SURFACE SCIENCE LETTERS

MULTILAYER DISTORTION IN THE RECONSTRUCTED (110) SURFACE OF Au

W. MORITZ * and D. WOLF

*Institut für Kristallographie und Mineralogie, Universität München, Theresienstrasse 41,
D-8000 München 2, Fed. Rep. of Germany*

A new LEED intensity analysis of the reconstructed Au(110)-(1×2) surface results in a modification of the missing row model with considerable distortions which are at least three layers deep. The top layer spacing is contracted by about 20%, the second layer exhibits a lateral pairing displacement of 0.07 Å and the third layer is buckled by 0.24 Å. Distortions in deeper layers seem to be probable but have not been considered in this analysis. The inter-atomic distances in the distorted surface region show both an expansion and a contraction compared to the bulk value and range from 5% contraction to about 4% expansion.

The reconstruction of the Au(110) surface has been a controversial topic for several years and recently has become of interest again as the development of new experimental techniques has contributed new results relevant to the understanding of this surface reconstruction. The new techniques are the method of glancing-incidence X-ray diffraction [1] and the direct imaging of surfaces by high resolution electron microscopy (HREM) [2]. In both methods an expansion of the bond lengths of the topmost atoms was found which contradicts the general rule that in the surface of most metals the atomic bond lengths are contracted. Otherwise, both methods confirmed the "missing row" model of the reconstructed Au(110) surface. The missing row model is consistent with the results of most other methods applied to the (110) faces of Pt, Ir and Au. All three faces are believed to exhibit the same reconstruction [3–11].

Though the previous structural results obtained by low energy electron diffraction (LEED) intensity analysis were somewhat unsatisfactory [3–6], a preference for the missing row model was always found. Most other models could be excluded by ion scattering studies [7–11]. The surface corrugation of the missing row model is also consistent with the results of a helium scattering

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* Present address: Department of Metallurgical and Mineral Engineering and Materials Science Center, University of Wisconsin, 1509 University Avenue, Madison, Wisconsin 53706, USA.

study [12] and with the topographic picture of the scanning tunneling micro-
scope [13]. A recently proposed saw-tooth model [14] which would have a
similar surface corrugation could be ruled out by an alkali impact collision ion
scattering spectroscopy (ALICISS) study of Pt(110)-(1 × 2) [15]. Further theo-
retical support for the missing row model comes from a total energy calcula-
tion [16]. Nevertheless, although various methods agree in the structure model,
up to now no consistent picture has been obtained about the atomic bond
lengths in the surface. An accurate knowledge of the bond lengths is necesary
in order to get a better understanding of the mechanisms of the reconstruction
and of the driving forces that bring it about.

In the "missing row" model each second row of close packed atoms in the
[1$\bar{1}$0] direction is omitted and the unit cell is doubled in the [001] direction.
This atomic arrangement in the surface certainly causes some distortions in the
underlying layers. A variation of the first two layer spacings and a row pairing
in the second layer have usually been considered. The main structure parame-
ter which the previous investigations have tried to determine is the top layer
spacing. The results differ not only in the amount but also in the direction of
the relaxation. From LEED a contraction of 15% was found for Au(110) [3]
and similarly for Ir(110) [6]. For Pt(110) two possible values were found for the
top layer spacing and the authors favored an expansion [5]. With ion-scattering
[7–11] no clear distinction between expansion or contraction for the first layer
spacing could be made but the value of 0.08 Å for the lateral pairing
displacement in the second layer found recently [11] agrees within the error
limits with the X-ray data [1] where a shift of 0.12 Å has been found. A recent
low energy ion scattering study [9] results in a contraction of 15–23% of the
top layer spacing and also indicates a lateral shift of the atomic positions in the
second layer. The direct image of the reconstructed Au(110) surface by HREM
[2] shows an expansion of the topmost layer spacing which is also favored in
the X-ray analysis [1], although the precision for this parameter was rather low
and only the lateral shift in the second layer could be measured with sufficient
reliability. It is clear that the interpretation of all experimental results, except
that of the HREM image, would be influenced by the assumption of further
distortions in deeper layers. In this paper we present the results of a new
LEED structure analysis which indeed results in a buckling in the third layer
and clearly rules out an expansion of the first layer spacing.

The experiment has been described in an earlier paper [3] and the same set
of *I–V* curves was used here. It consisted of 18 *I–V* profiles measured at
normal incidence by a Faraday cup. The energy range in the calculations was
limited to 200 eV in order to ensure convergence in the angular momentum
expansion series, where a maximum of 9 phase shifts was used. The calcula-
tions were performed using the layer doubling method [17] for interlayer
scattering in the bulk. For the strongly scattering gold atom it has been found
that the layer doubling method is not convergent below a layer spacing of 1.25

Å where a maximum of 80 symmetrized beams could be used. Because of this the matrix inversion method in direct space was applied for the top two layers and use has been made of all possible symmetry relations to reduce the size of the matrices to be inverted [18]. The crystal potential was constructed by superposition of relativistically calculated free atom potentials with an optimized α-parameter for the exchange term [19]. Spin averaged phase shifts were used in the multiple scattering program [20]. The bulk Debye temperature of 170 K [21] was taken for all layers, and the real part of the inner potential was assumed to be independent of energy. The imaginary part of the inner potential was set to $0.85E^{1/3}$ [eV], an optimization of these nonstructural parameters has not been tried. Two r-factors were applied for quantitative comparison between experiment and calculation, Zanazzi and Jona's r-factor [22] and Pendry's r-factor [23].

Maintaining the 2mm symmetry of the surface, an alternating row pairing and buckling is allowed in the layers below the top layer. Of these only a pairing in the second layer and a buckling in the third layer were considered here. Together with the first three layer spacings this resulted in 5 parameters which were varied independently in the model calculations (see fig. 1). The calculations proceeded in the following way. At first three parameters, the two uppermost layer spacings and a lateral shift in the second layer, were varied independently. The top layer spacing was varied in a wide range from 2.0–0.9 Å, taking account of large expansions found elsewhere. Further calculations were then performed by keeping the top layer spacing and the lateral shift in the second layer fixed and varying the buckling and the second and third layer spacings simultaneously. Finally, by independently varying all parameters it was checked that the true minimum of the fit had been reached.

A substantial improvement in the fit of the experimental data could not be reached without a buckling in the third layer. The strong backscattering of gold
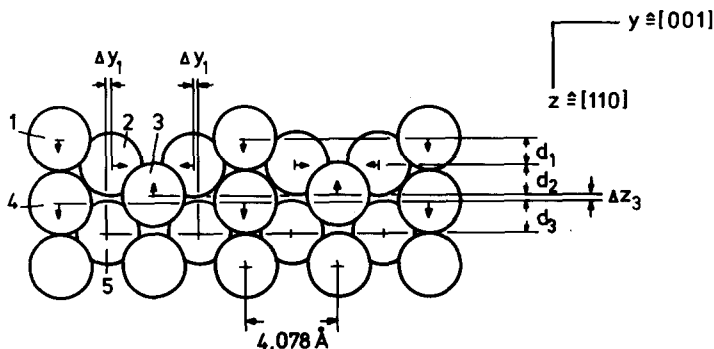

Fig. 1. Side view of the surface model. The distortions of atomic positions are exaggerated in the drawing.
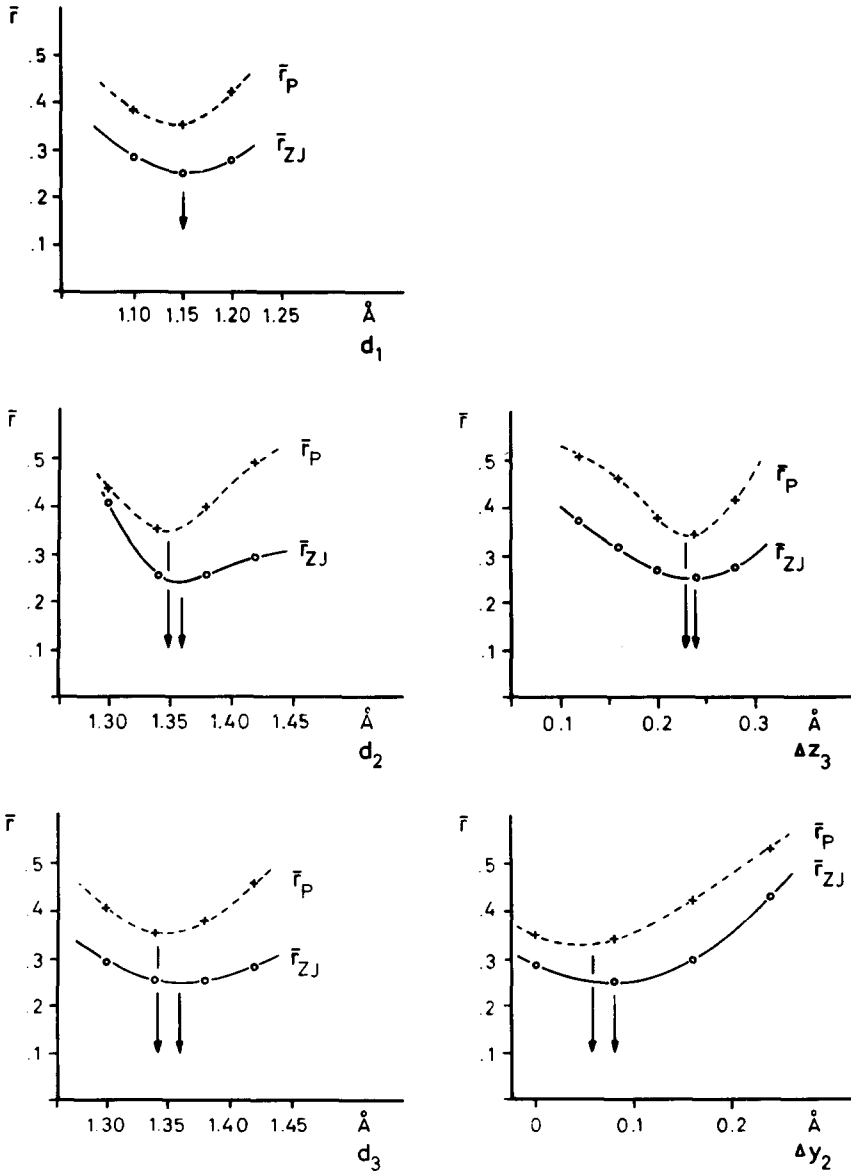
Fig. 2. Averaged r-factors as a function of a single structure parameter keeping the other structure parameters fixed at near-optimum values. Dashed line: Pendry's r-factor, solid line: Zanazzi and Jona's r-factor.

and the scattering geometry in LEED, with its emphasis on layer spacings and shifts of atoms normal to the surface, make the $I-V$ curves rather sensitive to a buckling, even in the third layer. The averaged r-factors keeping all but one parameter fixed near their optimum values are shown as a function of the variable parameter in fig. 2. The comparison of all experimental spectra with the calculated curves is shown in fig. 3.
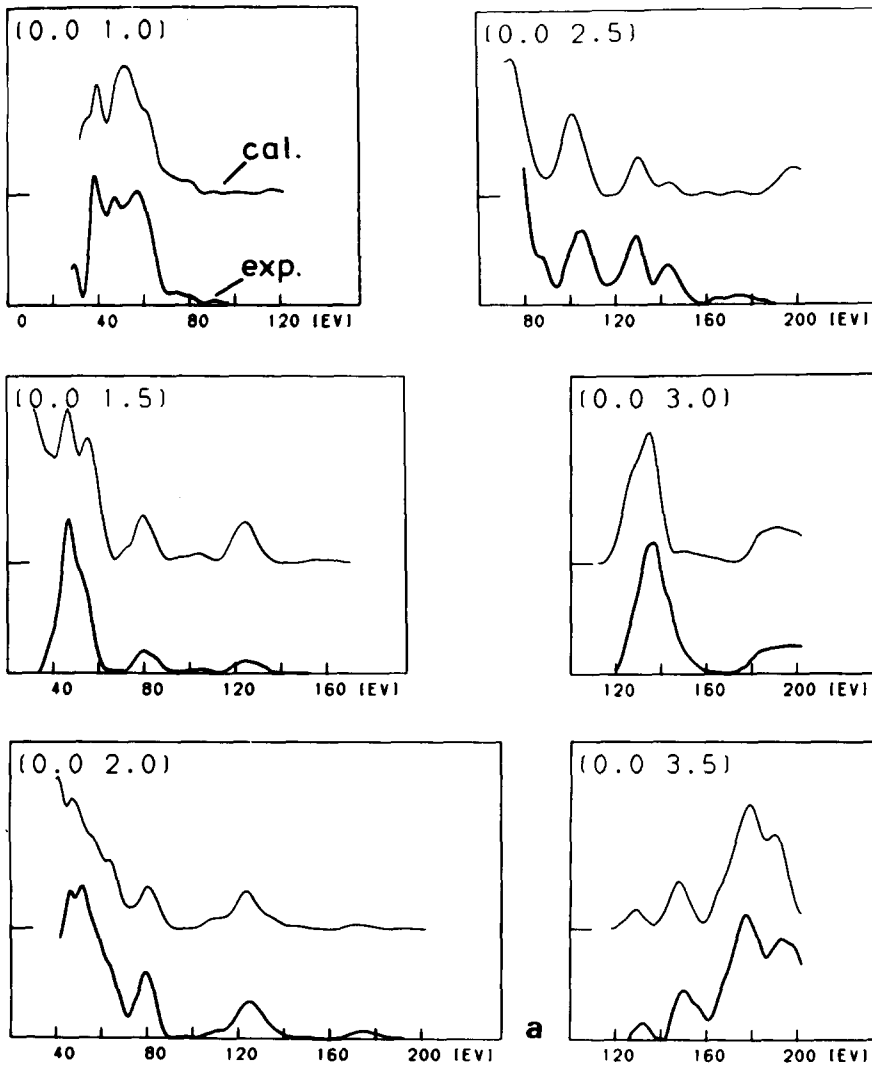
Fig. 3. Comparison between experimental and calculated $I-V$ curves at normal incidence. Temperature $T = 300$ K.

A good overall agreement is reached for each single spectrum. Although some discrepancies still remain between theory and experiment any other structural model can be excluded. The fact that both r-factors lead to nearly the same minima also indicates a high reliability for the resulting atomic bond lengths. The final averaged r-factors are $R_{ZJ} = 0.25$ and $R_P = 0.35$. Clearly, these values are not as good as those for clean unreconstructed surfaces. They are, however, similar to those obtained for adsorbate structures. An improvement of the fit could certainly be reached by optimizing the non-structural parameters such as the surface Debye temperature, which has been found to be
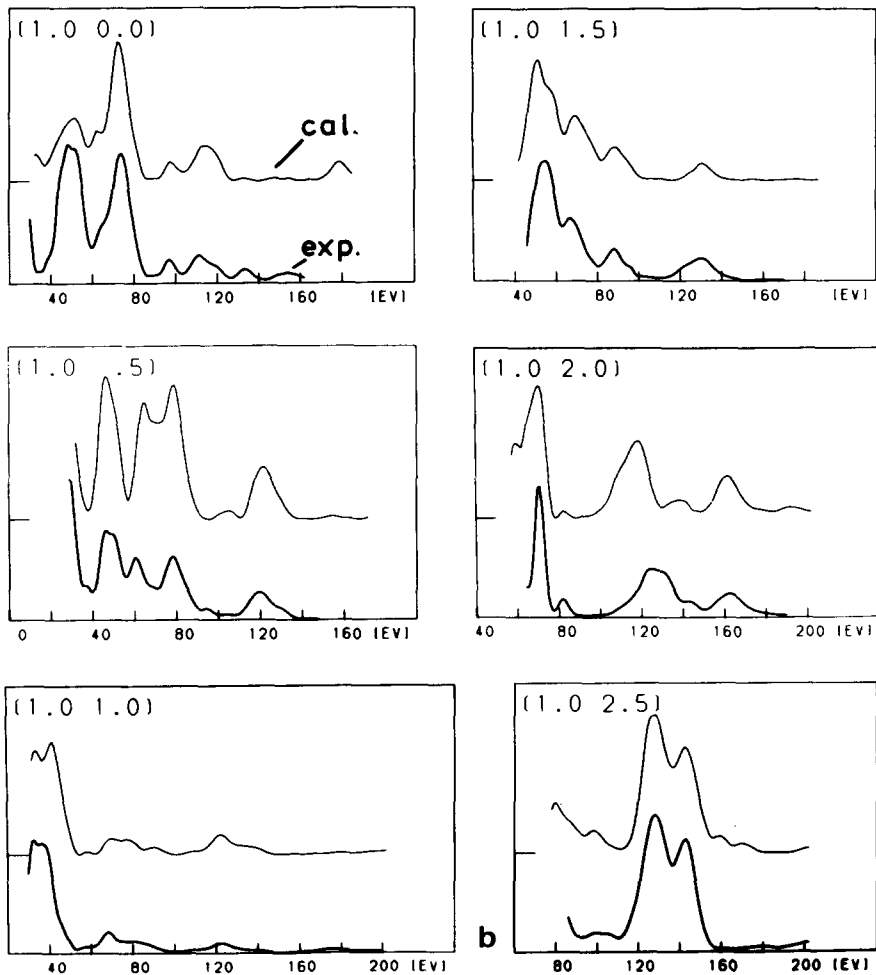

Fig. 3 (continued).

somewhat lower than that of the bulk by X-ray analysis [1], and the energy dependence of the real part of the inner potential. These parameters have not been fitted since it was found that the non-structural parameters have in general little influence on the structural result [24]. Also, further small atomic shifts in the fourth and fifth layer can be expected and from the observed
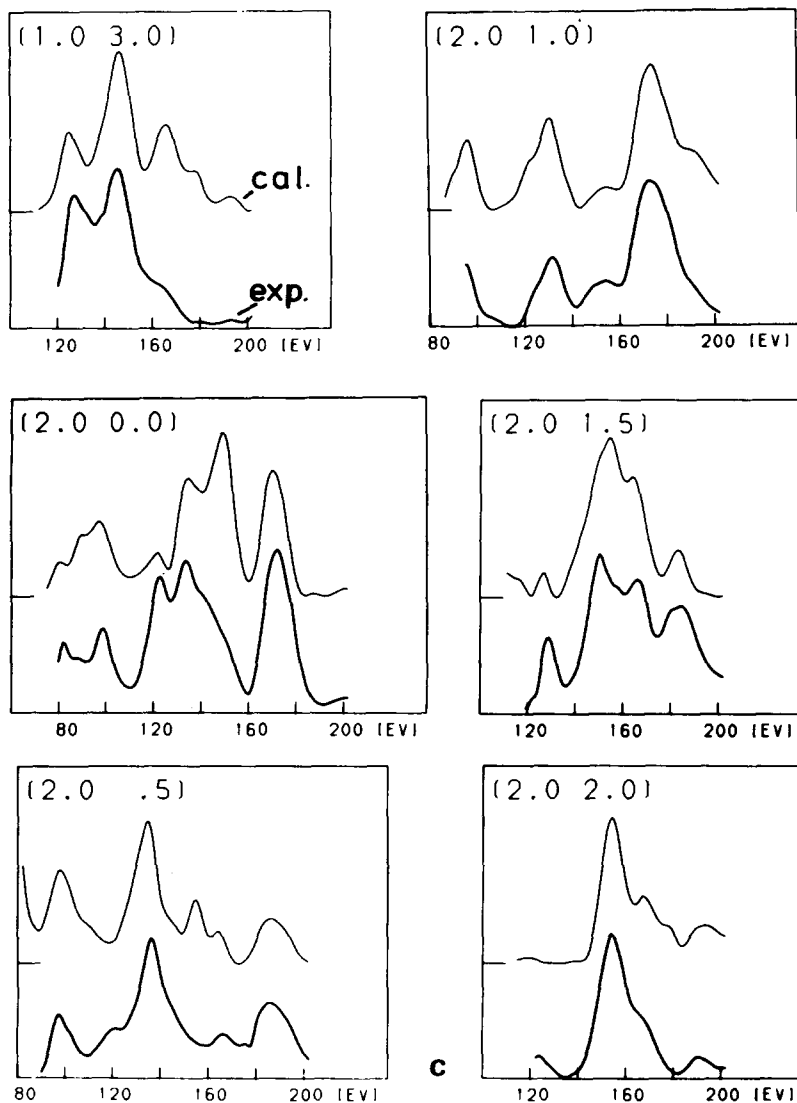

Fig. 3 (continued).

Table 1
Atomic positions in the surface unit cell; $a_0 = 2.88$ Å, $b_0 = 4.08$ Å

Atom number	x (Å)		y (Å)		z (Å)
1	0	0	0	0	0
2	0.5	1.44	0.259	2.11	1.15
3	0	0	0.5	4.08	2.50
4	0	0	0	0	2.74
5	0.5	1.44	0.25	2.04	4.09

sensitivity of the LEED spectra with respect to relatively small atomic shifts in the third layer we conclude that further distortions in deeper layers are mainly responsible for the remaining misfit. These atomic positions were not taken as free parameters since an independent variation of structural parameters as is usually done in a LEED intensity analysis is by far the most uneconomical method. As long as no reasonable procedure to fit a large number of variables is developed, as for example a least-squares fit used in X-ray structure refinement, further improvement cannot be expected. Another reason is that the data were taken from a relatively strongly disordered surface which certainly limits the agreement between theory and experiment.

The results of the structure analysis are shown in table 1; although a large contraction of the top layer spacing of about 20% occurs, the bond lengths are much less reduced due to the compensation by the lateral deviation in the second layer and the buckling in the third layer. The inter-atomic distances and their deviation relative to the bulk value are listed in table 2. As can be seen, the bond lengths split into two groups. The topmost row of atoms is attracted to the second layer and the nearest neighbor in the third layer. The bond lengths are reduced by 2.8% ($r_{12} = 2.80$ Å), and 5.0% ($r_{14} = 2.74$ Å) respectively. A similar contraction of bond lengths by 3.3% occurs between the

Table 2
Interatomic distances in the surface unit cell and their deviation from the bulk value; atoms are labeled as in fig. 1 and table 1

	r (Å)	Deviation from the bulk value (%)
r_{12}	2.80	-2.8
r_{14}	2.74	-5.0
r_{23}	2.79	-3.3
r_{24}	3.01	$+4.4$
r_{25}	2.94	$+2.0$
r_{35}	2.96	$+2.7$
r_{45}	2.84	-1.5

second and third layer at those rows of atoms where the top row is missing, thus causing the buckling in the third layer. Taking the center of mass in the third layer as the reference point, both the second and third layer spacings are slightly expanded by about 2%. It cannot be said whether an expansion or contraction in the fourth and fifth layer spacing occurs since these parameters were not determined. The oscillatory behavior of layer spacings observed on some clean metal surfaces [25] occurs here in a more complicated way which is related to the change of the translational symmetry in the surface.

A reliable estimate of the error bars is always somewhat arbitrary in a LEED structure analysis. From a statistical analysis of the single r-factor curves as well as from the difference between the minima from the two r-factors we estimate an average error of about 0.05 Å in the atomic positions. However, this limit might be too low for some parameters since the peak positions in the $I-V$ profiles are correlated leading to systematic errors. Furthermore, distortions in deeper layers were neglected in the present study and that would have an influence on all other parameters. The error bars might therefore be larger than usually assumed. Further non-structural parameters, such as local absorption and non-isotropic temperature factors, may also influence the result. A reliable estimate for the influence of these parameters cannot be given but certainly does not change the atomic geometry substantially.

There has been doubt about the missing row model because the transition from the (1×1) structure to the (1×2) structure (which is observed for Pt at 310 K) occurs within about 100 s and requires a relatively large mass transport in the surface [14]. Such a large mass transport would be in contradiction to the observed diffusion coefficients on surfaces. Therefore a saw-tooth model has been considered [14], in which every second row is simply shifted upwards to form a separate layer. The formation of the missing row model indeed cannot be explained with diffusion of surface atoms across the channels assuming jumps of one lattice spacing since the activation energy for this process is much to large. However, cross channel diffusion with an exchange mechanism requires a much lower activation energy [26] and this process has already been observed for diffusion of W on Ir(110) [27]. Its role in the self diffusion on Pt and Ir(110) surfaces has been recently discussed [28]. In view of the results of the present study, as well as of ion scattering studies [11,15], the saw tooth model can be ruled out and it seems very probable that the reconstruction takes place via an exchange process in cross channel diffusion. The reconstruction involves the creation or movement of steps in the surface where the mean diffusion length depends on the average terrace size. With the exchange mechanism the mean diffusion length is one quarter of the average terrace size.

All observations on the reconstructed Au(110) surface show that the surface is considerably disordered, while the state of order obviously depends on the

preparation of the surface. A LEED beam profile analysis from an electro-polished surface showed the existence of a stepped surface with an average terrace size of 4–5 unit cells [29]. With X-rays both a mechanically and an electropolished surface were investigated [1] and the mechanically polished showed an average terrace size of about 20 unit cells. Steps in the surface have been also found in a helium diffraction study [12] though no quantitative terrace size determination has been done there. A small terrace width and the low activation energies for the "cross channel diffusion" with an exchange process explain the $(1 \times 1) \to (1 \times 2)$ phase transition observed on Pt [14], where it is assumed that the (1×1) phase is ordered. This transition may be different from the $(1 \times 2) \to (1 \times 1)$ transition on the Au(110) surface which occurs at 700 K and has been explained by an order–disorder transition [29]. The feasibility of this transition has been demonstrated recently by Monte Carlo calculations [30].

Reconstructions with a (1×2) unit cell have been observed to occur during alkali adsorption on Cu and Ag(110) surfaces [31] and probably exhibit the same type of structure as the clean surfaces of Pt, Ir and Au. A preference for a missing row structure has also been found in a LEED $I-V$ analysis of the (1×2) reconstruction of Ni(110) induced by hydrogen [32]. The mechanism of the reconstruction on all these surfaces may assumed to be similar and in that case a high step density should be observable on these surfaces too.

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