Restructuring at surfaces

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1. Introduction

It is well known that the atomic force field at the surface can substantially deviate from that in the bulk, as established by the observation of changes in the interlayer spacing - "relaxation" - and even rearrangements in the two-dimensional structure parallel to the surface - "reconstruction" -. Various attempts have been undertaken to elucidate the forces responsible for these rearrangements at the selvedge of a crystal. An intuitive simple model is the point ion model of Finnis and Heine [1] based on the electron smoothing concept of Smoluchowsky and is exemplified in fig. 1. The electrons have the tendency to spill over the surface in order to create a geometrically smooth surface and thus lowering their kinetic energy.

This charge rearrangement leads to an increase of the charge density between the first and second layer, which causes an attractive force between the atoms of these layers, i.e. a surface stress. This particular vertical surface stress is relieved by the relaxation, i.e. contraction, of the first interlayer spacing. The charge redistribution leads however also to an increased charge density within the first layer, generating an inplane surface stress. This stress can only be relieved when the surface layer reconstructs to form more densely packed structures. Such inplane reconstructions are for instance observed for the (100) surfaces of Au and Pt, in which the surface layer forms a pseudo hexagonal close packed layer on top of the square bulk plane unit cell [2]. However, if no such reconstruction occurs, like in the case of Cu and Ni(100), the epitaxy between the outermost surface layer and the interior layers forces the nearest neighbor distance of surface atoms to be equal to those in the bulk. In this case the nearest neighbor surface distance no longer coincides with the minimum of the pair potential and its first derivative is nonzero.

The inplane stress of nonreconstructed surfaces can however be relieved by the charge rearrangement upon adsorbing atoms or molecules. The formation of a chemisorption bond on a metal surface involves the transfer of charge. Depending on the character of the adsorbate this charge is either transferred from the metal to the adsorbate (electron acceptor) or vice versa (electron donor). This charge transfer creates a dipole layer with positively (acceptor adsorbate) or negatively (donor adsorbate) charged surface metal atoms. In the case of a "positive" dipole layer the coulombic repulsion produces a weakening between the inter- as well as intralayer interatomic forces. The weakening of the bond between the first and second layer atoms is usually accompanied by an increase in bond length (outward relaxation, i.e. compensation of the inward relaxation of the clean surface) while the intralayer interatomic distances are only changed in extreme cases (adsorbate induced surface reconstruction). Typical representatives for adsorbates, which lead to a weakening of the metal-metal bonds at a surface are the chalcogenides and the halides. It is worthwhile to mention that the metal bond weakening is only marginally influenced by the ionic or covalent character of the adatom-metal bond. Even in the case of a nearly covalent bonds with localized charges, like the chalcogenides on Ni(100), the repulsive interaction between the incompletely screend metal nuclei, leads to a repulsive stress between the surface metal atoms, i.e. to a weakening of the metallic bonds [3]. The charge rearrangement upon adsorption of oxygen and sulfur counterbalances thus the attractive inplane surface stress of the clean Ni(100) surface; in the case of carbon or nitrogen adsorption the charge rearrangement even results in an adsorbate induced p4g reconstruction of the surface. In the surface phonon dispersion the bond weakening results in a pronounced phonon softening. The magnitude of this softening is determined by the amount of the removed metal charge per adatom, i.e. be determined by the coverage.

In the case of a "negative" dipole layer the situation is exactly inverse. The increased Coulombic attraction, due to the excess surface charge, results in a stiffening of the inter- and intralayer metal bonds. On transition metals atomic hydrogen, for example acts as an electron donor.

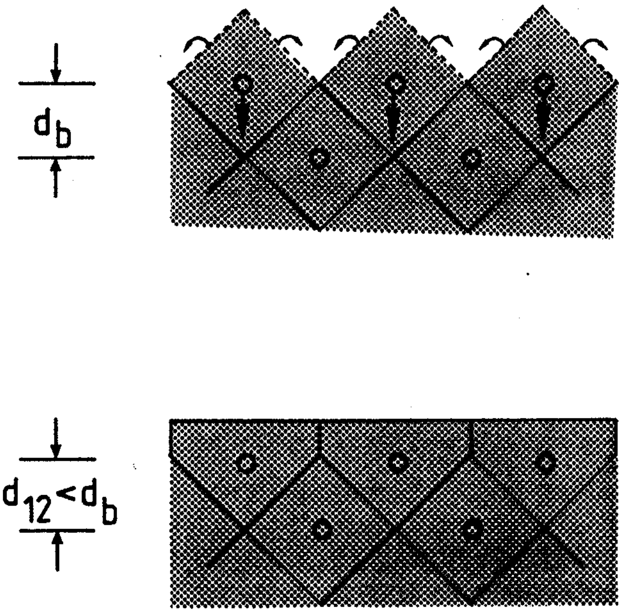


Fig.1 Surface relaxation in the charge smoothing model of Smoluchowsky.

So far we have ignored the temperature of the system. As the temperature rises, however, the lattice vibrational amplitude increases and the anharmonic terms in the interaction potential gain importance. Due to the reduced number of nearest neighbors in the surface (a maximum of 9 at the surface of a fcc-crystal with respect to the 12 nearest neighbors in the bulk of this crystal) the mean-square amplitude of the surface atoms is much larger than in the bulk. While in bulk Cu, for example, anharmonicity is negligible below 70-80% of the melting temperature, anharmonicity on the Cu(110) surface becomes important at temperatures above 40% of the melting temperature.

At the high temperature end it has been demonstrated recently that on a variety of surfaces a disordered quasi-liquid layer wets the surface well below the bulk melting temperature, i.e. the melting of a crystal can start from the surface layer [4]. In view of the Lindemann criterion of melting [5], which states that melting occurs when the mean-square displacement of the atoms surpasses a critical value (~ 10% of the interatomic equilibrium distance), the important role that surfaces play in the melting phase transition is not surprising. As already discussed the mean vibrational amplitude is substantially enhanced at the surface and the Lindemann-criterion predicts a surface instability around 0.75 T_M.

The picture developed above is based on a perfect defect free surface, which is, however, only at zero temperature the stable equilibrium state. At elevated temperatures a certain amount of defects like isolated adatoms and vacancies as well as clusters of those can be thermally excited. Both adatom islands as well as vacancy holes are bordered by steps. Frenkel [6] studied the structure of such steps and argued that they should contain a large number of kinks at finite temperatures. Thus, due to thermal fluctuations, every crystal surface with steps should have a certain roughness at nonzero temperature. Burton an coworkers [7], however, demonstrated that the thermal excitation of adatom and vacancy islands and thus the excitation of steps is negligible at low and medium temperatures but gave evidence for a microscopically rough surface at temperatures close to bulk melting. These authors predicted that on an atomic length scale the equilibrium structure of a crystal surface should exhibit a transition from a smooth state at low temperatures to a rough surface at higher temperatures. The critical temperature of this transition has been termed the roughening temperature, T_R. Burton et al. suggested that at the roughening temperature the free energy associated with the creation of a step vanishes. This was confirmed later by Swendsen [8] in a detailed calculation. One of the fundamental consequences of the existence of a roughening temperature for a certain crystallographic face below the melting temperature is that this face can occur on an equilibrium crystal only at temperatures below T_R.

In the following we will discuss the adsorbate and temperature induced restructuring of the (110) surface of face centered cubic metals. These surfaces are particularly attractive for two reasons. Firstly, the (110) surface has the most open structure of the three densest fcc-faces, (111), (100) and (110). The second aspect is surface reconstruction. The (110) surface of transition metals with face centered cubic (fcc) symmetry belong the two different classes (fig. 2). The first class, including the 3d-elements Cu, Ni and the 4d-elements Rh, Pd and Ag, have a nonreconstructed (1 × 1) ground state for the clean surface, i.e. they keep the bulk termination (they exhibit however large oscillatory interlayer-relaxations). The second class of fcc metals, including the 5d-elements Ir, Pt and Au, exhibits a reconstructed (1 × 2) ground state. The nature of the (1 × 2) reconstruction has been studied extensively by a number of different experimental techniques and there is a general agreement now that the (1 × 2) phase of all three 5d-metals is a missing row geometry.[9] with every second close packed [1$\bar{1}$0] row missing (see fig. 2).

It was suggested that reconstruction and roughening in these systems are indeed related [10]. As pointed out by Garofalo et al. the energies of the relaxed unreconstructed (1 × 1) surface and the energies for all possible missing-row states (1 × 2, 1 × 3, ..., 1 × n), are all energetically close to one another [11]. Locally the (1 × n) reconstructions represent microscopic (111) facets and are expected to be easily excitable at elevated temperatures. Trayanov et al. [10] speculate, that whatever the low-temperature ground state configuration (unreconstructed or reconstructed) it might roughen into a high temperature disordered phase, with a mixture of (1 × n) configurations.

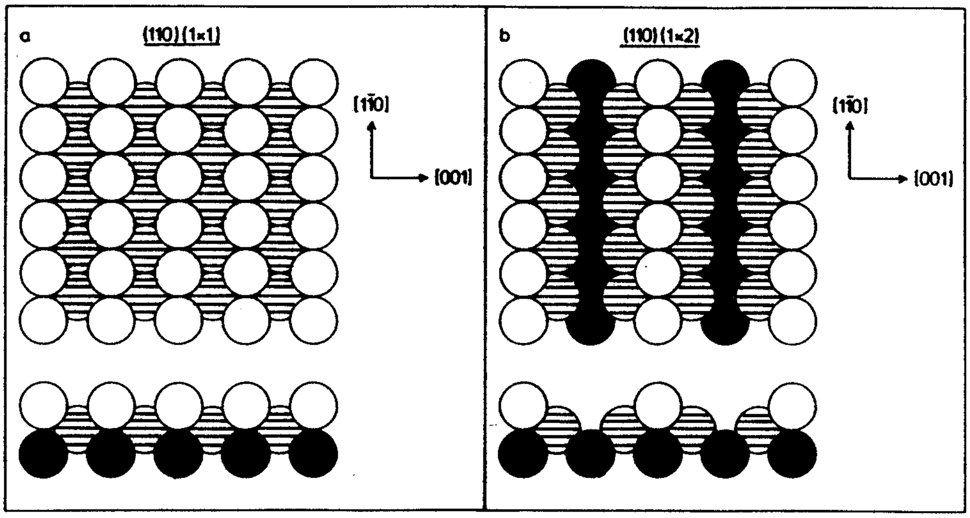


Fig.2 Structure of the unreconstructed and reconstructed (110) surface of face centered cubic metals.

2. Thermal restructuring of (110) fcc metal surfaces

2.1 Surfaces with nonreconstructed ground state

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 [12]. Similar effects have been seen recently in low energy ion scattering [13], in X-ray diffraction [14] and in thermal He scattering [15]. 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. [16] and Fauster et al. [13] proposed as explanation either anharmonic effects or some kind of disorder, Mochrie [14] 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. A He specular intensity measurement on Cu(110) versus temperature performed in our group shows (fig. 3a) that also above 870 K the intensity continues to drop (at 1000 K it is already 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. We have analyzed in detail the energy and angular distribution of the scattered He atoms in the whole temperature range up to 1000 K [15]. Recently we have extended these measurements up to 1100 K [17]. The analysis of the specular He-diffraction peak measured in near antiphase-scattering geometry reveals the onset of step proliferation to be located at $T_R = 1070$ K , 200 K higher then estimated by Mochrie.

It is generally accepted now that the surface roughening is preceded by two precursors : the onset of dynamical disorder through enhanced anharmonicity and the onset of static disorder through adatom-vacancy creation. In particular the sharp decrease in coherently scattered intensity above 0.35 T_M is ascribed to an anomalous large increase of the mean-square displacement of the surface atoms $< u_z^2 >$ due to a large anharmonicity in the metal potential at the surface. In fig.3b we show the mean-square displacements $< u_z^2 >$ at the Cu(110) surface which have been deduced from the fitting of the measured temperature dependence of its surface phonon frequencies and widths.

An enhanced surface anharmonicity on the open (110) surface of fcc metal crystals has been deduced also from theoretical [19] as well as experimental [20] studies of the thermal surface expansion coefficient. Nonreconstructed fcc(110) surfaces are strongly relaxed and the interlayer distance between the first and second plane of atoms d_{12} is contracted between 5 and 15% with respect to the bulk value d_b. This relaxation was found to vanish rapidly above ~ 0.4 T_M (i.e. $d_{12}/d_b \rightarrow 1$) which can only be ascribed to a substantial increase of the thermal surface expansion coefficient driven by a strong surface anharmonicity. The corresponding experimental graph for Pb(110) is given in fig. 4.

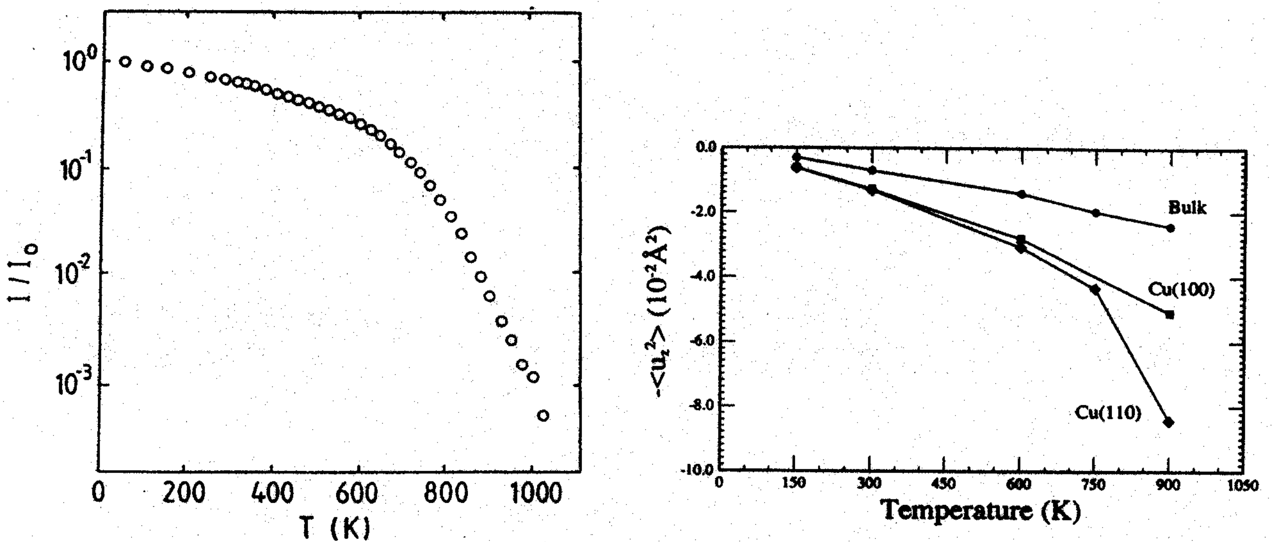


Fig.3 a)Thermal dependence of the He specular peak height from Cu(110); He beam energy 18.3meV and angle of incidence 90° [15]. b) Mean square displacements of surface atoms versus temperature [18].

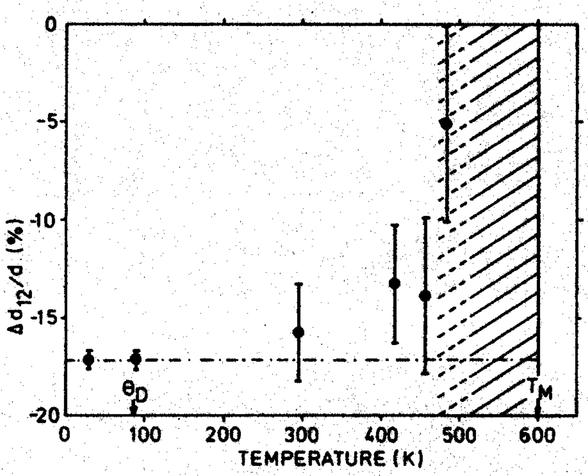


Fig.4 Surface relaxation of Pb(110) versus temperature [20].

The increase of $< u_z^2 >$ is however not sufficient to fully explain the substantial decrease of the coherent He-intensity in fig.3a . In particular above 800 K the dynamic disorder is to small to account for the dramatic intensity decay. This temperature marks indeed the onset of adatom-vacancy creation. The defect concentration can be deduced from the specular He-intensity data, assuming that the decay is induced by dynamic as well as static disorder, using the $< u_z^2 >$ values of fig.3b. In a simple Debye-Waller model with the assumption of a random distribution of additional adatoms and vacancies the attenuation of the specular He-beam I/I_0 is given by

$$I/Io = (1-\theta)^{n_s \cdot \Sigma} \cdot \exp^{<-2\,W(T)>}$$

here n_s is the number of lattice sites, Σ the cross section for diffuse scattering from isolated defects (~ 70 Å) and θ the defect concentration. With this simple model we estimate the concentration of isolated defects to be a few percent at 900K. The deduced onset of adatom-vacancy creation and their concentration is in nice agreement with recent molecular dynamics simulations of Häkkinen and Manninen [21].

Evidence for the roughening of the (110) surface has also been presented recently for the metals Ni [22], Pb [23], In [24], Ag [25] and Pd [26]. While the roughening of the (110) surfaces of Ni, Pb and In are generally accepted the experimental results for Ag(110) and in particular Pd(110) are disputed. For palladium Francis and Richardson [26] reported an order-disorder transition to occur around 250 K. This transition was, however, not be detected in a series of subsequent experiments [27], and today is believed to be an artifact due to the presence of impurities in the experiments of Francis and Richardson. Ag (110) is an interesting case. This surface was studied by Held et al. [25] with synchrotron x-ray diffraction. Based on a diffraction peak shape analysis they deduced the relatively low roughening temperature of 0.56 T_M. Robinson et al. [28] recently repeated the x-ray measurements on Ag(110) and came to a surprising result. They demonstrated that the Ag(110) surface below its roughening temperature coexists of flat (110) oriented regions and slightly inclined, rough regions. Thermal roughening takes place by the gradual replacement of the (110) faceted regions by the rough phase and the roughening temperature depends substantially on the misorientation of the crystal surface. For the perfect (110) face they extrapolated a value of $T_R \approx 0.65$ T_M.

Upon further increase of the temperature the nonrestructured (110) surfaces may start to melt well below the bulk melting temperature T_M. A disordered liquid surface layer can emerge which would grow in thickness as $T \to T_M$. This undercooled liquid layer which is intercalated between the vapor and the solid can then act as natural nucleus for the melting process of the solid.

Table I : The roughening temperatures of nonreconstructed fcc(110) metal surfaces.

Surface	T_R [K]	T_R/T_M	References
Ag(110)	800	0.65	25, 28
In(110)	290	0.69	24
Pb(110)	420	0.70	23
Ni(110)	1300	0.76	22
Cu(110)	1070	0.79	15, 17

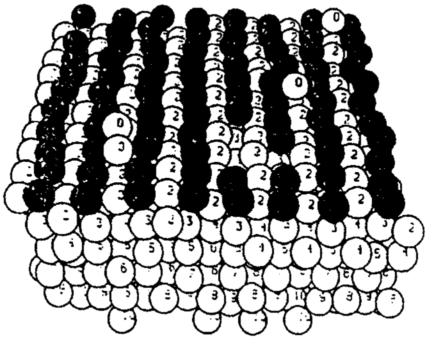
The physical law which governs the wetting of a solid by a liquid layer of its own, i.e. the premelting of a surface of given orientation [hkl], is the well known "Youngs equation"

$$\gamma_{sv}^{[hkl]} - \gamma_{sl}^{[hkl]} - \gamma_{lv} \equiv \Delta\gamma^{[hkl]} > 0$$

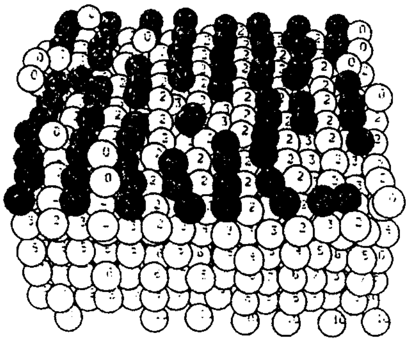
where $\gamma^{[hkl]}$ are the specific free energies at the interfaces between solid (s), liquid (l) and vapor (v). From the close packed surfaces the (110) surface of fcc solids are the most likely candidates for surface melting.

In fig. 5 we show the results of a molecular dynamics simulation of the Cu(110) surface which nicely demonstrates the evolution from a well ordered flat surface through adatom-vacancy creation and roughening to surface melting upon approaching the bulk melting temperature [21]. In the snapshots of the equilibrium configuration of the Cu(110) surface adatoms begin to appear on the surface above 800 K (a) leading eventually to the onset of surface premelting with planar disorder at and above 1200 K (d,a). The snapshots between 1000 K and 1100 K (b, c) show the adatom clustering and the surface roughening.

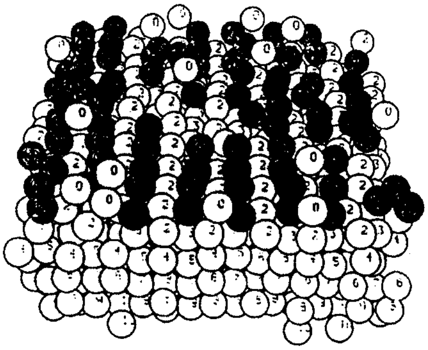
Experimental evidence for surface melting of fcc(110) surfaces has been found for Pb and Al, while the surface melting of the copper surface has not been studied so far. A detailed account of the experimental results and its implications can be found in ref. 29.



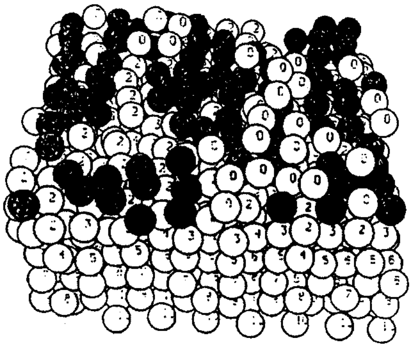
a) T = 798 K



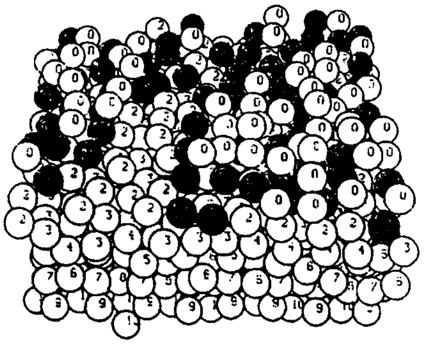
b) T = 1007 K



c) T = 1092 K



d) T = 1200 K



e) T = 1254 K

Fig.5 Molecular dynamics snapshots of configurations of the Cu(110) surface as a function of temperature [21]. The black atoms belong to the surface layer.

2.2. Surfaces with (1 × 2) reconstructed ground state

In theoretical studies of the reconstructed fcc(110) surfaces it has been shown that the (1 × 2) missing row configuration is indeed only marginally stable with respect to the "higher" missing row states (1 × 3, 1 × 4, ..., 1 × n). The energy difference between any of the (1 × n) 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 [30,31]. While Villain and Vilfan [30] have predicted a succession of two transitions, an Ising-like order-disorder transition at ~ 0.50 T_M with spontaneous proliferation of antiphase Ising-defects, followed by a roughening transition at ~ 0.57 T_M (onset of (111) micro faceting generating single height steps). Levi and Touzani [31] 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 [32] have studied the thermal behavior of the reconstructed Pt(110) surface. 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. [33] for the Au(110) (1 × 2) 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 monoatomic steps while Ising-like defects would only result in a symmetric peak broadening.

The basic result of this study has been that the half-order diffraction spots not only gradually disappear with rising temperature but also show a peak shift which is temperature dependent. Above $T > T_R = 1080\ K = 0.53\ T_M$ the half order diffraction peak broadens and shifts dramatically and completely reversible indicating the simultaneous proliferation of antiphase 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.

Indeed two recent He-diffraction studies of the same surface [34] and of the Au(110) (1 × 2) surface [35] clearly favour the model with two successive transitions, separated by about 50 - 60 K in both cases. It was also demonstrated that a small diffraction peak shift in the initial phase of the transition might also been obtained by a disordered flat phase with a stochastic mixture of odd and even (1 × n) configurations [36].

While the microscopic course of the order-disorder transition is under discussion, its occurence at substantially reduced temperatures with respect to the roughening temperature of nonreconstructed surfaces is obvious and can readily be ascribed to the more "open" structure of the missing row geometry.

No experimental search for the surface melting of the reconstructed fcc(110) (1x2) surfaces has been reported so far.

3. Adsorbate induced restructuring

The adsorbate-induced restructuring of surfaces, originally proposed by Langmuir in 1916 [37], has been matter of numerous experimental and theoretical investigations in the past two decades [38]. Oxygen adsorption on the (110) and (100) surfaces of Cu are among the most studied systems since the pioneering work of Ertl [39] who showed that the occurrence of (2 × 1) and c (6 × 2) LEED patterns of the Cu(110) surface upon adsorption of oxygen were due to alterations of the unit cell by displacements of Cu substrate atoms. Nevertheless it took more then twenty years until a consensus on the structure and the growth mechanism for the oxygen-induced (2 × 1) reconstruction of Cu(110) was reached.

The clean (110) surface of a copper crystal is known to exhibit a compressive inplane stress of $\tau_{[1\bar{1}0]} = -1.9 \times 10^3$ dyn/cm , trying to expand the surface along this direction [40]; i.e. the copper atoms try to avoid nearest-neighbor distances in the surface plane. Upon adsorption of oxygen the inplane stress is minimized through the reconstruction into a phase with a new (2x1) symmetry by the relocation of both substrate and adsorbate atoms in such a way that no more nearest-neighbor Cu-Cu distances are present in the outermost surface plane.

The detailed mechanism of this adsorbate induced restructuring has recently revealed by scanning tunneling microscopy [41]. These studies demonstrated that the (2 × 1) phase is formed by aggregation of mobile oxygen atoms on terraces with Cu adatoms diffusing in from step edges. Because of strongly attractive Cu-O interactions, long Cu-O strings are formed along the (001) direction on top of the substrate which act as nuclei for the growing reconstructed phase. With increasing oxygen coverage Cu{110} - (2 × 1)O islands grow by aggregation of Cu-O strings. At full coverage ($\theta_o = 0.5$) the

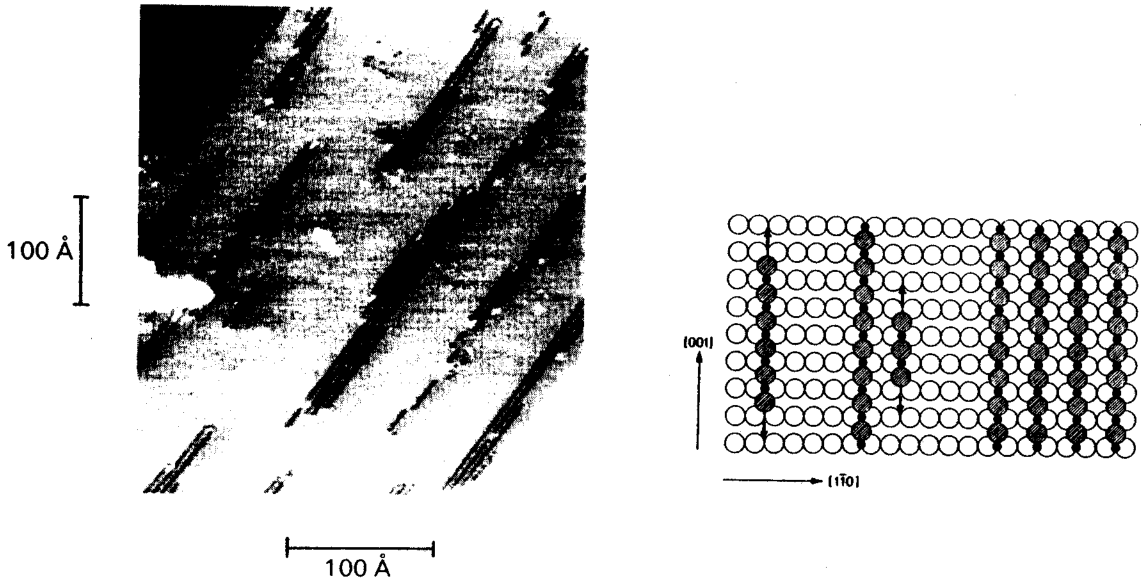


Fig.6 a) STM-image of (2 x 1)O islands on Cu(110) [44] and b) atomistic model of the nucleation and growth of the added-row structure [41].

structure is identical to the earlier inferred missing-row structure with the Cu-O strings 5.12 Å apart. In view of the formation process this structure is now more properly named the added-row structure.

In a wide intermediate coverage range this system "organizes" the islands formed by the Cu-O strings in a very spectacular way. The (2 × 1) reconstructed anisotropic Cu-O islands, each consisting of 4-22 Cu-O strings, arrange themselves in a one-dimensional periodic supergrating, with the stripes running along the [001] direction. The spacing of the supergrating depends on oxygen coverage and temperature and varies between 140 Å and 60 Å.

The picture of the spatial self-organization of the Cu-O islands is visualized by the real space image obtained with the scanning tunneling microscope and shown in fig.7 . In the image the Cu(110) surface was exposed to 2L of oxygen at ~ 550 K, resulting in a coverage of $\theta_0 = 0.26$. Over more than 1000 Å the Cu-O islands appear as dark regularly spaced stripes of nearly equal width and a lattice spacing of D = 86 Å. Most astonishing, the striped grating even extends practically undisturbed across monoatomic steps on the Cu-substrate. This grating is the smallest "optical element" ever fabricated.

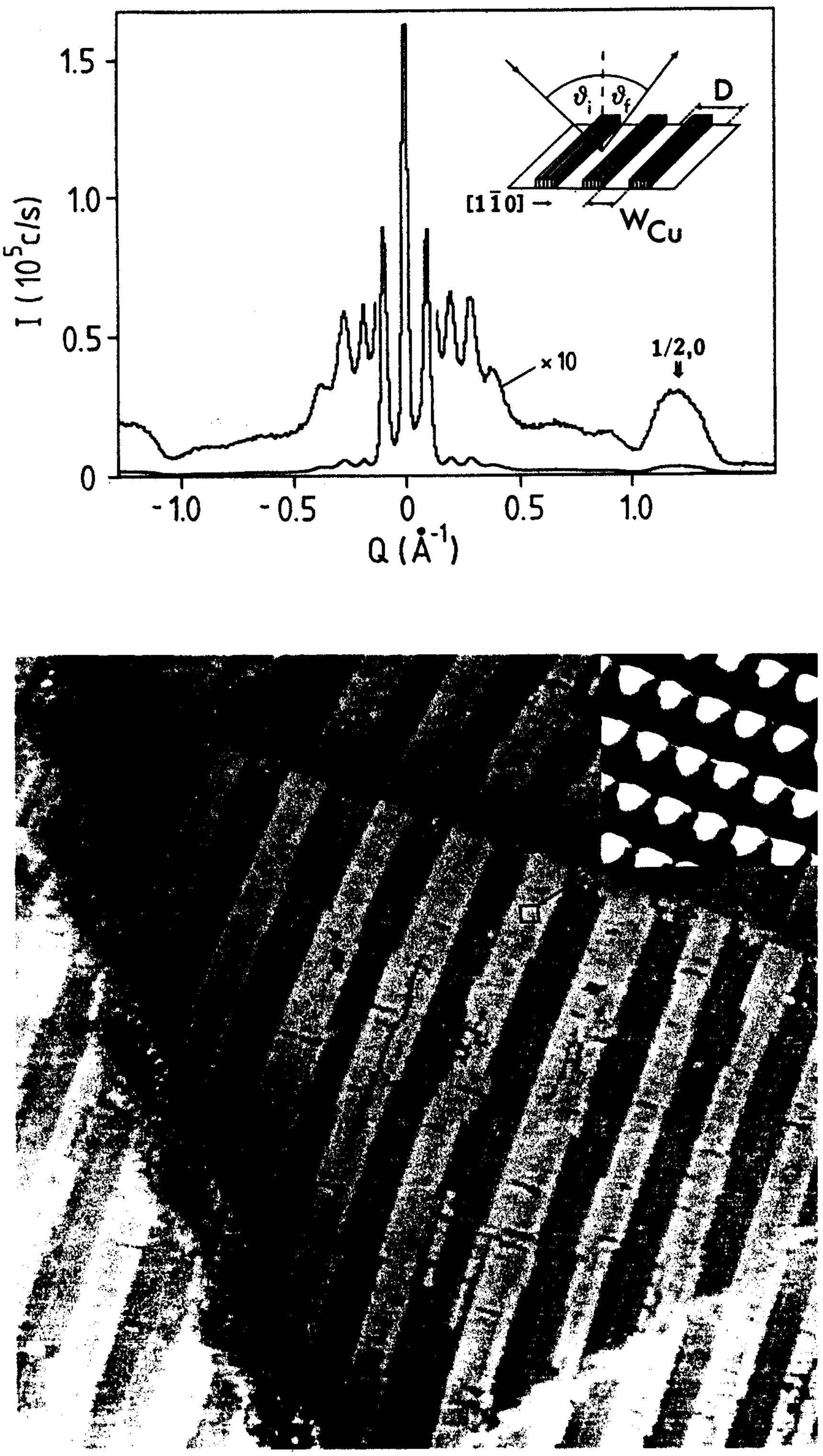


Fig.7 a) He-diffraction pattern and b) STM-image (930 x 930 $Å^2$) of the striped super-grating produced by adsorption of 1/4 monolayer of oxygen on Cu(110). The inset shows a STM-image (14 x 14 $Å^2$) of the clean surface.

The characteristics as "optical element" are demonstrated in the top part of fig.7 , where a He-diffraction pattern ($\lambda_{He} \approx 1$ Å) of the striped grating is shown. It was indeed this remarkable diffraction pattern which lead to the discovery of the mesoscopic spatial self-organization. The He-diffraction pattern from such a surface grating is particularly simple. The clean Cu(110) stripes reflect the helium beam almost mirrorlike, while the Cu-O islands have a 1-order-of-magnitude lower reflectivity. [This results from a comparison of the He reflectivities of the clean Cu(110) and of the saturated Cu(110) – (2 x 1)O surface]. The diffraction pattern is, therefore, analogous to that of light scattered by a periodic grating with broad slits, as discussed in most elementary textbooks. Here, the highly reflective Cu(110) stripes correspond to the slits, while the poorly reflecting Cu-O island stripes correspond to the opaque bars between slits. The comparison between the measured diffraction intensities and the intensities calculated with the classical optical diffraction theory is remarkable [42].

The microscopic origin of the spontaneous formation of mesoscopically ordered domain structures has yet not been solved. Two alternative explanations have been put forward [43]. In the first scenario surface stress effects can lead to the formation of ordered domain lattices when the energy gained from relaxation in the presence of the domain pattern is sufficient to overcome the energy cost of creating a domain boundary. Similarly electrostatic dipole-dipole interactions can be responsible for the formation of domain lattices under the conditions of phase segregation on metal surfaces. This effect is strongest when the work function difference between the clean and the adsorbate covered domains on the surface is large and the domain boundary energy is small. Unfortunately it is difficult to distinguish between the two explanations because both predict the same functional dependence of the lattice parameter as a function of the adsorbate coverage. In fig.8 we show the comparison between the experimental data and the theoretical results of the electrostatic dipole model. The agreement is striking, but would be as good for the stress model.

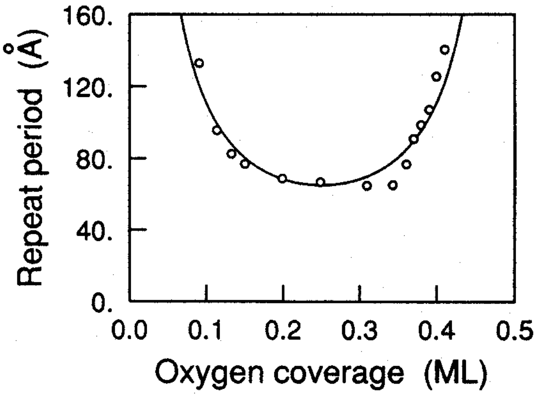


Fig.8 Theoretically calculated domain grating period (electrostatic interaction model) in comparison with experimental data [43].

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