Reliability of detailed LEED structural analyses: Pt(111) and Pt(111)-p(2×2)-O

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Abstract

As surface structures are being examined in more detail than ever before, the reliability of structural details becomes an important issue. To discuss necessary components of a high quality, reliable dynamical LEED studies, detailed dynamical LEED analyses of the clean Pt(111) and the Pt(111)-p(2×2)-O structures have been carried out utilizing different computer programs and search methods applied to a common set of experimental LEED I–V data. We have investigated the effects of various non-structural parameters, in particular those involved in the construction of the phase shifts, on the resulting structures of the clean Pt(111) and the Pt(111)-p(2×2)-O surfaces. The use of relativistic Pt phase shifts is found to be important in order to determine the adsorption structure accurately. For clean Pt(111), we find the top interlayer spacing is noticeably expanded by 0.025 ± 0.01 Å with a low R-factor value of 0.15. For the Pt(111)-p(2×2)-O system we find an R-factor of 0.18. O atoms in the p(2×2)-O overlayer are found to adsorb in fcc-hollow sites and induce buckling in both the first and second metal layers. In addition, there is an expansion of the first metal–metal interlayer spacing and a small contraction of the second.

Keywords: Chalcogens; Chemisorption; Electron–solid interactions, scattering, diffraction; Low energy electron diffraction; Low index single crystal surfaces; Metallic films; Platinum; Surface relaxation and reconstruction

1. Introduction

With the development of tensor low energy electron diffraction (TLEED) and other similar techniques [1], dynamical low energy electron diffraction (LEED) analysis has become increasingly capable of extracting detailed geometric information from experimental I–V curves. Information not only about adsorbate position, but also regarding its effect on the metal surface can be routinely determined. This is illustrated in a recent review of adsorbate induced relaxations [2]. As a result, when detailed relaxations of a surface structure are reported, the reliability of these fine details becomes an important issue. We describe and compare independent dynamical LEED analyses of the Pt(111)-p(2×2)-O system, using three different optimization schemes based on different implementations of TLEED [1,3–5]. These independent dynamical LEED analyses illustrate the reliability of different approaches to LEED analysis.

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in the similar structural results obtained with each. We have also investigated the effects of various non-structural parameters, particularly those involved in the construction of the phase shifts, on the resulting structures of the clean Pt(111) and the Pt(111)-p(2×2)-O surfaces.

The Pt(111)-p(2×2)-O system has been well studied using other techniques [6–8] due to the importance of Pt as a catalyst for oxidation reactions. Our sharp p(2×2) LEED pattern had an exceptionally large signal-to-noise ratio, which permitted the measurement of experimental I–V curves for many higher order diffraction spots. With only one O atom per unit cell (as established earlier [6–8]) different surface Pt atoms must have different O coordination. Due to this and in view of the strong chemisorption of O on Pt(111), considerable surface relaxations are expected. Correspondingly O/Pt(111) is an ideal system for use in investigating the extent to which the resulting relaxations (including interlayer spacings, buckling and lateral atomic displacements) are affected by the methodology of the LEED analysis.

In addition, the surface geometry of clean Pt(111) has been the subject of earlier LEED investigations using R-factor analyses [9,10]. These investigations have never yielded satisfactory R-factors as compared to other clean surfaces. Because clean Pt(111) normally has an unreconstructed bulk-periodic surface, these unsatisfactory R-factor values could not be caused by neglecting structural parameters. On the basis of I–V curves taken for clean Pt(111) we have investigated how non-structural parameters influence the LEED analysis. In particular, we have examined different parameters involved in obtaining the atomic phase shifts which describe the electron–atom scattering process. The consequences of varying these parameters on the resulting phase shifts and, in turn, on the quality of fit for both the clean surface and for the O overlayer are considered.

After a brief description of the experiment, this paper is divided into three main sections. In Section 3, we examine different approximations in the phase shift computation and their effects on both the quality of fit between experimental and theoretical I–V curves and the resulting structure of the clean Pt(111) surface. In Section 4, we report the structural results of the dynamical LEED analyses of the Pt(111)-p(2×2)-O structure obtained by different search schemes. In Section 5, we describe the effect on the optimal O/Pt(111) structure of the various non-structural parameters discussed in Section 3 for clean Pt(111). Following these three main sections, we draw conclusions in Section 6.

2. Experiment

Our experiments were carried out in a stainless steel ultrahigh vacuum chamber which was kept at or below 10−10 mbar throughout the experiments. The chamber is equipped with a quadrupole mass spectrometer, a Bayard–Alpert ion gauge, an ion sputter gun, a cylindrical mirror analyzer and an electron gun for Auger electron spectroscopy (AES). LEED data were collected for the Pt(111) crystal using a digital LEED detector [11]. This detector is capable of measuring the impact position of single diffracted electrons to digitally generate the diffraction pattern with an exceptional signal-to-noise ratio. Intensity versus energy (I–V) curves are generated for each individual diffraction spot in a LEED pattern at each energy, by integrating the intensity of a spot within a window and subtracting the intensity averaged over the window frame.

The Pt(111) crystal was cut to within 0.5° of the [111] direction and mounted on a manipulator capable of accurately positioning the sample normal to the LEED electron gun. The sample was cleaned by repeated cycles of ion bombardment and annealing followed by heating in O until no impurities could be detected by AES, and the LEED pattern of the clean surface was sharp and free of diffuse background intensities [12,13]. After flashing to 1000 K, the crystal was cooled to 90 K and the I–V curves of the clean surface were measured. The (1,0), (0,1), (1,1), (2,0) and (0,2) beams were measured from 50 to 250 eV at normal incidence for a total energy range of 690 eV. In addition, the (1,0), (0,1) and (1,1) beams were measured at 300 K. These experiments were repeated several times in order to insure the reproducibility of the I–V curves. The experimental I–V curves agree well with other work [9,10,14] and are reproducible.

The O chemisorption phase was prepared by exposing the clean surface to 7.5 langmuir (L) of molecular O2 at 270 K, followed by flashing the crystal to 300 K. This procedure resulted in the sharp (2×2) LEED pat-
tern shown in Fig. 1. Further experimental details can be found in Refs. [12,13]. After preparation of the O overlayer, the crystal was cooled to 90 K and the I–V curves for the p(2×2) LEED structure were measured from 20 to 350 eV at normal incidence. Five different LEED experiments were performed and resulted in nearly identical I–V curves. Normal incidence was confirmed by the good visual agreement between symmetry equivalent beams. A total of five integer order symmetry-averaged beams, the (1,0), (0,1), (1,1), (2,0) and (0,2), and nine fractional order symmetry-averaged beams, the (1/2,0), (0,1/2), (1/2,1/2), (3/2,0), (0,3/2), (1/2,1), (1,1/2), (1/2,3/2) and (3/2,1/2), was obtained by averaging the I–V curves from the two LEED experiments having the highest signal-to-noise ratios for a cumulative energy range of 3415 eV. The total energy range of the integer order beams was 1214 eV, and that of the fractional order beams was 2201 eV.

3. Clean Pt(111): non-structural parameters

The surface structure of the clean Pt(111) surface has been investigated with both dynamical LEED [9,10,14] and ion scattering [15,16]. Two LEED studies quantified the agreement between the experimental and theoretical I–V curves by computing reliability factors, or R-factors [17], which represent the quality of the fit. Ion scattering experiments [15,16] support the LEED results. Adams et al. found the first interlayer spacing to be possibly expanded by 0.04 ± 0.10 Å with a relatively large R2-factor [17] of 0.16 [9], while Hayek et al. found an unrelaxed surface within 0.05 Å and a high Rp-factor [18] of 0.43 [10]. In addition, Adams et al. noticed almost no change between the R2-factor value obtained using non-relativistic phase shifts and that obtained using spin-averaged or quasi-relativistic phase shifts. In contrast, we observe large differences in the R-factor values obtained utilizing phase shifts computed in different ways. This prompted us to re-examine the effects of the phase shift computation not only on the structure, but also on the quality of the fit between experimental and theoretical I–V curves.

3.1. LEED computations

We used the TLEED approximation combined with an automated search algorithm directed by R-factor values [1,19] to analyze the experimental I–V curves obtained for the clean Pt(111) surface. The TLEED approximation reduces the amount of computer time for trial geometries by determining how the amplitudes of the outgoing plane waves depend on small displacements from a reference structure [1,5,19–23]. To obtain this information, a conventional dynamical LEED computation [17,24,25] is required for the reference structure. The program then generates the tensor of beam amplitude dependencies by a generalization of the procedure described in Ref. [22], so that the tensor can be collected for layers containing more than one atom per unit cell. In this computation, the Pt(111) crystal was divided into a semi-infinite stack of layers. The scattering properties of each layer were computed treating multiple scattering within the layer exactly. Nine phase shifts at each energy were used to describe atomic scattering within a layer. Scattering between the layers and towards the bulk was modeled using renormalized forward scattering (RFS) with up to 37 plane waves.

The phase shift computations for LEED analysis have been described by many authors [17,24]. Briefly, the phase shifts used in our LEED computations were
obtained, within the muffin-tin approximation, by requiring the radial solution within the muffin-tin to smoothly match the spherical wave solution outside the muffin-tin. The muffin-tin approximation has been found to well describe the low energy electron scattering process [17,24]. The phase shifts were computed by numerically integrating either the Schrödinger or the relativistic Dirac equation using methods outlined by Loucks [26]. The relativistic phase shifts were spin-averaged (which we call quasi-relativistic) before they were used in the LEED computation [27]. The potential utilized in the integration was obtained from atomic wave-functions computed by numerical integration of either the Dirac–Fock or Hartree–Fock equation with electron exchange treated exactly. A muffin-tin potential was then computed, as in Loucks [26,28], after correcting the atomic charge densities for the effects of the surrounding atoms in the fcc crystal lattice. The total potential within the muffin-tin was computed by adding the Coulombic potential, which resulted from the spherically symmetrized charge densities, to the exchange correlation potential determined by the local density approximation. The muffin-tin zero was set equal to zero by subtracting the constant potential due to both the Coulombic and the exchange correlation potentials from the muffin-tin potential.

3.2. Results

3.2.1. Relativistic effects

Using a muffin-tin potential obtained from the bulk Pt lattice and a muffin-tin radius of 0.95 Å, the choice of which will be discussed later, phase shifts were generated starting from either relativistic or non-relativistic atomic charge densities. Although with five experimental beams measured at 90 K over an energy range of 100 to 250 eV a similar final structure is obtained using both quasi-relativistic and non-relativistic phase shifts, the quasi-relativistic phase shifts improved both the $R_2$-factor and the $R_p$-factor considerably. A smaller but significant improvement in both $R$-factors is observed if the experimental range is increased to 50 to 250 eV. These results are summarized in Table 1, and the $I-V$ curves generated with the quasi-relativistic phase shifts are shown in Fig. 2. Using non-relativistic phase shifts, the $R_2$-factor is comparable to the result of 0.18 obtained by Adams et al. [9]. Likewise, with non-relativistic phase shifts, the $R_p$-factor is in agreement with the result of 0.48 found by Hayek et al. [10].

The phase shift computation is naturally separated into two parts, the first determining the muffin-tin potential and the second dealing with scattering from each atomic sphere in the muffin-tin. The most important ingredient in the computation of the muffin-tin potential is the electron charge density, which is determined by a self-consistent atomic calculation [29,30]. Since relativistic effects make the potential in the atomic calculation more attractive in the core region as compared to the non-relativistic case, the self-consistent atomic charge density is pulled inward, or close to the core, thereby more effectively screening the nucleus. Therefore, the effective muffin-tin potential resulting from the relativistic charge density is weaker than that from the non-relativistic density.

Ignoring relativistic effects in the scattering portion for the moment, by numerically integrating the Schrödinger equation at each energy, we find that the phase shifts computed from the relativistic charge density lie under or below the phase shifts computed from the non-relativistic charge density. In Fig. 3 the phase shift for $l = 0$ computed using the relativistic charge...
density is shifted downward with respect to the phase shift computed with the non-relativistic charge density. In addition, for \( l = 4 \), the phase shift computed using the relativistic charge density is also shifted downward with respect to that computed with the non-relativistic charge density which coincides with the quasi-relativistic phase shift. These downward shifts are a direct result of the weaker relativistic scattering potential which results in a smaller phase difference between incoming and outgoing spherical waves. A LEED analysis of the clean Pt\((111)\) surface using the non-relativistic phase shifts generated from the relativistic potential results in an \( R_p \)-factor close to the fully non-relativistic \( R_p \)-factor in Table 1.

Incorporation of relativistic effects into the scattering portion of the phase shift computation increases the strength of the scattering potential. Ignoring these effects in the phase shift computation gives rise to phase shifts which reflect an unrealistically weak atomic scatterer. The addition of relativistic effects in the scattering portion effectively increases the atomic scattering power; thus, relativistic effects produce a large upward shift of the phase shifts. This large upward shift is illustrated in Fig. 3 for \( l = 0 \) and \( l = 4 \). At each energy, the phase shifts computed from the Dirac equation lie above the phase shifts computed from the Schrödinger equation. This effect also exists for the non-relativistic phase shifts computed with a non-relativistic muffin-tin potential. However, for \( l = 4 \), the non-relativistic phase shifts computed for the non-relativistic charge density are almost identical to quasi-relativistic phase shifts, as can be seen in Fig. 3. This is due to the fact that the inner core region, where relativistic effects are most important, is probed progressively less by the scattered electrons with larger \( l \). An important point is illustrated in Fig. 3: the non-relativistic phase shifts computed using the relativistic charge density lie under both the quasi-relativistic and the non-relativistic phase shifts computed with the non-relativistic charge density. This is due to the unrealistic screening of the nuclear charge. Inclusion of relativistic effects in only the atomic charge density computation and not the scattering portion yields a poorer \( R \)-factor than a fully non-relativistic computation. A LEED analysis of the clean Pt\((111)\) surface using quasi-relativistic phase shifts produced a low \( R_p \)-factor value of 0.15. Relativistic effects must be included in the scattering portion of the phase shift computation in order to obtain an improvement in the quality of fit between theory and experiment.

Although the introduction of relativistic effects improved the \( R \)-factor values, these effects have only
a small influence on the final structure of the clean Pt(111) surface. The features, or peaks and valleys, in an $I-V$ curve are caused by interference between different scattering paths. In the single scattering, or kinematic, limit the relative values, not the absolute values, of the atomic phase shifts are important. Therefore, one would not expect the structure of the clean surface to depend strongly on the absolute values of the phase shifts. However, the Pt(111)-p(2×2)-O system is a different case. In this system, even in the single scattering limit, the differences in the atomic phase shifts between O and Pt influence scattering paths between these atoms. This effect will be discussed later.

The addition of experimental data between 50 and 100 eV caused the $R_p$-factor value to increase from 0.15 to 0.22. The addition of these data increased the energy range by 18% for a cumulative energy range of 560 eV, but increased the $R_p$-factor by 50%. One possible explanation for the increase in the $R$-factor could lie in the neglect of spin in the LEED computation. By spin-averaging the phase shifts, one assumes that the LEED $I-V$ curves reflect a surface in which the LEED electron feels a spin-averaged interaction with the atomic scatterers. This is certainly not true even in the single scattering, or kinematic, limit where interference exists between the direct scattered wave and the spin-flip wave [31,32]. By examination of the phase shifts between 50 and 100 eV, one sees large differences between the spin up ($j=\frac{1}{2}$) and spin down ($j=-\frac{1}{2}$) phase shifts. Fig. 4 shows the resulting $I-V$ curves for the (1,0) and (0,1) beams computed using the spin up, the spin down, and the spin-averaged or quasi-relativistic phase shifts. The large differences between these $I-V$ curves in the low energy range support the assumption that the neglect of the effect of spin in the LEED computations may be the cause of the discrepancy between experimental and theoretical $I-V$ curves in the energy range between 50 and 100 eV, which was not fitted in the final structural analysis.

3.2.2. Role of the muffin-tin radius

Another factor in the phase shift computation is the choice of the muffin-tin radius. For a LEED computation in which scattering occurs primarily in the atomic cores, it is not obvious that the muffin-tin radius should equal one half the interatomic distance as is the case in lower energy band structure computations in which

![Graph showing $I-V$ curves for (1,0) and (0,1) beams with quasi-relativistic and spin-up/spin-down phase shifts.]

the crystal potential is solved self-consistently. Examination of the charge density for Pt shows the bulk of the charge density to be within 0.95 Å from the origin. Table 2 shows the optimal first interlayer spacing and both the $R_2$- and $R_p$-factor values obtained with phase shifts generated from different muffin-tin radii. In this table, one can see a slow decrease in the $R$-factor value with decreasing radius, followed by a rapid increase. In addition, correlation of the inner potential with the muffin-tin radius can be observed. This is due to the displacement of more charge density from the muffin-tin spheres into the flat region as the muffin-tin radius becomes smaller. Possibly due to the relative insensitivity of the $R_p$-factor to absolute intensities in the

<table>
<thead>
<tr>
<th>Radius</th>
<th>$R_p$</th>
<th>$d_{12}$</th>
<th>$V_0$</th>
<th>$R_2$</th>
<th>$d_{12}$</th>
<th>$V_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.38</td>
<td>0.18</td>
<td>-0.03</td>
<td>7.5</td>
<td>0.06</td>
<td>-0.05</td>
<td>6.8</td>
</tr>
<tr>
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<td>-0.03</td>
<td>8.5</td>
<td>0.06</td>
<td>-0.04</td>
<td>8.0</td>
</tr>
<tr>
<td>0.95</td>
<td>0.15</td>
<td>-0.02</td>
<td>10.5</td>
<td>0.06</td>
<td>-0.03</td>
<td>10.4</td>
</tr>
<tr>
<td>0.74</td>
<td>0.30</td>
<td>-0.02</td>
<td>14.2</td>
<td>0.13</td>
<td>-0.02</td>
<td>15.7</td>
</tr>
</tbody>
</table>
Table 3

\( R_2 \)- and \( R_p \)-factor values and the real part of the inner potential, for theoretical \( I-V \) curves computed for the Pt(111) surface with a muffin-tin radius of 1.38 Å obtained with relativistic phase shifts generated from muffin-tin potentials computed with different muffin-tin radii for the Pt atoms (independent fitting is done for each \( R \)-factor; because the "experimental" \( I-V \) curves were generated using a muffin-tin radius of 1.38 Å the resulting \( R \)-factors must be 0.00)

<table>
<thead>
<tr>
<th>Radius</th>
<th>( R_p )</th>
<th>( V_0 )</th>
<th>( R_2 )</th>
<th>( V_0 )</th>
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<td>13.0</td>
</tr>
<tr>
<td>0.74</td>
<td>0.38</td>
<td>16.4</td>
<td>0.20</td>
<td>16.6</td>
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</table>

\( I-V \) curves, we find that the variation of the first interlayer spacing is smaller for this \( R \)-factor than for the \( R_2 \)-factor. A computer experiment designed to quantify the effective size of the computed atomic scattering potential shows that most of the scattering is contained within 0.95 Å from the origin. \( R_2 \)- and \( R_p \)-factor values of the fit between \( I-V \) curves generated with a muffin-tin radius of 1.38 Å (one half the interatomic distance) and \( I-V \) curves generated with a muffin-tin radius of 1.38 to 0.74 Å show a rapid rise only when the muffin-tin radius is reduced below 0.95 Å (see Table 3). This supports the assumption that the scattered electron at typical LEED energies effectively feels the atomic charge density only out to about 0.95 Å. By increasing the muffin-tin radius, one adds charge density which is possibly inaccurate because the muffin-tin potential was not solved self-consistently. In a LEED computation, this charge density is better described by a constant, the real part of the inner-potential, which is then fit in the analysis. An additional important benefit of reducing the muffin-tin radius is a decrease in the number of phase shifts required in the LEED computation. The computational time decreases proportionally to the sixth power of the number of phase shifts. The muffin-tin radius should be viewed as an adjustable non-structural parameter in the LEED analysis, and we have found that a muffin-tin radius which excludes the valence charge density results in an improved \( R \)-factor value for other metals (Ni and Rh for example).

3.2.3. Effect of other parameters

In addition, the resulting structure and \( R \)-factor was found to be relatively insensitive to the other non-structural parameters: the Debye temperature \( (\Theta_D) \), the imaginary part of the potential \( (V_0) \), and the muffin-tin statistical exchange coefficient \( (\alpha) \). \( \Theta_D \) and \( V_0 \) were found to be the same as in Ref. [9]. Varying \( \alpha \) within a reasonable range of 0.5 to 0.9 results in only small changes in the \( R_p \)-factor value. The optimal value of 0.72 is similar to that determined in atomic structure computations for Pt [33]. The small effect of this parameter contrasts with findings from work done on the Mo(100) surface [34] but is in agreement with results from the clean Cu(100) and Ag(111) surfaces [35].

Finally, we have examined the influence on the final structure of smoothing the experimental \( I-V \) curves. The effect of smoothing was quantified by examining the resulting error bars given by Pendry’s method [18]. Because Pendry’s method depends both on the overall \( R \)-factor and on \( R \)-factor sensitivity to variation of the coordinate, an optimal amount of smoothing can be found by minimizing the error bar of a coordinate versus the amount of smoothing. As smoothing is increased, experimental noise is removed, thus reducing the overall \( R \)-factor. However, if it is increased until information is lost from the \( I-V \) curves, \( R \)-factor sensitivity to changes in a coordinate will be indirectly decreased. By minimizing the error bars versus amount of smoothing, we can decrease the amount of information lost and lower the final \( R \)-factor. For our experimental clean Pt(111) \( I-V \) curves, we find that one initial three-point smoothing of the experimental \( I-V \) curves on a 2 eV grid followed by one additional smoothing of both the experimental and theoretical \( I-V \) curves, after interpolating onto a common 0.25 eV energy grid, minimizes the \( R_p \)-factor value and maximizes the curvature of the \( R \)-factor versus the first layer distance.

3.3. Conclusions

The identification of the relative importance of various factors in the phase shift computation establishes a foundation which can be applied to different systems. A detailed examination of the scattering potential in our study of this system leads to a large improvement in agreement between theoretical and experimental \( I-V \)
V curves; the agreement represents a 50% improvement over older LEED results [9,10]. In addition, the averaging of spin-dependent phase shifts (as usually practiced) to correctly model the scattering properties is brought into question for the low energy range between 50 and 100 eV for Pt. This limitation of spin-averaged or quasi-relativistic phase shifts for Pt is supported by the excellent agreement in both peak position and height obtained for the clean Ni(111) I–V curves below 100 eV [36]. Unfortunately, fully relativistic LEED analysis has not been applied to intensity-only Pt(111) I–V curves, but only to spin polarization experiments [37]. However, the R-factor improvement for clean Pt(111) using the optimized spin-averaged phase shifts increases our confidence in the resulting clean surface structure and carries over to the analysis of overlayers on this surface.

I–V analysis of the clean surface shows excellent agreement with other experimental results [14-16,10]. We estimate the error bars using Pendry’s method [18]. The first and second interlayer spacings of the clean Pt(111) surface were determined to be 2.29 ± 0.01 Å and 2.27 ± 0.03 Å respectively, with an R_p-factor of 0.15. This corresponds to a 0.025 ± 0.01 Å expansion of the first metal layer spacing of the ideally terminated Pt(111) clean surface. I–V analysis of the I–V curves measured at 300 K gives identical conclusions. Within its error bars, the second interlayer spacing of the Pt clean surface agrees with the bulk value of 2.265 Å. It is plausible that the reorganization of electronic charge density at the surface is such that it is energetically more favorable to weaken the interlayer bonding in order to strengthen the intralayer bonding. If this is true, then it is quite possible that this would lead to both an expansion of the interlayer distance and an increase in surface stress. An examination of the computed surface stresses of the Ir(111), Pt(111) and Au(111) surfaces shows they are much greater than those of the equivalent 3d metals [38], which have a small contraction of the first interlayer spacing. The same surface forces which are also believed to cause the high temperature reconstruction of the Pt(111) surface [38,39] seen with X-ray diffraction [40] and scanning tunneling microscopy [41], may explain the anomalous expansion of the clean Pt(111) surface.

4. Pt(111)-p(2×2)-O: reliability of the structural fit

In this section, the structural results of the Pt(111)-p(2×2)-O system will be discussed. First we describe the computational details of the LEED calculations. This will be followed by a description of a coarse search over the high symmetry adsorption sites using both TLEED and conventional methods. Next, the surface relaxations of the first two metal layers for the best model found in the coarse search determined with three different schemes (a regular grid search, an automated search, and a direct method) will be compared. Optimization of non-structural parameters relating to the O/Pt(111) system will be discussed in Section 5.

4.1. LEED computations

The dynamical LEED computation used in the LEED analysis of the Pt(111)-p(2×2)-O structure divided the crystal, as in the case of clean Pt(111), into a semi-infinite stack of layers. A dynamical LEED calculation for a geometry, consisting of non-buckled layers, typically requires approximately one half hour of CPU time on a workstation (IBM RISC 6000). Search methods which require a dynamical LEED computation for each trial geometry, referred to as the conventional method, are computationally efficient enough to search over geometries which only vary interlayer spacings; such methods were used to fit the interlayer spacing for the O and the first two Pt layers for different high symmetry adsorption sites. Using conventional methods to exhaustively search for relaxations that break the symmetry of a layer, such as buckling, would be prohibitively time-consuming. If a trial geometry contains such a relaxation, the typical time required is 4–5 h of CPU time on a workstation (IBM RISC 6000) due to the Beeby matrix inversion method used to compute the scattering properties of a buckled layer.

The first search scheme among our different approaches used TLEED to explore relaxations on a regular grid of displacement values. The second scheme combined TLEED with an automated optimization algorithm, as described elsewhere [1]. The third scheme used a direct method based on TLEED in which a system of non-linear equations was solved iteratively for displacement parameters [3,4]. The TLEED approx-
imation was explained in Section 3.1, and additional information on the non-structural parameters and their effects on the resulting structure can be found in Section 5. Briefly, all analyses in this section used the same Pt and O phase shifts, computed utilizing the methods previously outlined for the clean Pt(111) surface (see Section 5 for more details). A Debye temperature of 230 K was used for the Pt atoms \((\gamma^2 = 0.01 \text{ Å}^2)\), implying a Debye temperature of 800 K for the O atoms, in order to match the vibrational amplitude of the O atoms to that of the Pt surface. The first and third search schemes used an imaginary potential of \(-6 \text{ eV}\) and 11 phase shifts, while the second used \(-5 \text{ eV}\) and 9 phase shifts. The first and third schemes used layer doubling with up to 200 beams to compute the total reflectivity of the surface. A 3 eV grid was used for calculating the theoretical \(I-V\) curves. Both the experimental and theoretical \(I-V\) curves were interpolated onto a 0.5 eV grid. The second search scheme used up to 200 beams between layers stacked by RFS. Theoretical \(I-V\) curves for this scheme were computed on a 4 eV grid and interpolated onto a 0.25 eV grid along with symmetry-averaged experimental \(I-V\) curves. Error bars for the first and second search schemes were estimated using Pendry’s method [18].

### 4.2. Results

The Pt(111)-p(2×2)-O system has been well studied using other techniques [6–8]. High resolution electron energy loss spectroscopy (HREELS) [6] of the p(2×2) overlayer shows only one vibrational peak corresponding to the O-Pt vibration. In addition, results from transmission channeling of protons through the crystal detected by a nuclear reaction with the adsorbed O support both the fcc site adsorption and 0.25 ML coverage [6]. Detailed relaxations of the metal surface due to O adsorption have not been reported. Given only one O atom in the p(2×2) unit cell, four high symmetry adsorption sites are possible: top, bridge, fcc-hollow and hcp-hollow.

We determined the adsorption site by a conventional analysis and a TLEED analysis coupled with an automated search algorithm, both restricted to the high symmetry sites. The conventional analysis, using all 14 non-equivalent experimental \(I-V\) curves from 30 to 350 eV, i.e. a 3355 eV total energy range, optimized O heights and the first two interlayer spacings on a regular grid for each model. The \(R_p\) factors obtained for each adsorption site are shown in Table 4 under the heading “Conventional.” In the analysis using TLEED combined with an automated search algorithm an energy range of 30 to 260 eV, i.e. a 2579 eV total energy range, was used for the fcc-, hcp- and top-site models. For the bridge-site model the initial TLEED search was restricted to the (1,0), (0,1), (1,1), (1/2,0), (0,1/2) and (1/2,1/2) beams giving an energy range of 100 to 250 eV for a total range of 882 eV. These beams have the lowest experimental noise and the largest total energy range. For each high symmetry site, automated searches were carried out over trial geometries with varying degrees of free-

### Table 4

<table>
<thead>
<tr>
<th>Site</th>
<th>Bulk</th>
<th>Planar</th>
<th>Buckled</th>
<th>Conventional</th>
</tr>
</thead>
<tbody>
<tr>
<td>fcc-hollow</td>
<td>0.40</td>
<td>0.40</td>
<td>0.19</td>
<td>0.49</td>
</tr>
<tr>
<td>hcp-hollow</td>
<td>0.58</td>
<td>0.54</td>
<td>0.48</td>
<td>0.75</td>
</tr>
<tr>
<td>top</td>
<td>0.66</td>
<td>0.65</td>
<td>0.57</td>
<td>0.64</td>
</tr>
<tr>
<td>bridge</td>
<td>0.55</td>
<td>0.50</td>
<td>0.45</td>
<td>0.68</td>
</tr>
</tbody>
</table>

The "Bulk" heading refers to automated TLEED searches (scheme 2) in which only the O height above the ideally terminated substrate was varied. "Planar" refers to additional automated TLEED searches (scheme 2) which varied only vertical displacements of the O and the two metal layers. "Buckled" refers to all vertical relaxations in the first two metal layers allowed by the local symmetry of the site and determined by automated TLEED searches (scheme 2). Finally, “Conventional” refers to a grid search that allowed only vertical displacements of the O and the two metal layers by conventional LEED methods. “Conventional” is similar to “Planar”, but using a search grid and a larger experimental data base.

![Fig. 5. Top(a) and side(b) views of the Pt(111)-p(2×2)-O structure. Geometrical parameters are labeled. The parameter which characterizes the second layer lateral expansion of the triangle of three metal atoms directly below the O (R2) is not shown.](image-url)
dom (see Table 4 and Fig. 5). The fcc-hollow site model clearly yields the best fit to the experimental data. Fig. 6 illustrates the improvements in the $I-V$ curves of the fcc-hollow site model with increasing degrees of freedom. The resulting $R_p$-factors for the other sites were obtained from structures which have large, possibly unrealistic displacements from the reference structures. Due to the growing inaccuracy of the TLEED approximation for larger displacements, the $R_p$-factor does not reflect the true $R_p$-factor value of the resulting structure. For example, the bridge site model has an $R_p$-factor of 0.45 with a large and unrealistic upward displacement of the O atom of 1.6 Å. In this case, a final $R_p$-factor value for the bridge site of 0.55 is obtained when the first two metal layers are allowed to relax and the O atom is kept fixed at a reasonable distance above the surface.

In both coarse analyses, Pendry's method [18] was used to rule out all sites other than the fcc-hollow. Note that buckling of the metal layers, which is responsible for the considerably lower $R_p$-factors of the TLEED analysis, was not needed to differentiate between the various possible adsorption sites. Using the best-fit fcc-site structure obtained by the conventional analysis, the normal incidence of the experimental data was verified by computing the $R_p$-factor values for an incident angle up to 1.0° from normal in the mirror plane. The lowest $R_p$-factor was obtained for normal incidence and varied by 0.1 over the whole range of angles.

The structure resulting from the initial analysis was used as a starting point for further refinement using the three different schemes. The automated TLEED method (scheme 2) iterated the structural search starting from new reference structures until the resulting structure was within a 0.01 Å radius of the last reference structure, thus eliminating any error caused by the TLEED approximation. We find that iteration, and thus recomputation of the reference structure, is imperative to minimize the errors induced by the TLEED approximation, since they can affect the final structure. Two iterations involving two new reference structures were required to obtain convergence within 0.01 Å. The maximum difference between the initial and final structures after two iterations was 0.02 Å in the second interlayer spacing. The TLEED approximation coupled with a grid search (scheme 1) yielded consistent results. In this analysis the whole available experimental data set up to 250 eV was used. A similar structure was obtained by the direct method (scheme 3) using the energy range from 30 to 250 eV. Deviations in the results from the different schemes are restricted to below 0.02 Å for layer distances and 0.06 Å for lateral distances, which the $R_p$-factor was less sensitive to due to normal incidence data. All parameters, illus-
trated in Fig. 5, were always within the error margins.

The three schemes involved searches using models with varying degrees of relaxation. The model (see Fig. 5) which contains only relaxations consistent with the three-fold rotational axis and the mirror plane symmetry (p3m1) of the fcc-hollow site was examined first. Other structural models, in which either the mirror plane was broken by allowing the triangle of three Pt atoms bonded to the O atom to rotate in-plane (p3-symmetry) or the rotational symmetry was broken by allowing two of three Pt atoms bonded to the O atom to move together and the third separately, were considered. Symmetry in the LEED pattern is regained by averaging beam intensities over the resulting domains. The small decrease in the \( R_p \)-factor value with an increasing number of parameters does not allow one to distinguish between these three different models.

The best-fit fcc-hollow site structure with lateral relaxations and p3m1 symmetry determined by the automated search (scheme 1) has the same number of parameters as does the grid-refined structure (scheme 2). A quantitative comparision of the resulting features shows similar adsorbate-induced relaxations of the metal surface. In both structures, there is an expansion followed by a contraction of the metal–metal interlayer spacings (defined as the distance between the centers of mass of two layers). The buckling of the first and second metal layers does not agree as well, although both structures show the same trend, and the displacements are within the stated error bars. It is important to remember that these structures were obtained using not only different amounts of experimental data and different computational parameters, but also dissimilar search schemes. The agreement of lateral displacements is also good. Comparing the \( R \)-factors of two structures obtained by relaxing the mirror plane and restricting the search to vertical displacements only, shows that the vertical displacements are relatively insensitive to the lateral displacements. Due to the normal incidence of the LEED data, it is difficult to distinguish between models which differ only by lateral displacements. This difficulty is evident in the maximum variance of 0.02 between the \( R_p \)-factor values obtained with the three different levels of relaxation, as well as in the large error bars for the lateral displacements. Fig. 7 shows the differences between the plots of the \( R_p \)-factor versus coordinate obtained by scheme 1 and 2 for the first metal–metal interlayer spacing and the lateral expansion of the triangle of three Pt atoms directly below the O.

4.3. Conclusions

Detailed LEED analyses of the Pt(111)-p(2×2)-O system carried out with different search schemes arrive at a similar final structure. Three different degrees of freedom ranging from no lateral displacements to displacements which break the rotational symmetry have insignificantly different \( R_p \)-factor values. For the final structure, we have chosen to accept a model containing lateral displacements consistent with the three-fold rotational axis and the mirror plane symmetry (p3m1) of the fcc-hollow site. The reliability of our relaxed fcc-site model for the Pt(111)-p(2×2)-O system is illustrated through its reproducibility using three different schemes of structural analysis. Reliability is also assessed by the assignment of error bars. Differences between the fcc-site structures obtained by these LEED analyses are consistent within error bars obtained by Pendry’s method [18].

5. Pt(111)-p(2×2)-O: non-structural parameters

In the structural analysis, we assumed that non-structural parameters have little effect on the resulting structure, as in the case of the clean Pt(111) surface. In this section, we will examine the effects of various non-structural parameters on the best-fit structure found by the three optimization schemes. We will investigate the changes caused by both muffin-tin potential and relativistic effects in the phase shift computation. In addition, changes in the final structure caused by both varying the total energy range and the ratio of fractional and integer order beams in the experimental \( I-V \) curves used in the \( R \)-factor computation will be examined. Finally, the effects of smoothing on both the structure and the error bars will be discussed. In this way, we will quantify the effects on the structure due to the non-structural parameters.

5.1. Phase shifts and the muffin-tin potential

The phase shifts used in the three structural optimization schemes were obtained using standard procedures [17]. To examine the effect of the phase shifts
on the resulting structure, additional phase shifts were computed using a muffin-tin potential computed from a slab. In this slab, the atomic O potential was arranged in a \( p(2 \times 2) \) overlayer and then placed on top of two \((1 \times 1)\) Pt layers. The muffin-tin potential was computed and the zero of this potential was adjusted to match the value found from an fcc Pt crystal. The muffin-tin zero of this slab was then offset to match the value obtained using a Pt fcc crystal and the muffin-tin radius of the O atom was chosen so the potential at this radius was the same as that at the Pt muffin-tin radius. The Pt phase shifts computed in this way were found to be almost identical to the phase shifts obtained from the bulk crystal and were virtually layer independent. It is possible that the reduction of the Pt muffin-tin radius to 0.95 Å is responsible for the insensitivity of the Pt phase shifts to the surrounding environment.

LEED computations for the Pt(111)-p(2x2)-O system were carried out to examine the effects of the muffin-tin radii of the O and Pt atoms used in the phase shift calculations on both the resulting structures and \( R \)-factor values. Using the \((1,0), (0,1), (1,1), (1/2,0), (0,1/2)\) and \((1/2,1/2)\) beams from 100 to 250 eV, which are found experimentally to have the highest signal-to-noise ratio, we find that a Pt muffin-tin radius of 0.95 Å gives an optimal \( R_p \)-factor. The O muffin-tin radius of 0.66 Å was chosen so that the potential at this radius was identical to that at the Pt muffin-tin radius. Adjustment of the O muffin-tin radius independently of the Pt muffin-tin radius was found to have little effect on the optimal \( R_p \)-factor. In addition, varying the Pt muffin-tin radius from 0.95 to 1.38 Å and the O radius from 0.50 to 0.90 Å had little influence on the resulting structure. The best-fit Pt muffin-tin radius and the reduction of 0.02 in the overall \( R_p \)-factor is in agreement with the result found for clean Pt(111). However, the lower sensitivity of the \( R_p \)-factor to the muffin-tin radius, as compared to the clean surface, is most likely due to greater experimental noise. If the optimization is repeated using all available experimental beams, one finds very little change in the \( R_p \)-factor value. However, the reduction of the Pt muffin-tin radius greatly reduces the number of phase shifts required in the LEED computation. We find that it is possible to generate theoretical \( I-V \) curves up to 350 eV using only nine phase shifts \((l_{\text{max}} = 8)\) with a great reduction in the amount of computer time. Using touching spheres, i.e. a muffin-tin radius of 1.38 Å for Pt, eleven phase shifts were required at 350 eV.

The inclusion of relativistic effects in the phase shift calculation has interesting consequences for the Pt(111)-p(2x2)-O system. When relativistic effects are included, the O phase shifts are not affected, due to
Table 5

Error bars computed using Pendry's method [18] with either the fractional, integer, or both beam sets (notice the low sensitivity of the integer order beams to the surface buckling); the geometrical parameters are illustrated in Fig. 5.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Error bars</th>
<th>$R_p$-both</th>
<th>$R_p$-fractional</th>
<th>$R_p$-integer</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{11}$</td>
<td>±0.02</td>
<td>±0.02</td>
<td>±0.05</td>
<td></td>
</tr>
<tr>
<td>$D_{12}$</td>
<td>±0.02</td>
<td>±0.02</td>
<td>±0.02</td>
<td></td>
</tr>
<tr>
<td>$D_{23}$</td>
<td>±0.03</td>
<td>±0.03</td>
<td>±0.03</td>
<td></td>
</tr>
<tr>
<td>$B_1$</td>
<td>±0.03</td>
<td>±0.03</td>
<td>&gt; ±0.1</td>
<td></td>
</tr>
<tr>
<td>$B_2$</td>
<td>±0.04</td>
<td>±0.04</td>
<td>&gt; ±0.1</td>
<td></td>
</tr>
<tr>
<td>$R_1$</td>
<td>±0.03</td>
<td>±0.03</td>
<td>&gt; ±0.1</td>
<td></td>
</tr>
<tr>
<td>$R_2$</td>
<td>±0.04</td>
<td>±0.04</td>
<td>&gt; ±0.1</td>
<td></td>
</tr>
</tbody>
</table>

the low atomic number of O, while the Pt phase shifts are shifted upward as explained in Section 3. Thus, the O position changes in order to compensate for the changing Pt phase shifts. We find that the O height is increased by 0.04 Å. Although the surface buckling and the interlayer spacing for the metal are only affected to a small degree, this represents a large systematic error. Correct inclusion of relativistic effects is necessary in the case of a light element adsorbed on a relativistic metal surface.

5.2. Additional factors

In determining the relaxation of the surface, an important parameter is the energy range ratio of the fractional order beams to the integer order beams. This importance is due to the greater sensitivity of fractional order beams to the surface relaxation than the integer order beams. This sensitivity is clearly illustrated in Table 5. Shown in this table are the error bars computed with Pendry’s method [18] for both the integer and fractional, only the integer, or only the fractional order beams. The large differences in the error bars shown in Table 5 are a direct result of the buckled atoms’ contributions to the intensities of fractional order beams. By comparing the $I-V$ curves of the non-relaxed model with those of the buckled model (Fig. 6), one can clearly see the improvement of the fractional order beams, particularly in the higher energy region. The stronger scattering power of the buckled Pt atoms with respect to that of the O atom results in increased intensity in the fractional order beams relative to that which would normally be expected from just the O atoms alone.

In addition to the importance of the ratio of fractional versus integer order beams, we find that the resulting structure is relatively insensitive to the addition of higher order beams. The structure obtained using the (1,0), (0,1), (1,1), (1/2,0), (0,1/2) and (1/2,1/2) beams is virtually identical to the structure obtained by using all 14 nonequivalent beams, even though the energy range in increased threefold. Also, error bars assigned with Pendry’s method [18] are directly dependent on the curvature of the plot of $R_p$-factor versus coordinate and inversely dependent on the square root of the cumulative energy range. Because of this, our error bars, obtained with Pendry’s method, proved insensitive to the addition of relatively noisy higher order beams. This observation supports the value of using a high quality experimental data set in the structural search, as opposed to a larger set that includes regions of greater experimental uncertainty.

As a last refinement we optimized the imaginary part of the inner potential and the surface Debye temperature of the Pt and O atoms using all 14 experimental beams from 30 to 350 eV. The optimal Debye temperature for the Pt atom was found to be the same as the value for the clean surface. For the O atom, we find a small improvement in the overall $R$-factor by reducing the Debye temperature by a factor of 2, which corresponds to vibration amplitude of 0.04 Å² or about 4 times greater than the an ms amplitude found for the Pt atoms. The optimal imaginary part of the inner potential was found to be −5.5 eV. However, these refinements resulted in very little (less than 0.01 Å) change in the final structure.

5.3. The final structure

The final structure obtained after including these non-structural refinements has O atoms adsorbed in fcc-hollow sites. Details of this final structure can be found in Table 6, and a comparison of final theoretical and experimental $I-V$ curves in Fig. 8. We find the O atom induces a buckling (see Fig. 5 for the relative displacements of the metal atoms within the layer) of 0.07±0.03 Å and 0.10±0.04 Å in the first and second metal layers, respectively. In addition, oxygen induces a probable expansion of 0.01 Å in the first metal–metal interlayer spacing and a possible small contraction of 0.02 Å in the second. A metal–oxygen bond length
of 2.02 Å was found. Lateral displacements consistent with the three-fold rotational and mirror plane symmetries yield a possible small lateral expansion of the triangle of three metal atoms directly bonded to the O. This expansion is within error bars of the bulk positions.

5.4. Conclusions

We have examined the effect of various non-structural parameters on the best-fit Pt(111)-p(2×2)-O structure. We find that details in the construction of the muffin-tin potential generated from a slab computation do not influence the resulting structure. Although the construction of the muffin-tin potential does not influence the structure markedly, we find that one must use the correct relativistic treatment of the phase shifts in the case of a light element on a relativistic or high Z metal surface. Failure to do so will result in a systematic increase in the overlayer's bond length to the metal surface. Finally, we find that the Debye temperature has little effect and the experimental beam selection is more important than the total energy range.

6. General conclusions

LEED I–V analyses of the clean Pt(111) surface show excellent structural agreement with earlier experimental results [9,10,14–16]. A detailed study of the scattering potential led to a large improvement in agreement between theoretical and experimental I–V
curves as compared to previous LEED studies [9,10] and correspondingly a considerable reduction of the error bars. The first and second interlayer spacings of the Pt(111) clean surface were determined to be 2.29 ± 0.01 Å and 2.27 ± 0.03 Å respectively, with an R_p-factor of 0.15. This corresponds to a 0.025±0.01 Å expansion of the first metal interlayer spacing of the ideally terminated Pt(111) clean surface. Within its error bars, the second interlayer spacing of the clean Pt surface agrees with the bulk value of 2.265 Å. Due to the general trend of contraction for clean metal surfaces, the question remains as to the cause of this expansion. Possibly, the lateral surface stress is offset by increased electron density or bonding between surface atoms, leading to a weakening of interlayer bonding and therefore an expansion. In addition, the use of spin-averaged phase shifts to model the scattering properties is in question for the low energy range between 50 to 100 eV. Because of this, the energy range between 50 to 100 eV was not used in the final structural analysis. The limitation of using spin-averaged phase shifts for Pt is supported by the excellent agreement in both peak position and height for the clean Ni(111) J–V curves [36]. The R-factor improvement for clean Pt(111) using the optimized spin-averaged phase shifts carries over to the analysis of O on this surface.

Detailed LEED analyses of the Pt(111)-p(2x2)-O system, carried out by different search methods, arrive at a similar final structure. An R_p-factor of 0.18 was obtained for the final structure. In this structure, O atoms adsorb in fcc-hollow sites and induce a buckling (again, see Fig. 5 for the relative displacements of the metal atoms within the layer) of 0.07 ± 0.03 Å and 0.10 ± 0.04 Å in both the first and second metal layers, respectively. In addition, there is a probable expansion of 0.01 Å in the first metal–metal interlayer spacing and possibly a small contraction of 0.02 Å in the second. A metal–oxygen bond length of 2.02 Å was found. Lateral displacements, including symmetry-breaking features, were found to be within error bars, however we do find a small lateral expansion of the triangle of three Pt atoms directly below the O. The fractional order beams proved to have much greater sensitivity to the surface relaxation than the integer order beams. In addition, relativistic phase shifts for the Pt(111)-p(2x2)-O structure were found to have important influences on the resulting metal–oxygen bond.

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