gradient causes a level splitting of the isomeric state characterized by three transition frequencies ($\omega_3=\omega_1+\omega_2$),

$$\omega_i=3c_i(\eta)\nu_Q/20 \quad (i=1,2,3) \text{ with } \nu_Q=eQV_{zz}/h\,, \tag{1}$$

where n_Q denotes the quadrupole coupling constant. The parameters $c_i(\eta)$ are known for a given asymmetry parameter η. The experimental counting rate ratio $R(t)$, which is formed by coincidence counting rates detected by a four γ detector setup [11], is a sum of cosine functions containing the transition frequencies

$$R(t)=A_{22,\text{expt}}\left[S_0+\sum_i S_i\exp(-\Delta\omega_i t)\cos(\omega_i t)\right]. \tag{2}$$

From the relative amplitudes S_i of the transition frequencies the orientation of the principal axis system with respect to the crystalline axes can be deduced [11].

In case the ensemble of ^{111}In probe nuclei is exposed to electric field gradients either varying from probe site to probe site or fluctuating in time, damping of the cosine functions occurs. The first case, namely, inhomogeneous broadening, conventionally is taken into account by assuming a Lorentzian distribution of electric field gradients with ΔV_{zz} characterizing the half-width. This leads to the exponential damping factors in Eq. (2). In the second case, where relaxation due to dynamical processes is considered, all amplitudes including the "hard-core" value S_0 are affected. In the motional narrowing regime, one single exponential is governing the reduction of all amplitudes.

Disks of 1 mm thickness and 12 mm diameter have been cut from a (001) oriented copper crystal rod along a plane parallel to the $(1\underline{1}0)$ direction and tilted by angles of 15.8(5)° and 11.4(5)° with respect to the (001) plane resulting in (115) and (117) surface orientations, respectively. After mechanical and electrochemical polishing, about twenty cycles of Ar^+ sputtering and annealing to 800 K were performed in order to clean impurities from the surface. The purity of the surfaces was determined by Auger-electron spectroscopy. The sample temperature was measured by a chromel-alumel thermocouple pressed onto the crystal surface. Before depositing radioactive $^{111}\mathrm{In}$ atoms onto the surface, the crystal was annealed for about 12 h at 740 K and cooled down to 300 K at a rate of 2 K/min. The base pressure of the ultrahigh vacuum system was kept well below 1×10^{-8} Pa during the PAC measurements.

Indium probe atoms were deposited onto the Cu(115) surface at 78 K. After annealing to room temperature, the indium atoms occupy substitutional sites within the steps and substitutional sites in the (001)-oriented terraces, characterized by $|V_{zz}|=8.0(12)\times10^{17}$ V/cm^2, $\eta=0.81(2)$ and $|V_{zz}|=9.0(14)\times10^{17}$ V/cm^2, $\eta=0.05(5)$, respectively [12]. The same quantities were detected in annealing experiments on various vicinal copper surfaces with (001) terrace orientation in order to study the diffusive behavior of In atoms in the low-temperature region, where in addition to substitutional step and terrace sites the occupation of adatomic terrace and step sites is detected [13].

In Fig. 1 selected PAC time spectra and corresponding Fourier transforms for $^{111}\mathrm{In}$ on Cu(115) for different sample temperatures are shown. In the Fourier transform in Fig. 1(a) three frequencies can be identified (due to the chosen sample-detector geometry not all transition frequencies are visible). They correspond to the two different probe sites introduced above, namely, substitutional step sites (f_{S2}) and substitutional terrace sites (f_0). Corresponding frequency triplets for the fractions f_0 and f_{S2} are indicated by the dashed and solid lines, respectively. The sample temperature for the experiment shown in Fig. 1(a) is 380 K, which corresponds to the critical temperature for surface roughening of Cu(115) found in helium diffraction experiments [8]. Since the electric field gradient distribution $\Delta V_{zz}/V_{zz}$ is in the same magnitude as found for well-annealed Cu(001) surfaces, the atomic configurations for different probe sites are assumed to be almost perfect. By increasing the sample temperature above 500 K [Figs. 1(b) and 1(c)] the amplitude of the transition frequencies ω_i decreases rapidly and in addition the broadening increases significantly. At sample temperatures of 650 K, the frequencies characterizing indium probes on substitutional terrace sites have disappeared, an indication that probes occupying this site at low temperatures are no longer exposed to this highly symmetrical structural configuration.

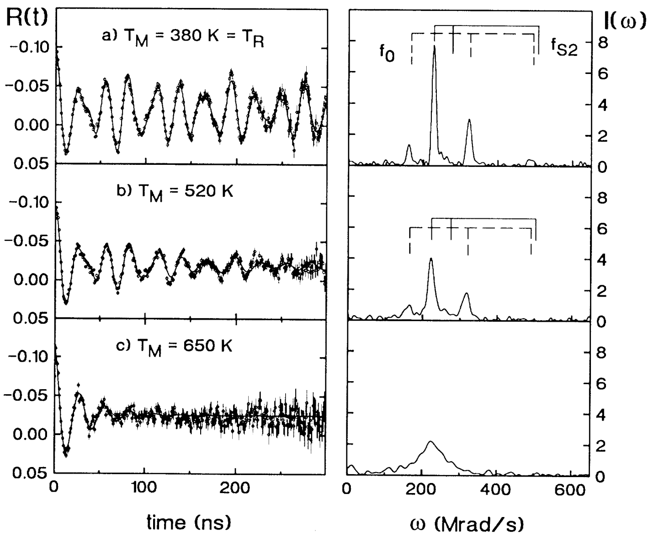

FIG. 1. PAC time spectra and corresponding Fourier transforms for $^{111}\mathrm{In}$ on Cu(115) surfaces for various measurement temperatures T_M. Corresponding transition frequencies describing the electric field gradients of the two different probe sites [substitutional step (f_{S2}) and terrace sites (f_0), respectively] are indicated.

It is important to note that the effect is completely reversible as indicated in Fig. 2, where the electric field gradient broadening is depicted for the $^{111}\mathrm{In}$ probes on substitutional step sites. Within the experimental error there is no difference between the data obtained for increasing (squares and circles) and decreasing (plusses) sample temperatures.

PAC results for $^{111}\mathrm{In}$ probes deposited on Cu(117) show qualitatively the same behavior as found for Cu(115). Again, there is no indication of an increased perturbation of the atomic surrounding around the In probes for temperatures up to at least 100 K above the

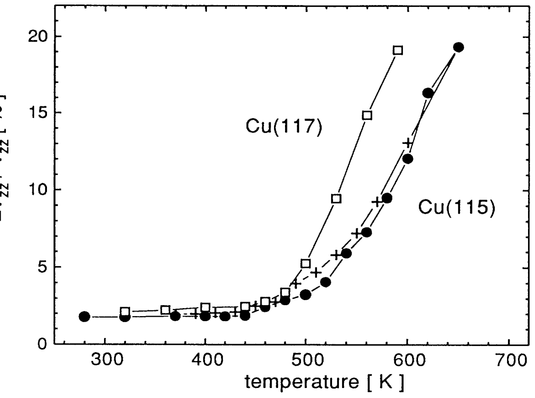

FIG. 2. Relative broadening $\Delta V_{zz}/V_{zz}$ of the electric field gradient $|V_{zz}|$ at $^{111}\mathrm{In}$ probes occupying substitutional step sites as obtained from least-square fitting of the experimental $R(t)$ spectra according to Eq. (2). Increasing (squares and circles) and decreasing (plusses) measurement temperatures are indicated.

critical temperature $T_R = 315$ K. For direct comparison of the two surfaces, Fig. 2 shows the electric field gradient broadening $\Delta V_{zz}/V_{zz}$ versus sample temperature for the case of substitutional step sites. For either probe site there is a drastic change in the linewidth for sample temperatures above 450 K. In addition, there is a significant difference between the two surfaces. In the case of the substitutional step sites the onset of increased damping on Cu(115) is shifted to higher temperature and less pronounced as compared to the Cu(117) surface.

The question arises how the observed broadening of the electric field gradients can be explained. The behavior shown in Fig. 2 can easily be interpreted in terms of disorder due to surface roughening. Since the critical temperature T_R is related to a vanishing free energy for kink site formation, this temperature can be regarded as the onset temperature for the meandering of steps. However, since the quantity detected in our measurements is only sensitive to the nearest-neighbor configuration around the probe atoms, meandering of steps does not necessarily change the local order around the probes. Only in the case of disorder on a scale of two or three atomic distances from the probe atom can a change in electric field gradients be expected. Since in the case of Cu(115) the repulsive step-step interaction is stronger than for Cu(117) the onset temperature for a decomposition of the step arrangement occurs at slightly elevated temperatures for Cu(115). The behavior found for indium probes on substitutional terrace sites is in agreement with the results obtained from the substitutional step sites.

From the data analysis it seems clear that the damping in the $R(t)$ time spectra is due to inhomogeneous broadening caused by a distribution of static electric field gradients. Static in this context means that there is no significant change in the atomic configuration during the lifetime of the intermediate nuclear state (≈ 100 ns). In the case of diffusive processes one would expect a motional narrowing behavior (Abragam-Pound damping) at high temperatures; i.e., the linewidth should decrease as the temperature is raised [14]. From the diffusion experiments mentioned earlier [13] one can estimate an average residence time for copper atoms of about 300 ns. Thus within the observation time of about 300 ns we do not expect an influence due to diffusive processes. A more crucial test to decide on dynamical processes is the investigation of the hard-core value (S_0 amplitude). In the case of high probe mobility $S_0(t)$ should show an exponential decay with increasing time, from which mean residence times can be extracted [15]. However, for $T_M = 650$ K there is no indication of an exponential decay and we therefore conclude that the effect of line broadening is due to a disordered surface. Fast diffusive processes with residential times on the order of nanoseconds as well as a liquidlike state can be ruled out from our data.

In our experiments the ^{111}In probes are impurities and a comparison with roughening data for pure copper surfaces has to be taken with some caution. Indium impurities do attract monovacancies in irradiated copper [16], exhibiting a tendency to stabilize In-vacancy pairs. These In-vacancy pairs break up above 320 K completely; at surfaces this effect of indium-vacancy attraction should be even less pronounced due to the relaxation of In out of the copper plane. The relaxation of In atoms out of regular lattice positions at Cu surfaces was indeed found by low-energy ion scattering [17]. Therefore self-stabilization of the In surroundings seems to be very unlikely.

Besides the measurement of the electric field gradient distribution, as we have discussed above, PAC spectroscopy also allows one to determine the temperature dependence of the average field gradient. This additional piece of information is interesting since the temperature dependence is governed by the vibration of the atoms in the vicinity of our probe atoms and can be characterized by a Debye-Waller-factor-like behavior. On surfaces this temperature dependence was found to be well represented by

$$\nu_Q(T) = \nu_Q(T = 0\ \mathrm{K})(1 - BT^n)\,, \qquad (3)$$

with an exponent n ranging between 1 and $\frac{3}{2}$ [11]. In Fig. 3 the results for ^{111}In occupying substitutional step sites on Cu(115) (filled circles) and Cu(117) (open squares) are shown. The temperature behavior below the roughening transition [$T_{R,\mathrm{Cu}(117)} = 315$ K, $T_{R,\mathrm{Cu}(115)} = 380(50)$ K [7]] is indeed well fitted with an exponent $n = \frac{3}{2}$, which is indicated by the solid line. Taking this as a reference, a drastic deviation of the data points above 400 K is visible. Such behavior has already been demonstrated in helium beam diffraction experiments [8,18]. There, in addition to a Debye-Waller-factor-like behavior, scattering fluxes show an enhanced intensity reduction which is attributed to the effect of surface roughen-

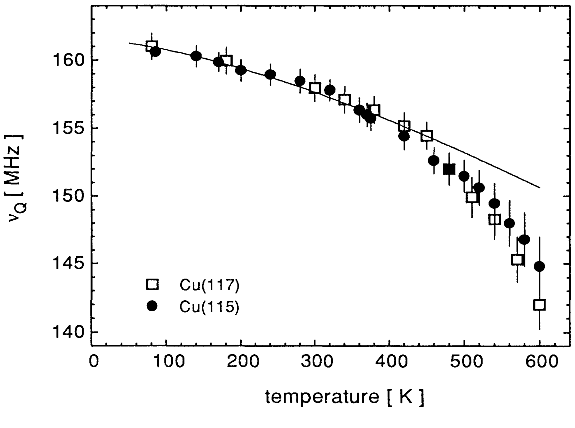

FIG. 3. Temperature dependence of the quadrupole coupling constant ν_Q for different probe sites on various Cu surfaces with (001) oriented terraces. Cu(117): open squares; Cu(115): filled circles. The solid line corresponds to a least-squares fit to data points for $T_M < 400$ K assuming at $T^{3/2}$ behavior.

ing [18].

Summarizing the statements given above we have shown that the onset of structural disorder in the course of surface roughening strongly depends on the length scale accessible in respective experiments. While typical scattering experiments have observed the step meandering only, the short-range character of the electric field gradient gives access to structural changes on an atomic scale. Using the PAC technique to determine this quantity we have shown that the critical temperature for the onset of disorder on this length scale is quite different from what was found in previous scattering experiments.

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