

## Efficient Determination of Multilayer Relaxation in the Pt(210) Stepped and Densely Kinked Surface

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The multilayer relaxation of the Pt(210) stepped and kinked surface is analyzed by low-energy-electron diffraction. This is the first application of the new real-space multiple-scattering theory of LEED, designed specifically for such open surfaces where conventional theories fail. Combined with an automated tensor LEED method, it efficiently detects nonalternating atomic relaxations which are oriented primarily perpendicular to the surface. These relaxations are in qualitative agreement with new embedded-atom-method results.

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Few structures of stepped surfaces have been determined on the sub-Å scale, despite their great importance in fields as diverse as catalysis, crystal growth, crack propagation, and tribology [1]. In particular, multilayer relaxations and adsorption geometries are expected to be crucial in the understanding of many phenomena involving stepped surfaces.

The step structures which have so far been analyzed mainly concern relatively low-Miller-index metal surfaces, in which the terraces between steps are very narrow [2]. A rare exception is Cu(410), studied by low-energy ion scattering [3] [the fcc (410) surface differs from (210) only in that the (100)-oriented terraces are 3 times wider]. While this Cu(410) study does not provide much reliable detail, relaxations of step edge atoms are proposed on the scale of 0.18 Å, such that the surface is made smoother. It is now generally accepted that relaxations of the atomic positions occur particularly at steps, including multilayer relaxations deeper into the surface.

The primary technique used to analyze steps has been low-energy-electron diffraction (LEED) [4]. Progress with LEED has, however, been hampered by difficulties in dealing with small interlayer spacings due to the stepped nature of the surface. Small spacings result from wide terraces and from kinks in the steps (kinks are nonalignments of step atoms, giving jagged step edges).

The Al(210) surface structure, very similar to that of Pt(210), was analyzed some years ago with LEED by Adams *et al.* [5] using the relatively robust layer-doubling method [4]. This was, however, only possible because of the unusually weak multiple scattering of electrons in aluminum, which permitted layer doubling to converge better than in almost any other metal. By contrast, platinum causes particularly strong multiple scattering and thus serves as a severe test case for a LEED theory. Several approaches [6-10] have been proposed in order to overcome these difficulties in LEED theory; the most recent ones [9,10] are based on the new real-space multiple-scattering theory (RSMST) [10]. Using RSMST, LEED intensities can be calculated under conditions where conventional methods fail. For instance, in the case of Pt(210), the layer-doubling method failed to converge sufficiently well for us to determine the surface structure. The structure could, however, be solved by applying the new method, coupled with an automated tensor LEED search [11,12] for the many unknown structural parameters.

A stepped surface is characterized by the relatively large area  $A$  of its two-dimensional unit cell and the small interplanar spacing  $d$  between atomic layers parallel to the surface. This causes two major difficulties in a LEED theory [4]. First, the size of the plane-wave basis

set necessary to represent electronic wave functions at a given energy scales roughly as  $A/d$ , which rapidly becomes prohibitively large for a stepped surface. Second, in a traditional LEED approach, one uses layer stacking methods to obtain the reflected-electron-beam intensities. This process also fails to converge for small interplanar spacings. Some improvement results from using a mixed plane-wave and spherical-wave basis, allowing the treatment of systems with smaller interplanar spacings than would be possible if one used only plane waves [6-8]. However, such a technique only delays the divergence, and does not cure it. An alternative approach is to use only spherical waves: That is, the approach of real-space multiple-scattering theory. As is indicated by our results, this last approach provides a powerful analytical tool for the study of stepped and kinked surfaces.

In our application of the RSMST [10] method, we still utilize the two-dimensional surface periodicity and use a Fourier transform to convert the surface problem into a one-dimensional problem. Then the concept of removal invariance is applied, which states that removing one layer from a semi-infinite periodic stack of layers does not change the surface properties. It leads to a self-consistent equation from which the scattering matrix for spherical waves from an unrelaxed half solid can be calculated. The amplitudes of the reflected electron beams can be obtained by a straightforward transformation from spherical- to plane-wave basis. Once the scattering matrix is known for an unrelaxed substrate, there are at least two ways to obtain the intensities for a given relaxed configuration. The first approach is to calculate the full scattering matrix within the spherical-wave representation by explicitly adding the relaxed layers on top of the unrelaxed substrate. The second approach is to use the tensor LEED technique [11,12], which is essentially a perturbation expansion of the scattering matrix in terms of the displacement of the atoms with respect to the (unrelaxed) reference structure. We chose the latter approach, coupled with an automated structural search method [11,12]: It is valid for relaxations less than about 0.4 Å, and is computationally extremely efficient, especially when fitting many unknown parameters. The former approach (layer addition), which should ideally be combined with the tensor LEED approach, would be used for reconstruction, overlayers of adsorbates, etc.

For comparison, we also calculated the Pt(210) surface relaxations and registry shifts using the embedded-atom method (EAM) [13]. This method has been employed in numerous studies of surface relaxations [13], including stepped surfaces [14,15]. For Al(210) and Pt(210), as well as other such surfaces, a  $(2 \times 1)$  reconstruction was predicted to be more stable than the  $(1 \times 1)$  unreconstructed surface [15]. We optimized the Pt(210) surface geometry with the standard EAM code using force minimization and previously published Pt embedding functions [13].

The LEED spectra were measured on a sample which was cut from a high-purity (99.999%) single-crystal rod and oriented within  $\pm 0.5^\circ$  using the Laue method. After polishing with diamond paste (0.25  $\mu\text{m}$ ) the sample was cleaned *in situ* by a combination of argon-ion sputtering (1 keV, 1000 K, 72 h), annealing (1200 K, 15-60 min), and oxygen treatment (1000 K,  $5 \times 10^{-7}$  mbar). This resulted in an impurity-free surface as judged by Auger electron spectroscopy, displaying a sharp LEED pattern. No reconstruction was observed down to 100 K, contrary to the earlier EAM prediction [15].

LEED intensities were taken near liquid-air temperature using a video camera operated under computer control [16,17]. Between the measurements of different beams, the surface was flashed in order to avoid residual gas adsorption which easily could affect the surface multilayer relaxation. Experimental spectra extend up to 300 eV, while the theory-experiment fit used only data between 15 and 120 eV, to limit the computational time for the unrelaxed surface (which increases fast as  $l_{\text{max}}$  increases with energy, similarly to conventional methods).

Experimental reasons prevented selecting exact normal incidence of the primary beam. However, it was possible to make the incident beam fall into the (001) surface mirror plane, causing  $(h,k)$  and  $(k,h)$  spots to be symmetrically equivalent. Intensity spectra of such spot pairs were averaged in order to increase the quality of the data. A total of eleven symmetrically inequivalent beams were measured, labeled (00), (10), (0-1), (11), (1-1), (21), (22), (0-2), (-1-2), (-2-2), and (32). Evaluation of the spot positions yielded an angle of incidence of about  $4.4 \pm 0.2^\circ$  off normal. This value was

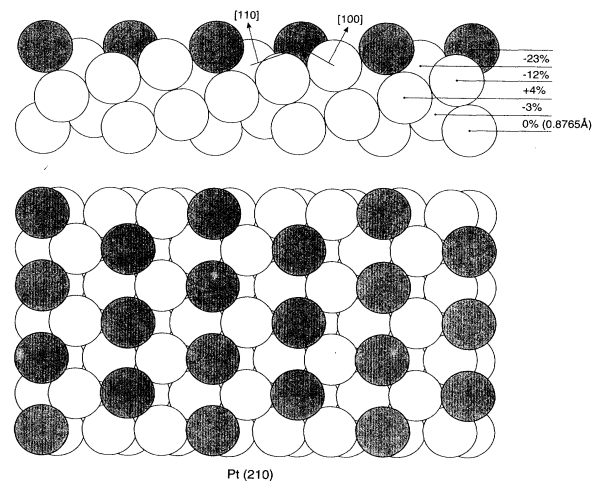


FIG. 1. Top view (bottom panel) and side view (top panel) of Pt(210), with outermost surface atoms shown in gray. Inter-layer spacing relaxations found by LEED are shown as percentages of the bulk value (which is given in parentheses).

TABLE I. Percentage relaxations of interlayer spacings  $\Delta d_i$  between layers  $i$  and  $i+1$ , with respect to the bulk spacing of 0.8765 Å for Pt(210) and 0.9026 Å for Al(210).

Relaxation	Pt-LEED (%)	Pt-EAM (%)	Pt-EAM <sup>a</sup> (%)	Al-LEED <sup>b</sup> (%)	Al-EAM <sup>a</sup> (%)
$\Delta d_1$	$-23 \pm 4$	-31	-23	$-16 \pm 2$	-27
$\Delta d_2$	$-12 \pm 5$	-10	-7	$-1 \pm 3$	+2
$\Delta d_3$	$+4 \pm 7$	+10	+6	$+9 \pm 4$	+5
$\Delta d_4$	$-3 \pm 7$	-7	-7	$-4 \pm 4$	-6
$\Delta d_5$	...	+2	+2	$-1 \pm 5$	-0

<sup>a</sup>Reference [19].

<sup>b</sup>Reference [5].

later optimized at the same time as the surface structure: The polar angle was treated as an additional parameter to be fitted in the calculation, by performing the structure optimization at several angles. The best-fit polar angle is  $4.1 \pm 0.3^\circ$ .

The nonstructural parameters for the LEED calculations were as follows. Phase shifts up to  $l_{\max}=6$  were included, based on a relativistic potential [18] for Pt. The muffin-tin zero was set at 10 eV below vacuum and later adjusted during the tensor LEED search to an optimum 14 eV. The mean free path was simulated by an imaginary part of the muffin-tin constant that was made proportional to the cubic root of the energy [18]. A Debye temperature of 230 K was used and the temperature was set at 100 K.

The resulting surface structure of Pt(210) is illustrated in Fig. 1. The relaxations found for the interlayer spacings are shown in Tables I and II. The relaxations parallel to the surface are within our error bars (which are largest parallel to the surface). The best-fit Pendry  $R$  factor is 0.218. These results are in reasonable agreement with those predicted by our calculation based on the embedded-atom method, also shown in Tables I and II. The corresponding LEED values for Al(210) [5] have somewhat similar magnitudes and trends, and also lateral relaxations within the error bars only. Our EAM results for Pt(210) are also included in Table I, together with other EAM results for Pt(210) (using a different embedding function) and Al(210) [19].

Not surprising is the magnitude of the contraction of the first interlayer spacing: It fits well with the trend for "rougher" surfaces to have larger relaxations [2]. Of particular interest is the nonalternation of the sign of the spacing relaxations, as if these occurred with an oscillation whose wavelength is badly mismatched to the interlayer spacing (for more compact, less open surfaces, a simple alternation of positive and negative relaxations is often found [2]). Such a behavior has occasionally been observed before, namely, for bcc Fe(111), Fe(210), and fcc Al(331) [2]. A trend emerges: Such nonalternation appears to occur only on the more open surfaces which expose the *third*-layer atoms most prominently to the vacuum. With fcc (210), the terrace plane has (110) orientation, exposing its deep-lying trough atoms. The exposure of highly coordinated metal atoms should be particularly beneficial for catalytic activity [20].

The success of the RSMST technique demonstrates that it is well suited for the structural study of stepped surfaces, especially when coupled with automated tensor LEED to determine many structural parameters. This study opens the way for the detailed analysis of stepped surfaces that were heretofore unreachable with LEED, including the most important case of adsorption.

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TABLE II. Absolute relaxations (in Å) of layer registries  $\Delta r_i$  in layers  $i$  measured parallel to the structural mirror plane, to be compared with the bulk registry shift from layer to layer of 1.7531 Å for Pt(210) and 1.8052 Å for Al(210). A positive  $\Delta r_i$  implies an outward expansion of the (110) terrace, i.e., edge atoms moving away from their neighbors in the (110) terrace and toward the (100) terrace.

Registry	Pt-LEED	Pt-EAM	Pt-EAM <sup>a</sup>	Al-LEED <sup>b</sup>	Al-EAM <sup>a</sup>
$\Delta r_1$	$+0.02 \pm 0.07$	+0.03	-0.02	$-0.00 \pm 0.05$	-0.02
$\Delta r_2$	$-0.03 \pm 0.08$	-0.02	-0.04	$-0.06 \pm 0.05$	-0.02
$\Delta r_3$	$-0.08 \pm 0.10$	-0.04	-0.05	$+0.03 \pm 0.05$	-0.04
$\Delta r_4$	$-0.01 \pm 0.10$	+0.01	+0.00	$-0.04 \pm 0.07$	+0.02
$\Delta r_5$	...	-0.01	+0.00	$-0.02 \pm 0.09$	-0.00

<sup>a</sup>Reference [19].

<sup>b</sup>Reference [5].

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