

Thermal dynamics of (110) fcc metal surfaces

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Abstract We discuss He- and x-ray diffraction data on the thermal behavior of the clean Cu(110) and Pt(110)(1x2) surface. The unreconstructed Cu(110) surface exhibits already at temperatures of $T \approx 0.4 T_M$ a pronounced thermal anomaly, attributed to an enhanced surface anharmonicity. Upon further increase of the temperature around $T_R \approx 0.8 T_M$ steps appear spontaneously and the surface roughens. On the reconstructed Pt(110)(1x2) surface, monoatomic steps are formed spontaneously already at temperatures $T_R \approx 0.53 T_M$.

The loss of vertical translational invariance at the surface changes the local force field with respect to the bulk forces. This charge redistribution is responsible for noticeable interlayer relaxations in the near surface region of most crystals. In some cases the changes in the force field can even cause a lateral atomic rearrangement in the surface plane, the surface reconstructs into a phase with new symmetry. The restructuring can either occur spontaneously or be activated by small amounts of adsorbates.

Restructuring can also be caused by simple temperature variations. As the temperature rises the lattice vibrational amplitude increases and the anharmonic terms in the interaction potential become important. Due to the reduced number of nearest neighbors in the surface the mean-square amplitude of the surface atoms is much larger than in the bulk, driving the surface to disorder at elevated temperatures. In particular crystal planes with an open structure are subject to surface roughening /1/ and surface melting phase transitions /2/.

The concept of a roughening transition has been developed by Burton, Cabrera, and Frank /3/. 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 the roughening temperature T_R at which the free energy for creation of a step becomes zero.

X-ray and He-atom diffraction has been used to study the thermal dynamics of the (110) surface of face centered cubic metals. These metal surfaces separate in two different classes. The first class, including the 3d-elements Cu, Ni and the 4d-elements Rh, Pd and Ag, have a nonreconstructed (1x1) ground state for the clean surface, i.e. they keep the bulk symmetry. The second class of fcc metals, including the 5d-elements Ir, Pt, and Au, exhibits a reconstructed (1x2) ground state with missing row geometry. As representatives of these two different classes we will discuss here result for Cu and Pt, respectively.

More than ten years ago it had been noticed that the intensities in the photoemission spectra taken from Cu(110) decrease dramatically with temperature above ~ 500 K /4/. Similar effects have been seen recently in low-energy ion scattering /5/, in X-ray diffraction /6/ and in thermal He scattering /7,8/. The dramatic intensity decrease observed in all cases above 450-500 K could not be accounted for by simple Debye-Waller effects. While Lapujoulade et al. /7/ and Fauster et al. /5/ proposed as explanation either anharmonic effects or some kind of disorder, Mochrie /6/ concluded categorically - without qualitative additional evidence - that he was observing the roughening transition. He even tentatively identified the temperature at which "the intensity has fallen essentially to zero" (870 K) with T_R . In a later study Ocko and Mochrie /6b/ realized that the sample used in the original experiments of Mochrie had a large miscut of about 0.8° and that such miscut samples did actually exhibit a reversible faceting transition with the coexistence of large flat (110) terraces and inclined rough regions (clustered steps) at low temperatures. Recently Robinson et al. /19/ observed a similar behavior for Ag(110), demonstrating that the roughening temperature is a rapid function of the surface miscut (decreasing T_R with increasing miscut).

A He specular intensity measurement on an almost perfect Cu(110) crystal with a miscut of less than 0.1° versus temperature performed in our laboratory shows that also above 870 K the intensity continues to drop (at 1000 K it is one order of magnitude lower) and that there is no sign of saturation even above 1000 K. Whether the intensity becomes "essentially zero" appears to depend on the dynamical range of the instrument, and is not a criterion for the choice of value of T_R . Zeppenfeld et al. /8/ have analyzed in detail the energy and angular distribution of the scattered He atoms in the whole temperature range up to 1000 K, and extended these measurements recently up to 1200K. This analysis showed that the anomaly at $T \approx 0.4 T_M$ is not accounted for by structural changes of the surface but due to an anomalous increase of the mean square displacement of the surface atoms above that temperature, which can be ascribed to an enhanced surface anharmonicity. A recent EELS study /9/ of the temperature dependence of the surface phonons has quantified this effect; according to this experiment the surface anharmonicity of the Cu(110) surface is enhanced about 5 times over that of bulk copper.

Upon further increase of temperature isolated defects start to appear at about 70-75% of the melting temperature and eventually around $T_R \approx 1070$ K $\approx 0.8 T_M$ steps appear spontaneously and the surface roughens. The measured roughening temperature of 1070 K coincides with the temperature at which the anisotropy in the activation energy for surface diffusion of adatoms on the Cu(110) surface vanishes /10/. Above this temperature the mass transport is isotropic, consistent with 2D step diffusion.

In theoretical studies of the reconstructed fcc(110) surfaces it has been shown that the (1x2) missing row configuration is indeed only marginally stable with respect to the "higher" missing row states (1x3, 1x4, ..., 1xn). The energy difference between any of the (1xn) phases of Au(110) has been calculated to be less than 10 meV per atom /11/. Based on this ground it has been argued by several authors that the missing row configuration should be thermally unstable with respect to the formation of (111) microfacets, giving rise to a "rough" surface at temperatures well below T_R of the non reconstructed (110) surfaces. While Villain and Vilfan /12/ have predicted a succession of two transitions, an Ising-like order-disorder transition at $\sim 0.50 T_M$ spontaneous proliferation of antiphase Ising-defects, followed by a roughening transition at $\sim 0.57 T_M$

(onset of (111) micro faceting generating single height steps), Levi and Touzani /13/ have found no evidence for an Ising-like transitions but predicted a direct roughening transition.

In a recent x-ray diffraction experiment Robinson, Vlieg and Kern have studied the thermal behavior of the reconstructed Pt(110) surface /14/. The experimentally observed half order diffraction peaks have two characteristics: they are broad in the [001] direction but sharp in the orthogonal [1 $\bar{1}$ 0] direction and always displaced slightly from the exact half order position along [001]. The uniaxial broadening and shift implies disorder in one direction only, i.e. must be associated with line defects oriented perpendicular to the [001] direction. An identical pattern of uniaxially shifted and broadened half order diffraction peaks was observed earlier by Robinson et al. /15/ for the Au(110)(1x2) surface and can be explained conclusively in terms of randomly distributed single height steps on the surface. It was further demonstrated that the peak shift of the half order spots is exclusively related to the density of these monatomic steps while Ising-like defects would only result in a symmetric peak broadening.

The basic result of this study is that the half-order diffraction spots not only gradually disappear with rising temperature but also show a peak shift which is temperature dependent. Above $T > T_R = 1080 \text{ K} = 0.53 T_M$ the half order diffraction peak broadens and shifts dramatically and completely reversible indicating the simultaneous proliferation of anti-phase Ising-defects and of steps. No separation in the proliferation of steps and Ising-defects were detected within the accuracy of the experiment. This and the observation of Ising-exponents for the transition has caused some controversial discussion /16-18/.

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