LEED STUDIES OF ADSORBATE-INDUCED
RECONSTRUCTION OF METAL SURFACES

by

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We accept this thesis as conforming
to the required standard

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Date September 17, 1993
Abstract

Using the technique of low-energy electron diffraction (LEED), the structures of three systems have been investigated, where small, electronegative atoms chemisorb and induce reconstruction at a metal surface; these surfaces are designated Ni(111)-(2x2)-O, Cu(110)-(2x3)-N, and Pd(100)-(\(\sqrt{5}\times\sqrt{5}\))R27°-O. In each case, experimental data consist of a set of intensity-versus-energy (I(E)) curves measured at normal incidence with a video LEED analyser. Multiple-scattering calculations were done for a number of proposed models of the surface structure, and comparisons were made between calculated and experimental I(E) curves. The objective in a LEED analysis is to find the geometry in the calculations which leads to the best match between the two sets of intensity curves. Reliability indices are used to quantify the level of correspondence between experiment and theory; a lower R-value indicates better agreement, and consequently the model is more likely to be correct. Two basic reliability indices were used in this work, and they are the modified Zanazzi-Jona R-factor and the Pendry R-factor. In addition to the more conventional LEED analysis, the recently-developed tensor LEED/directed search (TLEED) method was also used in the analyses of the N/Cu and O/Pd surfaces. As well as determining surface structure, this work has the further objective of using the details identified to develop some principles of surface structural chemistry and to relate these principles to the broader framework of structural chemistry.

For the Ni(111)-(2x2)-O structure, oxygen atoms chemisorb on 3-fold hollow sites which continue the fcc stacking of the nickel substrate. Top-layer Ni atoms which are bonding to O atoms are displaced both vertically toward (by 0.12 Å) and laterally away from (by 0.07 Å in a rotated manner) the O atoms, while those Ni atoms not bonding to O are displaced vertically toward the bulk. The determined surface O-Ni bond length of 1.83 Å agrees closely with the predicted value of 1.82 Å for 3-coordinate O on Ni, and the surface relaxations have been confirmed in a subsequent study with SEXAFS.
Nitrogen, activated by an ion gun, chemisorbs on the Cu(110) surface to form Cu(110)-(2x3)-N. Many techniques have been applied to study this surface, but little consensus exists as to its structure. Even structural conclusions from the present LEED analysis have been revised as new information, as well as TLEED program codes, became available. Currently, TLEED appears to favour a reconstruction in which the topmost layer is a pseudo-(100)-c(2x2)-N overlayer with substantial corrugation in the top two copper layers. Large lateral displacements of both N atoms in the overlayer and Cu atoms in the topmost Cu(110) layer result in a total of three 5-coordinate adsorption sites per unit mesh (as compared to one when no lateral relaxations are allowed). Average N-Cu bond lengths for the 5-coordinate sites (1.85 Å) agree well with prediction based on the structure of bulk Cu$_3$N, while the bond lengths for the 4-coordinate sites (1.94 Å) appear rather long. Very recently published STM images seem to suggest that nitrogen chemisorbs first on the 5-coordinate sites, before occupying the less favourable 4-coordinate sites, and that opens the possibility that the 4-coordinate sites may be only partly occupied under the experimental conditions of this work.

The Pd(100)-(\sqrt{5}x\sqrt{5})R27°-O surface is formed on extended O-dosing with the sample temperature at greater than about 550 K. A tensor LEED analysis of 15 independent beams supports a surface oxide model, as first postulated in outline by Orent and Bader. The detailed model which gives the best correspondence with experimental intensity data has a PdO(001) overlayer stacked onto the Pd(100) surface such that rumpling is induced in both the oxide and top two Pd(100) layers. The average O-Pd bond length for 2-coordinate O on the Pd surface (1.73 Å) is close to the predicted value of 1.76 Å based on the structure of bulk PdO. This analysis in particular highlights the potential advantages of the TLEED approach in opening up LEED crystallography for determining a wider range of surface structures than has typically been the case until now.
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The period during which the work in this thesis was performed has been a most educational one for me. I would like to thank my research advisor, Professor K.A.R. Mitchell, for directing me toward challenging surface structural problems and for his very careful reading of this thesis.

I thank Dr. H.C. Zeng and Ms. Y.K. Wu for introducing me to the LEED calculations, Prof. M.Y. Zhou for introducing me to the LEED experiment, and Mr. S.R. Parkin for providing the Cu(110) sample; I also acknowledge Ms. Wu for making LEED intensity measurements used in the analysis of the O/Ni system. I have greatly appreciated my interactions with Dr. Uwe Hess, Dr. J.R. Lou and Mr. Wei Liu and acknowledge in addition Mr. K.C. Wong and Dr. P.C. Wong among the other members of our surface science group.

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Dedication

Throughout this work, as throughout life, my family has been an invaluable source of support for me, always spiritually and sometimes financially. I thank all of my brothers and sisters for their unfailing belief in me, but one brother especially has had the greatest impact on my research for providing the computing resources for a significant portion of the tensor LEED calculations. To Anh Phuoc and to my parents, I lovingly dedicate this thesis.
1.1 Surface science and surface structure

A surface represents the transition region between a bulk material and the external environment. Whereas bulk atoms are surrounded on all sides by neighbours, surface atoms are surrounded by neighbours only on one side and thus have unsatisfied bonding capacity. As a result, surface free energy is higher than that of the bulk, and surface atoms experience a strong driving force to lower this energy either by bonding with foreign atoms, such as those from the gas phase, or by rearranging or reconstructing to increase their coordination number.

Surface science studies this region, which includes not only the topmost atomic layer, but also all those layers near the surface which may be involved in the reconstruction or reaction and which may be probed by a particular experimental method. Rapid progress in this field in the last thirty years has been due both to instrumental and theoretical improvements in the traditional methods, as well as the development of new techniques for revealing the structure and chemical composition of surfaces on an atomic scale. Information gained from fundamental surface structural studies provides the basis for the development of the theoretical framework for surface structural principles, which, when well established, can help increase understanding in a range of diverse fields of technological importance, including heterogeneous catalysis, corrosion, adhesion, and microelectronics. In particular, the connection should become better understood between studies of well-defined, single-crystal surfaces under ultrahigh vacuum (UHV) and those of "real" systems such as in high-pressure, metal-on-support catalytic chambers.

Of the many techniques now available to study surface structure (Table 1.1), low-energy electron diffraction (LEED) is the most developed surface crystallographic technique, and results from LEED studies are often used to test the accuracy of other
Table 1.1  A selection of surface science techniques which have been applied to study the three systems investigated in this thesis.

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techniques. LEED is possible because of the wave-particle nature of the electron, an idea first proposed by de Broglie in 1924. Diffraction by electrons impinging on a solid was first observed by Davisson and Germer in 1927, but not until the 1960s, with advances made in UHV technology, did LEED become widely adopted as a surface characterization technique. With theoretical development from around 1970 onwards, LEED has become an ideal tool for studying the location of atoms on the surface because of its strong dependence on the electron ion cores and its low sensitivity to the specific surface electron wave functions, unlike other techniques such as photoemission and scanning tunneling microscopy, which are sensitive to the electronic properties of the surface. Initially, LEED studies have concentrated more on low-Miller-index unreconstructed surfaces of metallic single crystals, but with the advent of faster and more sensitive measuring devices, as well as approximative calculation schemes, LEED is now being increasingly applied to study more complicated systems such as those involving surface reconstruction, disordered chemisorption, alloyed surfaces, et cetera.

1.2 Low-energy electron diffraction (LEED)

1.2.1 General principles

The LEED analysis is, at least in principle, simple. A beam of low-energy electrons is aimed at a single-crystal surface of known crystallographic orientation. Elastically back-scattered electrons are displayed on a fluorescent screen and form a diffraction (LEED) pattern if the surface is sufficiently well ordered. Diffraction occurs because at typical LEED energies of 30 to 300 eV, the wavelengths of these electrons

$$\lambda (\text{Å}) = \frac{h}{p} = \sqrt{\frac{150.4}{E \text{ (eV)}}}$$  \hspace{1cm} (1.1)
are comparable to the lattice spacings in most materials (h is Planck's constant, and p is the magnitude of the electron momentum). The LEED pattern gives information with respect to the size and shape of the unit mesh for the surface region probed by the LEED electrons. But in order to determine atomic positions, the intensities of the diffracted beams must be analyzed. It is most common to measure the intensity as a function of the incident electron energy to give intensity-versus-energy or I(E) curves. Based on a number of chemically plausible models of the surface, theoretical I(E) curves are also calculated and then compared to experimental data. Reliability- or R-factors are used as a quantitative and objective measure of the agreement between experimental and calculated I(E) curves; the lower the R-value, the better the agreement, hence, the more likely the model is to be correct.

The very factors that make LEED a surface sensitive technique also make it more difficult in practice than in principle. Strong inelastic scattering of low-energy electrons inside the target material limits the mean free path of the incident beam to the order of a few atomic layers, and this typically reduces the intensity of elastically back-scattered electrons to less than 2% of the incident beam current. The strong interaction between low-energy electrons and the surface complicates the LEED theory compared with that for X-ray (or neutron) diffraction. Before escaping the surface and being detected, low-energy electrons will often have been elastically scattered several times by the ion cores. The positions of spots in a diffraction pattern are determined by symmetry, but the distribution of intensity among different beams is affected by multiple scattering, and exact theoretical reproduction of experimental I(E) curves cannot generally be achieved without taking account of this effect. Furthermore, because of multiple scattering, LEED is traditionally forced to work by the trial-and-error approach of testing "reasonable" models of surface structure; even when the field is narrowed to only a few models, an exhaustive search over parameter space of atomic positions for each model can still have large
demands on computing time. Finally, R-factors must be used with caution, especially when the system being studied is complicated and no bulk structure exists to serve as a guide in predicting the surface structure. One problem is that R-factors can have local minima within parameter space, but the objective is always to find the global minimum. In addition, the choice of which R-factor to use can itself present a problem, there being no consensus as to which is the most effective LEED reliability index, particularly for analyzing completely unknown and complex surface structures.

The first step in a LEED analysis is the interpretation of the diffraction pattern in terms of the unit mesh basis vectors. The positions of spots on the screen, i.e., the direction of interference maxima, is determined by the 2-dimensional Laue conditions

\[(k_d - k_i) \cdot s_1 = \text{integer} \times 2\pi \]  \hspace{1cm} (1.2)

and

\[(k_d - k_i) \cdot s_2 = \text{integer} \times 2\pi \]  \hspace{1cm} (1.3)

where \(k_i\) and \(k_d\) are the wavevectors of the incident and diffracted beams, respectively, and \(s_1\) and \(s_2\) are the basis vectors describing the surface unit mesh. The condition of elastic scattering is satisfied when the magnitude of the wavevectors \(k_d = k_i = 2\pi/\lambda\). For a given incident beam energy and direction, an increase in the magnitude of the surface unit vectors will cause the differences in the diffracted beam directions to get smaller; in other words, the spots on the screen will appear closer together. A \((1\times1)\) LEED pattern results when the unit vectors \(s_1\) and \(s_2\) are the same as the unit vectors \(a_1\) and \(a_2\) of the substrate (i.e., bulk) planes parallel to the surface; that is, \(s_1 = a_1\) and \(s_2 = a_2\). As often happens in the case of chemisorption or reconstruction of the clean surface, the surface basis vectors are related to those of the substrate by \(s_1 = ma_1\) and \(s_2 = na_2\) (with \(m\) and \(n\) integers). The
resulting \((mxn)\) pattern will have extra spots which appear in between those of the \((1x1)\) pattern. Diffracted beams corresponding to the \((1x1)\) pattern are called integral beams, and extra beams in the \((mxn)\) pattern are called fractional (or superstructure) beams. In some cases, the surface basis vectors are rotated relative to the substrate \((1x1)\) vectors by an angle \(\alpha\). The Wood notation\(^{45}\) is commonly used to describe such a surface and hence the accompanying LEED pattern:

\[
S(hkl)-i(mxn)Ra-riA,
\]

where \(S\) and \(A\) are respectively the chemical symbols of the substrate and adsorbate, \((hkl)\) are the Miller indices describing the crystallographic orientation of the surface, \((mxn)Ra\) relates the size and orientation of the surface unit vectors to those of the substrate, \(\eta\) gives the number of adsorbed atoms in the surface unit mesh, and \(i\) is either \(p\) for primitive or \(c\) for centered. For primitive unit cells, the "\(p\)" is often omitted. Figure 1.1 illustrates these points for the three surface structures investigated in this work.

While the LEED pattern results from the diperiodicity of the surface region, the intensity of the diffracted beams depends strongly on the periodicity normal to the surface.\(^{46}\) In the single-scattering limit (\(e.g.,\) for X-ray diffraction where kinematic theory holds),\(^{47}\) intensity in a direction determined by Eqs. (1.2) and (1.3) is maximized when the third Laue condition

\[
(k_d - k_i) \cdot s_3 = \text{integer} \times 2\pi \tag{1.4}
\]

is satisfied; \(s_3\) is the basis vector normal to the surface, defined in this work as \(+x\) in the direction of the bulk. For the \((0 0)\) beam at normal incidence, primary Bragg peaks are expected when
Figure 1.1 Schematic diagrams of the real surface (left) and diffraction pattern (right) for the three surface structures investigated in this thesis. For the real surface, large open circles represent the substrate atoms, while small filled circles represent adsorbed atoms; dark and light arrows give, respectively, the substrate and surface unit vectors. In the diffraction patterns, filled circles correspond to integral beams from the clean surface, with additional fractional beams (open circles) for the chemisorbed surface. Note that the observed diffraction pattern for the O/Pd surface requires the presence of both domains on the real surface; ⊗ and ○ correspond respectively to diffracted beams from domain A and domain B.
s_3 (Å) = n_3 \lambda = n_3 \sqrt{\frac{150.4}{E (\text{eV})}} \quad (1.5)

In actual LEED experiments, however, intensity maxima are shifted by several volts toward lower energies compared with expectation from Eq. (1.5) alone. This is a manifestation of the lowering in potential which an electron experiences on entering the solid, and it relates to the concept of the inner potential. Corresponsingly, an electron gains kinetic energy inside the crystal so that its wavelength is effectively given by

\[ \lambda_{\text{crystal}} (\text{Å}) = \sqrt{\frac{150.4}{(E - V_0) (\text{eV})}} \quad (1.6) \]

as compared to the wavelength in vacuum as given by Eq. (1.1) (by definition, \( V_0 < 0 \)). In addition, rather than having intensity maxima at sharply defined energies, Bragg peaks are broadened by the uncertainty principle and the limited electron penetration depth, and multiple scattering leads to the appearance in I(E) curves of much secondary Bragg structure, which is not predicted by Eq. (1.5).

1.2.2 Multiple-scattering calculation of LEED intensities

Since the kinematic theory is insufficient for calculating LEED intensity spectra for comparison with experiment, a dynamical theory of diffraction is thus required. Mathematical details of the theory can be found in many references, and only a brief outline of the calculation schemes will be given here. In most LEED calculations, a muffin-tin model of the scattering potential is used, in which a spherically symmetric potential is assumed around each atom and a constant potential is assumed in the interstitial region outside of the spherical regions, which extend from each atomic nucleus to the appropriate muffin-tin radius. The latter are chosen to minimize the constant potential volume for non-overlapping atomic spheres. The real part of the constant
potential, $V_{0r}$, is treated as an adjustable parameter during the structural search, and it approximates to the experimentally-determined inner potential. In addition, the constant potential, $V_0 = V_{0r} + iV_{0i}$, is given an imaginary component ($V_{0i}$) which accounts for the removal of flux from the elastic beam by inelastic processes.

Calculation of LEED intensities (from squared amplitudes) is usually done in three steps (Fig. 1.2), starting with scattering by a single atom, from which the scattering properties of a layer are calculated, and contributions from different layers are then summed to give the total diffraction amplitude scattered by the surface. The spherical symmetry of the ion-core scattering potential favours a procedure whereby a plane wave representing the incident electron beam is decomposed into incoming and outgoing spherical waves, centered on each atom and characterized by angular momentum values $l = 0, 1, 2, \ldots$. For an incident plane wave given by

$$e^{ik \cdot r}$$

(1.7)

the scattered wave has the following asymptotic form

$$e^{ik \cdot r} + t(\theta) \frac{e^{ikr}}{r}$$

(1.8)

where $t(\theta)$ is the scattering amplitude at scattering angle $\theta$ and $r$ is the distance from the atomic nucleus. The scattering amplitude is expanded in Legendre polynomials $P_l$,

$$t(\theta) = \frac{4\pi}{k} \sum_{l} (2l + 1) t_l P_l (\cos \theta)$$

(1.9)

where $t_l$ is a t-matrix element given by
atom scattering
\( \delta_f \)

layer diffraction
\( M(k_g, k_g) \)

surface diffraction
\( A(k_g, k_0) \)

**Figure 1.2** Schematic diagram illustrating the three steps to calculate LEED diffracted intensities in terms of the phase shift \( \delta_f \), layer diffraction matrix \( M \), and scattered amplitudes \( A \); after Ref. 32.
\[ t_l = \text{i}e^{i\delta_l} \sin \delta_l \] (1.10)

Conservation of energy and angular momentum limits the difference between incoming and outgoing waves of the same \( l \) value to a phase factor, and the set of phase shifts \( \delta_l \) calculated for each element (i.e., each atomic potential) accounts fully for the intraatomic scattering. Additionally, thermal effects are included by the use of temperature-dependent phase shifts \( \delta_l(T) \), calculated from multiplying \( t(0) \) by an effective Debye-Waller factor

\[ e^M = \exp \left( -\frac{3(\Delta k)^2 T}{2mk_B \Theta^2} \right) \] (1.11)

where \( T \) and \( \Theta \) are the real and Debye temperatures, \( m \) is the atomic mass, \( k_B \) is Boltzmann's constant, and \( \Delta k = (k - k') \) is the momentum transfer due to diffraction from one plane wave into another.

Spherical waves which have been scattered by one atom can subsequently be multiply scattered by other atoms in the same layer. The scattering matrix of an atomic layer is obtained by combining and then transforming all partial waves into a set of plane waves, or diffracted beams, characterized by wavevectors \( k_g \). The two dimensional periodicity of a layer limits the number of wavevectors that need be considered; only those beams which can reach the next layer play a significant role in the diffraction process.

Although it is possible to calculate exactly the total surface diffraction using only spherical waves by considering the surface as a thick slab consisting of a finite number of sublayers, a more common approach is to stack the single layer diffraction matrices in order to build up the surface slab. In the layer-doubling (LD) scheme, \(^9\) diffraction matrices are calculated exactly for a pair of layers from the diffraction matrices of the
individual layers; diffraction matrices for the pair are then combined to give diffraction from a slab of four layers; each step in the iterative process doubles the thickness of the slab by combining two identical slabs; and layers are stacked in this manner until convergence of reflected intensities is reached. An alternative perturbative method (Renormalized-Forward-Scattering or RFS) is based on the idea that backward diffraction (or reflection) is weak compared to forward diffraction (or transmission). The incident beam is transmitted at each layer until the deepest layer is reached (in the presence of inelastic scattering); waves reflected at each layer are forward diffracted out of the crystal to give the first-order beams; reflection of these first order beams back into and then out of the crystal create second-order beams; and the process is repeated until higher order contributions become negligible, at which point convergence is reached. RFS is the fastest method for stacking layers, but it may fail to converge when interlayer multiple scattering is strong or when the interlayer spacing is small (∼1 Å). LD can be used for interlayer spacings as small as 0.5 Å.

For interlayer spacings less than 0.5 Å, as often occurs for chemisorption of small atoms on the more open metal surfaces, the combined-space method is used. The surface layers where the small interlayer spacings occur are treated as a composite layer consisting of two or more subplanes, each of which contain only one atom per unit mesh. Diffraction properties of the composite layer are calculated in the spherical-wave representation, while stacking of the composite layer onto the substrate is done in the plane-wave representation.

When the rotational symmetry of the surface is lower than that of the substrate, rotationally related domains are to be expected (e.g., for the Pd(100)-(\(\sqrt{5}\times\sqrt{5}\))-R27°-O surface in Fig. 1.1). At normal incidence, it is only necessary to calculate diffracted intensities from one domain, but appropriate averaging of diffracted beams is required to effect a summation of the different patterns from the different domains. The above
procedure assumes that domain sizes are large (compared to the instrumental transfer width) and that different domains are equally populated.\textsuperscript{6} These conditions are satisfied experimentally when a sharp diffraction pattern is observed, which contains fractional beams from all domains.

1.2.3 Structural analysis and reliability indices (R-factors)

The approach of LEED crystallography is to calculate theoretical I(E) curves for different models of the surface, and comparison with experimental I(E) curves is done both visually and with reliability indices to determine the best match (hence, the most likely correct model of the surface). Ideally, R-factors should be more sensitive to structural parameters such as atomic positions, and not so sensitive to nonstructural parameters such as the Debye temperature and $V_{\text{or}}$; in practice, however, $V_{\text{or}}$ must be optimized along with structural parameters. Two R-factors are especially used in this work: one is a modified form of that proposed by Zanazza and Jona ($R_{\text{MZJ}}$)\textsuperscript{44,53} and the other proposed by Pendry ($R_p$).\textsuperscript{54} The latter emphasizes peak positions, weighing all peaks in a spectrum equally; for each beam,

$$R_p = \frac{\int (Y_{\text{exp}} - Y_{\text{calc}})^2 \, dE}{\int Y_{\text{exp}}^2 + Y_{\text{calc}}^2 \, dE}$$  \hspace{1cm} (1.12)

where

$$Y = \frac{L}{(1 + L^2 V_{\text{or}}^2)}$$  \hspace{1cm} (1.13)

and $L$ is the logarithmic derivative of the intensity
\[ L = \frac{d \ln I}{dE} \]  

(1.14)

\( V_{0i} \) is the imaginary part of the constant potential. The original Zanazzi-Jona R-factor \( (R_{ZJ}) \) uses both the first and second order derivatives of intensity (\( I' \) and \( I'' \), respectively) and is designed to account for reproduction not only of peak positions, but also of relative peak intensities. For a single beam,

\[ R_{ZJ} = A_{ZJ} \int \frac{I''_{\text{exp}} - cI''_{\text{calc}}}{I'_{\text{exp}} - cI'_{\text{calc}}} \frac{I'_{\text{exp}}}{I'_{\text{exp}} + \max I'_{\text{exp}}} \, dE \]  

(1.15)

where

\[ A_{ZJ} = \frac{1}{0.027 \int I_{\text{exp}} \, dE} \]  

(1.16)

is a reducing constant chosen so that \( R_{ZJ} \sim 1 \) for uncorrelated curves,\(^{53}\) and

\[ c = \frac{\int I_{\text{exp}} \, dE}{\int I_{\text{calc}} \, dE} \]  

(1.17)

is a normalization constant to account for the different intensity scales between calculated and experimental \( I(E) \) curves. Van Hove and Koestner\(^{44}\) proposed a modified single-beam index, \( R_{MZJ} \), in which \( \max I''_{\text{calc}} \) replaces \( \max I''_{\text{exp}} \) in Eq. (1.15), and the reducing constant is redefined as

\[ A_{MZJ} = \frac{1}{\int I''_{\text{exp}} \, dE} \]  

(1.18)
When comparing I(E) curves for more than one diffracted beam, as in LEED crystallographic applications, Zanazzi and Jona suggested an average R-factor

$$R = \frac{\sum \Delta E^i R^i}{\sum \Delta E^i}$$

(1.19)

whereby individual beam R-values are weighted according to the energy range over which the comparison with experiment has been made. The summation in Eq. (1.19) is over each individual beam (i), and the multibeam index R can refer to either $R_p$ or $R_{MZJ}$.

All reliability indices have been defined so that their values are zero when identical curves are being compared, but often there is no clear meaning for a value when very different curves are compared. This point has been discussed by Van Hove and Koestner, and they proposed a further factor of $\frac{1}{2}$ in the definitions of both $R_p$ and $R_{MZJ}$ to ensure an upper value of $\sim 1$ when anticorrelated curves ($\sin^2 x$ and $\cos^2 x$) are compared. This latter definition has been followed in this work, namely $R_p = \frac{1}{2} R_p$ and $R_{MZJ} = \frac{1}{2} R_{MZJ}$, and a further index used is the average, defined as $R_{av} = \frac{1}{2} (R_p + R_{MZJ})$.

The first step in studying structure for chemisorption on metal surfaces is to determine the adsorption site and the corresponding adsorbate-metal bond lengths. The immediate result is the adsorbate to topmost metal layer spacing, usually with the metal atoms initially in their bulk positions. But work in our laboratory and elsewhere has shown that significant relaxations in the local metallic structure also occur, presumably to optimize the total bonding (adsorbate-metal and metal-metal). Both vertical and lateral displacements of metal atoms from the ideal bulk-terminated positions can create a metal surface layer with two-dimensional unit mesh different from that of the bulk, but the same as that of the chemisorbed overlayer. In some cases, identification of the correct adsorption site requires a gross reconstruction of the substrate so that the atomic density
in the top metal layer (or layers) is different from that of the clean surface. Each step in an analysis attempts to minimize the R-values in a search for the global minimum. The traditional trial-and-error method of LEED crystallography suffers from the uncertainty of whether a local or global minimum has been found at any stage, and this is combined with the large computing demands resulting from the multiple-scattering challenge (diffracted beams are coupled together so that, unlike X-ray diffraction, to calculate the intensity of one beam requires the intensity of all to be determined at the same time). Tensor LEED offers a more efficient, and perhaps more reliable, approach to the structural optimization, and this topic will be discussed in Chapter 2.

1.3 Auger electron spectroscopy (AES)

AES is the primary technique used in LEED experiments for the purpose of chemical identification of atoms in the surface region.\(^9\,10\) When energetic electrons (or electromagnetic radiation) strike atoms on the surface, electron emission can occur, which creates a hole in an inner electron shell. The ionized atoms may then relax to the electronic ground state either by X-ray emission or by Auger electron emission (Fig. 1.3). While the incident beam may ionize atoms deep within the crystal, only Auger electrons from those atoms near the surface can escape and be detected without loss in energy because of the short mean free path for low-energy electrons.\(^55\) Furthermore, the kinetic energy of an Auger electron depends only on the three energy levels involved, which are characteristic of each element. Shifts in Auger peaks may be observed to reflect differences in an atom's chemical environment, but such effects tend to be small in magnitude (a few eV) and usually do not affect the qualitative analysis aspect of AES. Chemical analysis is thus possible by assigning peaks in an Auger spectrum to a particular element with the aid of listed Auger energies.\(^56\,57\)
Figure 1.3  De-excitation processes of atomic core holes; KE is the kinetic energy of the Auger electron.
1.4 Outline

Three systems of increasing complexity were investigated in this thesis, using the combination of LEED and AES. Multiple-scattering calculations were done with the computer programs of Van Hove and Tong, as detailed in their book.\textsuperscript{48} Additionally, tensor LEED calculations used programs provided by Barbieri and coworkers;\textsuperscript{58-60} the tensor LEED approximation will be discussed in Chapter 2. Chapter 3 describes the general experimental methods employed. Chapter 4 gives results from the simplest surface studied, that formed by the chemisorption of oxygen on the (111) surface of nickel to give Ni(111)-(2x2)-O. Chapters 5 and 6 discuss structural features of the Cu(110)-(2x3)-N and Pd(100)-(\textit{\sqrt{5}x\sqrt{5}})R27°-O surfaces, respectively. In all cases, structural results were compared to those from other surface science techniques, in particular those listed in Table 1.1, and discrepancies were addressed. Finally, Chapter 7 reviews the current status of LEED crystallography and suggests directions for future research.
2.1 Introduction

As has been mentioned in the previous chapter, conventional full dynamical (FD) calculations of LEED intensities often have restricting requirements for computing (CPU) time, a large portion of which is spent in calculating the diffraction matrices for a composite layer. The CPU time scales roughly as $M^3$, where $M$ is the number of subplanes in the composite layer. An even more serious limitation of FD LEED is the trial-and-error procedure for determining surface structure, where times required scale roughly exponentially with the number of parameters being varied. Human selection of which structural parameter is to be studied in greatest detail limits not only the number of parameters to be investigated, but also the parameter space over which the structural search is done. Thus, the prospect of accurately determining the coordinates of more than five atoms is dim with the conventional procedure. Given the current interest in adsorbate-induced restructuring, often involving large unit cells containing many atoms, a new approach to LEED calculations is clearly needed to determine the many structural parameters involved. The recently developed tensor LEED method offers an alternative and faster approach to the standard LEED analysis.

2.2 General principles

Tensor LEED is an approximative scheme for calculating diffracted beam intensities, which attempts to recover the simplicity of X-ray diffraction in the LEED context. Weak atomic scattering of X-rays allows treating scattering as a first-order perturbation of the incident photon wavefield in vacuum. Furthermore, the probability of an X-ray photon being scattered by more than one atom (multiple scattering) is much lower than that of single scattering. Consequently, the amplitude of the scattered
wavefield can be expressed as a sum over all possible single-scattering events, and the diffracted intensity factorizes into the product of an atomic form factor $f$ and a geometrical structure factor $S$

$$I(k,k') = |f(\Delta k)|^2 |S(\Delta k)|^2 \quad (2.1)$$

$$S(\Delta k) = \sum_{j=1}^{N} e^{i\Delta k \cdot r_j} \quad (2.2)$$

where $(k,k')$ are respectively the wave vectors of the incident and diffracted waves and $\Delta k = (k-k')$ is the momentum transfer. Intensity calculations for any number of arrangements of atoms in the bulk unit cell can be accomplished by quick and simple resumming of the structure factor in Eq. (2.2) over atomic coordinates of the $N$ atoms in the unit cell.

The above equations cannot be directly used in calculating LEED intensities because of the strong atomic scattering of low-energy electrons so that the electron wavefunctions must be solved from the Schrödinger equation in which the crystal scattering potential is fully represented.\,\,\,6 Multiple scattering of low-energy electrons links the arrangement of atoms with the scattered wavefield so that the calculated intensities can no longer be simply separated into a form factor and a structure factor. Tensor LEED addresses these problems by starting not with the electron wavefunction in free space, but with the electron wavefield as calculated exactly for a reference surface using FD methods as outlined in the previous chapter. Small atomic displacements away from the reference structure can then be treated as a first-order perturbation of the reference structure, and diffracted intensities for more complicated trial structures can be calculated much more quickly than with conventional means.

Tensor LEED theory has been considered at three different levels of sophistication. The simplest, called Linear Tensor LEED, assumes that the change in the scattered
amplitude depends linearly upon the magnitude of atomic displacement; this approximation is accurate only for displacements of less than 0.2 Å at energies greater than about 100 eV and is therefore not very useful for many LEED crystallographic applications where intensity data often extend to 250 eV or higher. The most sophisticated version, called Cluster-Corrected Tensor LEED, attempts to correct for some multiple-scattering correlation between displaced atoms; this version has not been implemented, however, and will not be discussed here. The most widely available version of tensor LEED theory, which is used in this work, is simply called Tensor LEED (TLEED); an outline of TLEED theory follows.

First, an FD calculation is performed for a reference structure; the standard assumption of a spherically symmetric potential centered at each lattice point is made. Displacement of atoms from the reference structure positions is treated as a non-spherical distortion of the scattering potential (Fig. 2.1), as incorporated into the atomic scattering t-matrix:

\[ t'_j = t_j + \delta t_j (\delta r_j), \quad (2.3) \]

where \( t'_j \) and \( t_j \) are respectively the t-matrices for the displaced and undisplaced atom \( j \), \( \delta t_j \) is the change produced by the displacement \( \delta r_j \), all defined relative to the undisplaced atomic position \( r_j \). The change in each t-matrix element is given by

\[ \delta t^j_{l'm'} = \sum_{l'm_1m_1} G^j_{l_nl'_nm_1} (\delta r_j) t^j_{l'm_1} G^j_{l'_nm_1m} (-\delta r_j) - t^j_{l'm} \quad \delta \gamma \quad (2.4) \]

where \( G \) is a spherical wave propagator, which converts a spherical wave centered on \( r_j \) to a set of spherical waves centered on \( r_j + \delta r_j \), and \( \delta \gamma \) is the Kronecker delta (i.e., \( \delta \gamma \))
**Figure 2.1** Schematic diagram showing scattering of a plane wave (dashed lines) by an atom (solid circle) into spherical waves (open circles with arrows indicating some directions of propagation). The left panel corresponds to scattering by a spherically symmetric potential where the origin is located at the atomic center, while atomic displacement in the right panel leads to a non-spherically symmetric potential.
equals 1 if \( l = l' \) and 0 if \( l \neq l' \). The change in scattering amplitude of a LEED beam of parallel wavevector \( k_i \) is calculated from \( \delta t \):

\[
\delta A = \sum_j <\Psi^+ (k_i') | \delta t_j | \Psi^+ (k_i)>
\]  

(2.5)

which can be re-expressed \(^65\) as a product of a "form factor" \( F^j \) and a "structure factor" \( S^j \) for \( N \) displaced atoms as

\[
\delta A = \frac{1}{N} \sum_j \sum_{l_m, l'_m} F^j_{l_m, l'_m} S^j_{l_m, l'_m}
\]  

(2.6)

\[
F^j_{l_m, l'_m} = \sum_{l_{m1}, l_{m2}, l_{m3}} i^{l_1 + l_2} (-1)^{m_1 + m_2} T^j_{l_{m2}, l_{m3}} (C_{l_{m1}, l_1, l_{m2}, l_{m3}} - t_{l_2}^j \delta_{l_2 l_2})
\]  

(2.7)

\[
S^j_{l_m, l'_m} = (4\pi)^2 i^{l_f} (-1)^{m + m'} j_l (k\delta r_j) Y_{l_m} (\delta r_j) j_{l_f} (k\delta r_j) Y_{l'_m} (-\delta r_j)
\]  

(2.8)

\[
T^j_{l_{m2}, l_{m3}} = <\Psi^+ (k_i') | r_{l_1} | l_{m2} > < r_{l_2} | l_{m3} | \Psi^+ (k_i)>
\]  

(2.9)

\( j_l \) is a spherical Bessel function; \( Y_{l_m} \) is a spherical harmonic; \( C \) is a Gaunt coefficient; and \( | r_{l_1} ; l_m > \) is a state of angular momentum \( l_m \) centered on \( r_j \).

The tensors \( T \), hence \( F \), depend only on the property of the reference surface and need only be calculated once. \( I(E) \) curves for any number of trial structures, each of which would have required doing a new FD calculation in conventional LEED, can now be done quickly by reevaluating Eq. (2.8) (the CPU time now scales as \( N \), where \( N \) is the number of displaced atoms). In addition, since the terms \( S \) contain a product of two
Bessel functions and $j_l$ is a rapidly decreasing function of order $l$ so that $S \approx 0$ for $l + l' \geq k\delta r$, the sum in Eq. (2.6) can be truncated after

$$l + l' \geq k\delta r,$$

leading to a significant saving in CPU time. Previous tests$^{51-64}$ have shown that this version of tensor LEED can closely reproduce FD-calculated $I(E)$ curves for atomic displacements less than 0.4 Å, beyond which the theory becomes inaccurate as multiple scattering correlation between displaced atoms becomes important. For $\delta r = 0.4$ Å and maximum incident energy of 252 eV, the sum in Eq. (2.6) need only to be performed for $l + l' \leq 4$.

### 2.3 Automated search procedure

The speed with which $I(E)$ curves for a trial structure can be evaluated using TLEED naturally suggests implementation of an automated search procedure:$^{59-61}$ comparison between theoretical and experimental curves is done by the program, and the resulting increase or decrease in $R$-value is used to direct the choice of the next trial structure. This process is repeated until an $R$-factor minimum is reached. Previous tests of the TLEED method have mainly been of clean metals and "simple" overlayer structures; for the work in Chapters 5 and 6, the emphasis is on reconstructed surfaces where, to increase the likelihood of finding a global rather than local minimum, searches over many different chemically plausible reference surfaces are done. Figure 2.2 illustrates the automated search strategy as realized in the programs used in this work.$^{58-60}$

Three steepest-descent optimization schemes were available: the simplex and direction-set Powell algorithms are substantially modified versions of those contained in the book by Press et al.$^{70}$ and a direction-set search similar to the Rosenbrook
Figure 2.2 Directed search optimization scheme for structural analysis by tensor LEED
algorithm\textsuperscript{71,72} which provides information about the local geometry around the minimum in parameter space. Additionally, a fourth set of routines supplies information with respect to the explicit dependence of the R-factors on structural parameter variations in the vicinity of the minimum. This work used the Powell algorithm, a brief description of which follows.

Consider a search for the 3N coordinates of N atoms. R-factor minimization is done along 3N independent directions, initially chosen to be the Cartesian coordinates of each atom. Minimization along one direction begins by displacing an atom a distance $s$, calculating I(E) curves for this trial structure, and evaluating its R-factor. If the R-value has decreased relative to that for the initial structure, then a new trial structure is selected in which the atom is displaced a distance $\alpha s$, where $\alpha > 1.0$. Displacement in the same direction continues until an increase in R-value is encountered, then the step length is reduced and the direction is reversed by $\beta s$, where $\beta < 1.0$. Once this process has been performed for all 3N parameters, a new set of axes are defined in which one axis points along the direction of steepest descent, and the others point along directions of minimal change in R-factor. The minimization procedure is then repeated in the new coordinate system, and the search proceeds until no further significant variations could be observed in either structural parameters or R-values.

### 2.4 Some tests of TLEED

To assess the ability of TLEED and an automated search procedure for determining surface structures involving more complex unit meshes than have previously been considered, a number of tests were done using the TLEED program codes as provided by Barbieri \textit{et al.},\textsuperscript{58-60} with a simplified model of the O/Pd surface (Fig. 2.3). For all tests, the reference structure was the ideal Pd(100) surface with an O overlayer at 1.30 Å above the
Figure 2.3  Schematic diagram of reference structure model used to test tensor LEED. Large open circles and small shaded circles represent respectively Pd and O atoms. Four types of atomic displacement were separately considered, as indicated by arrows (top view) and dashed lines (side view).
surface and on bridge sites; the first-to-second Pd(100) layer spacing (d_{12}) was initially set at the bulk value of 1.94 Å. All FD calculations used an initial value of V_{0r} = -5.00 eV.

2.4.1 Reproducibility of full-dynamical calculations

The first test was of TLEED's ability to reproduce accurately full-dynamical calculations. I(E) curves were calculated by FD methods for four types of atomic displacement (\Delta_{Pd}, \Delta_{O}, D_{O}, D_{Pd}) by two different magnitudes (0.10 and 0.20 Å). These theoretical curves served as "experimental" curves; Table 2.1 summarizes the results from the TLEED calculations, and Figure 2.4 compares some TL vs. FD curves for this model surface. It is clear both from visual inspection of I(E) curves and from the low \(R_p\) values that TLEED can reproduce structural parameters to within 0.02 Å for initially assumed displacements of 0.10 Å or less. This is well within the error limit set by the uncertainty in experimental data, estimated to be about 0.03 Å,\(^\text{73}\) and, therefore, TL-calculated I(E) curves can be considered accurate for displacements in this range of values. Displacements of 0.20 Å gave worse agreement between TL and FD calculations, but this statement applies not so much to visual analysis or even to the significant rise in \(R_p\), but rather to the lack of reproducibility in the magnitude of the atomic displacements. Lateral displacements were reasonably well reproduced by TLEED, the error being 0.03 Å or less, whereas vertical displacements were somewhat underestimated, the error being as large as 0.1 Å. These observations are consistent with those of other workers\(^\text{61-63}\) and also serve as a guide as to how TLEED converges on the "correct" model:

(1) generally, for displacements less than 0.20 Å, structural results are the same from TLEED and conventional (FD) LEED;

(2) consequently, the difference in \(R_p\) between an FD and TL calculation should be \(\sim 0.05\) or less;
A test of the ability of the directed search/tensor LEED method for reproducing initially assumed structural details. "Experimental" curves were calculated by FD methods for four types of atomic displacements (defined in Fig. 2.3) by two different magnitudes (DISP), and the optimization was done over all three Cartesian coordinates of the four O atoms and five top-layer Pd atoms. For both sets of results, initially assumed first-to-second interlayer spacing $d_{12} = 1.94 \text{ Å}$, and DISP = 0.10 and 0.20 Å for the left and right sets, respectively. $\delta V_{0\alpha}$ is the difference between the TL-optimized $V_{0\alpha}$ value and that assumed initially. The values reported for the vertical displacements ($D_O$ and $D_{Pd}$) do not correspond to a simple displacement of the particular atom under investigation (e.g., O for $D_O$); hence the parentheses around these values.

<table>
<thead>
<tr>
<th></th>
<th>DISP</th>
<th>$d_{12}$</th>
<th>$\delta V_{0\alpha}$ (eV)</th>
<th>$R_p$</th>
<th>DISP</th>
<th>$d_{12}$</th>
<th>$\delta V_{0\alpha}$ (eV)</th>
<th>$R_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta_{Pd}$</td>
<td>0.10</td>
<td>1.95</td>
<td>0.10</td>
<td>0.011</td>
<td>0.17</td>
<td>1.92</td>
<td>1.84</td>
<td>0.052</td>
</tr>
<tr>
<td>$\Delta_O$</td>
<td>0.12</td>
<td>1.94</td>
<td>0.53</td>
<td>0.013</td>
<td>0.22</td>
<td>1.95</td>
<td>-0.03</td>
<td>0.023</td>
</tr>
<tr>
<td>$D_O$</td>
<td>(0.08)</td>
<td>1.93</td>
<td>1.14</td>
<td>0.017</td>
<td>(0.15)</td>
<td>1.91</td>
<td>2.58</td>
<td>0.055</td>
</tr>
<tr>
<td>$D_{Pd}$</td>
<td>(0.09)</td>
<td>1.93</td>
<td>1.23</td>
<td>0.019</td>
<td>(0.16)</td>
<td>1.92</td>
<td>2.27</td>
<td>0.048</td>
</tr>
</tbody>
</table>
Figure 2.4  Comparison of FD- and TL-calculated I(E) curves for the four types of displacement illustrated in Fig. 2.3. "Experimental" FD curves were obtained by full-dynamical methods for a displacement of magnitude 0.20 Å (LP2 corresponds to Δ_p, LO2 to Δ_o, DO2 to D_o, and DP2 to D_pd). See Table 2.1 for more details.
(3) therefore, a new iteration of the TL search procedure starting from the last TL-optimized result is probably not necessary.

2.4.2 Lateral vs. vertical displacement

Even without the autosearch procedure, tensor LEED provides a very efficient, and hence powerful, method for correlating changes in calculated I(E) curves with a particular displacement of a particular atom. Figure 2.5 illustrates this point. Comparison was made between real experimental data and FD-calculated curves for the reference structure as well as four sets of TL-calculated curves (all displacements as defined in Fig. 2.3), and the following conclusions can be drawn:

(1) For normal incidence, vertical displacements generally have a greater effect than lateral displacements of the same magnitude (e.g., beam (0 2)). This is to be expected, since at normal incidence the momentum transfer $\Delta k$ is mainly in the direction perpendicular to the surface.

(2) For the same number of atoms, displacement of a stronger scatterer (e.g., Pd) will change calculated curves more than the same displacement of a weaker scatterer (e.g., O, beams (0.2 0.6) and (0.6 0.8)). This, too, is as expected.

(3) In some cases, a lateral displacement can have a greater effect than vertical; beam (0.4 1.2) in Fig. 2.5 shows a significant change which is due solely to the lateral displacement of Pd.

These observations are useful in cases where visual analysis suggests that a particular change is needed to improve agreement between calculated and experimental I(E) curves. Furthermore, as will be apparent in Chapters 5 and 6, the directed-search procedure relies solely on R-factors, but until there is a better understanding of the most
Figure 2.5  Comparison of the effect of different types of displacement (defined in Fig. 2.3) on calculated I(E) curves. 4BO curves are FD-calculated curves for the reference structure, while LP1t, LO1t, DO1t, and DP1t are TL-calculated curves for displacements of magnitude 0.10 Å of type Δpd, ΔO, Dχ, and Dpd, respectively.
appropriate R-factor to use in different contexts, it appears preferable to back an R-factor analysis with visual comparison as well as by consistency with some general chemical principles for structural results.

2.4.3 Interlayer spacings and $V_{0r}$

Results of a third test qualify the last conclusion of Section 2.4.1. A new FD calculation was done in which four out of the five Pd atoms in the first Pd(100) layer were vertically displaced toward the bulk, with a corresponding decrease of $d_{12}$ to 1.74 Å; TL curves were also calculated by displacing the same atoms in the reference surface so that all structural parameters in the two calculations are identical (Fig. 2.6a). When the two sets of calculated curves were compared to real experimental data, however, different optimized values of $V_{0r}$ were obtained (-10.23 eV for FD and -5.50 eV for TL), and visual inspection of the two sets of curves (Fig. 2.7a) showed similar profiles, but with a systematic shift in the energy scale of about 5 eV.

Since comparison against an unknown real structure (i.e., using real data) seems rather arbitrary, another series of tests similar to the first set of tests was done, using the FD-calculated curves as "experimental" data and allowing tensor LEED to find the "true" structure through the automated search procedure. Figure 2.6b shows that TLEED was unable to locate the correct structure to within the experimental error limit of 0.03 Å when the search was done over all three Cartesian coordinates of the nine atoms; nor was it able to locate the correct $V_{0r}$ value. Of particular concern is the fact that all atomic displacements were small (~ 0.1 Å), which suggests, in terms of the conclusions by Rous that the calculations should have converged to the correct structure and that a new calculation should not be needed. Clearly, this is not the case. When the search was restricted, however, to the vertical coordinates only (all lateral displacements being fixed at zero), the automated search procedure reproduced closely not only the correct structure
Figure 2.6  Structural models of the type shown in Fig. 2.3 involved in tests of tensor LEED. FD-calculated curves for model (a) were used as experimental data. The other models show results of three optimization schemes corresponding to (b) full optimization over three Cartesian coordinates of all nine atoms; (c) optimization restricted to vertical displacements only (lateral displacements being fixed at zero); and (d) full optimization after an initial $V_0$ shift of -5.0 eV. Dashed lines show displacements relative to the reference structure as indicated by solid lines.
Figure 2.7  (a) Comparison of FD- and TL-calculated curves for the assumed structure shown in Fig. 2.6a; note the systematic shift in energy scale of about 5 eV due to differences in the optimized $V_{or}$ value.  (b) Comparison of FD-calculated curves for the model shown in Fig. 2.6a and TL-calculated curves for the optimized structure shown in Fig. 2.6c.
(Fig. 2.6c), but also the correct value for \( V_{or} \) (-9.76 eV vs. the "true" value of -10.23 eV; Fig. 2.7b). The implication, then, is that an analysis of an unknown structure should begin by optimizing the vertical displacement of atoms (and consequently \( V_{or} \), with subsequent fine-tuning of the structural details by allowing lateral displacements in the latter TLEED cycles. A third test allowed displacements along all three coordinates but only after an initial \( V_{or} \) shift of -5.00 eV; TLEED-optimized results are similar to those obtained from not allowing lateral displacements. This last test would not be useful in practice, however, since the real value of \( V_{or} \) is usually not known \textit{a priori}. Nevertheless, it shows that TLEED can produce the essentially correct structure after only one cycle provided that the initial values of either \( V_{or} \) or the interlayer spacings are not too far from the true values.

2.4.4 Reference structure selection

A final test was performed to verify the claim that TLEED can produce superstructure beams which are not present in the reference surface. A missing-row model of the Cu(110)-(2x3)-N surface was used (LBbMR in Chapter 5), where all remaining long-bridge sites were occupied by N atoms, effectively removing the "3" periodicity; relaxations in the top two layers were allowed. The optimization procedure produced very small (< 0.05 Å) displacements for Cu atoms which would effectively restore the "3" periodicity in the \( <1\overline{1}0> \) direction. Nevertheless, no intensity was obtained for any of the four fractional beams needed for comparison with experimental data. It will be concluded, therefore, that while tensor LEED may be able to produce intensities in superstructure beams for sufficiently large atomic displacements, the autosearch procedure cannot be relied upon to produce such displacements and that some care is needed in choosing a reference structure which reflects the observed diffraction pattern.
2.5 General comments

Each full dynamical calculation in Section 2.4 (as part of the TLEED programs) takes about 12800 CPU seconds on an IBM RISC/6000. With a conventional LEED structural search, each variation in atomic position would require almost the same amount of CPU time, such that a thorough structural search would tend to be very limited by computing resources and power. TLEED calculation takes only an additional 30 CPU seconds for each of the above variations, while even full optimization of the atomic coordinates of nine atoms and $V_{\theta r}$ takes only 671 CPU seconds! For a more complicated real structure, e.g., an PdO(001) overlayer on Pd(100), the reference structure (FD) calculation takes about 5 CPU hours with an additional 1 CPU hour for the TL optimization where the coordinates of 18 atoms were varied. Clearly, it would be extremely difficult to explore parameter space in sufficient detail during a trial-and-error search of such a structure. This would in turn easily lead to identification of local rather than global minima in R-factors, and hence to incorrect conclusions (see Chapter 5 for N on Cu(110)). The power, validity, as well as the limitations of the combined tensor LEED and automated search procedure have been assessed in relation to some model situations. Application of TLEED to two real systems will be discussed in Chapters 5 and 6.
3.1 UHV equipment

A modern surface science experiment requires the use of an ultrahigh vacuum (UHV) chamber, where the base pressure should be maintained in the range $10^{-10}$ Torr or less. Although three different experimental chambers were used in this work, many aspects are common to all chambers and will be described here. Figure 3.1 illustrates the pumping arrangement for the chamber that was used in the study of Cu(110)-(2x3)-N surface. UHV is achieved by a series of pumps connected to the non-magnetic stainless steel chamber; vacuum seals between flanges are made using copper gaskets pinched between steel knife edges. Gas pressure inside the chamber and at the diffusion pump is monitored with ionization gauges, whereas gas-line pressure is measured using thermocouple gauges or the gauge on the small ion pump.

Pump down from atmospheric pressure to UHV is done in stages:

1. A liquid nitrogen-cooled adsorption pump reduces the chamber pressure to about $10^{-3}$ Torr.

2. A water-cooled, liquid nitrogen-trapped oil diffusion pump lowers the pressure to about $10^{-7}$ Torr.

3. A sputter-ion pump is then turned on and maintained as the primary pump for the vacuum chamber. Before baking, a pressure of only about $10^{-8}$ Torr is reached.

4. The chamber is baked at about 150°C for 12 hours or more to desorb and remove gases from the chamber walls. After baking and while the chamber is still warm, all filaments used in the chamber are degassed thoroughly to avoid contaminating the surface during an experiment. The baking and degassing procedures are repeated as necessary to lower the pressure to UHV range. Additionally, a
Figure 3.1  Schematic diagram of the pump and gas line configuration of the Varian 240 vacuum chamber used for the N/Cu experiment.
titanium sublimation pump (TSP) is available for use during degassing and normal operations.

The single-crystal sample sits inside a molybdenum sample cup, which is equipped with a resistive heater and to which is attached a thermocouple for measuring crystal temperature. The whole assembly is mounted on a manipulator to allow five degrees of movement for the sample: translation along three orthogonal directions (x,y,z), and variation of the polar angle (θ) and flip angle (ψ). Gases used for cleaning and for chemisorption studies are introduced into the chamber from the gas side line through a variable leak valve. An ion-bombardment gun and the LEED/AES optics complete the basic UHV chamber for surface study (Fig. 3.2).

3.2 Instrumentation for LEED and AES

This work used a standard front-view LEED display system (Fig. 3.3a). An electron gun provides the incident electron beam of desired energy. Four concentric hemispherical grids located in front of the fluorescent screen work to repel inelastically scattered electrons, while elastically scattered electrons are accelerated onto the positively biased screen to form the diffraction pattern. The first of the four grids is grounded to provide a field-free region around the sample. Linked together and biased at a negative potential several volts below the accelerating voltage, the second and third grids act as an energy selector. The fourth grid, grounded, isolates the positive screen potential from the retarding potential of grids 2 and 3, which in turn improves the resolution of the grid system, especially when it is being used as an energy analyzer for Auger electron spectroscopy.
Figure 3.2  Schematic diagram of the UHV chamber used in the N/Cu study; Ref. 74.
Figure 3.3 Schematic diagram showing the (a) LEED and (b) AES optics setup used in the N/Cu study; Ref. 74.
Figure 3.4 The CMA setup used in the O/Ni experiment; after Ref. 77.
The four-grid optics can also serve as the retarding-field analyzer (RFA) for AES, and the same gun used for LEED provides the primary electron beam with energy around 2 keV (Fig. 3.3b\textsuperscript{74}). In Auger mode, the retarding potential on the repeller grids (2 and 3) is modulated about the ramp voltage $V_r$ and the spectrum is recorded in $dN(E)/dE$ vs. $E$ format in order to extract the Auger peaks from the background. Besides its obvious convenience, the RFA system suffers from a number of disadvantages. It cannot be used to study many kinetic processes occurring on the surface because of the relatively long time required to obtain a full spectrum (several minutes). The large primary beam current needed (40 $\mu$A in the current study) leads to heating of the surface, and care is needed to ensure that the nature of the adsorbed layer is not significantly changed. Poor signal-to-noise ratio also makes difficult the detection of small impurity Auger peaks from background noise.

The cylindrical mirror analyzer (CMA), introduced by Palmberg et al.,\textsuperscript{76} has greatly improved signal-to-noise characteristics compared with the RFA. Figure 3.4\textsuperscript{77} shows the CMA set up for the Ni(111)-(2x2)-O study. A glancing incidence electron gun enhances the Auger yield from the topmost atomic layer relative to that of the substrate.\textsuperscript{75} Emitted electrons enter the analyzer and are deflected by a potential $V_a$ applied between two coaxial cylindrical electrodes. Only electrons with kinetic energy $eV_e$ will pass through the exit slit and arrive at the collector. A small modulating voltage $V_m$ superimposed on $V_a$ yields the $dN(E)/dE$ vs. $E$ spectrum, which can be recorded fast enough to be displayed on an oscilloscope. For the CMA, the relative resolution ($\Delta E/E$) is constant at all energies so that the resolution ($\Delta E$) and consequently the sensitivity are greater at high energies than low; by contrast, $\Delta E$ of the RFA is constant with energy for a constant modulating voltage so that the sensitivity is greater at low energies than high. In favourable cases, the sensitivity of a CMA can get down to around 0.1% of a monolayer of impurity and is generally an order of magnitude better than for the RFA.
3.3 Sample preparation and cleaning

Samples used in these studies were thin discs cut from single-crystal rods. Laue X-ray diffraction was used to orient the rods, and cutting by spark erosion exposed a surface of desired crystallographic plane (e.g., the (111) plane). Initial surface polishing was done with a planetary lapping system with progressively finer grades of diamond paste (from 9 to 3 μm), while final polishing was done by hand with either 0.05 μm alumina or 1 μm diamond paste on a deer skin-covered, flat glass plate. After polishing, optical face alignment was checked with a He/Ne laser (Fig. 3.5), and X-ray diffraction was again used to ensure that the desired crystallographic plane and the optical face are parallel to each other (to within 0.5°).

For the purpose of LEED crystallography, the single-crystal surface must be clean and well ordered. The sample was first degreased with trichloroethylene, acetone, and methanol and rinsed with distilled water. Once inside the UHV chamber, surface impurities were removed by Ar+ bombardment. Subsequent annealing induced surface ordering as well as surface segregation of bulk impurities. Cycles of Ar+ bombardment followed by annealing were repeated until AES indicated no impurity signals and LEED showed a sharp (1x1) pattern. After each chemisorption experiment, the clean, well-ordered surface was recovered by a shorter period of ion bombardment and annealing.

3.4 LEED intensity measurement using the video LEED analyser (VLA)

Experimental I(E) curves in the current study were measured at normal incidence with a commercial VLA, shown schematically in Fig. 3.6. A silicon-intensified TV camera placed in front of the viewing window allowed the diffraction pattern to be displayed on a monitor. The camera defined the viewing area as a 256x256-pixel frame and recorded the intensity of each diffracted beam by summing the digitized intensities
Figure 3.5 Schematic diagram showing He/Ne laser alignment of crystallographic and optical planes of the single-crystal sample. For large R, θ (rads) = r/2R.
Figure 3.6  Block diagram of the Video LEED analyser (VLA) for collecting LEED intensity data.
inside a 10x10-pixel window, which completely covered the spot and which automatically tracked the moving spots as the incident electron energy was varied by a microcomputer unit. Theoretically, up to 49 beams can be measured at the same time, but typically only up to eight symmetry-equivalent beams were measured in one pass. Two or three passes were made for each set of beams to improve the signal-to-noise ratio. In addition, it was necessary to use different gain level settings for integral-order and fractional-order beams, as the latter were often much weaker than the former.

Measurement of LEED intensities in this work was made at normal incidence, and fixing of the direction was done by comparing spectra of symmetrically equivalent beams. At normal incidence, the LEED pattern has the highest rotational symmetry that often corresponds to the rotational symmetry of the substrate (see Section 1.2.2 for a discussion of rotationally related domains). The sample orientation was adjusted until the measured I(E) curves reflected this symmetry.

Further treatment of the experimental data was needed before they can be used in a structural analysis. First, raw intensities were normalized to constant incident beam current (the experimental beam current increases linearly from low energy to about 100 eV, at which point it becomes constant at approximately 1 µA). Second, symmetrically degenerate beams were averaged together to minimize experimental errors such as slight misalignment of the surface away from normal incidence. Finally, the average I(E) curves were smoothed to reduce noise which would adversely affect the R-factor analysis. In some cases, a correction for background intensity was also made, and data from different experiments can also be averaged together to reduce statistical error. Figure 3.7 illustrates these procedures as applied to the treatment of experimental data for the N/Cu system.
Figure 3.7  Treatment of LEED experimental data for use in the structural analysis of the Cu(110)-(2x3)-N surface. (a) Symmetrically equivalent beams from one experiment are averaged and smoothed. (b) Data from different experiments are averaged to reduce statistical error.
4.1 Introduction

The first structural analysis for the Ni(111)-(2x2)-O surface, which was a LEED study by Marcus et al.,\textsuperscript{80} identified that the O atoms chemisorb at 3-coordinate hollow sites in the close-packed nickel surface, but that work was unable to make a choice between the two types of hollow site. Indeed, neither of the later studies on this surface, by high-energy ion scattering (HEIS)\textsuperscript{81} and surface-enhanced electron energy loss fine structure\textsuperscript{82}, clarified further the details of the adsorbate layer, although these analyses did suggest that there are significant O-induced relaxations in the metal structure. For example, Narusawa et al.\textsuperscript{81} reported with HEIS that three quarters of the Ni atoms in the top layer are relaxed outward by about 0.15 Å in a direction perpendicular to the surface. Displacements of this magnitude could have significantly affected the results of the 1975 LEED analysis.\textsuperscript{80} Also, the structural parameters deduced by Marcus et al.\textsuperscript{80} correspond to a O-Ni bond length of 1.88 Å, which is somewhat longer than the prediction of 1.82 Å\textsuperscript{83} made with a bond length-bond order relation deduced for related bulk structures. These observations suggested the need for a new LEED crystallographic analysis for the Ni(111)-(2x2)-O surface structure.\textsuperscript{84} Furthermore, at the time this work was done, it was by no means clear to what degree LEED could reliably identify relaxations in metal surfaces induced by chemisorbed species. Such topics provide the subject of this chapter.

4.2 Experiment

This project used LEED intensity data measured by Y.K. Wu,\textsuperscript{85} and the details for these measurements are outlined here. The starting point was the preparation of a clean, well-ordered Ni(111) surface as characterized by the cylindrical mirror analyzer showing no detectable Auger signals for impurity elements (Fig. 4.1a) as well as by LEED showing
Figure 4.1  (a) Auger spectra for clean Ni(111) and Ni(111)-(2x2)-O taken with the CMA setup in Fig. 3.4.  (b) Schematic diagram of the (2x2) LEED pattern.  Solid and hollow dots correspond respectively to integral and fractional beams, and boxes indicate one beam from each symmetrically equivalent set for which I(E) curves were measured.
a sharp (1x1) pattern. Such a surface at room temperature was exposed to O$_2$ gas at about 1 x 10$^{-8}$ Torr, and I(E) curves were then measured at normal incidence for optimal sharpness of the (2x2) LEED pattern for the three integral and seven fractional beams designated (Fig. 4.1b)

(1 0), (0 1), (1 1), (1/2 0), (0 1/2), (1/2 1/2), (1 1/2), (1/2 1), (3/2 0), and (0 3/2).

Intensity measurements were made with the VLA over a total energy range of about 1300 eV.

4.3 Calculation

The LEED multiple-scattering analysis for this system followed procedures outlined in Chapter 1. The atomic potential in the substrate was characterized by phase shifts up to $\varphi = 7$ derived from a band structure calculation for nickel, and the real part of the constant potential ($V_{0r}$) between all muffin-tin spheres was initially set at -7.2 eV. However, values of $V_{0r}$ were effectively refined for each structural model during the comparisons of the experimental and calculated I(E) curves, which were done both visually and with the LEED reliability indices $R_{M2J}$ and $R_p$. The oxygen phase shifts were those derived by Marcus et al. from a superposition of charge densities model, and the imaginary part of the constant potential between all atomic spheres was equated to -0.9 $E^{1/3}$ eV (where E is the electron energy in eV). The Debye temperatures for nickel and oxygen were taken as 440 and 843 K, respectively. Diffraction matrices for the relaxed topmost nickel layer were calculated using the combined-space method, layer stacking being done with RFS routines.
4.4 Structural analysis

The first part of the analysis aimed to determine the adsorption site, where all structural parameters except the the oxygen-to-nickel top layer spacing \(d_{01}\) were fixed at bulk values. Three possibilities with O atoms chemisorbed in 3-coordinate hollow sites were considered (Fig. 4.2a). The first two are represented as (C)ABC... and (B)ABC..., where O is identified by its registry in brackets with respect to the Ni layers; these two cases correspond respectively to O chemisorbed in "expected" 3f sites (which continue the fcc ABC... packing arrangement) and O chemisorbed in the alternative 3h sites which correspond to the hcp stacking arrangement for the O and top two Ni layers. Also considered was a "graphitic" O layer which corresponds to (B+C)ABC..., and is the structure proposed by Joebst\(^90\) for the Pt(111)-(2x2)-O surface. Based on results from other techniques for the Ni(111)-(2x2)-O surface,\(^91-95\) no calculation was done for any model where oxygen dissolved into the substrate to form an underlayer, although that could be expected at higher coverages and/or temperatures when a surface oxide forms.\(^91,92,96,97\) Nor was any model tested where three rotationally related (2x1) domains give rise to the observed (2x2) pattern: the measured\(^92\) oxygen coverage for the (2x2) surface is \(\theta_O = 0.25\) ML, whereas that of a (2x1) structure is \(\theta_O = 0.50\) ML. The existence of a higher coverage (\(\theta_O = 0.33\) ML) Ni(111)-(\(\sqrt{3} \times \sqrt{3}\))R30\(^\circ\)-O surface also precludes a (2x1) model of the (2x2) surface.

Visual analysis indicates clearly that the "expected" (C)ABC... model gives the best fit with experiment; Figure 4.2b compares the experimental and calculated I(E) curves for these three basic model types. Furthermore, R-factor analyses arrive at consistent and better results for the 3f model compared with the 3h model: for the former, both \(R_p\) (0.2326) and \(R_{MZJ}\) (0.2184) indicate an optimal value of \(d_{01} = 1.10\) Å, whereas two different values were obtained for the latter (\(R_p = 0.3026\) for \(d_{01} = 1.30\) Å; \(R_{MZJ} = 0.2383\) for \(d_{01} = 1.50\) Å). The best correspondence at this stage is still quite mediocre, consistent
Figure 4.2  (a) Schematic diagram of the three basic models considered in the adsorption-site
determination for the Ni(111)-(2x2)-O surface. (b) Comparison of experimental (dashed curves)
and calculated I(E) curves for the models illustrated in (a).
Figure 4.3  Schematic diagram illustrating the types of metal relaxations considered for the Ni(111)-(2x2)-O surface. Positive displacements are indicated.
with observations from the earlier history of LEED crystallography that chemisorbed O often did not immediately give as good a correspondence between experimental and calculated I(E) curves as, for example, could be obtained with chemisorbed S. Since this was the situation on Ni(111), it was important to establish the reasons, and in particular to establish whether the LEED method as used was limited in its scope for oxygen chemisorption, or whether the basic geometrical structure had simply not been fully refined.

Figure 4.3 defines the structural parameters included in the refined analysis for the Ni(111)-(2x2)-O surface structure. A positive value of $D_{1/1}$ indicates a vertical displacement toward oxygen of those Ni atoms which are bonded to O. Additionally, two types of lateral displacement were considered for the topmost Ni layer. That which corresponds to a radial displacement is designated $\Delta_{\text{rad}}$, while the twisted or rotated displacement is designated $\Delta_{\text{rot}}$. Table 4.1 summarizes the ranges of values considered for each structural parameter, although the ranges were effectively reduced as the optimization procedure developed; also tabulated are optimal values and the corresponding $R_{\text{av}}$. The second-to-third interlayer spacing for nickel, and all below, were fixed throughout at the bulk value (2.03 Å).

The first part of this refined study emphasized $\Delta_{\text{rad}}$ rather than $\Delta_{\text{rot}}$ for the lateral displacement, and indeed it was soon apparent that inclusion of both vertical and lateral relaxations in the top layer of Ni were needed in the calculations in order to improve agreement between calculated and experimental I(E) curves. Figure 4.4 compares calculated intensity curves for lateral and no vertical relaxation ($\Delta_{\text{rad}} = 0.10$ Å, $D_{1/1} = 0.0$, curves marked (c)), for vertical and no lateral relaxation ($\Delta_{\text{rad}} = 0.0$, $D_{1/1} = 0.10$ Å, curves marked (d)), and for vertical and lateral relaxation ($\Delta_{\text{rad}} = 0.10$ Å, $D_{1/1} = 0.10$ Å, curves marked (e)). It was found that the correspondence with experiment improved on average along the progression of curves marked (c), (d), and (e) in Fig. 4.4, although problems do
Table 4.1  Ranges of relaxation parameters considered for model (C)ABC... are given, along with optimized values; increment sizes are in parentheses, and ranges were reduced as the structural search progressed.

<table>
<thead>
<tr>
<th></th>
<th>( D_{11} ) (Å)</th>
<th>( d_{01} ) (Å)</th>
<th>( d_{12} ) (Å)</th>
<th>( \Delta_{\text{rad}} ) (Å)</th>
<th>( V_{\text{or}} ) (eV)</th>
<th>( R_{\text{av}} )</th>
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<tbody>
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<td>Range</td>
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<td>0.90 (0.10) 1.35</td>
<td>1.90 (0.04) 2.14</td>
<td>-0.10 (0.05) 0.15</td>
<td>-13.2 (2.0) -1.2</td>
<td></td>
</tr>
<tr>
<td>Optimal</td>
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<td>1.10 Å</td>
<td>1.96 Å</td>
<td>0.09 Å</td>
<td>-6.8 eV</td>
<td>0.1560</td>
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</table>

<table>
<thead>
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<th></th>
<th>( D_{11} ) (Å)</th>
<th>( d_{01} ) (Å)</th>
<th>( d_{12} ) (Å)</th>
<th>( \Delta_{\text{rot}} ) (Å)</th>
<th>( V_{\text{or}} ) (eV)</th>
<th>( R_{\text{av}} )</th>
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<td>1.08 (0.02) 1.14</td>
<td>1.94 (0.04) 2.14</td>
<td>0 (0.05) 0.15</td>
<td>-13.2 (2.0) -1.2</td>
<td></td>
</tr>
<tr>
<td>Optimal</td>
<td>0.12 Å</td>
<td>1.09 Å</td>
<td>1.95 Å</td>
<td>0.07 Å</td>
<td>-7.8 eV</td>
<td>0.1219</td>
</tr>
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</table>
Figure 4.4 Comparison of experimental (dashed) with calculated (solid) I(E) curves (structural parameters are specified in Fig. 4.3). Those marked (a) and (b) are for models (B)ABC... and (C)ABC..., respectively, with no metal relaxation and \( d_{01} = 1.10 \) Å, \( d_{12} = 2.03 \) Å. The set of curves marked (c) \( (\Delta_{rel} = 0.10 \) Å, \( D_{11} = 0.00 \) Å), (d) \( (\Delta_{rel} = 0.00 \) Å, \( D_{11} = 0.10 \) Å), (e) \( (\Delta_{rel} = 0.10 \) Å, \( D_{11} = 0.10 \) Å), (f) \( (\Delta_{rel} = 0.10 \) Å, \( D_{11} = 0.10 \) Å) correspond to the relaxed model with \( d_{01} = 1.11 \) Å, \( d_{12} = 1.98 \) Å. Calculated curves marked (g) give the best agreement with experiment; with structural parameters \( d_{01} = 1.09 \) Å, \( d_{12} = 1.96 \) Å, \( D_{11} = 0.12 \) Å, \( \Delta_{rel} = 0.07 \) Å.
still remain (e.g., for the (0 3/2) beam) and that suggested the need to try the other type of lateral displacement. The curves marked (f) in Fig. 4.4 are for $\Delta_{rot} = 0.10 \text{ Å}$ and $D_{1/1} = 0.10 \text{ Å}$. This change had a negligible effect on the integral beams, while the correspondence with experiment for most of the fractional beams (except (3/2 0)) was improved.

The average of the two R-factors mentioned above, namely $R_{av} = \frac{1}{2} (R_{MZJ} + R_p)$, was used for a full optimization of the structural parameters with the rotated lateral relaxation in the topmost Ni layer. The best correspondence between the experimental and calculated intensity curves was then obtained with the values $d_{01} = 1.09 \text{ Å}$, $D_{1/1} = 0.12 \text{ Å}$, $d_{12} = 1.95 \text{ Å}$, $\Delta_{rot} = 0.07 \text{ Å}$ (the optimal value of $V_{O}$ is -7.8 eV, and the values of $R_{MZJ}$ and $R_p$ are 0.1087 and 0.1326, respectively); the uncertainty in these structural values is estimated at 0.03 Å (the amount by which visual observation suggests the correspondence has deteriorated, even if only slightly). Calculated I(E) curves corresponding to these optimal structural values are shown in Fig. 4.4, curves (g). In this structure, the topmost close-packed layer of Ni distorts appreciably: specifically, those Ni atoms which neighbour an O atom relax in a way to emphasize the formation of a local Ni$_3$O cluster. The O-Ni bond length of 1.83 Å agrees closely with the value (1.82 Å) predicted by a relation which relates O-Ni bond lengths to O coordination numbers in solid structures; interestingly, the same predictive model suggests an O-Ni bond length of 1.93 Å for O chemisorbed on the (100) surface of nickel, again very close to the latest experimental value of 1.92 Å.

The radial relaxation, vertical relaxation, and radial combined with vertical relaxation parameters were also applied to the (B)ABC... model. The match between experimental and calculated I(E) curves, as observed visually and indicated by R-factor analyses, was decreased when relaxation parameters were included. This is in contrast to the improvements observed for the (C)ABC... relaxed models, and further supports the latter as the correct structure of the Ni(111)-(2x2)-O surface.
The finding here of a vertical relaxation ($D_{11}$) in the top Ni(111) layer of about 0.12 Å agrees to within the stated uncertainty with the value reported earlier by HEIS,\textsuperscript{81} although this latter technique did not identify the specific adsorption site. This relaxation can be understood qualitatively by the strong bonding between the three Ni atoms and O, and a consequent reduction in bonding between these Ni atoms and their other neighbours (including those below in the second layer). Previous works\textsuperscript{81,82} did not detect, however, displacement toward the bulk of the non-oxygen-bonded Ni atoms, resulting in a contracted interlayer spacing of $d_{12} = 1.96$ Å. The net effect of the two displacements is to give for the center-of-mass distance between first and second Ni layers a value of 2.05 Å, which is only slightly greater than the bulk value of 2.03 Å.

The lateral relaxation of about 0.07 Å had not been reported before in this context. At least two factors are involved in determining the direction of the lateral displacement. First, Ni atoms which are bonded to O will have partial positive charges due to the polar nature of the bonds to O, and increased electrostatic repulsion between the three Ni atoms will lead to an expansion of the adsorption site. The second factor is related to the ideal tendency for O to have bond angles near or greater than 90°,\textsuperscript{99} and expansion of the adsorption site acts to increase the Ni-O-Ni bond angle. The Ni-O-Ni bond angle for the optimal structure in this study is 88.3°, compared with an angle of 86.9° for the non-relaxed model.

Lateral expansion of each occupied adsorption site is accompanied by contraction of an adjacent unoccupied site, associated with which is an energy penalty that increases as the minimum Ni-Ni distance decreases. With the radial type of lateral displacement, groups of neighboring Ni atoms move directly toward one another, and for a given magnitude of displacement, the minimum Ni-Ni distance is shorter than with the rotated or "twisted" type of displacement. Thus, the energetics for $\Delta_{\text{rot}}$ should be more favourable than for $\Delta_{\text{rad}}$, an observation which is consistent with the results of this study.
distortions found here in the topmost Ni layer can be expected to cause some further disturbances in the second layer, and detailed considerations of such features may help to reduce the remaining discrepancies between the experimental and calculated I(E) curves. Nevertheless, O-induced metal relaxations observed in here have been further confirmed by a more recent work using SEXAFS.100

Structural details of the (2x2) surface can also be compared to those subsequently measured for the Ni(111)-(√3 x √3)R30°-O surface formed at higher oxygen coverage. LEED analysis of the latter101 revealed no lateral relaxation, while a vertical buckling of the topmost layer was precluded by symmetry. A very slight uniform expansion of the topmost nickel layer spacing (2.05 Å), was observed, however, with an optimal second-to-third layer spacing (2.02 Å) at essentially at bulk value. These spacings are comparable to those from the current work, when the center-of-mass distance is used, and in addition, the oxygen height above its nearest nickel neighbours (on 3f sites) are the same in both studies, resulting in similar O-Ni bond lengths (d_{01'} = 1.08 Å and b_{O-Ni} = 1.80 Å for the √3 surface). Since phase diagram measurements as well as Monte Carlo simulations102 have predicted a restructuring during the p(2x2) → (√3 x √3)R30° phase transition, perhaps it is not surprising that the former is reconstructed while the latter is not. Furthermore, oxygen coverage on the √3 surface (θ_O = 0.33 ML) is higher than that on the (2x2) surface, and in the limit of a monolayer coverage, no metal relaxation can be expected (other than a uniform metal interlayer spacing expansion).

4.5 Comments on Ni(111)-(2x2)-S

In light of these results for the Ni(111)-(2x2)-O system, it seemed appropriate to reanalyze the corresponding sulfur-nickel system since the correspondence between calculated and measured LEED intensities is now at a higher level for chemisorbed O than
for chemisorbed S, an observation contrary to that of earlier experience. A previous LEED study of the Ni(111)-(2x2)-S surface reported a very small non-rotated lateral relaxation of 0.03 Å in the top Ni layer, accompanied by a uniform vertical expansion of both the first and second metallic layers. Second layer expansion has been questioned, however, since the commonly observed trend is a contraction of second-to-third interlayer spacing when the first-to-second spacing is expanded.

Therefore, new models containing rotated lateral relaxation were tried. Some of these models included either uniform vertical expansion or contraction, or 3/4 ML expansion or contraction, of the top metal layer. Unlike the O-Ni system, calculated I(E) curves for these models for the S-Ni system did not change significantly as different structural parameters were varied by small amounts. Furthermore, results for the S-Ni system indicate uniform rather than 3/4 ML expansion and non-rotated rather than rotated lateral expansion. This is consistent with the previous report.

In a further attempt to improve agreement between experiment and theory, models which included hydrogen were considered. Coadsorption of hydrogen and sulfur from hydrogen sulfide on Ni(111) at room temperature has been reported from a SIMS study. Thus, calculations were performed to stack a graphitic overlayer consisting of one hydrogen and one sulfur per (2x2) unit mesh on a bulk-like Ni(111) surface. Sulfur sits on the 3f site as before, and hydrogen sits on the adjacent 3h site. \( R_p \) is slightly lower for this structure (0.19) than for the corresponding structure without hydrogen (0.20), but as expected, calculated I(E) curves have not changed much visually, and the problem beams appear unaffected by the addition of hydrogen to the surface. Models in which a hydrogen remains bonded to the sulfur which is in turn chemisorbed onto the Ni(111) surface gave the same \( R_p \) as without hydrogen. Unlike the graphitic-overlayer model, however, the intensities of some of the peaks have changed enough to be discernible.
4.6 Summary

Even with these new considerations, little progress was achieved with the S-Ni system. The reported model\textsuperscript{103} remains the best reached thus far, if the only criterion is the lowest overall R-value. The fact that there was a decrease in agreement for five of the ten beams in the relaxed model, however, is a problem that needs to be addressed. It is possible that this problem can be solved by incorporating hydrogen into the bulk, rather than on the surface. Perhaps such a model can also explain why there is a uniform vertical expansion of the substrate surface layers for the H\textsubscript{2}S on Ni case, whereas O on Ni shows a differential vertical expansion of the top Ni layer.

The bonding geometry of chalcogen overlayers on Ni(111) has previously been discussed in terms of Ni\textsubscript{3}X clusters, where X is a member of the chalcogen family.\textsuperscript{106} This model is perhaps most markedly illustrated in the case of O on Ni, where the interaction between oxygen and Ni atoms is so strong as to cause a lattice expansion of 3/4 ML of the top Ni layer with a lateral displacement to increase the Ni-O-Ni bonding angle. Thus, this work not only has helped to increase knowledge of the structure of the Ni(111)-(2x2)-O surface, but also has confirmed the ability of conventional LEED methods to refine structural details for O chemisorption on metal surfaces when sufficiently exhaustive structural searches are undertaken in the calculations.
5.1 Introduction

Chemisorption of activated nitrogen on to the (110) surface of copper yields a surface of (2x3) translational symmetry which shows high stability. Such a surface has also been observed on the fcc(110) surface in other contexts including nitrogen on Ni(110), hydrogen on Ni(110) and sulphur on Pd(110); moreover, facets which form on Cu(210) and Ni(210) under N chemisorption have also been interpreted as corresponding to (110)-(2x3) surfaces. Since the Cu(110)-(2x3)-N surface appears significant in the development of surface structural principles, both because of its high stability and its unestablished structure, the present work attempted to identify structural details for it and provide some satisfactory explanation of the specific translational symmetry.

Despite the large number of techniques which have been used to study this surface, no consensus exists as to the correct structure of the Cu(110)-(2x3)-N surface. Studies using HREELS and XPS concluded that N atoms occupy only one type of adsorption site, and that is the long-bridge site. In addition, XPS data suggested that the nitrogen coverage $\theta_N = 2/3$ ML (where 1 ML corresponds to 6 N atoms per (2x3) unit mesh), whereas Auger measurements from a different work gave a value of $\theta_N < 1/4$ ML. Two separate low-energy ion scattering studies (LEIS and NICISS) arrived at completely contrary structural models of the (2x3) surface, although each of these conclusions have received support from other techniques. Specifically, with photoelectron diffraction, Ashwin, Robinson and coworkers proposed a pseudo-(100) reconstruction where the overlayer has four rows of copper atoms for every three on the clean surface in the $<1\bar{1}0>$ direction; with STM images, Spitzl et al. concluded that every third $<1\bar{1}0>$ row is missing so that the copper density in the topmost layer ($\theta_{Cu}$) is 2/3 that of the clean
surface. The most recent technique to be applied is X-ray reflectivity, which indicated that \( \theta_{\text{Cu}} = 4/3 \),\(^\text{116}\) supporting the (100)-reconstruction model of Ashwin et al.

An initial conventional LEED crystallographic analysis (this work) suggested yet another model, where every other <001> row is missing in the topmost layer (\( \theta_{\text{Cu}} = 1/2 \)),\(^\text{115}\) but tensor LEED currently favours the pseudo-(100) model over that of conventional LEED. Results from each analysis will be discussed separately in this chapter, along with summarizing remarks on the difference in conclusions between the two studies.

5.2 Experiment

The UHV chamber is as described in Chapter 3. The Cu(110) sample was cut from a high-purity single-crystal rod\(^\text{123}\) and cleaned under UHV by cycles of Ar\(^+\) bombardment and annealing at 820 K. These cycles were repeated until the retarding field analyzer showed no detectable Auger signal for impurity elements and LEED showed a sharp (1x1) pattern.

Such a cleaned and ordered surface was exposed at room temperature to (5-9) \( \times 10^{-5} \) Torr nitrogen activated by the ion gun for glancing incidence at 200, 350, or 500 eV for varying lengths of time. The lowest dose which gave a sharp (2x3) pattern, after annealing at 610-650 K, was 5 minutes at 200 eV and 2 \( \mu \)A at the surface (corresponding to 600 \( \mu \)C), and the highest was 20 minutes at 500 eV and 1 \( \mu \)A (corresponding to 1200 \( \mu \)C). These surfaces were stable over a period of some weeks at 4 \( \times 10^{-10} \) Torr vacuum. The (2x3) LEED pattern remained even when the surface was kept for several days at about \( 10^{-5} \) Torr, although it became less sharp and additional annealing did not improve the pattern.
I(E) curves were measured at normal incidence for optimal sharpness of the (2x3) LEED pattern for five integral and four fractional beams designated 

(1 0), (0 1), (1 1), (2 0), (2 1), (2/3 1/2), (4/3 1/2), (4/3 1), and (5/3 1),

using the beam notation indicated in Fig. 5.1. Intensity measurements were made at all three activation energies over a total energy range of about 920 eV for each. Comparison of experimental I(E) curves showed no significant differences among the three sets of data (Fig. 5.2), and the analysis was done using the averaged set of I(E) curves.

5.3 Calculation

The combined-space formalism was used to calculate diffraction matrices for up to four atomic layers, with N atoms being included in the topmost Cu layer. Layer stacking was accomplished with either the layer doubling (conventional LEED) or RFS method (conventional and tensor LEED). Atomic potential in the substrate was characterized by phase shifts up to $l = 7$ derived from a band-structure calculation for copper,\textsuperscript{124} whereas nitrogen phase shifts were those derived by Imbihl $et$ $al.$\textsuperscript{125} from a superposition of free-atom potentials. $V_{or}$ was initially set at -7.0, -10.0, or -12.0 eV, depending on the model type, and $V_{oi}$ was fixed throughout at -5.0 eV. Debye temperatures for copper and nitrogen were taken as $343^{126}$ and 731 K, respectively; the latter was chosen to give a constant root-mean-square vibrational amplitude for all atoms.\textsuperscript{127}

Refined values of $V_{or}$ were obtained during R-factor comparison of calculated and experimental intensity curves, which was also done visually. Special care was taken in the tensor LEED analysis to ensure consistency between visually observed changes and changes in individual beam R-factors. The average LEED reliability index $R_{av} = \frac{1}{2} (R_{M2I} + R_{p})$ was used to assess overall agreement between experiment and theory.
Figure 5.1 Auger spectra for the clean Cu(110) and Cu(110)-(2x3)-N surfaces taken with a CMA; two consecutive scans were made for the clean surface, whereas the scans for the (2x3) surface were made for two different experiments. The inset gives a schematic diagram of the (2x3) LEED pattern. Solid and hollow dots correspond respectively to integral and fractional beams, and boxes indicate one beam from each symmetry-equivalent set for which I(E) curves were measured.
Figure 5.2  A comparison of I(E) curves measured for the Cu(110)-(2x3)-N surface with N activated at 200, 350, and 500 eV. The average of the three experimental data sets was used in the comparison with theoretically calculated curves.
Figure 5.3  (a) The bulk structure of Cu$_3$N; (b) the ideal Cu$_3$N(110) surface; and (c) the ideal Cu$_3$N(100) surface. Small circles represent N atoms, while large circles represent Cu atoms. Shading indicate atoms belonging to the same layer.
The bulk structure of Cu$_3$N\textsuperscript{128} served as a guide for estimating the chemical reasonableness of a particular model. In Cu$_3$N (Fig. 5.3), each nitrogen atom bonds octahedrally to six copper atoms with a bond length of 1.91 Å, but a shorter N-Cu bond length would be expected on a surface where the nitrogen atom bonds to fewer Cu atoms. Specific estimates can be made from bond length-bond order considerations, such as through Equation (5.1), deduced from bulk structural information.\textsuperscript{83,129} Equation (5.1) relates the bond length of a bond of order $s$ to the single bond length $b_1$ by

$$b_s = b_1 - 0.85 \log s$$  \hspace{1cm} (5.1)

For $n$ non-equivalent bonds, there will be $n$ different bond orders whose total $s_1 + s_2 + ... + s_n = \text{valency } v$, insofar as the adsorbate species alone determines the total bonding capacity. If all $n$ bonds are equivalent, $s = v/n$. For nitrogen, $v = 3$, and $b_1 = 1.65$ Å when N is bonding to three Cu atoms. An average bond length value of 1.76 Å would be expected for four-coordinate nitrogen, which would occur, for example, when N chemisorbs on long-bridge sites on the Cu(110) surface, or when N is held substantially above its nearest copper neighbours on the (100)-reconstructed surface. In the latter case, a fifth bond can form between nitrogen and second layer Cu atoms when N is nearly coplanar to the reconstructed layer; the average predicted bond length is then 1.84 Å.

Table 5.1 lists the names of all the models considered, along with the figures in which they are illustrated, and calculational details will be given in the next two sections.
Table 5.1 General notation used to name structural models of the Cu(110)-(2x3)-N surface in terms of the chemisorption sites and types of reconstruction. Also tabulated are model names, the figures (and page numbers) where the models are defined, and the section under which they are discussed. Models in bold are not defined in figures, but are described in the text (on the page noted) and are related to those for which there are schematic diagrams.

<table>
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<tr>
<th>Type of site</th>
<th>Type of reconstruction</th>
<th>Variations of basic model</th>
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<tr>
<td>LB = long bridge</td>
<td>MA = missing atom</td>
<td>a, b, c, A, B, C, D, E, F, G</td>
</tr>
<tr>
<td>HOL = hollow</td>
<td>MR = missing row</td>
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</tr>
<tr>
<td>U (ULB) = underlayer, &quot;long bridge&quot;</td>
<td>100 = pseudo-(100)</td>
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<tr>
<th>Analysis</th>
<th>Figures and Tables</th>
<th>Model names</th>
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<tr>
<td>Conv. LEED, I; § 5.4.1</td>
<td>Fig. 5.4 (p. 75)</td>
<td>LBa → LBae, HOLa, HOLc, LBaMA → LBcMA, LBaMR, LBBMR, LBaMR', LB2a, LB2b, LBM2R, ULBa (p. 78), ULBbMR, ULBbMR', 10002X2, PS100, PS100X2</td>
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<td>Conv. LEED, II; § 5.4.2</td>
<td>Fig. 5.6 (p. 81)</td>
<td>100C2X2, 100A → 100E, LBbMR</td>
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<td>Tensor LEED; § 5.5.1</td>
<td>Fig. 5.4 (p.75)</td>
<td>LBaMR', LB2a, LB2a' (p. 83)(^a)</td>
</tr>
<tr>
<td>Tensor LEED; § 5.5.2</td>
<td>Fig. 5.7 (p. 87), Fig. 5.8 (p.88), Table 5.4 (p. 91), Fig. 5.4 (p.75)</td>
<td>LBBMR, MRA, UMR, UMRa (p. 84)(^b), ULBbMR</td>
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<td>Fig. 5.7 (p. 87), Fig. 5.8 (p.89), Table 5.5 (p. 92)</td>
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<td>Fig. 5.7 (p. 87), Fig. 5.8 (p.89), Table 5.6 (p. 100)</td>
<td>100G, UMRa (p. 84)(^b)</td>
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</table>

(a) LB2a' is the same as LB2a, except N atoms occupy all LB sites exposed by the missing row.

(b) UMRa is the same as the <001>-missing row model illustrated in Fig. 5.7, except that the overlayer contains only 2 N atoms (labelled N\(_1\)) per (2x3) unit mesh.
5.4 Structural analysis, I: conventional LEED

5.4.1 Initial comparison of 25 models

Conventional LEED analysis of the Cu(110)-(2x3)-N surface was done in two separate stages. In the first study, 25 structurally distinct models were tested (Fig. 5.4). These cover a variety of local environment, with nitrogen coverage ranging from 1/6 to 2/3 ML. Simple overlayer models include nitrogen chemisorption on long-bridge (LB) sites at 1/6 ML (LBa), 1/3 ML (LBb), 1/2 ML (LBc), and 2/3 ML (LBD, LBE) and nitrogen chemisorption on hollow (HOL) sites at 1/6 ML (HOLa) and 1/2 ML (HOLc). Multiple scattering calculations were done for these models with variations in the nitrogen height relative to the top Cu layer and the first-to-second Cu interlayer spacing. Comparisons made with the experimental I(E) curves lead to the following conclusions:

(1) Both visual and R-factor analyses show that LB models give a better account of the experimental I(E) curves than the HOL models. This appears to support the HREELS result\textsuperscript{107} that nitrogen chemisorbs on long-bridge sites.

(2) The simple adsorption models seem unlikely to be correct. Reasonable agreement between experimental and calculated I(E) curves from simple LB-type models could be achieved only for integral beams, but not for fractional-order beams (e.g., curves for LBD in Fig. 5.5).

(3) In each simple adsorption model, $R_{av}$ was greater than 0.280 at the geometry which minimized $R_{av}$. On visual analysis, none of these models showed a sufficient match between experimental and calculated I(E) curves to warrant considering them further.
Figure 5.4 Schematic diagram for 21 out of the 25 models considered in the first conventional LEED analysis. Small and large circles represent respectively N and Cu atoms; shading decreases progressively toward the bulk. Side views are included for two underlayer models and for LB6MR.
Table 5.2  Ranges of structural parameters considered for those models for which I(E) curves are provided in Fig. 5.5. Included are increment sizes (in parentheses) and optimal values.

<table>
<thead>
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<th>Model</th>
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<th>Lateral parameters (Å)</th>
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<td>$d_{12}$</td>
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<td>-0.02</td>
</tr>
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</tr>
<tr>
<td></td>
<td>Optimal</td>
<td>-0.10</td>
<td></td>
</tr>
<tr>
<td>LB2b</td>
<td>Range</td>
<td>-0.10 (0.10) 0.10</td>
<td>-0.10 (0.10) 0.10</td>
</tr>
<tr>
<td></td>
<td>Optimal</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>LBd</td>
<td>Range</td>
<td>-0.10 (0.10) 0.10</td>
<td></td>
</tr>
<tr>
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<td>Optimal</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>100C2X2</td>
<td>Range</td>
<td>-0.20 (0.10) 0.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Optimal</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

(a) The range applies to displacement of either N-bonded Cu atoms only or the whole row of Cu atoms; optimal value corresponds to the latter displacement.
(b) The same range was used for $d_{23}$, optimal value being given in brackets.
Figure 5.5  Initial conventional LEED results comparing experimental with FD-calculated I(E) curves for the models listed in Table 5.2 and illustrated in Fig. 5.4. Only eight of the nine beams used in the analysis are shown.
The restructured models considered comprise three types: the first has N in LB sites on the (110) surface supplemented by missing Cu atoms or missing rows of Cu atoms; the second has N in LB sites in overlayer/underlayer combinations; and the third has an N environment like that established for hollow site chemisorption on the Cu(100) surface. The last type (100C2X2) was suggested by Ashwin et al.,\textsuperscript{108-110} while one of the missing-row models (LBaMR') was based on STM and NICISS results.\textsuperscript{113,114} Geometrical variations of the basic reconstructed models (Table 5.2) gave the following observations:

(1) Of the pseudo-(100) models, 100C2X2 could better account for experimental data than either PS100 or PS100X2. The last two maintain the total number of Cu atoms on an ideal Cu(110) surface and have N atoms at or near LB sites for total coverages of 1/3 and 2/3 ML, respectively. The optimal 100C2X2 structure, at this stage, has N coplanar to a non-rumpled (100) overlayer with a first-to-second interlayer spacing ($d_{12}$) of 2.18 Å. Visual comparison of calculated and experimental I(E) curves showed problems for all fractional beams (e.g., (2/3 1/2) and (5/3 1) in Fig. 5.5) and verified the somewhat large value of $R_{av}$ (0.312).

(2) Calculated I(E) curves for models in which N atoms occupy LB sites both in the overlayer and varying numbers of underlayers also gave poor correspondence with experimental data. The underlayer is either unreconstructed (ULBa, not shown) or is of the missing-row type (ULBbMR and ULBbMR', Fig. 5.4). For ULBa, four specific models were considered corresponding to one, two, three and infinite number of N underlayers. In all cases, agreement with experimental I(E) curves, especially for the integral beams, was much worse than for the corresponding single overlayer models (i.e., LBa and LBBMR, respectively).

(3) All remaining restructured models in Fig. 5.4 have N in equivalent, 4-coordinate LB sites on the Cu surface. Initial comparison of I(E) curves suggested that
missing-row (MR) models can better account for experimental data than missing-atom (MA) models (c.f. LBbMR and LBbMA) and that the missing row is in the <001> direction, rather than in the <110> direction as proposed by Niehus et al.,113,114 (c.f. LBaMR and LBaMR', respectively). Furthermore, models with a lower N coverage tended to give lower values of $R_{av}$ than those with higher coverage. For example, the minimum $R_{av}$ for the basic (unrelaxed) LBaMR' ($\theta_N = 1/6 \text{ ML}$) is 0.263 as compared to 0.287 for model LB2a ($\theta_N = 1/3 \text{ ML}$).

Metallic relaxations in the basic reconstructed LB models include rumpling ($D_{11}$) as well as lateral displacements ($\Delta_{Cu_1}$) of top-layer Cu atoms from the ideal Cu(110) position. Also considered in model LBbMR was a lateral displacement ($\Delta_N$) of N from the ideal long-bridge position. R-factor and visual analyses support two <001>-missing row models, which differ only in the number of N atoms on the surface ($\theta_N = 1/6 \text{ ML}$ for LBaMR, and $\theta_N = 1/3 \text{ ML}$ for LBbMR).

Structural details were consistent between LBaMR and LBbMR, as well as between these models and Cu$_3$N. The bulk structure of Cu$_3$N has N atoms at the corners of a cube with Cu atoms at midpoints on the cube edges,128 and the ideal Cu$_3$N(110) surface has rows of (Cu-N-Cu-N)$_x$ alternating with "missing rows" in the <001> direction (Fig. 5.2). In LBbMR, every third N atom is missing from the chain to give the surface unit (Cu$_a$-N-Cu$_b$-N-Cu$_p$)$_x$, whereas every third site is occupied in LBaMR to give the surface unit (Cu$_b$-Cu$_a$-N-Cu$_a$-Cu$_b$)$_x$. Although LBaMR gives a slightly lower $R_{av}$ value than LBbMR, the higher coverage model LBbMR does appear more consistent with the stoichiometry of Cu$_3$N.

In the optimized LBbMR surface structure, N atoms lie 0.32 Å above the plane containing those copper atoms (Cu$_p$) which are bonded to only one nitrogen, while Cu$_a$ are displaced laterally away from the nitrogen atoms by about 0.07 Å. The substrate
relaxation gives rise to asymmetric N-Cu surface bond lengths in the chain; specifically, $b_{\text{Cu}_a}$ equals 1.90 Å and $b_{\text{N-Cu}_b}$ equals 1.83 Å. The bond lengths of 1.88 Å between each N atom and the two neighbouring Cu atoms in the second layer is achieved by a reduction in the first-to-second copper interlayer spacing ($d_{\text{Cu}_a-\text{Cu}_2}$) to 1.06 Å from 1.15 Å in the clean surface (1.28 Å in the bulk).

A small expansion of each occupied adsorption site is also observed as Cu$_a$ atoms are displaced laterally away from the center. Thus, on the reconstructed missing-row surface, one out of three long-bridge sites in the (2x3) unit mesh is contracted and is, therefore, unoccupied. To have all sites occupied would require a substantial expansion of the (110) surface in the $<00\overline{1}>$ direction to allow longer N-Cu bond lengths. Such an expansion would destroy the (2x3) periodicity seen in the LEED pattern and maintained in the optimized LBbMR model. The first stage of the conventional LEED analysis of the Cu(110)-(2x3)-N surface structure thus favours an $<00\overline{1}>$-missing row model, similar to the Cu$_3$N(110) surface.

5.4.2 Further analysis of 100C2X2 and LBbMR

Subsequent to the first study, X-ray reflectivity results became available, supporting the (100)-reconstruction model. Structural details of the X-ray model were significantly different from those considered in the previous LEED analysis, however, and so a second series of FD calculations were done for five pseudo-(100) models not previously tested: the X-ray model included corrugation in the top four copper layers (100E), three models restricted buckling to the top two copper layers (100A, 100B, 100C), and one had no rumpling but the top two copper layers were (100) reconstructed (100D). Additional calculations were also performed for model LBbMR, to allow second-layer relaxations. Figure 5.6 specifies the ranges and optimized values of structural parameters for (100)-type models, while Table 5.3 lists those considered for LBbMR.
Figure 5.6 (100)-reconstruction models considered in the second conventional LEED analysis. Ranges of structural parameters are given in Å, with optimized values in brackets and $V_{s}$ and $R_m$ under each model name. Calculations for models 100A, 100B, and 100C also included second Cu layer relaxation in the opposite sense (i.e., $D_{22} = -0.1150$ Å).
Table 5.3  Ranges and optimized geometrical parameters, including those for the second metal layer, for model LBbMR during the conventional LEED analysis. A comparison is made with results from the first study when no second layer relaxations were allowed.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Optimal</th>
<th>Previous optimal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{N_1}$ (Å)</td>
<td>0 (0.10) 0.30</td>
<td>0.20</td>
<td>0.32</td>
</tr>
<tr>
<td>$D_{11}$ (Å)</td>
<td>0 (0.05) 0.05</td>
<td>~ 0</td>
<td>0.01</td>
</tr>
<tr>
<td>$\Delta_{Cu_1}$ (Å)</td>
<td>-0.05 (0.05) 0.15</td>
<td>0.08</td>
<td>0.07</td>
</tr>
<tr>
<td>$\Delta_{N_1}$ (Å)</td>
<td>-0.05 (0.05) 0.05</td>
<td>~ 0</td>
<td>-0.01</td>
</tr>
<tr>
<td>$D_{22}$ (Å)</td>
<td>-0.10 (0.05) 0.10</td>
<td>-0.05</td>
<td>0</td>
</tr>
<tr>
<td>$d_{12}$ (Å)</td>
<td>0.98 (0.05) 1.23</td>
<td>1.07</td>
<td>1.06</td>
</tr>
<tr>
<td>$d_{23}$ (Å)</td>
<td>1.18 (0.05) 1.38</td>
<td>1.25</td>
<td>1.28</td>
</tr>
<tr>
<td>$V_{tr}$ (eV)</td>
<td>-9.4</td>
<td>-8.6</td>
<td></td>
</tr>
<tr>
<td>$R_{av}$</td>
<td>0.2305</td>
<td>0.2368</td>
<td></td>
</tr>
</tbody>
</table>
Consistent with the previous LEED results, model LBbMR gave a lower \( R_{av} \) than any of the (100)-type models; of the latter group of models, \( R_{av} \) was lowest for the single Cu(100)-c(2x2)-N overlayer, with N coplanar to the non-rumpled reconstructed Cu layer. Furthermore, optimized top-layer relaxation parameters in LBbMR were essentially unchanged by the inclusion of a small vertical splitting of the second Cu layer. Neither R-factor nor visual analysis could detect, however, any significant improvement in agreement between calculated and experimental I(E) curves for any of the models, as compared to the previous work. Therefore, no new conclusions can be drawn at this time from conventional LEED methods.

### 5.5 Structural analysis, II: tensor LEED

Three model types were considered (Figs. 5.7 and 5.8): those based on LBbMR, which allowed relaxations of the top three Cu layers, those based on 100C2X2, which restricted relaxations to the top two Cu layers (set by currently available TLEED programs), and those based on the STM model, which included the top two Cu layers. In the following discussion, numerical subscript on each atom indicates the layer to which it belongs, e.g., \( N_i \) represents a nitrogen atom in the first layer, \( Cu_j \) a copper atom in the third layer. Additionally, for (100)-type models, \( N_t, N_o, \) and \( N_b \) refer respectively to N atoms which are on-top, off-top, and on bridge sites with respect to the topmost Cu(110) layer; and Cu\( h \) and Cu\( l \) identify Cu atoms in the (100) layer which are farther away from (higher) and closer to the bulk (lower), respectively. Figure 5.7 specifies further the convention for labeling atoms and structural parameters used in this section.
5.5.1 $<1\bar{1}0>$-missing row models

Reference structure (FD) calculations were done for three models where every third $<1\bar{1}0>$ row is missing: LBaMR', LB2a, and LB2a'. The first two are illustrated in Fig. 5.4; the last is similar to LB2a, except that N atoms occupy all sites in the second layer exposed by the missing row. TLEED optimization gave the following preliminary conclusions:

1. Similar displacements of top layer Cu atoms were observed for models LBaMR' and LB2a'. Specifically, those which are bonded to nitrogen are laterally displaced away from the nitrogen to give bond lengths $b_{N_1-Cu_1}$ of 2.10 and 2.08 Å, respectively.

2. The magnitudes of displacements of second layer Cu atoms were different between LBaMR' and LB2a', although the direction was the same in each case. $b_{N_1-Cu_2}$ for LBaMR' and LB2a' are, respectively, 1.56 and 1.99 Å.

3. For LB2a', displacements of N atoms in the second layer resulted in a rather short bond length to copper atoms in the third layer ($b_{N_2-Cu_3} = 1.82$ Å).

4. R-factor analysis could not distinguish between LBaMR' and LB2a' ($R_{av} = 0.235$ for both), although visual analysis showed some differences between calculated I(E) curves for the two models. The previous LEED analysis for LBaMR' gave $R_{av} = 0.256$.

It may be inferred from (4) above that the effect of the weakly scattering N atoms on the LEED I(E) profiles is small compared with the effect of the gross rearrangement of the metal atoms. The optimized atomic displacements, especially in the topmost Cu layer, seem somewhat implausible in that they give a longer $b_{N_1-Cu_1}$ as compared to $b_{N_1-Cu_2}$. This is against expectation when the second layer Cu atoms must necessarily bond to more Cu.
neighbours than those in the top layer (ten as compared to six). Since structural models must ultimately be based on chemical principles, and since no significant improvement in visual or R-factor analysis could be observed, no further calculations were done for <110>-missing row models.

5.5.2 <001>-missing row models

TLEED calculations were performed for five different models where every other <001> row is missing, and they can be classified as follows: a single missing-row overlayer with two or three N atoms on the remaining LB sites (LBbMR and MRa in Fig. 5.8), a two-N-atom missing-row overlayer with two- or three-N-atom underlayer in an otherwise unreconstructed Cu(110) surface (UMR and UMRa), and a two N-atom missing-row reconstruction in both the first and third Cu layers (ULBbMR in Fig. 5.4). The last is based closely on the ideal Cu$_3$N(110) surface, but with every third site empty; both the first and last models had been studied before (Section 5.4.1), while the remaining models arose as TL-optimized displacements suggested them as possibilities worth investigating. Relaxations in the top three layers were allowed so that the number of geometrical parameters being varied is similar between LBbMR-type and (100)-type models.

Table 5.4 defines the reference structure coordinates and gives the TLEED-optimized geometrical parameters for the first type. Models LBbMR, MRa, and UMR can be considered fully optimized within the context of tensor LEED, the magnitude of displacements in the final TL cycle being ≤ 0.1 Å. Both ULBbMR and UMRa contain large displacements in the range where TL fails to reproduce FD calculations. Furthermore, the displacements gave unreasonably short N-Cu bond lengths (as compared to bulk Cu$_3$N) so that no additional calculations were done for these two models; Section 5.5.4 gives a more detailed discussion of the failure of the automated search procedure with respect to UMRa.
Of the three optimized models, $R_{av}$ indicates that agreement with experimental data is better achieved by having (1) every third LB site empty rather than all sites filled with nitrogen ($R_{av} = 0.194$ and $0.204$ for LBbMR and MRa, respectively) and (2) a single N-overlayer rather than an overlayer/underlayer combination ($R_{av} = 0.200$ for UMR). Nevertheless, the differences among these models are not great in either R-factor or visual analysis, and a possible explanation for this observation lies in the very similar atomic coordinates obtained for each model (Table 5.4 and Fig. 5.8); this is consistent with results from the previous section where R-factor analysis could not distinguish between two models which differ essentially only in the number of N atoms on the surface. It is also interesting to note that MRa gives the observed (2x3) periodicity only because of the large displacement of a Cu atom in the third layer, in contrast to the test case results of Section 2.4.4, where the periodicity in the $<1\bar{1}0>$ direction was not reproduced by atomic displacements of small magnitude.

Further discussion of $<001>$-missing row models will be limited to LBbMR, first because it gives the best account of experimental data among these types, and second because it was favoured in the conventional LEED study. Full TL-optimization of the top three layers in LBbMR gave first-layer displacements which differ not only in magnitude but also in direction from those of conventional (FD) LEED. Specifically, from FD calculations, Cu atoms which are bonded to only one N atom are laterally displaced away from nitrogen ($\Delta_{Cu_1} = 0.07 \text{ Å}$), whereas $\Delta_{Cu_1} = -0.06 \text{ Å}$ from TL, such that the unoccupied third site is expanded rather than contracted. Although the height of nitrogen above the first Cu layer is similar between the two analyses ($D_N \sim 0.3 \text{ Å}$), TL indicated a movement of N atoms toward the center ($\Delta_N = -0.04 \text{ Å}$) where FD suggested none (or negligible at $-0.01 \text{ Å}$). Finally, first-to-second Cu interlayer spacing is somewhat longer from TL (1.10 Å) than from FD (1.06 Å). The most significant difference among these three parameters is clearly $\Delta_{Cu_1}$. Arguments for the empty site presented in Section 5.4.1 are no longer
Figure 5.7 Schematic diagram showing the atom-labelling scheme used in the tensor LEED analysis of the Cu(110)-(2x3)-N surface. Small filled circles represent N atoms. Large, hollow circles represent top-layer Cu atoms, while second-layer Cu atoms are filled. 100S1 and 100S2 are (100)-reconstruction models which exhibit glide-line symmetry.
Figure 5.8  Top views show explicitly TL-optimized lateral displacements of magnitudes specified in Tables 5.4 and 5.5 for six models of the Cu(110)-(2x3)-N surface structure. Thick solid lines indicate the plane through which side views are taken. Solid lines in the side views locate the center of mass for each Cu layer, while broken lines indicate vertical displacements. Shading of top-layer Cu atoms have been removed for clarity.
Figure 5.8, continued
Figure 5.9  Comparison of experimental and TL-calculated curves for the optimized geometry of two (100)-reconstructed models (100C2X2 and 100G) and two <001>-missing row models (LBbMR and UMR).
Table 5.4  TLEED-optimized geometrical parameters for three \textless 001\textgreater-missing row models. D and Δ correspond respectively to vertical and lateral displacements from the ideal positions (i.e., bulk for Cu or coplanar, long-bridge for N); negative displacement is toward the bulk or toward the origin as specified in Fig. 5.7; d gives the center-of-mass interlayer spacings, and b the N-Cu bond lengths. The initial reference structure, defined for LBbMR, fixed all parameters at zero except $D_{N1} = +0.300$ Å, $d_{12} = 1.080$ Å, $d_{23} = 1.280$ Å, and $d_{34} = 1.278$ Å.

<table>
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<th>UMR</th>
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<td>+0.379</td>
<td>+0.386</td>
<td>+0.373</td>
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<td>n/a</td>
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<td>+0.014</td>
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<tr>
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<td>-0.032</td>
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<td>-0.130</td>
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<tr>
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<td>-0.098</td>
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</tr>
<tr>
<td>$D_{Cu3a'}$</td>
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<td>+0.012</td>
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<td>$D_{Cu2b'}$</td>
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<td>+0.286</td>
<td>+0.342</td>
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<td>-0.082</td>
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<td>n/a</td>
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<td>-8.02 [0.2041]</td>
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Table 5.5  Geometrical parameters defining the initial reference structures, as well as optimized values, for TLEED calculations of (100)-reconstruction models. D and A correspond respectively to vertical and lateral displacements from the ideal positions (negative displacement is toward the bulk or toward the origin as specified in Fig. 5.7); d gives the center-of-mass interlayer spacings, and b the N-Cu bond lengths.

<table>
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<td>+0.650</td>
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<td>0</td>
</tr>
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</tr>
<tr>
<td>V_{ox} (eV) [R_{av}]</td>
<td>-9.22 [0.2114]</td>
<td>-9.06 [0.2350]</td>
<td>-9.02 [0.1908]</td>
</tr>
</tbody>
</table>
valid (hence, the TL calculations for MRa). Nevertheless, it must be concluded that the TL-optimized geometry is more reliable. First, visual analysis supports the lower $R_{av}$ value (0.194 vs. 0.237 from FD). Second, although a thorough structural search was performed in the FD study, the traditional trial-and-error method necessarily leaves much of the parameter space unexplored, and the link between different atomic displacements could be missed.

It appears that the improvement in correspondence with experimental data is due in large part to a substantial rumpling in the third Cu layer. This observation was verified as follows. In the initial reference structure calculation for LBbMR, all Cu atoms (except for the missing row) were kept at bulk positions. The first set of TL-optimized geometrical parameters was then used to calculate I(E) curves for displacements within each separate layer. Relative to the undisplaced coordinates ($R_{av} = 0.258$), neither visual nor $R$-factor analysis showed any increased agreement between calculated and experimental I(E) curves when first-layer, second-layer, or first-plus-second-layer displacements were considered individually ($R_{av} = 0.274$, 0.262, and 0.267, respectively). $R_{av}$ dropped to 0.226 when only third-layer relaxations were included, first and second layers being fixed at the reference structure positions. Even with all displacements except one set at 0.00 Å ($D_{33} = 0.46$ Å), $R_{av}$ decreased to 0.232. Full optimization of all three layers gave the lowest $R_{av}$ (0.190). Atomic coordinates obtained at this stage were somewhat unreliable, however, since TL optimization gave a displacement of 0.46 Å away from the reference structure positions and this is beyond the range of validity of the tensor LEED approximation. Thus, a second calculation was done starting from the previous result.

After three FD/TL cycles, TLEED converges on an optimal set of geometrical parameters for LBbMR (Table 5.4). The asymmetric N-Cu surface bond lengths remain ($b_{N-Cu_1} = 1.80$ and 1.83 Å), although not as pronounced as in the conventional LEED
study. Metal relaxations appear chemically reasonable in that they tend to strengthen N-Cu bonding, Cu atoms in both the first and second layers moving toward nitrogen. A longer bond length to the second layer \((b_{N-Cu_2} = 1.90 \text{ Å})\) gives an average N-Cu bond length of \(1.86 \text{ Å}\), which is still rather long compared to the predicted value of \(1.76 \text{ Å}\). Nevertheless, having \(b_{N-Cu_2} > b_{N-Cu_1}\) reinforces arguments put forth in Section 5.5.1 (that a delicate balance exists between bonding to nitrogen and bonding to its nearest neighbours, especially for second-layer Cu atoms). Missing from the first study are lateral displacements in the second and third metal layers and a significant rumpling in the third.

5.5.3 Pseudo-(100) models

Five models belonging to two diperiodic space groups (\(p2gg\) and \(p2mm\)) served as reference structures for (100)-reconstruction calculations (Figs. 5.7 and 5.8 and Table 5.5). Initial optimization of structural parameters for models 100S1 and 100S2 indicated that the glide-line symmetry was being incorrectly treated by the automated search routines; for example, different displacements were obtained for the two top-layer Cu atoms marked 1 and 6 in Fig. 5.7, model 100S1. Furthermore, a vertical displacement of \(\sim 0.8 \text{ Å}\) for atom "1" gives a first-to-second Cu bond length of \(2.01 \text{ Å}\), which corresponds to a 21% contraction compared to the metallic distance of \(2.556 \text{ Å}\). Although significant interlayer contractions are often observed on open surfaces, changes in metal bond lengths are not as great (e.g., for clean Cu(110), \(d_{12} = 1.15 \text{ Å}\) is a 10% contraction relative to the bulk value of \(1.278 \text{ Å}\), but the metal-metal bond length reduces to \(2.49 \text{ Å}\), only a 2.4% contraction from the distance in the bulk metal). \(R_{av}\) does not rule out 100S1 or 100S2 as possible structures of the Cu(110)-(2x3)-N surface, but until the TLEED programs available can correctly treat surfaces exhibiting glide-line symmetry, additional calculations will not be done for these models.
Figure 5.10  Comparison showing dramatic improvement in agreement between experimental and calculated I(E) curves for model 100F after only one FD/TL cycle. FDO are full-dynamical calculated curves, while TLO were obtained after optimization by the directed search method.
Two of the remaining three models contain metal corrugations of magnitudes suggested by X-ray reflectivity measurements\textsuperscript{116} (100F and 100G), while one maintained a non-rumpled (100) overlayer with N coplanar to the reconstructed layer (100C2X2) as in the first LEED study. Dramatically improved agreement with experimental data was immediately achieved even after only one FD/TL cycle for the rumpled models. For example, FD calculated I(E) curves for 100F showed very poor correlation with experiment, by both visual and R-factor analyses ($R_{av} = 0.524$); after TL optimization, $R_{av}$ decreased to 0.196, and visual analysis confirmed the improvement (Fig. 5.10, e.g., beams (2/3 1/2) and (4/3 1)). TL displacements are still large at this stage, however, the maximum magnitude being 0.25 Å, and so a second calculation was performed starting from the first TL results. After two FD/TL iterations, geometrical parameters for 100F can be considered closely optimized within the context of tensor LEED (maximum displacement $\sim$ 0.10 Å). Although the final TL-optimized $R_{av}$ value of 0.235 is somewhat higher than that obtained after the first cycle, atomic coordinates from the second TLEED calculation should be more reliable because of the smaller shifts from the reference structure positions. It is also important to note that, compared to conventional LEED results of Section 5.4.2, the directed search method had given significantly better agreement between calculated and experimental I(E) curves so that the Cu(110)-(2x3)-N surface structure could now be considered as likely to be (100) reconstructed as <001>-missing row reconstructed.

A similar, though not as dramatic, improvement was also observed for the non-rumpled, N-coplanar 100C2X2 model. Convergence to the optimal geometry was achieved after two cycles, $R_{av}$ dropping from 0.298 to 0.211. The slightly lower $R_{av}$ value for 100C2X2 as compared to 100F appears to favour a nearly flat (100) overlayer to one which is highly corrugated (Table 5.5). Visual comparison of integral beam curves
supports R-factor analysis (Fig. 5.9, e.g., beams (1 0) and (2 0)), although problems remain for fractional beams (e.g., (2/3 1/2)).

Without rumpling in the topmost Cu layer, a (100)-reconstruction model is inconsistent with both STM images and X-ray results. Thus, a new series of TL calculations was started from a reference structure where metallic corrugation is as in model 100F, but with N nearly coplanar to the reconstructed layer. The initial height of N (D_N) above its local Cu neighbours gave an average N-Cu bond length of 1.87 Å (predicted bond length is 1.85 Å for 5-coordinate N); the Cu-Cu metallic distance determined the initial interlayer spacings (model 100G in Table 5.5 and Fig. 5.8). Observations regarding the failure of the automated search procedure in some instances will be discussed in the next section, and only a summary of the results will be given here. After eight FD/TL iterations, the coordinates of 18 atoms in the top two layers are sufficiently refined that all displacements in the final cycle are less than ~0.1 Å.

At this stage, 100G gives the best account of experimental data of the (100)-type models. Although R-factor analysis cannot distinguish between 100G and LBbMR (R_{av} = 0.19 for both), visual analysis might favour the former (c.f. integral beams in Fig. 5.9). Further support for 100G as the correct structure of the Cu(110)-(2x3)-N surface comes from comparison with X-ray results. TL-optimized first-layer corrugation D_{11} = 0.494 Å is close to the stated error limit of 0.639 ± 0.089 Å from the latter work. Additionally, first-to-second (d_{12}) and second-to-third (d_{23}) interlayer spacings equal 1.890 and 1.289 Å, respectively; X-ray reflectivity measurements give d_{12} = 2.006 ± 0.153 and d_{23} = 1.304 ± 0.064 Å. Similar magnitudes were obtained for second-layer rumpling (D_{22}) and N vertical height between the two techniques, although the details of the displacements differ. For example, TL indicates three different values for D_N ranging from 0.068 to 0.284 Å and corresponding to nitrogen being in three different local environments, where X-ray suggests only one (0.75 ± 0.5 Å). Perhaps it is not surprising that LEED is more
sensitive than X-ray scattering to the position of a weak scatterer such as nitrogen, while coordinates of Cu atoms were more closely reproduced between the two techniques.

TLEED also gave other structural parameters not observed in the X-ray study. Most notable of these are lateral displacements of $N_0$ and second-layer Cu atoms to allow the formation of a fifth N-Cu bond, which is not significantly present in the absence of these relaxations (Fig. 5.8). Consequently, three out of the four nitrogen atoms become 5-coordinate as they would be on the true Cu(100)-c(2x2)-N surface. One N atom remains 4-coordinate resulting from the need to maintain a physically reasonable Cu$_1$-Cu$_2$ metallic distance. The average N-Cu bond lengths of 1.836 (N$_i$) and 1.855 Å (N$_o$) for 5-coordinate nitrogen are close to both the expected value and that obtained for Cu(100)-c(2x2)-N,$^{131}$ while the value of 1.936 Å for 4-coordinate nitrogen (N$_b$) is somewhat long compared to the predicted value of 1.76 Å. Nevertheless, these bond lengths appear more consistent with prediction than those (1.93 and 2.08 Å) reported by Baddorf et al.,$^{116}$ as the latter are rather longer than the value of 1.91 Å for 6-coordinate nitrogen in bulk Cu$_3$N.$^{128}$

5.5.4 Anomalies in TLEED results

The last two sections noted concern with respect to TLEED results in two instances: those for 100G and for UMRa. An intermediate TL calculation of 100G, for example, gave a nitrogen-to-second layer Cu bond length which is much shorter than that to first-layer Cu atoms ($b_{N_i-Cu_j} = 1.71$ Å vs. $b_{N_i-Cu_i} = 1.93$ Å), and since this contrasts with the N-Cu bond lengths observed on the true Cu(100)-c(2x2)-N surface ($b_{N-Cu_2} = 2.00$ Å, $b_{N-Cu_1} = 1.81$ Å), the question arises whether the TLEED analysis got misdirected in this case. For example, visual analysis showed a substantial decrease in agreement for the fractional beam (2/3 1/2) (c.f. curves marked opt3 and opt4 in Fig. 5.11), with only a marginally improved correspondence in the integral beams (1 1) and (2 0). These
Figure 5.11  Comparison of experimental data with TL-calculated curves for models 100G and UMRa, illustrating the need to reset some TL-optimized displacements. For 100G, opt3 are TL-optimized curves for the third FD/TL cycle; opt4 are TL-optimized curves for the fourth FD/TL cycle; alt4 are TL-calculated curves with some atomic displacements from the fourth cycle reset. Note the improved agreement with experimental beam (2/3 1/2) going from opt4 to alt4. For UMRa, TL-calculated curves with (a) full optimization of all atomic coordinates, including a vertical displacement of N$_y$ (D$_{ney}$) by 1.13 Å; (b) as (a) with D$_{ney}$ fixed at zero; (c) partial optimization, atomic displacement being reset to give chemically plausible N-Cu bond lengths. See Table 5.6 for structural details.
observations together suggested that it may be worth resetting some atomic positions during the analysis to increase $b_{N_1-Cu}$, decrease $b_{N_1-Cu}$, and at the same time improve correspondence between calculated and experimental intensities for the beam (2/3 1/2).

Table 5.6 gives bond lengths for one such set of alternate coordinates, and Fig. 5.11 indicates that the match was indeed better for the alternate positions (curves marked alt4) than for the fully optimized model (curves marked opt4) for beam (2/3 1/2), with no observable change in other beams (consequently, $R_{av}$ remains comparable between the two calculations at 0.171 and 0.165, respectively). Thus, based on visual analysis as well as bond-length considerations, the subsequent FD/TL cycle was started from the alternative set of atomic positions.

Calculations for model UMRa also revealed the need to check the directed search results for chemical reasonableness. (Refer to Fig. 5.7 for atomic labels.) Full optimization ($R_{av} = 0.173$; Fig. 5.11, curves a) gives two physically implausible N-Cu bond lengths in the underlayer: vertical displacement of $N_3$ ($D_{N_3}$) by 1.13 Å produces a nitrogen-to-fourth layer Cu bond length of 1.31 Å, and a lateral displacement of $N_3$ by 0.48 Å gives a value of 1.51 Å for $b_{N_3-Cu_{3a}}$. Neither R-factor (Table 5.6) nor visual analysis (Fig. 5.11, curves b) could detect any significant decrease in agreement between calculation and experiment when $D_{N_3}$ was fixed at zero, while resetting this displacement gave an N-Cu bond length more consistent with six-coordinate nitrogen ($b_{N_3-Cu_{4a}} = 1.91$ Å). Figure 5.11 also shows calculated I(E) curves (marked c) corresponding to $b_{N_3-Cu_{3a}} = 1.81$ Å ($R_{av} = 0.183$). Visual comparison of the three variations appears to suggest that TL-optimized displacements of large magnitude may not always be necessary (or even reliable) and that chemical input may be useful in resetting atomic positions. Finally, the low $R_{av}$ value for the fully optimized model UMRa (a in the table below) can certainly be dismissed as unreliable due to the large displacements beyond the range of validity of tensor LEED.
Table 5.6  Comparison of N-Cu bond lengths (in Å) for models 100G and UMRa for the I(E) curves shown in Fig.5.11. DISP indicates the magnitude (in Å) of maximum displacement in each set of calculation.

<table>
<thead>
<tr>
<th></th>
<th>DISP</th>
<th>b_{N-Cu}</th>
<th>b_{N-Cu}</th>
<th>R_{av}</th>
</tr>
</thead>
<tbody>
<tr>
<td>100G</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>alt4</td>
<td>0.24</td>
<td>1.88</td>
<td>1.86</td>
<td>0.1713</td>
</tr>
<tr>
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<td>0.1650</td>
</tr>
<tr>
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<td>0.1766</td>
</tr>
<tr>
<td>UMRa</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>(a)</td>
<td>1.13</td>
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<td>1.31</td>
<td>0.1731</td>
</tr>
<tr>
<td>(b)</td>
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<td>1.51</td>
<td>1.91</td>
<td>0.1711</td>
</tr>
<tr>
<td>(c)</td>
<td>0.35</td>
<td>1.81</td>
<td>1.91</td>
<td>0.1833</td>
</tr>
</tbody>
</table>

5.6 Summary

Results from this chapter clearly illustrate the limitations of the conventional LEED method compared with the tensor LEED method. First, even with an extensive search in parameter space using the trial-and-error procedure, structural details were missed in the calculations for the <001>-missing row model LBbMR. Second, models where the topmost Cu layer is (100)-reconstructed were ruled out simply because the geometrical parameters had been insufficiently refined by conventional means, as there had been no indication to encourage further investigation of these models. At the present time, the R-factor analysis from tensor LEED and the directed search method appears to favour both model types equally (R_{av} around 0.19), although the latter, in particular model 100G in Fig. 5.8, appears more likely to be the correct structure of the Cu(110)-(2x3)-N surface for a number of reasons.

A highly corrugated pseudo-(100)-c(2x2)-N reconstruction model with N nearly coplanar with the topmost Cu layer can account not only for LEED data (Fig. 5.9) in the current work, but also for results from other techniques. Specifically, the copper density in the topmost Cu layer has been indicated to be increased relative to that on the clean surface (X-ray reflectivity,^{116} PED and LEIS^{108-110}), while a nitrogen coverage of 2/3 ML agrees with XPS measurements of Baddorf and Zehner.^{112} Rumpling of the pseudo-(100)
layer by 0.494 Å is consistent with observations of Baddorf et al.,\textsuperscript{116} and can perhaps reconcile an added-row model with STM images by Neihus, Spitzl and coworkers.\textsuperscript{114} In addition, average N-Cu bond lengths in model 100G (~ 1.85 Å) generally agree with prediction\textsuperscript{83,129} based on the bulk structure of Cu$_3$N; two aspects remain to be resolved, however: (1) the rather long N-Cu bond length for 4-coordinate, "bridge-site" N atoms, and (2) bond lengths which are shorter to second-layer Cu atoms than to first-layer Cu atoms for "on-top" N. The second point may not present a serious problem, however, since bonding to second layer Cu atoms is constrained in part by the short Cu(110) interlayer spacing on the pseudo-(100) surface in contrast to the longer interlayer spacings on the true Cu(100)-c(2x2)-N surface. It is expected that structural details for 100G can be further refined, and an improved account of experimental data be achieved, as future versions of the tensor LEED programs allow more complete calculations, for example, to include third and fourth metal layer relaxations as suggested by X-ray reflectivity measurements.

5.7 Addedum

After this chapter was completed, a new high resolution STM study of the Cu(110)-(2x3)-N surface became available;\textsuperscript{132} Figure 5.12 identifies the structures seen. At low N dosage, Leibsle \textit{et al.} observed the paired rows of bright spots (labelled as B features by the authors) in the <1\bar{1}0> direction, like those seen previously by Neihus \textit{et al.}\textsuperscript{114} Additional bright spots (labelled A) appeared, however, at the center of the four local B features, the surface density of A features increasing with the N dosage. Also important is the imaging of atoms (labelled C) in the dark bands between the paired rows, previously attributed to a missing row in the <1\bar{1}0> direction. These features can be explained in terms of model 100G as follows, \textit{if} it is the N atoms which are principally imaged. The B and C features correspond respectively to N atoms which are off-bridge
(N_o) and on-top sites (N_t) with respect to the Cu(110) surface. There are two N_o atoms in every (2x3) unit mesh, imaged as pairs of bright spots, and N_t atoms are less bright because they are lower than N_o atoms \textit{(i.e., closer to the bulk)}. "Bridge-site" N_b atoms are highest on the surface and are thus most brightly imaged as the A features. STM shows the (2x3) surface structure exists even when the density of the A features is very low, which is consistent with the N_b sites being occupied only at higher dosages since chemisorption on the 4-coordinate "bridge-site" would be less favourable than on the other two types of sites, where the coordination is five. Furthermore, the rather long N_b-Cu bond length obtained in the current LEED analysis may perhaps indicate that the N_b sites are not occupied, or only partly occupied, under our experimental conditions. These observations give strong evidence that the model which can best explain the structure of the Cu(110)-(2x3)-N surface, and which is most consistent with the multitude of techniques which have been applied to study this system, is a highly corrugated, pseudo-(100) reconstruction of the topmost copper layer.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Cu110-2x3-N.png}
\caption{STM images (Ref. 130) of the Cu(110)-(2x3)-N surface at (a) low and (b) high N-dosages.}
\end{figure}
6.1 Introduction

Considering that palladium plays an important catalytic role in certain oxidation reactions, for example of CO and NO in catalytic converters, it is surprising how very little quantitative structural work has been done on O/Pd chemisorption systems compared with, for example, O/Ni systems. Previous LEED studies on low Miller index surfaces of palladium have been restricted to observations of patterns and suggestions of models to account for the observed patterns. The additional techniques most often employed are HREELS and TPD, but these only give indirect evidence for the surface structure through comparison with similar systems. For example, Stuve et al. compared the loss peak at 370 cm\(^{-1}\) measured for the Pd(100)-p(2x2)-O surface to those of O chemisorbed on Ag(110) and Pt(111) and concluded a 4-coordinate (hollow) adsorption site for O atoms.

Oxygen chemisorbs on Pd(100) to form four ordered surface structures: p(2x2), c(2x2), p(5x5), and (\(\sqrt{5}\times\sqrt{5})R27^\circ\). Room-temperature chemisorption results in only the p(2x2) and c(2x2) surfaces, with respective ideal coverages (\(\theta_0\)) of 0.25 and 0.50 ML, where 1 ML corresponds to one oxygen per palladium surface atom. The p(5x5) structure (proposed \(\theta_0 = 0.64\) ML) develops with extended O\(_2\) dosing and sample heating above \(\sim 400\) K, while a temperature of \(\geq 550\) K is needed to create the (\(\sqrt{5}\times\sqrt{5})R27^\circ\) surface (proposed \(\theta_0 = 0.80\) ML). The oxygen coverages for the latter two surfaces have been estimated using Auger and TDS, assuming ideal \(\theta_0\) values for the p(2x2) and c(2x2) surfaces. He diffraction study of the p(2x2) structure places O atoms in hollow sites on the unreconstructed Pd(100) surface, which supports the interpretation given by the HREELS results. No structural analysis exists for the latter two surfaces, although two very different models have been postulated. In an earlier energy loss study, Orent and Bader suggested that the two high coverage structures correspond to
reconstructions with the formation of a PdO layer on top of the Pd(100) substrate, specifically, PdO(110) for the p(5x5) surface and PdO(001) for the (√5x√5)R27° surface (Fig. 6.1). Such oxide overlayer reconstruction is commonly observed for high-temperature oxygen chemisorption on metal surfaces, e.g., for the O/Ni(110) system. An alternative interpretation for both structures was suggested by Simmons et al.; the authors reported a HREELS loss peak at 430 cm\(^{-1}\) (in addition to that at 350 cm\(^{-1}\)) and proposed a model where oxygen atoms chemisorb on distorted 4-fold hollow sites, with significant lateral displacements of both O and surface Pd atoms to give O-Pd bond lengths of 1.576, 2.460, 2.504, and 3.138 Å for each chemisorbed O atom. The need for an independent analysis is clearly indicated, especially since knowing the surface structure is fundamental and prerequisite to understanding catalytic reactions occurring at the surface. Thus, a LEED structural analysis has been undertaken for the Pd(100)- (√5x√5)R27°-O surface, and the results are reported in this chapter.

6.2 Experiment

Experimental data at normal incidence were provided by Oden Warren at Ames Laboratory, Iowa, for 15 independent beams (Fig. 6.2) corresponding to

\[(0 \ 1), (1 \ 1), (0 \ 2), (0.2 \ 0.4), (0.2 \ 0.6), (0.6 \ 0.8), (0.4 \ 0.8), (0.4 \ 1.2),
(0.6 \ 1.2), (0.6 \ 1.8), (0.4 \ 1.8), (0.2 \ 1.4), (0.2 \ 1.6), (0.8 \ 1.6), (0.8 \ 1.4).
\]

Briefly, the Pd(100) sample was cleaned by a three step process. First, Ar\(^+\) bombardment during heating in UHV removed impurities, such as sulfur and phosphorus, which segregated to the surface. Second, the other main contaminant, carbon, is removed by reaction with oxygen to form CO. Finally, any excess oxygen is removed by annealing the surface in vacuo at 1150 K for about 2 min. The (√5x√5)R27° surface was formed by
Figure 6.1 (a) The PdO bulk structure; Ref. 145. (b) The PdO(001) overlayer model of the Pd(100)-(\sqrt{5}x\sqrt{5})-R27°-O surface, as proposed by Orent and Bader; Ref. 137. Oxide Pd atoms have been labelled to identify their registry with respect to the Pd(100) substrate: Pd_t and Pd_h correspond respectively to "on-top" and "hollow-site" Pd atoms, while Pd_{bt} and Pd_{bh} refer to "bridge-site" Pd atoms along the string containing Pd_t and Pd_h, respectively. (c) The distorted hollow-site model of Simmons et al.; Ref. 142. Additional legend in Fig. 6.3.
Figure 6.2  Schematic diagram of the LEED pattern from the Pd(100)-$(\sqrt{5}\times\sqrt{5})R27^\circ$-O surface, showing beams from two domains which are mutually rotated by 90° (see Fig. 1.1). Solid and hollow dots correspond respectively to integral and fractional beams, and boxes indicate one beam from each symmetrically equivalent set for which $I(E)$ curves were measured.
dosing O₂ at 5 x 10⁷ Torr onto the cleaned Pd(100) surface for 15 min. with the crystal
temperature being held at about 570 K. Intensity measurements were made for a total of
81 beams before averaging (30-200 eV, 1-eV grid), and background subtraction was
performed locally during the measurement.

6.3 Calculation

Oxygen phase shifts were the same as those used by Marcus et al.⁸⁰ in their O/Ni
calculations, while substrate phase shifts up to 𝑙 = 7 were calculated from the Moruzzi-
Janak-Williams atomic potential for metallic palladium.¹²⁴ The real part of the constant
potential between muffin-tin spheres was initially set through visual comparison at \( V_{0x} \)
equals -10.0, -5.0, or 0.0 eV depending on the basic model type, but was always refined
during the structural search; the imaginary part was fixed at \( V_{0i} = -5.0 \) eV. Debye
temperatures of 270 and 696 K were used for Pd and O, respectively.

Initial analysis used the conventional LEED programs as provided by Van Hove
and Tong.⁴⁸ Because structural models of the Pd(100)-(\( √5 \times √5 \))R27°-O surface generally
have a large number of parameters to be varied, however, this procedure was abandoned
in favour of the tensor LEED method (see Chapter 2), as working TLEED computer
codes became available. This system, in turn, served as a test case for assessing the
efficiency of the tensor LEED method for determining a challenging surface structure, for
which no hard information is available. As discussed in Section 2.4.1, the cycle of FD
calculation followed by directed search was repeated until the final TL-optimized structure
contained displacements away from the current reference structure which were all less
than \( ~0.1 \) Å, the amount within which TL accurately reproduces FD results. For the
analysis of the Pd(100)-(\( √5 \times √5 \))R27°-O surface structure, \( R_p \) was used to assess the
agreement between calculated and experimental I(𝐸) curves.
6.4 Structural analysis: tensor LEED

6.4.1 Reference structures

A range of chemically plausible models of the Pd(100)-(√5x√5)R27°-O surface structure was proposed. Relaxations in the top three Pd layers were allowed, and each oxygen layer contained either four or two O atoms. Bulk Pd-Pd distances and parametrized O-Pd bond lengths (see, e.g., Section 5.3) determined the atomic coordinates in the first reference structure, while subsequent reference structures were taken from TL-optimized displacements. All models except one (2BU1, θ₀ = 0.40 ML) have an oxygen coverage of 0.80 ML, as suggested by Orent and Bader and measured by other workers.\textsuperscript{137-139,142} Figure 6.3 illustrates schematically the twelve basic model types which were considered in some detail and which can be roughly divided into three groups:

(1) O overlayer on Pd(100). Three adsorption sites were considered on the unreconstructed surface: symmetrical 4-coordinate hollow (4F), symmetrical 2-coordinate bridge (4BO), and off-bridge (4FB), where O atoms were initially placed exactly half way between the hollow and bridge sites. An alternative 4-coordinate hollow site (4FMA) is created by having O nearly coplanar with a reconstructed top layer where one out of every five Pd surface atoms is missing. The distorted hollow-site model of Simmons and coworkers\textsuperscript{142} (Fig. 6.1) was not tested explicitly, as it is only a variation of 4F.

(2) O underlayer in Pd(100). One-underlayer models (4BU and 2BU1) have O atoms in tetrahedral holes between the first and second Pd layers; a two-underlayer model (2BU2) has an additional 2-O-atom layer between the second and third substrate layers. One model (2BOU) combines a bridge-site overlayer with an underlayer between first and second Pd layers.
Figure 6.3 Schematic diagrams of the initial reference structures for nine out of the twelve models of the Pd(100)-\(\sqrt{5} \times \sqrt{5})R27^\circ-O\) surface. Models 4BU and 2BU1 have an oxygen underlayer between the first and second Pd layers with O atom positions directly below the positions shown in models 4BO and 2BOU, respectively; model 2BU2 has two O underlayers between the first-and-second and the second-and-third Pd layers.
(3) PdO(001) reconstruction. The slightly expanded PdO(001) overlayer can be stacked onto the substrate in two ways: one (PDO) has Pd atoms in the oxide layer on three different sites (top, bridge, and hollow) and is that proposed by Orent and Bader, while the other (PDOS) has all overlayer Pd atoms in equivalent environments relative to the Pd(100) surface. A variation of the latter (PDOMA) has one out of every five atoms missing in the first Pd(100) layer. Finally, a two-layer reconstruction model (PDOU) consists of an O layer between two oxide Pd layers. (Figure 6.1 illustrates the bulk structure of PdO.)

For model PDO, the difference in adsorption sites of Pd atoms in the oxide layer gives hard-sphere stacking distances of 1.94, 2.38, and 2.75 Å, respectively, for hollow-site (Pd$_h$), bridge-site (Pd$_{bh}$ and Pd$_{bt}$), and on-top Pd atoms (Pd$_t$) (Fig. 6.1). Therefore, four separate initial reference structures were considered, corresponding to (1) no rumpling in either the oxide or the Pd(100) layers and a value of 2.75 Å for the interlayer spacing ($d_{12}$) between the oxide and topmost Pd(100) layers; (2) corrugation restricted to the oxide layer (i.e., $D_{ht}$, defined as the difference in height between Pd$_h$ and Pd$_t$) of magnitudes 0.80 Å ($d_{12} = 1.94$ Å) and (3) 0.40 Å ($d_{12} = 2.34$ Å); and (4) rumpling within both the oxide and topmost Pd(100) layers by 0.40 Å, for an effective $D_{ht} = 0.80$ Å. Initial analysis favoured the last type, and thus subsequent calculations were based on type (4) of model PDO.

6.4.2 Results

Full optimization, as determined by convergence within the tensor LEED approximation, was achieved for all models but one (Table 6.1); after six FD/TL cycles, calculations were discontinued for model PDOMA for two reasons. First, rather than converging toward smaller displacements with increasing numbers of iterations, the magnitude of maximum displacement was still 0.17 Å at this stage. Furthermore,
agreement between experimental and calculated I(E) curves decreased during the latter cycles; for example, \( R_p = 0.3101 \) for the fourth reference structure, while \( R_p = 0.3186 \) for the sixth. Decrease in agreement was also observed for the TL-optimized geometries (Table 6.2). This would appear to indicate that the optimization procedure was diverging rather than converging toward an optimal set of geometrical parameters for this model, thus suggesting that PDOA is unlikely to be the correct structure of the \((\sqrt{5} \times \sqrt{5})R27^\circ\) surface.

Of the remaining 11 models, R-factor analysis indicates that model PDO gives the best account of experimental data. That is to say that the most likely structure of the Pd(100)-\((\sqrt{5} \times \sqrt{5})R27^\circ\)-O surface is an oxide reconstruction with a single PdO(001) overlayer on top of the Pd(100) substrate (Fig. 6.4). \( R_p \) equals 0.2323 for fully optimized PDO, while the next closest minimum \( R_p \) value of 0.2514 (for PDOS) is sufficiently higher to rule out the other models tested. Although only \( R_p \) was used during the optimization procedure, \( R_{av} \) was additionally used to assess the agreement between experimental and \textit{FD-calculated} I(E) curves (i.e., those from reference structures at each FD/TL cycle); this served to verify the trend indicated by \( R_p \), that improved account of experimental data was being achieved, irrespective of the tensor LEED approximation and the particular R-factor used. Table 6.2 illustrates this point for model PDOA in particular, but the same observations could be made for the other models. For example, \( R_p \) decreased steadily from an initial value of 0.4294 for the first set of FD-calculated curves to 0.3101 by the fourth set, but \( R_{av} \) increased to 0.3161 for the fifth set. The corresponding \( R_{av} \) values are 0.3380, 0.2285, and 0.2397 and show the same trend as \( R_p \).

Visual analysis (Fig. 6.5) of 15 beams for 12 models requires some care, but it appears to support the R-factor analysis. For model PDO, the correspondence between experimental and calculated I(E) curves appeared best for beam (0.2 1.4), with generally good agreement for beams (0 1), (0.2 2), (0.2 0.4), (0.6 0.8), (0.4 0.8), (0.4 1.2), (0.2 1.6),
Table 6.1  Comparison of the level of agreement achieved between calculated and experimental I(E) curves for the 12 models in Fig. 6.2, with the model giving the overall best fit in bold. Values listed are for the final FD/TL cycle. $R_{av}$ for the final reference structure are included to verify the trend indicated by $R_p$. DISP indicates the level of convergence achieved within the context of tensor LEED, as given by the type and magnitude of maximum displacement in the final cycle. Only one cycle was performed for model PDOU since the value of DISP is within the range of validity of the tensor LEED approximation.

<table>
<thead>
<tr>
<th>Model</th>
<th># cycles</th>
<th>FD: $R_p$ ($R_{av}$)</th>
<th>TL: $R_p$</th>
<th>$V_0$ (eV)</th>
<th>DISP (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDO</td>
<td>10</td>
<td>0.2429 (0.2061)</td>
<td>0.2323</td>
<td>0.04</td>
<td>$\Delta_{pd} = 0.07$</td>
</tr>
<tr>
<td>PDOS</td>
<td>8</td>
<td>0.2874 (0.2196)</td>
<td>0.2514</td>
<td>-3.51</td>
<td>$\Delta_{pd} = 0.09$</td>
</tr>
<tr>
<td>PDOMA</td>
<td>6</td>
<td>0.3186 (0.2353)</td>
<td>0.2708</td>
<td>0.76</td>
<td>$\Delta_{pd} = 0.17$</td>
</tr>
<tr>
<td>PDOU</td>
<td>1</td>
<td>0.4590 (0.3354)</td>
<td>0.3152</td>
<td>0.16</td>
<td>$\Delta_{pd} = 0.11$</td>
</tr>
<tr>
<td>4F</td>
<td>10</td>
<td>0.3296 (0.3207)</td>
<td>0.3093</td>
<td>-5.83</td>
<td>$\Delta_{pd} = 0.08$</td>
</tr>
<tr>
<td>4FB</td>
<td>2</td>
<td>0.3502 (0.2800)</td>
<td>0.3306</td>
<td>-4.87</td>
<td>$\Delta_{o} = 0.06$</td>
</tr>
<tr>
<td>4FMA</td>
<td>6</td>
<td>0.3505 (0.2869)</td>
<td>0.3283</td>
<td>-5.13</td>
<td>$\Delta_{pd} = 0.08$</td>
</tr>
<tr>
<td>4BO</td>
<td>3</td>
<td>0.3253 (0.2618)</td>
<td>0.2921</td>
<td>-1.29</td>
<td>$\Delta_{pd} = 0.06$</td>
</tr>
<tr>
<td>4BU</td>
<td>3</td>
<td>0.3683 (0.2948)</td>
<td>0.3328</td>
<td>-3.43</td>
<td>$D_{pd} = 0.10$</td>
</tr>
<tr>
<td>2BU2</td>
<td>3</td>
<td>0.3218 (0.2821)</td>
<td>0.3129</td>
<td>-10.00</td>
<td>$D_{o} = 0.04$</td>
</tr>
<tr>
<td>2BU1</td>
<td>3</td>
<td>0.3904 (0.3133)</td>
<td>0.3722</td>
<td>-5.22</td>
<td>$\Delta_{pd} = 0.05$</td>
</tr>
<tr>
<td>2BOU</td>
<td>3</td>
<td>0.3566 (0.3055)</td>
<td>0.3512</td>
<td>-4.68</td>
<td>$D_{pd} = 0.03$</td>
</tr>
</tbody>
</table>
Figure 6.4 Top views showing explicitly TLEED-optimized lateral displacements in the final cycle for two PdO(001)-reconstruction models (PDO and PDOS), a bridge-site overlayer model (4BO), and a hollow-site overlayer model (4F), with the corresponding I(E) curves in Fig. 6.5. Atomic coordinates are given for model PDO because it is the structure which gives the overall best account of experimental data. Some atoms are labelled to correspond to the displacements listed in Table 6.3; also defined are some vertical displacements.
Figure 6.5 TL-calculated curves for the optimized structures in Fig. 6.4. R-factor analysis indicates that PDO gives the best agreement with experimental data ($\beta_p = 0.232$).
Figure 6.5, continued
Figure 6.5, continued
Table 6.2  \( R_p \) and maximum displacement (DISP) for the sequence of FD/TL calculations done for PDOMA. Note the decrease in agreement, as indicated by a higher value for \( R_p \), after the fourth cycle; \( R \)-values which are lower in the previous cycles may be unreliable due to the large values of DISP in those cycles. FD values are obtained from comparison with experiment of full-dynamical calculated I(E) curves, while TL values result from optimization of each reference structure.

<table>
<thead>
<tr>
<th>Iter. #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>FD : ( R_{av} )</td>
<td>0.3380</td>
<td>0.2678</td>
<td>0.2488</td>
<td>0.2285</td>
<td>0.2397</td>
<td>0.2353</td>
</tr>
<tr>
<td>FD : ( R_p )</td>
<td>0.4294</td>
<td>0.3547</td>
<td>0.3267</td>
<td>0.3101</td>
<td>0.3161</td>
<td>0.3186</td>
</tr>
<tr>
<td>TL : ( R_p )</td>
<td>0.3036</td>
<td>0.2727</td>
<td>0.2615</td>
<td>0.2551</td>
<td>0.2484</td>
<td>0.2709</td>
</tr>
<tr>
<td>DISP (Å)</td>
<td>( D_O = 0.32 )</td>
<td>( \Delta P_d = 0.21 )</td>
<td>( \Delta P_d = 0.25 )</td>
<td>( \Delta P_d = 0.24 )</td>
<td>( \Delta O = 0.27 )</td>
<td>( \Delta P_d = 0.17 )</td>
</tr>
</tbody>
</table>

Table 6.3  Some optimized structural parameters for model PDO; CM is center-of-mass spacing. Other parameters are defined in Fig. 6.4.

<table>
<thead>
<tr>
<th>Vertical (Å)</th>
<th>Lateral (Å)</th>
<th>CM spacing (Å)</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_{11} )</td>
<td>0.1001</td>
<td>( \Delta O ) +0.0133</td>
<td>( d_{12} ) 2.2318</td>
</tr>
<tr>
<td>( D_{11}' )</td>
<td>0.3428</td>
<td>( \Delta O' ) +0.1060</td>
<td>( d_{23} ) 2.2018</td>
</tr>
<tr>
<td>( D_{ht} )</td>
<td>0.2782</td>
<td>( \Delta_{2b} ) +0.0566</td>
<td>( d_{34} ) 1.9851</td>
</tr>
<tr>
<td>( D_{22} )</td>
<td>0.3783</td>
<td>( \Delta_{2h} ) -0.4888</td>
<td>( d_{23} ) 2.2018</td>
</tr>
<tr>
<td>( D_{22}' )</td>
<td>0.4816</td>
<td>( \Delta_{2h} ) -0.4888</td>
<td>( d_{34} ) 1.9851</td>
</tr>
<tr>
<td>( D_{33} )</td>
<td>0.0505</td>
<td>( \Delta_{3} ) -0.1702</td>
<td>( d_{34} ) 1.9851</td>
</tr>
<tr>
<td>( D_{33}' )</td>
<td>0.0429</td>
<td>( \Delta_{3}' ) +0.1220</td>
<td>( d_{34} ) 1.9851</td>
</tr>
</tbody>
</table>
and (0.8 1.4). Although relative peak intensities were not closely reproduced for the last beam, the more important peak positions seemed to match those of the experimental curve. The double peak between 40 and 60 eV of beam (0.4 0.8) emerged for no model other than the fully optimized PDO model; even after many refinements in the conventional LEED analysis (see Section 6.4.3), only a single peak could be obtained in this range for PDO. Both R-factor and visual analyses indicate poor agreement for beams (0.2 0.6) and (0.6 1.8), the latter extending only over a short energy range of 50 eV, while the former covers a 160 eV range with many structures in the experimental I(E) curve to match. The calculated I(E) curve for beam (0.2 0.6) also contains a number of peaks but is less complex than the experimental curves, and the peaks do not line up with those of the experiment. Nevertheless, considering the unusually large data base of 15 beams, 12 of which are fractional order beams, and that a reasonably good level of correspondence has been reached for many of the beams for a relatively complex surface structure, model PDO most likely resembles closely the actual structure of the Pd(100)-(\(\sqrt{5}\times\sqrt{5}\))R27°-O surface. This model will, therefore, be discussed further in relation to structural chemical principles.

In PDO, coincidence with the Pd(100) lattice requires a slight expansion of the PdO(001) overlayer; Pd-Pd distance in the plane of the unrelaxed overlayer is 3.075 Å, whereas that in bulk PdO is 3.043 Å. In addition, registry with respect to the Pd(100) substrate is such that Pd atoms from the oxide layer are placed on three very different "adsorption" sites: one atom per unit mesh sits on-top, two on bridge, and one on hollow sites. As a result, significant expansion of the first-to-second interlayer spacing and/or rumpling of the top metal layers would be expected since the hard-sphere stacking distance of hollow-site atoms is 1.94 Å above the Pd(100) surface while that of on-top atoms is 2.75 Å. Both types of relaxations are observed for the final TL-optimized geometry of PDO (Table 6.3). Rumplings of magnitude 0.28 Å in the oxide layer and
0.48 Å in the topmost Pd(100) layer give an effective difference in height of 0.76 Å between on-top and hollow-site Pd atoms, which is close to the expected difference of 0.81 Å. The center-of-mass distances indicate a large expansion in the first three interlayer spacings, but these values are deceptive in that they do not account for the substantial lateral displacement of Pd atoms, often resulting in a contracted Pd-Pd bond distance. Consider, for example, the top two Pd(100) layers, where a second-to-third center-of-mass spacing of 2.20 Å implies a 13% expansion relative to the bulk distance of 1.94 Å. Lateral displacements actually lead to a minimum distance of 2.70 Å between Pd-Pd nearest neighbours in the second and third layers, corresponding to a 2% contraction, while expansion of the remaining Pd-Pd bond distances (between second and third layers) was typically less than 7%. In addition, Pd atoms tend to be laterally displaced along directions which minimized corrugation in the top metal layers: two atoms in the topmost Pd(100) layer are displaced (Δ2h) toward the hollow-site atom, while two are displaced (Δ2b) toward bridge-site atoms lying along the string containing on-top atoms (Fig. 6.4). The effect is to increase the height of the lower Pd atoms within the oxide layer and thus reduce the height difference between higher and lower Pd atoms. A balance is thus achieved between the drive toward maintaining an ideally flat PdO(001) surface and the need to optimize the total bonding at the surface, in particular, to maximize Pd-Pd bonding (without rumpling, Pd_h atoms would sit too high above the surface to bond to Pd atoms in the layer below).

Oxygen displacements also appear chemically reasonable in that shorter bond lengths (i.e., stronger bonding) are observed for those Pd atoms which have fewer Pd nearest neighbours. For example, O atoms are displaced toward on-top Pd atoms (Pd_t), which have only one Pd-Pd bond (to the layer below). The resulting bond length b_O-Pd_t equals 1.60 Å, whereas b_O-Pd_b equals 1.94 Å for the bond to bridge-site atoms which have two Pd nearest neighbours. Similarly, b_O-Pd_h equals 1.71 Å and b_O-Pd_bh equals 1.65 Å for
bonds to hollow- and bridge-site Pd atoms, respectively, along the other string. The average O-Pd surface bond length of 1.73 Å is close to the predicted value of 1.76 Å for 2-coordinate oxygen.

6.4.3 Comparison with other models

An oxide-reconstruction model of the Pd(100)-(\sqrt{5}x\sqrt{5})R27°-O surface does not agree with the distorted hollow-site model of Simmons et al. However, structural features of the latter model appear chemically implausible, based on the structure of PdO (Fig. 6.1) as well as the general behaviour of oxygen chemisorbed on metal surfaces. The driving force for adsorbate-induced reconstructions is presumably to optimize total bonding at the surface, often in terms of maximizing the coordination number (CN) of the adsorbed atom. While oxygen chemisorbed in a hollow site (CN=4) may be more favourable than on a reconstructed oxide layer (CN=2), the large lateral displacement (0.688 Å) of O atoms suggested in the HREELS study lead to an effective oxygen coordination of one. The shortest O-Pd bond length of 1.576 Å is close to the predicted value of 1.504 Å for O bonding to one Pd atom, essentially forming an O-Pd double bond, and the largest value of 3.138 Å is too long for a meaningful bond to exist. The remaining two bond lengths of 2.460 and 2.504 Å are also longer than that (2.024 Å) reported for bulk PdO, where O bonds to four Pd atoms. Allowing an oxygen coordination of three and averaging the first three values give an O-Pd bond length of 2.18 Å, which is still rather long compared to the predicted value of 1.91 Å (for CN=3). Interestingly, the TL-optimized 4F model in the present study also indicated the formation of an unrealistically short O-Pd bond (1.40 Å), but the longest value is only 2.49 Å, giving an average of 1.99 Å for 4-coordinate oxygen. The 4F model was not favoured by TLEED, however: Rp = 0.3093 for the optimal geometry, and this is significantly higher than that obtained for PDO (Rp = 0.2323).
The \((\sqrt{5}x\sqrt{5})R27^\circ\) structure has also been observed for oxygen chemisorption on Mo(100), and a recent X-ray scattering study\(^{146}\) determined its structure to be a missing-atom reconstruction similar to model 4FMA, but Table 6.1 shows clearly that this cannot be the correct structure of the Pd(100)-\((\sqrt{5}x\sqrt{5})R27^\circ\)-O surface. It is not surprising, however, that oxygen induces two different reconstructions, both exhibiting the same diffraction pattern, on Pd(100) and Mo(100). First, palladium is an fcc metal, while molybdenum is bcc, so that Mo(100) is a much less densely packed surface than Pd(100). O atoms are still 4-coordinate in model 4FMA, whereas they are 3-coordinate on the reconstructed Mo(100) surface. Furthermore, molybdenum has a large range of oxide stoichiometry and structures, unlike palladium which exists in the bulk just as \(\text{PdO}^{145,147,148}\).

The preliminary conventional LEED analysis also supported PDO-type model, although structural features were not sufficiently refined to allow significant distinction between PDO- and 4F-type models. After 14 full-dynamical calculations to vary atomic positions within the top two Pd layers of PDO, \(R_p\) only decreased to 0.3609 from an initial value of 0.4084. The situation was even worse for 4F: \(R_p\) dropped to 0.3771 from 0.4368 only after 40 FD calculations. These values can be compared to those in Table 6.1, where a maximum of 10 FD calculations was performed for any particular model, yet TLEED optimization clearly indicated PDO as the model giving the best account of experimental data and hence the model which most likely identifies the essential features of the \((\sqrt{5}x\sqrt{5})R27^\circ\) surface structure.

### 6.5 Summary

The present tensor LEED I(E) analysis favours an oxide-reconstruction model (PDO in Fig. 6.4 and Table 6.3) for the Pd(100)-\((\sqrt{5}x\sqrt{5})R27^\circ\)-O surface structure: a PdO(001) overlayer is stacked onto the Pd(100) surface such that significant rumpling is
induced in both the oxide and topmost Pd(100) layers. An average O-Pd bond length of 1.73 Å agrees closely with predicted value for 2-coordinate oxygen, and structural details of the optimized model PDO appear chemically reasonable in that a balance is maintained between adsorbate-metal and metal-metal bonding. This model can also explain why the formation of the (√5x√5)R27° surface is an activated process, requiring O chemisorption at an elevated temperature: the Pd atom density in the oxide layer is 4/5 that of the clean surface, so that mass transport is involved during the creation of such a surface. Similarly, the p(5x5) surface is only formed at a high surface temperature and most likely corresponds to a PdO(110) overlayer as suggested by Orent and Bader.137
7.1 Further work on Ni(111)

The better level of agreement achieved for the Ni(111)-(2x2)-O surface structure compared with the corresponding sulfur system suggests the need to reanalyze the Ni(111)-(2x2)-S surface, perhaps by incorporating hydrogen into the bulk. Tensor LEED can be used to explore a larger volume of parameter space in the S/Ni system than was possible with conventional LEED. In addition, the well-established O/Ni surface structure, with both vertical and lateral relaxations in the close-packed Ni(111) surface, can serve as a further test of the ability of the TLEED method for reproducing FD results.

7.2 Further work on Cu(110)-(2x3)-N

This system has perhaps demonstrated most clearly the limitations of the LEED technique, as determined by the R-factor analysis. The same R-values \( R_{av} = \frac{1}{2} (R^{Mz} + R_p) \approx 0.19 \) were obtained for two very different reconstruction models of the Cu(110)-(2x3)-N surface: one has alternating <001>-missing rows, while the other is a highly corrugated pseudo-(100)-c(2x2)-N overlayer (100G in Fig. 5.8). The (100)-reconstruction model, however, appears to be more consistent with results from many of the techniques that have been applied to study this surface. In particular, recently available STM images suggest a high- and a low-N-coverage (2x3) surface, which can be explained in terms of the adsorption of N preferentially on 5-coordinate sites (as opposed to 4-coordinate sites) on a (100)-reconstructed surface. Since all LEED calculations of the (100)-type models have been based on the high coverage structure (with four N atoms per (2x3) unit mesh), one possibility for improving the agreement between experimental and calculated I(E) curves for model 100G is to start a new series of tensor LEED
calculations based on a low-coverage (100) structure, with N atoms occupying only 5-coordinate sites. A better approach would be to combine in various proportions the diffracted intensities from the low- and high-coverage calculations to account for the not well-defined experimental coverage. In addition, a new series of experiments should be carried out to measure the evolution of the I(E) curves with N dosage, to cover a much wider range than was done in the current study; the nitrogen coverage should be determined as well on a more absolute scale, using, for example, the nuclear reaction analysis technique. A LEED analysis of the Ni(110)-(2x3)-N surface may also provide insight into the surface structure of both systems. Interestingly, while bulk Cu$_3$N exists, the corresponding nickel compound is not well known, yet chemisorbed nitrogen induces a (2x3) reconstruction not only on the (110), but also on the (210) surfaces of both these metals.

7.3 Further work on Pd(100)-(\sqrt{5}\times\sqrt{5})R27°-O

The current tensor LEED analysis of the high coverage O/Pd(100) system has identified some key features of the Pd(100)-(\sqrt{5}\times\sqrt{5})R27°-O surface structure: a single surface oxide overlayer is formed, which is stacked onto the Pd(100) substrate such that significant rumpling is induced in both the oxide and the top two Pd(100) layers. The overall level of correspondence between experimental and calculated I(E) curves is best for this type of model, but some discrepancies remain, e.g., for beam (0.2 0.6). R-factor analysis indicates that the next most likely model of the (\sqrt{5}\times\sqrt{5})R27° surface is also an oxide reconstruction, which differs from the first type mainly in its registry with respect to the Pd(100) surface. Visual comparison of I(E) curves suggests that including some features of the shifted oxide model into the favoured oxide model may help improve
agreement with experimental data. New calculations could thus be undertaken to combine features from both model types, and additional R-factors can be used during the optimization procedure (as discussed below).

7.4 Critique of the LEED analysis

Fundamental to understanding surface reactions is knowing the surface structure, as for example, how the structure of a catalyst affects the rate of reaction. Since most systems of practical interest are too complicated for detailed structural analysis, the approach of surface science is to start with simple systems such as clean, single-crystal (metal) surfaces, on which gases are adsorbed in a controlled manner under UHV. Information gained from the three chemisorption systems investigated in this thesis have thus contributed to our basic knowledge of surface structures, in particular of adsorbate-induced reconstruction of metal surfaces. In addition, this work has provided some insight into the power as well as the limitations of LEED as a surface structural technique. For a simple system such as that formed by the chemisorption of oxygen onto the Ni(111) surface to form Ni(111)-(2x2)-O, the trial-and-error procedure of the conventional LEED method can locate with some certainty fine structural details such as small lateral and vertical displacements of the local metallic structure, provided that a sufficiently exhaustive search has been done in parameter space. Analysis of the more complicated surfaces of Cu(110)-(2x3)-N and Pd(100)-($\sqrt{5}$x$\sqrt{5}$)R27°-O was hampered both by the numerous models and by the large number of parameters within each model that need be considered. Evidence from the N/Cu study clearly shows the limitation of the traditional method of LEED crystallography, but even the newly developed tensor LEED/directed search method (TLEED) has problems which should be addressed. One of these problems
is the lack of "chemical sensibility" of the directed search method: the search for an optimal geometry is based solely on R-factors, but care is always needed in assessing whether the R-factor used is a reliable measure of the agreement between experimental and calculated I(E) curves. Figure 7.1 illustrates using two beams from the N/Cu analysis where, in the absence of redeeming corrections from the other beams, R-factor analysis would clearly fail. For beam (4/3 1/2), visual analysis suggests little difference in the level of correspondence with experiment for the two calculated curves: of the six peaks and valleys to be matched in the experimental curve, FD matches only the one peak near 70 eV, and TL matches that in addition to the valley at 97 eV; the I(E) profiles are similar between FD and TL over much of the energy range. Yet, the Pendry $R_p$ value is significantly higher for one curve (0.5639 for FD) than for the other (0.3493 for TL). Visual comparison of beam (5/3 1), on the other hand, indicates that the level of agreement should be much better for the FD curve than for the TL curve, the latter having no peak between 110 and 120 eV (although the TL curve appears to match the minimum at 130 eV better than the FD curve) and an intensity scale which is 10 times that of the experiment; nevertheless, compared with the numerical difference seen for the (4/3 1/2) beam, somewhat comparable $R_p$ values were obtained for the (5/3 1) curves (0.2943 and 0.3406, respectively, for FD and TL). These observations are not limited to the Pendry R-factor; of the other nine R-factors summarized by Van Hove and Koestner, all gave similar numerical analysis of beam (4/3 1/2), and only three (ROS, R1, R2; see Ref. 44) gave R-values which were consistent with visual analysis of beam (5/3 1). The observed R-values could be explained as follows:

(1) For beam (4/3 1/2), the minimum at 97 eV in the FD curve falls almost exactly at the maximum in the experimental curves. As a result, in the range 80 to 100 eV,
Figure 7.1  Comparison of two sets of calculated I(E) curves with those from the N/Cu experiment. $R_p$ values are given to illustrate the failure of R-factor analysis for these two beams.
the FD and experimental I(E) curves have exactly opposite slopes. Consequently, $R_p$ is much higher for the FD curve than for the TL curve.

For beam (5/3 1), the slope between experimental and both calculated curves are similar over much of the energy range of interest. Thus, despite the visually different calculated curves, similar R-values are obtained (for FD and TL).

It could be argued that the R-factor comparisons in Fig. 7.1 show sufficiently poor overall agreement to indicate an incorrect structure; thus, for a given change in geometry (e.g., from FD to TL), it is not critical that changes in individual beam R-values be on the same quantitative scale (e.g., a substantial decrease in R-value for beam (4/3 1/2), but only a small increase for beam (5/3 1)). R-values should, in practice, however, indicate quantitatively and consistently changes which give better and worse agreement, since tensor LEED must follow trends in total R-factors and structural analysis of a completely unknown and challenging surface inevitably starts from a position of poor agreement. Nevertheless, R-factors must remain the primary tools to quantify the level of correspondence between experiment and calculations in any LEED structural search: visual comparison of I(E) curves for many beams and many models (e.g., for O/Pd) is difficult, if not impossible, and lacks objectivity. But, as seen above, a numerical R-factor is "objective" only in its own limited context, and it may not always mimic trends seen by the human eye.

The goal is thus to improve the reliability of R-factors, a measure of which was done by Van Hove and Koestner through a series of extensive tests. These authors showed that the ten R-factors tested exhibited differing sensitivity to different features such as relative peak heights, widths and positions. Furthermore, in the neighborhood of the correct geometry, minima will generally coincide for (1) different R-factors averaged
over all beams, (2) different beams averaged over R-factors, and (3) different energy ranges taken from the same beam. These points can be checked in a conventional LEED analysis, but point (1) is probably most often used as it is the overall agreement between experimental and calculated I(E) curves which ultimately determines the best structural model of the surface under investigation. With tensor LEED, separate searches could be performed, each using a different R-factor, and coincidence of structural details could in principle be used to measure reliability. When only one R-factor is used in an analysis, that proposed by Pendry\cite{Pendry} is often used for its sensitivity to peak positions (which can be more easily reproduced than, for example, relative peak heights), for its mathematical basis (which should give an upper limit of unity when comparing completely uncorrelated curves), and for its apparent physical basis (which measures in terms of $V_{0i}$ the effect of inelastic scattering on peak widths). In addition, $R_p$ can be calculated much more quickly than, for example, $R_{M2J}$ (by about a factor of ten). One approach then is to use $R_p$ to explore parameter space on a course scale, to match peak positions first; fine-tuning of structural details can be done by including other R-factors which emphasizes other features of I(E) curves. This procedure has generally been used for the work in this thesis.

As there is no generally accepted "best" R-factor, it remains essential even with TLEED to continue to make visual inspections of I(E) curves to ensure consistency between lower R-values and improved correspondence with experimental data (as discussed in Section 5.5.4). In addition, there should be a check regarding the chemical reasonableness of a particular geometry; ultimately, surface structural models should show broad agreement with bond length-bond order predictions based on well-established bulk structures. These checks are especially important in cases where R-factors apparently cannot distinguish between two very different model types (e.g., missing-row and (100)-reconstruction for N on Cu(110)), yet even more similar model types have been
unambiguously differentiated in other cases (e.g., the 3f and 3h sites for O on Ni(111)). For both the Cu(110)-(2x3)-N and Pd(100)-(\sqrt{5x\sqrt{5}})R27°-O surfaces, the discrepancies between experimental and calculated I(E) curves which remain suggest that, although the essential elements of the surface structure have been established, further refinements are needed.

Even with its limitations, LEED is still by far the most developed surface crystallographic technique. Many other techniques give only broad structural features, whereas LEED can determine structural details such as bond lengths and surface relaxations to within 0.03 Å, if a high level of correspondence has been reached between calculations and experiment (e.g., for O/Ni). These details are important toward the development of a predictive framework, which helps establish principles of surface structural chemistry. To the extent that R-factor analysis may sometimes fail to identify reliable trends, and that a number of proposed models are still needed as reference structures in tensor LEED calculations, LEED as a surface structural technique can never be completely automated. With the cautions noted above, however, the TLEED method has greatly increased the ability of LEED to solve more complex, and consequently more application-oriented, surface structures.
References

[34] S.Y. Tong, Prog. in Surf. Sci. 7 (1975) 1.


[58] The Tensor LEED programs were derived from the LEED package of Van Hove.


