STUDIES IN LEED CRYSTALLOGRAPHY

by

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Abstract

This thesis is involved with the use of low-energy electron diffraction (LEED) for determining the geometrical structures of well-characterized surfaces of single crystals. Specific applications are to surfaces of rhodium, both clean and when containing adsorbed species.

A preliminary problem concerned discrepancies reported previously in the details of the geometrical structures for the clean (100) and (111) surfaces when using rhodium potentials from either a band structure calculation or from the linear superposition of charge density procedure for a metal cluster. A correction has now been made in the calculation of phase shifts for the band structure potential, and reinvestigations of the (100), (110) and (111) surfaces of rhodium with this potential resolve the discrepancies. These results now support the suggestion, as shown previously in this laboratory for Cu(111), that the superposition potential provides a good approximation to a band structure potential for the purpose of LEED crystallography.

In the structural determinations made here, the degree of correspondence between intensity versus energy curves for different beams from experiment and from multiple-scattering calculations were assessed with the reliability-index $r_f$ proposed by Zanazzi and Jona. A new aspect considered involved the use of this index for determining the non-structural parameters required in the multiple-scattering calculations. Included in the latter for Rh(111) are variations of the imaginary part of the constant potential ($V_{oi}$) between the muffin-tin spheres and the surface Debye temperature ($\Theta_{D,surf}$). Structural conclusions from $r_f$ are compared with visual analyses wherever possible, and this work generally supports the use of the Zanazzi-Jona index in LEED crystallography.
The experimental part of this study involved the (100) and (110) surfaces of rhodium. A series of diffraction patterns were observed for the chemisorption of \( \text{O}_2 \) and \( \text{H}_2\text{S} \). Intensity versus energy curves were measured for the available diffracted beams for the surface structures designated Rh(100)-(3\times1)-\( \text{O} \), Rh(100)-p(2\times2)-S and Rh(110)-c(2\times2)-S. The latter two systems were analyzed by multiple-scattering calculations (using the renormalized forward scattering and layer-doubling methods) and surface structures determined. In each case S atoms adsorb on the centre sites; on Rh(100) S bonds to four neighbouring Rh atoms at a distance of 2.30 Å (very close to the Pauling single-bond value 2.29 Å), and on Rh(110) each S atom is 2.12 Å from the Rh atom directly below in the second layer and 2.45 Å from the four neighbouring Rh atoms in the top metallic layer.

An investigation was also made for the use in LEED crystallography of the quasidynamical method recently proposed by Van Hove and Tong. This scheme includes interlayer multiple-scattering properly, but neglects multiple-scattering within individual layers, and has the potential for considerable savings in computing time and core storage. This method was investigated for the clean and sulphur-adsorbed (100) and (110) surfaces, and results compared with the more-complete multiple-scattering methods. The quasidynamical method appears to have some promise for making initial selections of the most significant trial structures prior to the more-detailed testing with full multiple-scattering calculations.
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CHAPTER 1

Introduction
1.1 Modern Surface Science

Studies of the properties of solid surfaces have assumed great interest over the past decade, in part because such surfaces have dominant roles in various technological processes (e.g. friction and wear, electronic devices and heterogeneous catalysis) [1,2]. Traditional research emphasized the properties of real surfaces, usually of polycrystalline materials, which could not be well-characterized at the atomic level [3]. However, modern surface science has introduced the "clean surface" approach where carefully characterized surfaces are studied with the objective of developing principles which can lead to better understandings of the atomistic aspects of surface processes, including those of technological interest [4,5]. In the clean surface approach, single crystals are used and the properties of surfaces corresponding to well-defined crystallographic planes are studied under conditions such that the surface is not contaminated by unwanted impurities. This requires experiments to be carried out under ultra-high vacuum (<10^{-9} torr). The necessity for this provision follows from the kinetic theory which predicts that, for an ambient pressure of 10^{-6} torr, a surface can be covered by an adsorbed monolayer in 1 second, assuming that all colliding molecules stick to the surface.

With the availability of ultra-high vacuum facilities, many experimental techniques have been developed recently for the characterization of solid surfaces with regard to chemical composition, geometrical and electronic structure as well as chemical bonding, vibrational structure and energy exchange with impinging molecules. Among the techniques available,
Auger electron spectroscopy (AES) is commonly used for qualitative chemical analyses of surfaces, whereas ultraviolet photoemission spectroscopy (UPS) [6] is popular for indicating electronic structure and low energy electron diffraction (LEED) gives information on geometrical structure. Reflection high energy electron diffraction (RHEED) [7] and the scattering of molecular and ion beams [8,9] also have high potentials for surface studies. Research on well-defined surfaces with a variety of techniques has established that surface properties depend not only on the particular material involved, but also on the specific crystallographic plane exposed [10]. For example, chemisorption and molecular beam scattering studies have shown that sticking probabilities and reaction rates can be very different on stepped surfaces of platinum compared with low-index surfaces of the same metal [11].

At the present time LEED appears as the most direct technique for the determination of surface geometrical structure. This potential was recognized in 1927 when the experiment was first performed by Davisson and Germer [12]. However the development of this technique to its full potential was inhibited by many theoretical and experimental difficulties, and it was only during the 1970's that these problems were overcome sufficiently for some surface structures to be determined. In current LEED studies it is considered advantageous, if not essential, to utilize other techniques simultaneously for characterizing the surface. The most commonly-used complementary technique is AES. Historically, electrons produced by the Auger process were discovered in 1925 [13], and although their potential in surface analysis was recognized by Lander [14] in 1953, it was not until the late 1960's that they could be
detected routinely in surface experiments [15-17]. Indeed the development of AES as a method for qualitative surface analysis encouraged the development of reproducible LEED experiments, and in turn the development of adequate theories for LEED. The existence of the latter represented a necessary requirement for the development of LEED crystallography (i.e., the determination of surface geometrical structure by LEED).

1.2 Introduction to Low Energy Electron Diffraction

A LEED experiment involves directing a beam of low-energy electrons (typical energy <500eV) with known angles of incidence onto a well-defined surface of a crystalline solid and observing the intensity distribution of electrons which are elastically back-scattered from the surface. The de Broglie hypothesis relates electron energy (E in eV) to wavelength (λ in Å) according to

$$\lambda = \sqrt{\frac{150.4}{E}}$$

(1.1)
electrons in the low-energy range therefore have wavelengths which are comparable with interlayer spacings in the solid. Low-energy electrons are particularly "surface sensitive" because they experience strong inelastic scatterings in solids. A helpful parameter for discussing inelastic scattering is the electron mean free path length (L) which can be expressed in terms of

$$I = I_o \exp \left[ -\frac{L}{L} \right]$$

(1.2)
where the incident intensity $I_o$ at a particular energy is attenuated to I on passage through a distance $L$. The general form of the dependence of the mean free path length on electron energy is shown in figure 1.1. Electrons
Figure 1.1: Schematic diagram of the mean free path length \( L \) (Å) of electrons in a metallic solid as a function of energy (eV).

Figure 1.2: Schematic energy distribution \( N(E) \) of back-scattered electrons for a primary beam of energy \( E_0 \).
in the low-energy range are associated with values of L of just a few Ångstroms, and therefore they are ideally suited for investigation of the top few layers of a solid. Further information on electron mean free path lengths has been reviewed by Brundle [18], Ibach [19] and Powell [20].

A monoenergetic beam of low-energy electrons incident upon a solid surface typically gives an energy distribution for the back-scattered electrons of the type shown in figure 1.2. The narrow "elastic peak" on the right hand side involves the electrons which are studied in the conventional LEED experiment. This peak includes the genuinely elastically-scattered electrons, as well as those electrons which have undergone phonon scattering with small energy changes (≤0.1 eV). This latter group of electrons can be referred to as quasielastic electrons. Typically only 1-5% of the incident electrons contribute to the "elastic peak". Most electrons experience strong inelastic scattering, associated especially with single-electron and plasmon excitations [21,22], and those excitations contribute to the comparatively short mean free path length indicated in figure 1.1. The emission of Auger electrons, which typically corresponds to a current of ~10^-12 A on a background of ~10^-7 A, appears as small peaks superimposed on a slowly-varying background in the intermediate range of figure 1.2. Peaks due to Auger electrons can be distinguished from loss peaks due to plasmon or single-electron excitations because the former occur at energies which are independent of the primary electron energy. The large peak at low energy in figure 1.2 involves the so-called "true secondary" electrons which are associated with a series of inelastic scatterings in a cascade-type process [23].
The principle of the LEED experiment is illustrated in figure 1.3a. The incident electrons are scattered by the surface region and the elastically back-scattered electrons are separated from others by energy selecting grids. The elastically scattered waves interfere constructively to give diffracted beams along certain directions, and each beam shows as a bright spot when these electrons are accelerated onto a fluorescent screen. The distribution of these spots is referred to as the LEED pattern. Because of strong inelastic scattering, the elastically-scattered electrons do not normally experience a regular periodicity normal to the crystal surface and consequently the region probed by the LEED electrons is diperiodic (i.e., it can be characterized by two unit translation vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \)). The corresponding diffraction pattern (figure 1.3b) involves the associated translational vectors in reciprocal space, namely \( \mathbf{a}_1^* \) and \( \mathbf{a}_2^* \) defined by

\[
\begin{align*}
\mathbf{a}_1^* &= 2\pi \frac{\mathbf{a}_2 \times \mathbf{z}}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{z}}, \\
\mathbf{a}_2^* &= 2\pi \frac{\mathbf{a}_1 \times \mathbf{z}}{\mathbf{a}_2 \cdot \mathbf{a}_1 \times \mathbf{z}}
\end{align*}
\] (1.3)

where \( \mathbf{z} \) is the unit vector perpendicular to \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \).

Pendry [24] has given a detailed analysis showing how a LEED pattern is a direct consequence of the surface translational symmetry. Assuming the incident electrons can be described by a plane wave

\[
\psi_0 = B \exp[i \mathbf{k}_0^+ \cdot \mathbf{r}],
\] (1.4)

where \( B \) is an appropriate normalization constant, \( \mathbf{r} \) is a general position vector and \( \mathbf{k}_0^+ \) is the incident wave vector which relates to electron energy through

\[
E = \frac{\hbar^2}{2m} |\mathbf{k}_0^+|^2,
\] (1.5)
Figure 1.3: a) Schematic diagram of the LEED experiment.
b) The principle of the formation of a diffraction pattern in LEED experiment.
then wave vectors $k_g^-$ for the diffracted electrons are determined by conservation of energy

$$E(k_g^-) = E(k_o^+)$$

and by the conservation of momentum parallel to the surface

$$k_g^\parallel = k_o^\parallel + g(hk), \quad (1.7)$$

where

$$g(hk) = h\xi_1 + k\xi_2$$

$h$ and $k$ being integers. As illustrated in figure 1.3b, the direction of each diffracted beam (wave vector $k_g^-(hk)$) is determined by $E$, $k_o^+$, and $g$. For given values of $k_o^+$ and $E$, each spot in a diffraction pattern is associated with a particular $g$, and hence may be identified with the indices $(hk)$. For a given energy, only a limited number of beams can reach the screen; if $|g|$ is sufficiently large $k_g^-$ becomes complex and corresponds to an evanescent (or surface) wave which cannot escape from the solid.

The (00) beam is made up of electrons which have interacted with the surface without momentum transfer parallel to the surface ($k_g^\parallel = k_o^\parallel$), and it is frequently called the "specular beam". The direction of the specular beam remains constant as $E$ changes, as long as the electrons move in a field-free space outside the crystal and the direction of the incident beam is fixed. With increasing energy, more diffracted beams are observed, the non-specular beams move towards the (00) beam, the symmetry of the LEED pattern remains unchanged, but the beam intensities vary continuously.

In practice, incident electron beams in LEED are coherent only over restricted distances ($\pm 10^2 \text{ } \text{Å}$) [25], and this limits the range over which
surface order can be recognized in the diffraction experiment. Some disorder is inevitably present at surfaces, and this can affect spot patterns by broadening the diffracted beams, by introducing streaks, rings and spot splittings, and by increasing the background intensity [26]. Frequently LEED patterns are affected by domain structure in which two or more equivalent orientations of the structure are possible on the surface. In the presence of domain structure, provided that the dimensions of the domains are greater than the coherence width associated with the incident electron beam, observed LEED patterns represent direct superpositions of the patterns from the individual domains. This can be particularly important for adsorption systems, and examples are given later.

For a given surface, the intensities of the diffracted beams vary with the electron energy E, the direction of incidence (specified by angles θ, ϕ; see figure 1.4) and the temperature. Most often intensity data are presented as a function of energy (i.e., as I(E) curves for each diffracted beam) with all other parameters being held constant. A typical example of I(E) curves is given in figure 1.5. Davisson and Germer [12], at the time of the first LEED experiment, realized beam intensities contain information on surface bond distances, but nearly 50 years elapsed before detailed surface geometries could be extracted from measured intensities. The basic method utilized at the present time involves the trial-and-error approach in which I(E) curves are calculated for different possible surface geometries, and a search is made for that geometry which allows the best match up with the experimental I(E) curves for the various diffracted beams. The main content of this thesis is involved with the application of this approach to LEED crystallography.
Figure 1.4: Conventions for the incident angle of an electron beam on a surface; $\theta$ is a polar angle relative to a surface normal and $\phi$ an azimuthal angle relative to a major crystallographic axis in the surface plane.
Figure 1.5: \( I(E) \) curve for the specular beam from Ni(100) at \( \theta = 3^\circ \). The bars indicate energies where primary Bragg conditions are satisfied (after Andersson [48]).

Figure 1.6: A schematic comparison of overlayer and substrate regions, both of which are diperiodic in the x and y directions.
1.3 **Surface Crystallography**

The definition of surface is very much a function of the particular probe used to study it. For LEED from a crystalline solid, it is convenient to refer to the "surface region" as the region probed by the LEED electrons (i.e., over the range of mean free path length corresponding to the elastically-scattered electrons). Figure 1.6 also indicates the "substrate" whose structure is generally known from X-ray crystallography and is that for which the bulk triperiodicity is established. The objective of surface crystallography is then to determine the position of all atoms beyond the substrate surface (i.e., the topmost substrate plane). The surface region may involve an overlayer whose diperiodic translational symmetry is different from that of a substrate plane. The appropriate periodic translational symmetry for LEED is that for the overall surface region, and is described by the unit translational vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \). These vectors may result from the combination of the diperiodic symmetries of the substrate and the overlayer.

The vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) define a unit mesh which is analogous to the unit cell of triperiodic crystallography. The vector

\[
\mathbf{t} = m\mathbf{a}_1 + n\mathbf{a}_2
\]

(1.9)

translates from one point in a surface region to another with an identical environment, and a two-dimensional net can be generated from all integral values of \( m \) and \( n \); this is the diperiodic analogue of the triperiodic lattice used in X-ray crystallography. Five types of diperiodic nets are possible and they are analogous to the 14 Bravais lattices in triperiodic crystallography. There are 17 possible space groups in diperiodic crystallography, and they are detailed in the International Tables for X-ray Crystallography [27].
Adsorption on clean surfaces typically gives increased surface periodicities and therefore extra LEED spots, as shown in figure 1.7. Such extra spots are frequently called "fractional order" spots when the same notation is used for corresponding beams from the adsorption structure as for the clean surface structure. Generally it is convenient to use a notation for surface structures and diffracted beams which is based on the substrate. For example in Wood's nomenclature [28], a surface is designated

$$\left( \frac{a_1, a_2}{b_1, b_2} \right)_\theta$$

where \((a_1, a_2)\) and \((b_1, b_2)\) are the unit diperiodic vectors of the surface region and substrate respectively, and \(\theta\) is the angle of rotation between the surface and substrate unit meshes (for more complex surfaces, where such an angle of rotation is not applicable, a matrix notation has been introduced [29] and discussed further by Estrup and McRae [30]). With Wood's notation, the symbols \(p\) or \(c\) are frequently added to indicate whether the surface mesh is primitive (one atom per unit mesh) or centred (with an extra atom at the centre of the unit mesh), respectively. For the examples of S adsorbed on (100) and (110) surfaces of rhodium (figure 1.7) the structures obtained are designated as Rh(100)-p(2×2)S and Rh(110)-c(2×2)S respectively; the latter could alternatively be designated as Rh(110)-(√3×√3/2)S4S although the first is always used for simplicity.

A diffraction pattern usually allows a specification of the surface periodicity, but never of the actual surface structure. The latter requires analysis of beam intensities. For S adsorbed on the (110) surface of rhodium, there are four particularly important locations for the S atoms. These are
Figure 1.7: Schematic diffraction patterns of clean and overlayer structures.
Four possible structural models for Rh(110)-c(2×2)S which are consistent with the observed diffraction pattern. The adsorbed sulphur atoms are represented by the filled circles.

- On-top (1F) model
- Centre (4F) model
- Short-bridge (2SB) model
- Long-bridge (2LB) model
shown in figure 1.8, and all are consistent with the $c(2\times2)$ diffraction pattern. The adsorption sites are designated as centre or four-fold (4F) sites, on-top or one-fold (1F) sites, short-bridge (2SB) sites or long-bridge (2LB) sites. To determine the actual adsorption site it is necessary to calculate the $I(E)$ curves of the diffracted beams for the various models and compare them with the experimental $I(E)$ curves to assess which model gives the best agreement.

1.4 Auger Electron Spectroscopy

The Auger process is depicted in figure 1.9. It is initiated by the ionisation of a core electron either by electron impact or by photon interaction. An electron from a higher energy level then drops down to fill the inner vacancy, and this process releases energy either by photon production (e.g. X-ray fluorescence) or by ejection of an Auger electron whose kinetic energy depends directly on the energy levels involved in the process [23,31]. Generally Auger emission is the more probable process if the initial ionisation involves an electron whose binding energy is less than -2keV. The key point for surface analysis is that the kinetic energies of Auger electrons are characteristic of the particular element from which the electrons originate; chemical shift effects are observed, but these effects are small compared with the differences between different elements [32,33]. Qualitative analysis in practice involves comparing the energies of observed Auger peaks with the listed values [34-36]. Most elements, with the exception of hydrogen and helium, can be detected uniquely even if several are present in a surface region. A typical example of an Auger spectrum from this work is shown in figure 1.10; this is for a Rh(110) surface contaminated with sulphur,
Figure 1.9: The production of an $L_{2,3}V$ Auger electron in aluminum. X-ray energy levels are indicated relative to the Fermi level.
Figure 1.10: Auger spectrum of a heavily contaminated Rh(110) surface, $E_o = 1.5$ keV, $I_o = 10$ microamps.
carbon and phosphorus. The spectrum is presented in the derivative form (\(dN(E)/dE\)) to enhance the weak Auger features. Using standard LEED optics as a retarding field analyzer \([16,17]\), amounts of around 1-5% of a monolayer can be detected for most elements; higher sensitivities are possible with a cylindrical mirror analyzer \([37]\). The flux of Auger electrons produced depends especially on the ionization cross-section of individual elements, and this generally varies with energy.

In this thesis, AES is used only for qualitative chemical analysis, although there are continuing attempts to develop this technique for quantitative analysis \([38,39]\). With suitable calibrations, this technique can give important information on surface kinetics \([40]\). It also has potential value for assessing aspects of surface band structures \([41]\).

1.5 Aims of Thesis

The overall objective of this thesis is to contribute to an increase in knowledge associated with LEED crystallography, both by determining some unknown surface structures and by assessing possible new or modified procedures.

The catalytic aspects of rhodium have been well known for a long time \([42]\) but the crystallography of its surfaces has not been thoroughly investigated. In earlier work, Watson et al. \([43,44]\) reported discrepancies in the geometrical structures of the (100) and (111) surfaces of rhodium, associated with the use of atomic potentials from two different sources which were expected to give essentially equivalent results. These discrepancies are resolved in this thesis.
An important recent emphasis in LEED crystallography involves the development of suitable reliability factors for making routine comparisons between experimental and calculated I(E) curves. The most complete R-factor appears to be that introduced by Zanazzi and Jona [45]. This reliability factor is studied here both in actual surface structure determinations and by assessing its value for fixing some non-geometrical parameters required in the multiple scattering calculations of LEED intensities.

In the experimental parts of this thesis, the adsorptions of oxygen and sulphur on the (100) and (110) surfaces of rhodium have been studied and diffracted beam intensities measured for various structures. Complete LEED crystallographic analyses with full multiple-scattering calculations have been made for the surface structures designated Rh(110)-c(2×2)S and Rh(100)-p(2×2)S. These structures have proved useful for gaining some insights into surface chemical bonding.

A problem with the present schemes for calculating LEED intensities concerns the large computational times and computer core storages required. A simpler scheme called the quasidynamical method has recently been proposed by Tong and Van Hove [46]; it is faster and requires much less core storage than the complete methods. Initial studies indicate that it could be useful for systems of weak scatterers [46,47], and further investigations are reported here, particularly for structures involving sulphur adsorbed on surfaces of rhodium.
CHAPTER 2

Calculation of LEED Intensities
2.1 Characteristics of $I(E)$ curves

A typical $I(E)$ curve has already been illustrated in figure 1.5; this is specifically for the specular beam diffracted from a Ni(100) surface. Such a curve shows considerable structure, that is the intensity exhibits a number of maxima and minima as the energy is varied. Also as noted in section 1.2, the elastic reflectivity corresponds to only a few percent of the total incident electrons. Early attempts to explain $I(E)$ curves in LEED based on the kinematical theory (which is applicable when scattering cross-sections are very low e.g. X-ray diffraction [49]) were unsuccessful. For a surface whose structure corresponds to that of the bulk, the kinematical theory predicts peaks in $I(E)$ curves for the triperiodic diffraction condition

$$\mathbf{k}^- = \mathbf{k}_0^+ + \mathbf{g}(hk\ell)$$  \hspace{1cm} (2.1a)

where $\mathbf{g}(hk\ell)$ is a vector of the reciprocal lattice. For the $(hk)$ beam in LEED, equation (2.1a) becomes equivalent to

$$\mathbf{k}^- = \mathbf{k}_0^+ + \mathbf{g}(00\ell)$$ \hspace{1cm} (2.1b)

Peaks in $I(E)$ curves which satisfy (2.1b) are termed "primary Bragg peaks" and may be designated by the index $\ell$. Further relevant observations from $I(E)$ curves of the type in figure 1.5 are as follows:

1) Peaks in experimental $I(E)$ curves which are close to satisfying the primary Bragg condition (equation 2.1b) are generally found at lower energies than expected. This suggests an inner potential correction is necessary as a consequence of the reduced potential experienced by an electron inside the crystal [50].

2) Often more peaks are observed in experimental $I(E)$ curves than expected
from equation 2.1. This suggests multiple-scattering is significant; this is consistent with the cross-sections for scattering of low-energy electrons being of the order of unit mesh areas [51] (and hence several orders of magnitude greater than those for the scattering of X-rays).

3) Peaks in I(E) curves generally show increasing widths with increasing energy [52]. Peak widths are related to uncertainties in energy and hence to finite life-times via the uncertainty principle [24]; the average life-time can be interpreted as the time for the electron to traverse the mean free path length (L) introduced in section 1.2.

4) The diffracted beam intensities decrease with increasing temperature often in an exponential manner [53,54].

Such observations suggest that the LEED process is a dynamical process in which the non-geometrical parameters play an important role in its description. The fixing of these parameters, together with multiple-scattering of electrons through ordered surface regions, represent complications for an analysis of the diffraction process.

2.2 Physical Parameters required in LEED Theory

It has already been indicated that the incident electrons in LEED experience strong elastic and inelastic scatterings; clearly the crystal potential must be chosen carefully to accommodate these two important features in LEED intensity calculation. The "muffin-tin" potential provides a convenient model for this purpose. In this approximation (figure 2.1), the potential is taken as spherically symmetric in the vicinity of atoms and
Figure 2.1: Muffin-tin potential
a) in cross-section as contours,
b) along xx' ( $V_0$ is the constant intersphere potential ).

Figure 2.2: Illustration of the relationship between energies measured with respect to the vacuum level and those measured with respect to the lowest level of the conduction band.
constant elsewhere. The real part of the constant potential \( V_{\text{or}} \) is often equated to the empirical inner potential noted above; \(|V_{\text{or}}|\) is roughly equal to the sum of the Fermi energy and the work function as illustrated in figure 2.2. \( V_{\text{or}} \) is negative and it can be regarded as giving the position of the muffin-tin zero below the vacuum level; it is associated with the potential well that confines the conduction electrons to solids. Typical values of \( V_{\text{or}} \) range from -10 to -20 eV. The effect of this potential well is to speed up the incident electrons inside the crystal. Although \( V_{\text{or}} \) is strictly dependent on energy [55], because of exchange and correlation effects, this dependence is often sufficiently weak that it can be ignored for the purpose of calculating \( I(E) \) curves [56]. To a good approximation, changes in \( V_{\text{or}} \) give a rigid shift in calculated \( I(E) \) curves; this enables values of \( V_{\text{or}} \) used in calculation to be refined by translating the calculated \( I(E) \) curves along the energy scale until optimal matching with the corresponding experimental \( I(E) \) curves is obtained [57].

Inelastic scattering is conveniently incorporated into calculation schemes by giving an imaginary contribution to the intersphere potential, that is expressing the constant part of the potential as

\[
V_0 = V_{\text{or}} + iV_{\text{oi}} . \tag{2.2}
\]

For an electron wave function with time dependence

\[
\psi(\mathbf{r},t) = \psi(\mathbf{r}) e^{-iEt} ; \tag{2.3}
\]

the intensity decays with time as \( e^{2V_{\text{oi}}t} \) provided \( V_{\text{oi}} \) is negative. Pendry [24] established the relation

\[
\Delta E_w = 2|V_{\text{oi}}| . \tag{2.4}
\]
where ΔE is the peak width at half maximum height in an I(E) curve and
the analysis uses atomic units (h^2=m_e=e=1). Equation (2.4) is helpful for
estimating values of V_01 from experimental intensities; typically V_01 is
around -5 eV with a fairly weak energy dependence [58]. Demuth et al. [56]
proposed the use of the functional form

V_01 = -αE^{1/3} \quad (2.5)

In practice, especially for an overlayer, the crystal potential close to
the topmost atoms can be different from that of the substrate region [59];
a schematic representation of the crystal potential is indicated in figure 2.3.

Ideally the potential used in LEED calculations is constructed from
self-consistent band structure calculations [60]. However suitable potentials
of this type are not always available, and a plausible alternative involves
constructing potentials from the superposition of atomic charge densities in
finite clusters [22,61]. In either case, the exchange potential experienced
by an electron of wave function ψ(x) is most often represented by Slater's
local density approximation [62]

V_{ex}(x)ψ(x) = -6 \left( \frac{3ρ(r)}{8\pi} \right)^{1/3} ψ(x) \quad (2.6)

where ρ(r) is the local charge density.

The scattering of an electron plane wave by a spherically symmetric
ion-core potential yields a spherical wave, and the total wavefield at
large |x| has the form [63,64]

ψ_s(x) = e^{i\kappa \cdot x} + \frac{1}{|x|} \left[ e^{i\kappa \cdot x} \frac{1}{|x|} \right]. \quad (2.7)
Figure 2.3: Muffin Tin model of an adsorbate covered surface (after Marcus et al. [59]).
The scattering amplitude \( f(\theta) \) is commonly expanded as

\[
f(\theta) = \frac{2\pi}{|k|} \sum_{l=0}^{\infty} (2l+1) \exp(i\delta_l) \sin \delta_l P_l(\cos \theta),
\]

where \( \delta_l \) is the phase shift which characterizes scattering by ion-cores for angular momentum \( l \), and \( P_l \) is a Legendre polynomial. For a particular atomic potential, phase shifts are found by solving the Schrödinger equation inside the muffin-tin sphere and joining the asymptotic form of the solution smoothly at the boundary of the sphere to those solutions obtained by solving the Schrödinger equation for the outside region. In practice for LEED it is found that \( f(\theta) \) converges fairly rapidly so that only a limited number of \( l \) values are needed. Typically in LEED calculations for energies up to and around 200 eV, the maximum value of \( l \) (i.e. \( l_{\text{max}} \)) needed in expressions such as (2.8) is about 7.

The effect of the thermal motion of ion-cores is generally treated by adding an isotropic Debye-Waller-type contribution into the atomic scattering factor. Jepsen et al. [57] showed that the atomic scattering factor for such a vibrating lattice can be related to that \( (f(\theta)) \) of the rigid lattice but with some modifications to the phase shifts. Specifically for the \( p \)th atom,

\[
f(\theta, T) = f(\theta) \exp[-M_p(k' - k)^2],
\]

where a wave characterized by \( k \) is scattered into \( k' \),

\[
M_p = \frac{1}{2} \langle u_p \rangle ^2,
\]

and \( u_p \) is the vibrational amplitude in the direction of the momentum transfer.
(k' - k). In the high temperature limit (T > θ_D), u_p is related to the Debye temperature (θ_D) by

\[ \langle u_p^2 \rangle_T = \frac{\hbar^2 T}{M k_B^2 θ_D^2} \]

where M_p is the atomic mass and k_B is the Boltzmann constant.

Computational procedures for LEED intensities developed rather slowly, in part because of the complexity associated with the multiple-scattering. However, during the 1970's a number of schemes have been derived, and helpful reviews have been given by Duke [22], Tong [65] and Stoner et al. [66]. The earliest calculations neglected inelastic scattering [67]; Duke and Tucker [68] were among the first to emphasize the necessity for including inelastic scattering in computational schemes. The first substantial agreement between calculated and experimental I(E) curves was produced in 1972 in the work of Jepsen et al. [57] on the (100) surface of aluminium, silver and copper. These calculations assumed:

i) Surface geometries that correspond to undistorted truncations of the bulk structures.

ii) Electron-ion core interactions can be represented by potentials from band structure calculations.

iii) Absorption effects can be incorporated with an imaginary potential from uniform electron-gas theory [62].

iv) Lattice vibrations can be treated by a Debye-Waller type factor as indicated above.

v) The inner potential correction (V) can be chosen empirically by aligning theoretical and experimental I(E) curves.
This work of Jepsen et al. established that the dominant aspects of the elastic LEED process were essentially understood, even though numerical agreement was not obtained for absolute intensities. The latter appears to relate especially to incomplete order for the surfaces, but in any event this discrepancy did not inhibit the development of LEED crystallography, since it was found that the positions of structure in I(E) curves could be calculated to within experimental error.

Calculations of LEED intensities generally involve treating the scattering of a plane wave by a surface region of perfect diperiodic symmetry. The total wave field outside of the crystal has the form

\[ \psi(r) = \phi(r) + \sum \frac{c^g}{k^g} e^{i \mathbf{k}^g \cdot \mathbf{r}} \]

where \( \phi(r) \) is the incident plane wave. The objective is to calculate beam reflectivities

\[ R^g = \left| \frac{k^g}{k^o} \right| \left| c^g \right|^2 \]

which relate to the measured intensities. Brief descriptions of some of the important procedures now available for calculating beam reflectivities are given in the following sections.
2.3 T-Matrix Method

The T-matrix method was formulated by Beeby [70] and has since been detailed further by Tong [65]. This method starts by writing the wave function for an electron inside the solid as

\[ \psi(x) = \phi(x) + \int G(x-x') V(x') \psi(x') \, dx' \]  

(2.13)

where the Green's function \( G(x-x') \) describes the propagation of an electron from \( x' \) to \( x \). This equation can be solved by defining a total scattering matrix \( T \) for the solid

\[ V(x') \psi(x') = \int T(x,x') \phi(x) \, dx \]  

(2.14)

With the muffin-tin approximation for the potential, substitution of (2.14) into (2.13) yields

\[ T(x_2,x_1) = \sum_R t_R(x_2-R,x_1-R) + \sum_{R \neq R'} \left\{ t_{RR'}(x_2-R',x_3-R') G(x_3-x_4) t_R(x_4-R,x_3-R) \right\} \]  

(2.15)

where

\[ t_R(x_2-R,x_1-R) = V_R(x_2-R) \delta(x_1-x_2) + \int V_R(x_2-R) G(x_2-x) t_R(x-R,x_1-R) \, dx \]  

(2.16)

is the t-matrix for the single ion core at \( R \). In (2.15), the first term covers all single ion core scattering, the second term represents all double scattering events, etc. Equation 2.15 therefore sums all possible inter-atomic and intra-atomic scattering events involved with the electron going from \( x_1 \) to \( x_2 \) inside the solid.

For the actual evaluation of the \( c_x \) in (2.11), and hence the beam
reflectivities, the crystal is divided into subplanes parallel to the surface such that each subplane has the same Bravais structure and contains the same kind of atoms. The final result is

$$c_{\ell} = \gamma_0 \sum_{LL'} \frac{Y_L(k_0 \hat{z}) Y_{L'}^*(k_o \hat{z})}{|k_o \hat{z}|} \sum_{\alpha} e^{i(k_o \hat{z} - k_0 \hat{z}) \cdot d_\alpha} T_{LL'}^{\alpha} (k_o)$$

(2.17)

where $L$ stands for the angular momentum quantum numbers $l,m$, $Y_L$ is the associated spherical harmonic, the second summation is over all subplanes and $d_\alpha$ is the vector from the overall origin at the interface to the origin chosen for subplane $\alpha$. In (2.17) $T_{LL'}^{\alpha} (k_o)$ is the element of the total scattering matrix for subplane $\alpha$ in the angular momentum representation

$$T_{LL'}^{\alpha} (k_o) = \mathcal{T}_{LL'}^{\alpha} (k_o) + \sum_{L_1 L_2} \mathcal{T}_{L_1 L_2}^{\alpha} (k_o) \sum_{\beta \neq \alpha} G_{L_1 L_2}^{\alpha \beta} (k_1) T_{L_2 L_1}^{\beta} (k_o) ,$$

(2.18)

$\mathcal{T}_{LL'}^{\alpha} (k_o)$ is the $LL'$ element of the planar scattering matrix ($\mathcal{T}_{LL'}$) for the subplane $\alpha$

$$\mathcal{T}_{LL'}^{\alpha} (k_o) = \mathcal{T}_{LL'}^{\alpha} (k_o) [1 - G^{SP}(k_1) t_{L_2}^{\alpha} (k_o)]^{-1},$$

(2.19)

and $t_{L_2}^{\alpha} (k_o)$ is the diagonal $t$-matrix for a single ion core in subplane $\alpha$. The non-zero elements of this matrix relate to the phase shift $\delta_k$ by

$$t_{L_2}^{\alpha} (k_o) = \frac{\hbar^2}{2m} \left[ \frac{e^{2i\delta_k} - 1}{2ik_o} \right].$$

(2.20)

Also needed in (2.18) and (2.19) are the intraplanar structural propagators $G^{SP}$ and the interplanar propagators $G_{L_1 L_2}^{\alpha \beta}$. These are complex matrices which are dependent on the inelastic scattering and the geometries associated with the ion core sites.
Successful calculations have been made with this method for clean metal surfaces. In principle it is exact and can work for any type of surface structure; in practice, however, the solving of the set of equations (2.18) to give the matrix $T$ is very time consuming and requires a large amount of computer core storage if an appreciable number of subplanes have to be included. This method is only practical in the presence of inelastic scattering, a feature that Beeby neglected in the initial formulation. The extension to include thermal motion of the ion cores was made by Tong and Rhodin in 1971 for the (100) surface of aluminum [71].

2.4 Bloch Wave Method

This method was introduced by McRae [67,73] and developed by Pendry [74], Kambe [75,76] and Jepsen et al. [57,77]. A detailed account has been published in Pendry's book [24]. In this approach, the muffin-tin approximation is again used and an infinite crystal is built up of parallel layers. For the region of constant potential between successive layers, each Bloch wave can be expanded in terms of plane waves. The scattering situation at a single layer is depicted in figure 2.4, where a set of incident plane waves

$$\psi_i(\mathbf{r}) = \sum_{\mathbf{g}} b^+ \exp(\mathbf{i} \mathbf{k}^+ \cdot \mathbf{r})$$

(2.21)

is directed onto the crystal, and scattered waves

$$\psi_s(\mathbf{r}) = \sum_{\mathbf{g}} M_{\mathbf{g}}^{+\dagger} b^+ \exp(\mathbf{i} \mathbf{k}^+ \cdot \mathbf{r})$$

(2.22)

propagate both in the outward direction ($\mathbf{k}^+$) and in the inward direction ($\mathbf{k}^-$). The matrices involved in this formulation are expressed in terms of...
Figure 2.4: Schematic representation of a set of plane wave incident from the left and multiply scattered by a plane of ion cores.

Figure 2.5: Schematic diagram of transmission and reflection matrices at the \( \alpha \)th subplane. The broken lines are the central lines between the subplanes.
the linear momentum (K-space) representation; this contrasts with the angular momentum (L-space) representation in the T-matrix method. \( M^{++}_{g_g} \) is an element of the layer diffraction matrix \( M^{++}_{g_g} \) where both incident and diffracted beams move into the crystal. The notation \( M^{++}_{g_g} \) covers all four combinations of directions.

It is clear for the situation in figure 2.4 that all the diffracted beams become coupled together. The coefficients for plane waves between layers \( a \) and \( a+1 \) can be expressed in a compact matrix notation

\[
\begin{align*}
\mathbf{b}_{a+1}^+ &= T^{++}_{a_g} \mathbf{b}_{a}^+ + R^{+-}_{a_g} \mathbf{b}_{a+1}^- \\
\mathbf{b}_{a}^- &= T^{--}_{a_g} \mathbf{b}_{a+1}^- + R^{+-}_{a_g} \mathbf{b}_{a}^+
\end{align*}
\]

where, for example, the components of the column vector \( \mathbf{b}_{a}^+ \) are the various values of \( b^+ \) between layers \( a \) and \( a+1 \). For a crystal composed of identical layers, which are separated by a constant displacement \( \xi \), the transmission and reflection matrices can be expressed as

\[
\begin{align*}
T^{++}_{g_g} &= p^+ \cdot (I_i + M^{++}_{g_g}) \mathbf{p}^+ \\
T^{--}_{g_g} &= p^- \cdot (I_i + M^{--}_{g_g}) \mathbf{p}^- \\
R^{+-}_{g_g} &= p^+ \cdot M^{+-}_{g_g} \mathbf{p}^- \\
R^{-+}_{g_g} &= p^- \cdot M^{-+}_{g_g} \mathbf{p}^+
\end{align*}
\]

where \( p^+ \) represents inward propagation with wave vector \( k^+_g \) through one half of an interlayer distance while \( p^- \) represents the corresponding outward propagation with wave vector \( k^-_g \).
The \( P^\pm \) in equation (2.24) are elements of a unit matrix. Schematic representations of the reflection and transmission matrices are shown in figure 2.5.

Corresponding coefficients between successive layers must satisfy the Bloch conditions

\[
b^+_\alpha+1 = e^{i k \cdot g} b^+_\alpha \tag{2.26a}
\]

\[
b^-_\alpha = e^{-i k \cdot g} b^-_{\alpha+1} \tag{2.26b}
\]

Substitution of (2.23) and (2.24) into (2.26) yields the eigenvalue equation

\[
\mathbf{L} \begin{bmatrix} b^+_\alpha \\ b^-_\alpha \end{bmatrix} = \lambda \begin{bmatrix} b^+_\alpha \\ b^-_\alpha \end{bmatrix} \tag{2.27}
\]

where

\[
\mathbf{L} = \begin{pmatrix} L^+ & R^- \\ -L^- & R^+ \end{pmatrix} \tag{2.28}
\]

and

\[
\lambda = \exp i k \cdot g \tag{2.29}
\]

Pendry [24] has discussed the evaluation of the layer diffraction matrices \( M^{\pm \pm} \) in terms of the scattering properties of the individual ion-cores. For a layer which involves a single atom per unit mesh, the elements satisfy

\[
L^{\pm \pm} = \sum_{LL'} Y_L^+(k^+_L) [1-X]^{1-L} Y_L^+(k^+_L) \exp(i\delta^+_L) \sin \delta^+_L, \tag{2.30}
\]
where $\chi$ describes multiple scattering within the layer. Given $M_{zz}^{\pm \pm}$ for a particular system, the transmission and reflection matrices in equations (2.24) can be set up and hence (2.27) can be solved by standard methods to give eigenvectors, which fix the Bloch waves, and the corresponding eigenvalues which fix possible wave vectors along with the requirement of conservation of momentum parallel to the surface.

Only half of the $2n_g$ possible solutions (where $n_g$ is the number of vectors $g$ included in the calculation) are physically acceptable (i.e. correspond to waves which either propagate or decay exponentially in the $z$-direction). To complete the calculation of diffracted beam reflectivities it is necessary to match each wave function, and its first derivative with respect to $z$, at both sides of the solid-vacuum interface. Corresponding wave matching procedures are involved in extending this scheme to situations where one or more top layers are different from the rest (e.g. for an adsorbed layer). This basic approach involves less computer core storage than the T-matrix method, but the solution of equation (2.27) becomes time consuming when $n_g$ is large.
2.5 Perturbation Methods

The T-matrix and the Bloch wave methods are exact in the sense that they include all multiple scattering events in the crystal. These methods have proved valuable for calculating LEED intensities of clean surfaces, although they require long computational times and large core storage. Such considerations limit the use of these exact multiple scattering methods to the more complex surface structures of interest in LEED crystallography, and therefore encourage the development of approximate schemes based on perturbation expansions. Part of the motivation for this comes from the realization that with inelastic scattering the comparatively short mean free path length must limit the order of multiple scattering that can be important. This suggests that it should be possible to reduce computational times by formulating in terms of perturbation theory. Tong et al. [72] made the T-matrix calculation to third order, and showed that it can work well for weak scattering metals like aluminum. However the approach of utilizing perturbation theory within the T-matrix method seems less helpful for stronger scatterers; basically this approach becomes too clumsy and unwieldy at above third order.

Pendry has developed convenient iterative schemes which are based on the Bloch wave method and have the significant property that the contribution from each additional order has the same basic form as those from the previous orders (this is unlike the situation for the third order calculation [72] noted above for Al(100)). These new methods are the layer doubling and renormalized forward scattering methods; multiple scattering calculations described in this thesis utilized these methods extensively.
2.5 (a) **Layer Doubling Method**

This method \([24,78]\) requires that inelastic scattering is sufficiently strong so that a semi-infinite crystal can be approximated by a slab of finite thickness. Two layers are considered first, then four layers, and at each level of iteration the number of layers is doubled. This method starts with a calculation of the reflection and transmission matrices as in equations (2.24), and then generates the corresponding matrices for a stack of two layers.

\[
T_{2C}^{++} = T_{2B}^{++} \left( \frac{1}{2} R_{A}^{++} R_{B}^{++} - I \right)^{-1} T_{2A}^{++} \quad (2.31a)
\]

\[
R_{2C}^{--} = R_{A}^{--} + T_{1B}^{--} R_{B}^{--} \left( \frac{1}{2} R_{A}^{++} R_{B}^{++} - I \right)^{-1} T_{2A}^{--} \quad (2.31b)
\]

\[
R_{2C}^{+-} = R_{B}^{+-} + T_{1B}^{--} R_{A}^{--} \left( \frac{1}{2} R_{A}^{++} R_{B}^{++} - I \right)^{-1} T_{2B}^{+-} \quad (2.31c)
\]

\[
T_{2C}^{--} = T_{2A}^{--} \left( \frac{1}{2} R_{B}^{++} R_{A}^{++} - I \right)^{-1} T_{2B}^{--} \quad (2.31d)
\]

where the individual subplanes are denoted by A, B and the resulting composite layer is denoted by C. The doubling process is shown schematically in figure 2.6; the same set of equations (2.31) are used to extend the crystal stack to 2, 4, 8, 16... layers. This process is continued until the reflection amplitudes have converged; typically this requires 8 or 16 atomic layers. Once convergent reflectivities have been obtained for the substrate, surface layers can be systematically added still using equations (2.31). A convenient feature of this method is that a surface layer can be shifted either laterally or vertically, without having to recompute the bulk reflectivities.
Figure 2.6: Stacking of planes to form a crystal slab and illustrate the layer-doubling method. Planes A and B are first stacked to form the two-layer slab C; the process is continued to form a four-layer slab. (After Tong [65].)
This method is considerably faster than the full Bloch wave method and yet it can provide good numerical accuracy. Each iteration involves inversions of two matrices of dimension \( n_g \) (the number of beams included in the calculation). A limitation is that this method is not suitable for very small interlayer spacings \((c<0.5\,\text{Å})\) when \( n_g \) is required to be excessively large [79].

2.5 (b) **Renormalized Forward Scattering method**

The renormalized forward scattering (RFS) method was introduced by Pendry [24] and discussed further by Tong [65]; its characteristic features are that the intralayer scatterings are calculated exactly, while the interlayer scatterings are iterated for the various possible paths in the crystal. The principle of this method is illustrated schematically in figure 2.7.

The crystal is again represented by a finite number of layers; the actual number used \((n)\) is such that the total elastically scattered amplitude that would reach the \((n+1)^{\text{th}}\) layer is less than a predetermined fraction \((\text{e.g. } 0.003)\) of its incident amplitude. Clearly the stronger the inelastic scattering, the smaller is the number of layers that are needed. Following Tong [65], \( A^i_{\alpha}(g) \) designates the amplitude at the local origin between the \( \alpha^{\text{th}} \) and \((\alpha+1)^{\text{th}}\) layers for the electron wave characterized by \( g \) propagating into the crystal; the index \( i \) is the order of iteration which identifies the number of times the electron has propagated into the crystal along this particular path. For the first iteration we have

\[
A^1_{\alpha}(g) = \sum_{g'} T^{+*}_{\alpha} (gg') A^1_{\alpha-1}(g') ,
\]

(2.32)
Figure 2.7: a) Illustration of the renormalized forward scattering method. Vertical lines represent layers. Each triplet of arrows represents the complete set of plane waves that travel from layer to layer.
b) Propagation steps of the inward-travelling waves.
  c) Propagation steps of the outward-travelling waves.
  (After Van Hove and Tong [81].)
but no waves propagating in the inward direction are included after the $n^{th}$ layer. Waves propagating in the outward direction are represented by $B^i_{\alpha}(g)$ in an analogous notation. Except at the deepest layer, the outward travelling waves consist of two components (figure 2.7c): the reflected portions of the inward travelling waves, and the transmitted portion of the outward-travelling waves. In general, the amplitudes of the outward-directed waves satisfy

$$B^i_{\alpha}(g) = \sum_{g'} R^+_{\alpha+1}(gg')A^i_{\alpha}(g') + \sum_{g'} T^-_{\alpha+1}(gg')B^i_{\alpha+1}(g');$$

(2.33)

$$\alpha = n-1, n-2, \ldots, 0,$$

where $n$ is the deepest subplane reached in the appropriate iteration. The corresponding expression for the inward-directed waves is

$$A^i_{\alpha}(g) = \sum_{g'} R^-_{\alpha}(gg')B^i_{\alpha}(g') + \sum_{g'} T^+_{\alpha}(gg')A^i_{\alpha-1}(g');$$

(2.34)

$$\alpha = 1, 2, 3, \ldots, n.$$

Equations (2.33) and (2.34) are solved iteratively in the RFS method until the reflectivity has converged. This approach is computationally convenient since no eigenvalue equations or matrix inversions are involved. The computation times scale as $n^2$, where $n$ is the number of beams included; this is more favorable than the layer doubling method for which computation time scales as $n^3$. The RFS method has proved to be an excellent method for calculating LEED intensities for many systems provided the electron damping is sufficient. Otherwise its only limitation is a failure to converge when any two layers are closer than about 1 Å. In the latter event the layer doubling method may be applicable.
2.6 **Further Multiple Scattering Methods**

The RFS and layer doubling methods have proved to be reliable and convenient for LEED crystallographic analyses of many clean and simple overlayer surface structures. A limitation in all procedures which utilize the K-space representation (including the full Bloch-wave method) is that the number of plane waves required in the calculations increases rapidly with decreasing interlayer separations [79]. Once matrices of dimension of the order of $10^2$ are involved the K-space methods become increasingly unwieldy and numerically unreliable; effective limits are set with interlayer spacing of around 0.5 Å for both the layer doubling and the Bloch wave methods ($\sim 1$ Å sets the lower limit for the RFS method).

For models where close interlayer spacing are required, there are two possible approaches: (i) to stay with the K-space representation but treat the two layers as a composite layer (with consequent increase in matrix dimensions and requirements for computing time and storage), or (ii) to work with the L-space representation (as in the T-matrix method). The dimensions of matrices involved in L-space calculations are independent of the number of beams required for the calculations, hence this approach starts to have advantages over the K-space representation when $n_g$ is large. To make the T-matrix method more efficient, Zimmer and Holland [80] introduced a reverse-scattering iterative procedure which essentially represents an equivalent of the RFS method in the L-space representation. This approach again fully accounts for forward scattering events, but approximates the back-scattering. The reverse scattering procedure of Zimmer and Holland requires matrices of
dimensions \((\ell_{\text{max}} +1)^2\). Typically \(\ell_{\text{max}} +1 \leq 8\) for electron energies less than 200 eV, thus this iterative method appears advantageous over the RFS method if the number of beams required exceeds about 64. However this L-space iteration approach requires the evaluation and storage of \(n(n-1)\) square matrices \(C_{\alpha\beta}\) for an \(n\)-layer crystal, and moreover these matrices have to be recalculated for every change made to the surface layer. This represents a less satisfactory feature of the method.

Recently Van Hove and Tong [79] described a combined-space method which utilizes both the L-space and K-space representation to achieve optimal advantages of each. Specifically the calculation is made in the L-space representation for those layers which are closely spaced, while the K-space representation is used for the rest of the calculation where the interlayer spacings are larger. Discussions of approaches and the associated computer programs for the various methods now available for surface crystallography with LEED have been described in a recent book by Van Hove and Tong [81].
2.7 General Aspects of Computations

2.7 (a) Structural Parameters and Use of Symmetry

The basic approach to surface crystallography with LEED involves postulating a series of trial structures and searching for that particular model which gives the best agreement between calculated and experimental I(E) curves. The models postulated must be consistent with the symmetries indicated by the observed LEED pattern. The substrate structure is generally known from X-ray crystallography, but atoms in the upper layers of a clean surface need not occupy exactly the positions they would in the infinite crystal. Many clean metals have surfaces whose translational symmetries are found by LEED to be identical with those of the corresponding substrate structure (the surface is said to be unreconstructed if the normal registries are maintained, although there may be changes in the vertical spacing); by contrast LEED patterns show directly that many are reconstructed [86]. In general, for both clean surfaces and adsorption systems, the topmost interlayer spacing must be varied in the LEED intensity calculations and lateral variations should also be considered. For models where domain structures are possible appropriate beam intensities need to be averaged in the calculations in order to accommodate the expectation that the incident beam in the experiment samples all the domain types. For example, for sulphur adsorbed on the bridge sites of the Rh(100) surface, as in figure 2.8, an averaging of the intensities of the (10) and (01) beams is necessary for the calculations to become consistent with the four fold symmetry observed in the experimental LEED pattern.
Figure 2.8: Schematic diagram of three simple models for Rh(100)-p(2×2)S. In reciprocal space, sets of symmetrically equivalent beams are indicated by a common symbol.
The computational effort can be reduced when the direction of incidence coincides with a symmetry axis or a symmetry plane [81]; this depends on the inevitable equivalences in the diffracted beams as a result of the symmetry elements in the model. The simplifications in the multiple-scattering calculations represent a standard application of the group theory. Utilizing symmetry reduces the dimensions of the matrices required within the K-space representation [82], specifically only one g vector is needed for each set of symmetry-related beams. For the particular examples of the model types shown in figure 2.8 for Rh(100)-p(2x2)>S, it is readily seen that, with normal incidence, the 4F and 1F models preserve two mirror planes of symmetry perpendicular to each other as well as a C4 rotation axis, whereas the 2F model contains only two mirror planes. A consequence of the C4 axis is the equivalence of the following 8 fractional order beams

\[(1 \frac{1}{2}) \equiv (1 \frac{1}{2}) \equiv (\bar{1} \frac{1}{2}) \equiv (\bar{1} \frac{1}{2}) \equiv (\bar{1} \frac{1}{2}) \equiv (\bar{1} \frac{1}{2}) \equiv (\frac{1}{2} \bar{1}) \equiv (\frac{1}{2} \bar{1})\]

for both the 4F and 1F models. The situation for the 2F model is that these fractional order beams separate into two sets of 4 equivalent beams,

\[(1 \frac{1}{2}) \equiv (1 \frac{1}{2}) \equiv (1 \frac{1}{2}) \equiv (\bar{1} \frac{1}{2}) \not\equiv (\frac{1}{2} \bar{1}) \equiv (\frac{1}{2} \bar{1}) \equiv (\frac{1}{2} \bar{1}) \equiv (\frac{1}{2} \bar{1}).\]

Similarly, the 4F and 1F models have the equivalences

\[(0 1) \equiv (0 \bar{1}) \equiv (1 0) \equiv (\bar{1} 0)\]

whereas the corresponding situation for the 2F model involves

\[(0 1) \equiv (0 \bar{1}) \not\equiv (1 0) \equiv (\bar{1} 0).\]

The calculations for the 2F model therefore require more beams, and correspondingly larger matrices, than the 4F and 1F models.
Table 2.1: Numbers of symmetrically-inequivalent beams actually used in calculation of various surface structures. The models for the overlayer structures are designated as in figure 1.7 and 2.8.

<table>
<thead>
<tr>
<th>Surface structure</th>
<th>Surface model</th>
<th>Type of symmetry</th>
<th>Number of symmetrically inequivalent beams used in calculation</th>
<th>Equivalent total number of beams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(100)</td>
<td>unreconstructed</td>
<td>2 perpendicular mirror planes + $C_4$</td>
<td>9</td>
<td>53</td>
</tr>
<tr>
<td>Rh(110)</td>
<td>unreconstructed</td>
<td>2 perpendicular mirror planes</td>
<td>23</td>
<td>71</td>
</tr>
<tr>
<td>Rh(111)</td>
<td>unreconstructed</td>
<td>3 mirror planes at $60^\circ$ to each other + $C_3$ along z-axis</td>
<td>10</td>
<td>37</td>
</tr>
<tr>
<td>Rh(100)-p(2x2)-S</td>
<td>4F, 1F, 2F</td>
<td>same as Rh(100)</td>
<td>35</td>
<td>221</td>
</tr>
<tr>
<td></td>
<td>4F, 1F</td>
<td>same as Rh(110)</td>
<td>49</td>
<td>175</td>
</tr>
<tr>
<td></td>
<td>2SB, 2LB</td>
<td>same as Rh(110)</td>
<td>49</td>
<td>175</td>
</tr>
</tbody>
</table>
Calculations reported here with the RFS and layer doubling methods utilize symmetry as in the discussion and computer programs given by Van Hove and Tong [81]. In these routines symmetry is accommodated by listing the \( g \) vectors in the input data together with appropriate code numbers to identify the symmetry type of each beam. The code number enables the program to use the appropriate symmetrized wave functions and to set up the simplified diffraction matrices. Listed in Table 2.1 are the numbers of symmetrically inequivalent beams needed for calculations on the various surfaces studied in this thesis.

2.7 (b) Program Flow

The flow-chart in figure 2.9 summarises the sequence of events that occur in a multiple-scattering calculation. The programs start by reading in all the relevant structural and non-structural parameters as well as a list of diffracted beams with their symmetry code numbers. At each energy, the dimensions of the matrices are set equal to the number of propagating beams (i.e. those beams with real \( k \)) plus the first few evanescent beams. The layer diffraction matrices \( M^{++} \) are calculated; different subroutines are available depending on whether the layer corresponds to a simple Bravais net or to a composite layer-type. The stacking of layers is performed by either the layer doubling or the RFS methods. Each method can include overlayers with structures which differ from the appropriate layer of the substrate; a special case of this involves a variation of the topmost layer spacing for example for clean metal surfaces. Generally the calculations are made for the energy range 40-200 eV in increments of 2 eV up to 80 eV, and in increments
Figure 2.9: Flowchart showing principal steps in a multiple-scattering LEED calculation, using the RFS or layer doubling programs.
of 4 eV above 80 eV; the reflected intensities in the high energy range are then interpolated to give values in 2 eV intervals. The calculated intensities are stored on magnetic tape and can be plotted for visual comparison with the experimental I(E) curves; alternatively the calculated intensities can be compared with experimental values by means of a reliability index as discussed in the next sections.

2.8 Evaluation of Results

2.8 (a) Introduction

In LEED crystallography it is necessary to find the structural model which gives the best correspondence between the calculated and experimental I(E) curves. This opens the need to be able to evaluate the similarity, or otherwise, between two sets of curves on varying structural, and some non-structural, parameters. Such a search has most often been done by visual comparisons (e.g. by matching up the positions and relative intensities of peaks, dips and other structural features), but this approach suffers the disadvantage of being unwieldy when the numbers of beams and variation parameters are large. As a consequence there has been considerable encouragement for the development of numerical indices for guiding these comparisons. Among the simplest possibilities is

$$\Delta E = \frac{1}{N} \sum_{i=1}^{N} |E_{i}^{\text{cal}} - E_{i}^{\text{obs}}|$$

(2.35)

which only compares peak positions. In (2.35), the $E_{i}$ represent energies at which the $i^{th}$ peak occurs in the calculated and observed curves, and $N$
is the total number of peaks compared \[83,84\]. Clearly the better the correspondence in peak positions between the experimental and calculated \(I(E)\) curves, the lower the value of \(\Delta E\). In practice this criterion seems incomplete because it ignores the actual intensity values, it gives an equal weighting to each peak, and it is ambiguous when a peak present in one curve is either absent or appears as an incompletely developed feature (e.g. a shoulder) in the other curve. Van Hove et al. \[85\] proposed an extension involving five simple indices, where each gives a different emphasis in the comparison. However, the most complete index so far is that proposed by Zanazzi and Jona \[45\]. This index attempts to compare numerically all the features included in a visual comparison.

2.8 (b) Zanazzi and Jona's Proposals

The reliability index proposed by Zanazzi and Jona \[45\] compares curve shapes via their derivatives. For the \(i\)th beam the reliability index is:

\[
\begin{align*}
    r_i &= \int_{E_{1i}}^{E_{2i}} w(E) | c_i I_i', \text{cal} - I_i', \text{obs} | \, dE \left/ \int_{E_{1i}}^{E_{2i}} I_i', \text{obs} \, dE \right. \\
    &\quad \left/ \int_{E_{1i}}^{E_{2i}} I_i', \text{cal} \, dE \right. \\
\end{align*}
\]

(2.36)

where intensities are compared between energies \(E_{1i}\) and \(E_{2i}\), and the primes indicate first derivatives for the calculated and observed \(I(E)\) curves. The weight function

\[
w(E) = \left( \frac{c_i I_i'', \text{cal} - I_i'', \text{obs}}{| I_i', \text{obs} | + | I_i', \text{obs} |_{\text{max}}} \right) ,
\]

(2.37)

emphasizes the extrema of the experimental curve and other portions with high curvature; the double primes in (2.37) indicate second derivatives.
The scaling constant

\[ c_i = \int_{E_{li}}^{E_{2i}} I_{i,\text{obs}} \, dE / \int_{E_{li}}^{E_{2i}} I_{i,\text{cal}} \, dE \]  \hspace{1cm} (2.38)

allows for an arbitrary scale of intensity in the experimental curves; comparisons of relative intensities are sufficient for LEED crystallographic studies at the present time.

One total reliability index given by Zanazzi and Jona for a set of diffracted beams is

\[ \bar{r} = \sum_i (r_i) \Delta E_i / \sum_i \Delta E_i , \]  \hspace{1cm} (2.39)

where \( \Delta E_i = E_{2i} - E_{li} \), \( (r_i) \) is the reduced single beam index

\[ (r_i) = r_i / \rho , \]  \hspace{1cm} (2.40)

and \( \rho \) was equated to 0.27, a mean value of \( r_i \) found by matching random pairs of curves. In (2.39), an average is taken over the single beam indices, where they are weighted according to the energy range over which the comparison between experiment and calculation is made.

A variation of (2.39), also proposed by Zanazzi and Jona, is

\[ R = \left( \frac{3}{2n} + \frac{2}{3} \right) \bar{r} , \]  \hspace{1cm} (2.41)

where \( n \) is the number of different beams treated in the comparisons. The advantage of (2.41), over (2.39), is that it mitigates against a low value of the overall reliability index resulting from a comparison involving just a small number of beams; it is generally believed that a reliable LEED crystallographic analysis requires comparisons involving \( I(E) \) curves for 10
different diffracted beams. \( R \) in (2.41) was set up with the objective of being consistent with the following possibilities for values obtained from comparisons of experimental and calculated \( I(E) \) curves for a particular proposed model: \( R<0.20 \) suggests the model is "very probable", \( 0.20<R<0.35 \) suggests the model is "possible", and \( R>0.35 \) suggests the model is unlikely.

2.8 (c) Further Developments

As part of an investigation of the proposal of Zanazzi and Jona, Watson et al. [43] plotted \((r_{r})_i\) as a function of topmost spacing for the (111) surface of copper. This is shown in figure 2.10 where \(\Delta d\%\) gives the topmost spacing expressed as the percentage change from the bulk spacing, (i.e.

\[
\Delta d\% = \frac{d - d_0}{d_0} \times 100
\]

where \(d_0\) is the bulk interlayer spacing and \(d\) is the topmost interlayer spacing). The curves shown in figure 2.10 are specifically for \(V_{or} = -9.5 \text{ eV}\); of the 16 beams available only 9 are shown for clarity. The reduced reliability index \((\tilde{r}_r)\) for the 16 beams is plotted as the dashed line in the same figure, and the associated error

\[
\varepsilon_r = \left\{ \left[ \sum_i \Delta E_i ((r_{r})_i - \tilde{r}_r)^2 \right] / \left[ (n-1) \sum_i \Delta E_i \right] \right\}^{\frac{1}{2}}
\]

(2.42)
corresponding to the minimum of \(\tilde{r}_r\) is indicated by the arrows. In (2.42), \(n\) is the number of beams considered.

Watson et al. [43] concluded that \(\varepsilon_r\) indicates an unrealistically large error in \(\Delta d\%\) for the data available. In fact the top layer spacings indicated
Figure 2.10: Plots for Cu(111) of $(r_r)_i$ for 9 individual beams versus $\Delta d\%$ with $V_{or} = -9.5$ eV. The dashed line shows the reduced reliability index $(\bar{r}_r)$ for the total 16 beams.

(After Watson et al. [43].)
by the minima for all the individual curves are rather close to the spacing for the minimum in the dashed line, and this suggests that the uncertainty in spacing associated with the minimum value of $\tilde{r}_r$ could be given by the standard error found from the distribution of toplayer spacings $(d_{\text{min}}^i)$ indicated by the minimum for each individual curve,

$$
\varepsilon_d = \left\{ \left[ \sum_i \Delta E_i (d_{\text{min}}^i - \bar{d}_{\text{min}}) \right]^2 / \left[ (n-1) \sum_i \Delta E_i \right] \right\}^{\frac{1}{2}}, \quad (2.43)
$$

where

$$
\bar{d}_{\text{min}} = \left( \sum_i \Delta E_i d_{\text{min}}^i \right) / \left( \sum_i \Delta E_i \right) \quad (2.44)
$$

Figure 2.10 shows $\bar{d}_{\text{min}} \pm 2\varepsilon_d$; this corresponds to $-4.1\pm1.2\%$. The introduction of $\varepsilon_d$ by Watson et al. makes a start on the problem of estimating uncertainties in results from LEED crystallography. Certainly numerical reliability indices are required for this purpose; it is very hard to see how uncertainties could be helpfully evaluated solely from visual evaluations of I(E) curves. Another advantage of numerical indices is that they can be easily plotted in contour form. Again this was introduced by Watson et al., and the example in figure 2.11 shows a contour plot of $\tilde{r}_r$ versus $V_{or}$ and $\Delta d\%$ for Cu(111). According to the proposal of Zanazzi and Jona, the overall minimum in $\tilde{r}_r$ in figure 2.11 corresponds to the values of $V_{or}$ and $\Delta d\%$ which give the best agreement between the complete set of experimental and calculated I(E) curves. Error bars shown for the minimum represent $\pm \varepsilon_d$ and $\pm \varepsilon_v$ (the standard error associated with the distribution of values of $V_{or}$ for the minima of $(r_i^r)$ and defined analogously to $\varepsilon_d$); these indicate 68% confidence limits associated with the minimum of $\tilde{r}_r$. 


Figure 2.11: Contour plot for Cu(111) of \( \tilde{r} \) versus \( \Delta d\% \) and \( V_{OR} \).

(After Watson et al. [43].)
CHAPTER 3

Preliminary Work
3.1 **General Experimental Procedures**

3.1 (a) **LEED Apparatus**

As in all work on well defined crystal surfaces, LEED experiments must be carried out at low pressure (i.e. \( \leq 10^{-9} \) torr). This section describes the general features of the conventional type of LEED apparatus which has been used in the majority of LEED experiments made so far. The discussion will be brief, but a lot more information can be obtained from the references provided. A review of the various modifications of LEED instruments is available [87].

A schematic diagram of the LEED apparatus used in this work is shown in figure 3.1. This involves a Varian FC12 chamber which is constructed of non-magnetic stainless steel and is connected to a series of pumping facilities below the main chamber indicated in figure 3.1. The initial sorption pumping is done with high surface area molecular sieves (zeolites) in containers which are cooled by liquid nitrogen. These pumps can reduce the pressure of the system to \(-10^{-3}\) torr when the main sputter ion pump \((200 \text{ l s}^{-1})\) can be started. After baking the whole system for \(-12\) hours at \(200^\circ\text{C}\) (to remove adsorbed gases from the chamber walls), it is necessary to out-gas thoroughly all components of the system that are heated during an experiment. A titanium sublimation pump is available for extra pumping during both out-gassing and the actual experimental periods. Gases for adsorption studies or for ion-bombarding in the cleaning process can be introduced into the whole chamber through a leak valve from a gas inlet manifold. This part of the system is pumped by its own small ion pump \((20 \text{ l s}^{-1})\) and it can be baked separately.
Figure 3.1: (a) Schematic of the Varian FC12 UHV chamber.
(b) Diagramatic representation of the pumping system:

IP = Ion Pump;
TSP = Titanium Sublimation Pump;
SP = Sorption Pump.
Figure 3.2:  (a) Schematic diagram of the electron optics used for LEED experiments.
(b) Diagram showing sample mounted on a tantalum supporting ring.
(c) Electron bombardment sample heater. Hatched lines represent stainless steel parts while the stipple pattern indicates the ceramic insulator.
from the main chamber. The objective here is to limit the amount of impurities in the admitted gases to very low proportions in the main chamber. Details of pumping methods, measurement of pressure and associated techniques are given in reviews by Hobson [88], Lange [89] and Tom [90].

The sample manipulator (Varian 981-2528) holds the crystal sample and enables the crystal to be translated as well as rotated both about the axis of the chamber (to enable the sample which is off-set by $\frac{21}{2}$" to be directed to different facilities) and about an axis in the horizontal plane (to enable the beam from the electron gun to make different angles of incidence ($\theta$) with respect to the crystal). The sample holder has facilities for electron bombardment heating (figure 3.2(c)); the temperature of the crystal is measured with a Pt/13%Rh-Pt thermocouple junction in contact with the sample.

The electron gun (Varian 981-2125) produces an electron beam by thermionic emission from a hot tungsten cathode; these electrons are accelerated and collimated through anode plates. The typical incident beam used for LEED in this work (energy range 30-230 eV) has a current of about 1 $\mu$A, and a beam diameter at the sample of $\leq 0.75$ mm. The same gun was used for Auger analysis at a typical energy of 1 keV and current of 10 $\mu$A. Reviews of the design and technology of low voltage electron guns includes those by Rosebury [91] and Kohl [92].

The electron optics (Varian 981-0127) (figure 3.2a) consists of a hemispherical phosphor screen and four concentric grids each of ~80% transparency; the sample is positioned at the common centre of curvature of the grids and screen for LEED. In the usual mode of operation, the specimen and the grid closest to the sample are grounded to ensure that electrons travel through an
electrostatically field-free space between the sample and the optics (the final anode of the electron gun is also grounded). The second and the third grids are connected together and are held at a potential which is close to that on the cathode in the electron gun; the objective is to stop those electrons which have lost energy on interacting with the sample, while permitting only the elastically scattered electrons to pass through. The fourth grid is earthed. The elastically scattered electrons, after penetrating this grid, are accelerated through about 5 keV onto the phosphor screen, where each beam diffracted from an ordered crystal surface shows up as a bright spot. The whole diffraction pattern on the screen can be observed directly through the glass window and photographed.

Another accessory needed for the LEED experiment is the sputtering gun (Varian 981-2043) for cleaning the crystal by ion bombardment. The chamber is surrounded by three orthogonal sets of square Helmholtz coils to reduce the residual magnetic field to a level where its effect on the motion of electrons being studied is minimized.

3.1 (b) Crystal Preparation

The experiments reported in this thesis involve surfaces of rhodium cut from two sources of single crystal; one was purchased commercially [93] (99.99% purity), the other was provided by another laboratory [94]. To start the preparation process, the single crystal is oriented to the required surface plane by the Laue X-ray back-reflection technique [95] and cut by spark erosion ("Agietron", AGIE, Switzerland). To correct for small deviations of orientation from the desired crystal face, the crystal slice is mounted in
acrylic resin ("Quickmount" Fulton Metallurgical Produce Corp., USA) and polished with 5, 3 and 1 micron diamond paste on a polishing wheel ("Universal Polisher", Micrometallurgical Limited, Thornhill, Ontario.). After this process, it is necessary to check again that the finished surface still has the required crystallographic plane. This is done by placing the crystal on the Laue X-ray diffractometer so that the desired plane is perpendicular to the X-ray beam; the whole goniometer and crystal assembly is then transferred to an optical bench where a Ne-He laser beam is directed perpendicularly onto the surface and the angle of reflection is detected. This provides a test of whether the physical surface coincides with the required crystal plane. Generally we aim to have the surface oriented to within $\frac{1}{2}$° of the desired crystal plane. At this stage the back of the sample is spot welded onto a supporting tantalum ring (figure 3.2(b)), which in turn is mounted onto the manipulator. The sample and manipulator is then placed in the vacuum chamber, the latter is closed and the chamber is pumped down to a base pressure of $-1\times10^{-10}$ torr after the standard out-gassing processes.

AES indicates that sulphur, phosphorus and carbon are the impurities generally present in the rhodium crystals used in our experiments; no substantial amounts of boron (Auger peak at 180 eV) has been detected although some other research groups [96,97] have reported appreciable amounts of this impurity in their rhodium samples. The cleaning processes are generally performed by cycles of heat treatment (700-1000°C for 10-60 min.) to drive most bulk impurities to the surface, and argon ion bombardment to sputter off the impurities at the surface. All impurities except carbon, can be removed from
Figure 3.3: Auger spectra of clean Rh(110) surface as a function of crystal temperature indicating carbon concentrated around the surface region at 200°C and diffused back into the bulk at 300°C.
rhodium surfaces by argon ion bombardment (typically $10^{-6}$ torr of Ar at 0.1-1 microamps and -1 keV for 10-30 min.). Immediately after sputtering, the carbon Auger signal (282 eV) always showed a relative increase; this appears to be associated with the low sputtering cross-section of carbon. However, after annealing at 700°C for a few minutes, AES indicates that the level of carbon contamination on the surface is reduced (presumably by back diffusion into the bulk) and LEED indicates that the surface has become ordered again. In preliminary studies, Auger spectra of the clean Rh(110) surface were studied as a function of crystal temperature (figure 3.3), and it was found that below 300°C carbon diffuses to the surface whereas above this critical temperature carbon apparently diffuses back into the bulk. Further general discussions on the preparation of clean surfaces are given in reviews by Farnsworth [98], Bauer [99] and Jona [100].

3.1 (c) Detection of Surface Impurities

Surface impurities were detected in this work by means of Auger electron spectroscopy using the LEED optics as a retarding field analyzer [16,17]. Auger electrons of characteristic energies are present as small peaks superimposed on the high (but relatively constant) background of the intermediate regions of N(E) vs E curve (figure 1.2), and these peaks can be enhanced by electronic differentiation [116]. With reference to figure 3.4, the final anode of the gun, the sample, the first and fourth grids are grounded as for the normal LEED experiment, but for detecting Auger electrons the retarding potential applied on the two middle grids has a small modulating voltage $\Delta V=V\sin \omega t$ (typical values of V used in these experiments are <10 eV). With this modulating voltage, the total current collected on the screen (held at
Figure 3.4: Schematic diagram of LEED optics used as a retarding field analyzer for Auger electron spectroscopy:
MCA = multichannel analyzer.
Table 3.1: Observed and calculated Auger transition energies for rhodium.

<table>
<thead>
<tr>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
<th>(f)</th>
<th>Assignment</th>
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<td></td>
<td></td>
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<td>303</td>
<td>100</td>
<td>303.0</td>
</tr>
</tbody>
</table>

(a) this work
(b) Grant and Haas [102]
(c) Palmberg et al. [36]
(d) Castner et al. [96]
(e) Chan et al. [118]
(f) Coghlan and Clausing [103]
a positive potential of about 300 eV) is modulated. Using a lock-in amplifier
the components of the current corresponding to the first and second harmonics
(frequencies $\omega$ and $2\omega$ respectively) are readily identified. A plot of the
amplitude of these harmonic components as a function of the retarding energy
E produces the secondary electron distribution $N(E)$ (figure 1.2) and its first
derivative $dN(E)/dE$ respectively [31]. The typical Auger spectrum shown in
figure 1.10 is plotted in $dN(E)/dE$ form. Theoretically, the sensitivity of
the spectra measured by this method is approximately 1% of a monolayer
[16,17]. Higher sensitivities to impurities are possible when Auger spectra
are measured with a cylindrical mirror analyzer [101]. Such an analyzer was
not available at the time the experimental work reported in this thesis was
done.

Measured peak energies and relative peak heights for the Auger spectrum
of rhodium are summarized in Table 3.1. The variations in peak energies from
other published measurements must be attributed to errors in the energy scale
and to the lack of an appropriate contact potential correction; also uncer-
tainties are inevitably increased for low-intensity peaks. Energies calculated
by Coghlan and Clausing [103] for free atoms with an ionization correction
are also listed in the table; these values are helpful for guiding the
assignment to particular Auger transitions.

3.1 (d) LEED Intensity Measurements

Diffraeted beam intensities in LEED have most often been measured either
directly as diffracted beam currents with a moveable Faraday cup collector
inside the chamber [104] or indirectly as the brightness of spots on the
phosphor screen with an external spot photometer [105]. A variant of the latter approach is the photographic technique introduced by Stair et al. [106] and developed further by Frost et al. [107], who employed a computer-controlled Vidicon camera to analyze the photographic film and thereby produce experimental I(E) curves. This latter procedure has been used in the present work. Basically photographs of the LEED screen are taken at a series of electron energies and measurements are made of the integrated optical densities for the diffracted spots on the film negatives. Assuming the measured optical density (D) for a spot is proportional to the amount of light which caused the darkening, and hence to the associated electron flux which hits the screen, then D divided by the incident electron current is proportional to the diffracted beam intensity. Such measurements inevitably give relative beam intensities.

The LEED patterns displayed on the phosphor screen were photographed through the window of the vacuum chamber using a Nikon F2 35 mm camera with an 85 mm f1.8 lens and a K2 extension ring. Photographs were taken generally for the range of incident beam energies 30-250 eV in 2 eV intervals using fixed exposures of 1 s at f4, the incident current and energy being recorded for each photograph. Using a motor-driven unit to wind the film and a 250 exposure film back, LEED patterns could be photographed over this energy range in less than 5 minutes. After taking a set of photographs, the surface purity was routinely checked with AES to assess whether any contamination occurred during data collection.
Standard Kodak Tri-X emulsion film was used and the film was processed in a continuous length in "Acufine" developer at 73°F for 7 minutes. The photographic negatives were analysed with the system indicated in figure 3.5. The vidicon camera and associated electronics comprise part of the Computer Eye System (Spatial Data System Inc.) which was interfaced to a mini-computer (Data General Nova 2). The film held on the light table is scanned continuously by the camera and the image is displayed on the TV monitor in a 512x480 (xy) array. The intensity (z value) of any element of the image may be sampled by triggering the digitizer with appropriate instructions from the computer. The profiler displays directly on the monitor the variation of intensity along any selected vertical line of the image. The joystick controls the position (coordinates) of the flashing spot on the TV monitor, and is used to start the analysis [107] by pointing at the spot to be analysed.

Assuming a Gaussian distribution for the spot intensity, the background intensity \( z_{\text{back}} \) is estimated by averaging the z-value of all elements lying in an annulus of mean radius \( 2\sigma \) (where \( 2\sigma \) is the width at half maximum of the intensity distribution). The integration procedure involves summing all the values of \( (z-z_{\text{back}}) \) within the circle of radius \( 2\sigma \) and this value is divided by the incident beam current to give a measure of the diffracted beam intensity. After the integration, the coordinates of the intensity maximum are determined and stored as the new starting coordinates for the next frame. Since the area scanned for each spot always includes the position of that spot on the next frame, the computer can automatically follow each spot as it moves toward the centre of the screen with increasing energy. The whole analysis of each spot takes less than 30 seconds and the \( I(E) \) curves may be displayed on an oscilloscope and plotted on an xy recorder.
Figure 3.5: Schematic diagram of the apparatus used to analyse the photographic negatives of LEED patterns.
3.2 Structural Determinations of Low Index Surfaces of Rhodium

3.2 (a) Previous LEED Intensity Calculations for Rhodium Surfaces

Watson et al. [43, 44, 108, 109] analysed measured I(E) curves from low index surfaces of rhodium with multiple-scattering calculations and their structural conclusions are summarized in Table 3.2. These calculations used two types of atomic potential:

i) The self-consistent band structure potential provided by Moruzzi, Janak and Williams [110]; this potential was designated $V_{\text{MJW}}^{\text{Rh}}$.

ii) The superposition potential calculated for the central atom in a Rh$_{13}$ cluster by a linear superposition of atomic charge densities. This potential was designated $V_{\text{Rh13}}$.

With reference to Table 3.2, Watson et al. obtained discrepancies between the two atomic potentials which resulted in different geometrical structures and inner potential values reported for the same surface. Generally a band structure potential is likely to be preferred [60] although it has been suggested [61] that the superposition potential can produce very similar results to the band structure potential for the purpose of LEED crystallography. Watson et al. [43] supported this suggestion in a determination of the geometrical structure of the Cu(111) surface.

However for rhodium, upon evaluating the level of agreement between experimental and calculated I(E) curves, both with visual analyses and reliability indices, Watson et al. were unable to select one of these atomic potentials as being preferred. This thereby left significant uncertainties in the details of the structures of the Rh(100) and (111) surfaces. One of the objectives of my initial research was to perform further studies on these surfaces in order to elucidate this problem.
Table 3.2: Structural determination of low index surfaces of rhodium.
(Watson et al.)

<table>
<thead>
<tr>
<th>Surface</th>
<th>$\Delta d_{%}^{\pm \epsilon_d}$ (%)</th>
<th>$V_{\text{or}}^{\pm \epsilon_V}$ (eV)</th>
<th>$\bar{\tau}_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(100)</td>
<td>-1.8±1.0</td>
<td>-19.6±0.8</td>
<td>0.17</td>
</tr>
<tr>
<td>Rh(111)</td>
<td>-4.2±0.5</td>
<td>-18.6±0.5</td>
<td>0.16</td>
</tr>
<tr>
<td>Rh(110)</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Rh(110)</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 3.3: Structural determination of low index surface of rhodium.
(This work)

<table>
<thead>
<tr>
<th>Surface</th>
<th>$\Delta d_{%}^{\pm \epsilon_d}$ (%)</th>
<th>$V_{\text{or}}^{\pm \epsilon_V}$ (eV)</th>
<th>$\bar{\tau}_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(100)</td>
<td>1.0±0.9</td>
<td>-12.8±0.4</td>
<td>0.09</td>
</tr>
<tr>
<td>Rh(111)</td>
<td>-1.6±0.8</td>
<td>-11.2±0.6</td>
<td>0.08</td>
</tr>
<tr>
<td>Rh(110)</td>
<td>-3.3±1.5</td>
<td>-10.9±0.8</td>
<td>0.12</td>
</tr>
<tr>
<td>Rh(110)</td>
<td>-0.5±0.7</td>
<td>-9.6±0.9</td>
<td>0.09</td>
</tr>
</tbody>
</table>
3.2 (b) Further Studies

In this work, multiple scattering calculations were repeated for normal incidence on the (100), (110) and (111) surfaces of rhodium, and the calculated LEED intensities were compared with the experimental I(E) curves previously produced by Watson et al. for the (110) and (111) surfaces. Although a new set of experimental data for normal incidence on Rh(100) was obtained, and used in the comparison in this work, these new experimental I(E) curves did not show any significant deviations from the previous data [111].

Prior to making the multiple scattering calculations, the calculation of phase shifts from the two different atomic potentials was completely re-investigated. In doing this an error was detected in the value used previously for the potential at the muffin-tin radius, and this resulted in an incorrect set of phase shifts associated with the potential $V_{\text{Rh}}^{\text{MJW}}$. After making the correction for the band structure potential, a new set of phase shifts was generated for different $\ell$ to a maximum value of 7 (figure 3.6). These new phase shifts values generated from the band structure potential of Moruzzi, Janak and Williams are designated as $[V_{\text{Rh}}^{\text{MJW}}]$ to avoid confusion with the erroneous $V_{\text{Rh}}^{\text{MJW}}$ of Watson et al.

With the corrected phase shifts from the band structure potential, multiple-scattering calculations for normal incidence were repeated for the (100), (110) and (111) surfaces assuming regular packing arrangements as indicated previously [43,44,108,109]. The non-structural parameters were kept unchanged from those used in the previous work. Specifically, the surface atomic vibrations were assumed to be isotropic and layer-independent, the

†The possibility of a numerical error was first suggested to K.A.R. Mitchell by J.J. Rehr (Univ. of Washington). The actual error was later detected by P.R. Watson and W.T. Moore while calculating some phase shifts for zirconium.
Figure 3.6: Energy dependence of rhodium phase shifts ($\ell=0-7$) for the potential $[V_{Rh}^{MJW}]$. 
surface Debye temperature being taken as 406 K (i.e. \( \sqrt{0.7} \) times the bulk value of 480 K \([112,115]\)). The imaginary part of the inner potential (\( V_{oi} \)) was equated to \(-1.17E^{1/3} \), guidance being provided by the widths of primary Bragg-type peaks in experimental I(E) curves according to equation (2.4) and the energy dependence proposed in equation (2.5). All the interlayer spacings below the second rhodium layer were fixed at the bulk values (i.e. 1.9022 Å for Rh(100), 1.3452 Å for Rh(110) and 2.1960 Å for Rh(111)). The topmost interlayer spacings (i.e. the perpendicular distance between the first and second rhodium layers) were allowed to vary from a 10% contraction from the bulk value to a 5% expansion in increments of 2.5% for the (100) and (111) surfaces, while for the (110) surface calculations were made with the topmost spacing varying from a 12.5% contraction to a 2.5% expansion. The multiple-scattering calculations over the energy range of 30-250 eV were done for the (10), (01), (11), (02) and (12) beams for all three surfaces (beam notations are illustrated in figure 3.7). The calculations utilized the RFS method for the (100) and (111) surfaces, whereas the layer-doubling method was used for the (110) surface to avoid any possibility that the reflected intensities might not converge for the smaller interlayer spacings.

Intensities calculated with the corrected phase shifts from the band structure potential for the (100) surface were compared with the new experimental I(E) curves. Visual analysis suggested that the best correspondence occurred when \( \Delta d\% \) is between 0 and 2.5% (here \( \Delta d\% \) indicates the topmost interlayer spacing (d) expressed as the percentage change from the bulk value \( d_o \) (i.e. \( \Delta d\% = [(d-d_o)/d_o] \times 100 \)). The analysis with the reliability
Figure 3.7: (a) Schematic diagrams of the (100), (110) and (111) surfaces of rhodium. The dotted circles represent rhodium atoms in the second layer.
(b) The corresponding LEED patterns indicating the beam notation as used in text.
index proposed by Zanazzi and Jona [45] indicated that the minimum value for \( r \) was 0.085 and occurred when \( \Delta d^% = 1.0 \pm 0.9% \) and \( V \text{or} = -12.8 \pm 0.4 \text{ eV} \).

To assess the correspondence between the two potentials \( V_{\text{Rh13}} \) and \( [V_{\text{MJW}}] \), another comparison with \( \tilde{r} \) was made between the same experimental \( I(E) \) curves and the curves calculated from \( V_{\text{Rh13}} [108] \). This time the minimum value of \( \tilde{r} \) was again 0.085, although for the conditions \( \Delta d^% = 0.5 \pm 1.2% \) and \( V \text{or} = -14.0 \pm 0.6 \text{ eV} \). These two results, which are summarized in Table 3.3, are in contrast to the previous report of Watson et al. (Table 3.2). Also summarized in Table 3.3 are the conditions for minimum \( \tilde{r} \) from comparisons of intensities calculated using \( [V_{\text{MJW}}] \) with one set of experimental data for the (110) and (111) surfaces; each set of experimental data covers 5 beams in the energy range 30-200 eV. Corresponding results from the potential \( V_{\text{Rh13}} \) obtained previously by Watson et al. are in Table 3.2.

Comparisons of our new results obtained from the corrected phase shifts from the band structure potential \( [V_{\text{MJW}}] \) for three low-index surfaces of rhodium (Table 3.3) with those obtained previously from the superposition potential \( V_{\text{Rh13}} \) (Table 3.2), allows the conclusion that the values of \( \Delta d^\% \) and \( V \text{or} \) given by the two potentials are equal to within the indicated uncertainties for each set of experimental measurements. This suggests that the two rhodium potentials are equivalent for the purpose of LEED crystallography, and provides support for the suggestion [61] that the superposition potentials from cluster calculations can be useful when self-consistent band structure potentials are unavailable. This situation for the rhodium surfaces is now consistent with that found previously for Cu(111) [43].
3.3 Studies with the Reliability Index of Zanazzi and Jona

3.3 (a) Introduction

The basic approach for surface crystallography with LEED involves varying structural and non-structural parameters in the multiple-scattering calculations in order to find the best correspondence between calculated and experimental I(E) curves for all diffracted beams [113]. At present the high cost of the multiple-scattering calculations inhibits a full variation of non-structural parameters to maximize the agreement in these comparisons, and so far only $V_{qi}$ has been subjected to much variation [57]. In part this has been because of a common feeling that the other non-structural parameters do not have a strong effect on determined geometries. Thus, the usual procedure in LEED crystallography involves finding a plausible choice of non-structural parameters (e.g. $V_{oi}$, $\theta_D$) at the start of the calculation and keeping these parameters fixed from then on [56]. This philosophy is tested here, particularly with the reliability index $r^r$ suggested for LEED by Zanazzi and Jona [45]. The variation of non-structural parameters appears to provide a fairly stringent test of $r^r$. Hence one objective of this work is to assess where the use of $r^r$ for the variation of non-structural parameters is able to give results similar to a visual analysis and where it does not. The content of this section has already been published along with some supplementary observations of P.R. Watson and S.J. White [150].

3.3 (b) Relations between Reliability Index and the Imaginary Potential

The imaginary part of the inner potential ($V_{oi}$) provides a phenomenological description of the inelastic scattering of electrons by a solid; the life times of electrons of well defined energy in the solid place a
restriction (via the uncertainty principle) on peak widths in I(E) curves according to equation (2.4). Increase in $V_{oi}$ corresponds to a reduction in the proportion of the elastically scattered electrons and to a broadening of peaks in the I(E) curves.

The initial selection of a value of $V_{oi}$ for rhodium was made (utilizing equations (2.4) and (2.5)) from the measured widths of "kinematical" peaks in experimental I(E) curves; on this basis a plausible expansion for $V_{oi}$ is $-\alpha E^{1/3}$ with $\alpha$ equal to about 1.17. A point of interest here is to see whether changes in $\alpha$ would modify conclusions on the geometries of rhodium surfaces, and whether the reliability-index analysis would indicate that $\alpha=1.17$ is the most appropriate value of $\alpha$. In order to examine this, further multiple-scattering calculations were made for normal incidence on the (111) surface of rhodium at a series of values of $\alpha$, specifically 1.17, 1.47, 1.76, 2.05 and 2.34, with all other non-structural parameters fixed at the values used previously in section 3.2 (b). The (111) surface was convenient for this study, since the calculations required a comparatively small number of beams and the RFS method was applicable.

I(E) curves for the (01) beam for the five values of $\alpha$ with a 2.5% contraction of the topmost layer are shown in figure 3.8 together with the experimental data. The main features of each individual curve are maintained, although increase in $\alpha$ gives a general lowering of intensities and, most significantly, a broadening of the peaks. Visual evaluations of all diffracted beams suggested the best agreement between experimental and calculated I(E) curves occurred when $\alpha$ is in the range 1.47 to 1.76. These comparisons were
Figure 3.8: The experimental $I(E)$ curve for the (01) beam at normal incidence from the Rh(111) surface compared with five corresponding curves calculated with the potential $[V_{\text{Rh}}^{\text{MJW}}]$ and $\Delta d\% = -2.5\%$ for the parameter $\alpha$ varying from 1.17 to 2.34.
also made with the numerical reliability index, and conditions for minimum $\tilde{r}_T$ for each value of $\alpha$ are summarized in Table 3.4. These results indicate that variation of $\alpha$ has only a minor effect on the determined topmost interlayer spacing, and this supports the common assumption that variation of $V_{oi}$ is not essential in LEED crystallography. It is satisfying also that the insensitivity of geometrical structure to $V_{oi}$ is recognized by $\tilde{r}_T$. Nevertheless it must be noted that even though closely similar geometrical structures are indicated by the different values of $\alpha$, the values of $\tilde{r}_T$ at the different minima are not equivalent. The lowest $\tilde{r}_T$ value corresponds to $\alpha$ close to 1.76, and this suggest that the initial choice of 1.17 may not be optimal. Both visual and $r$-index evaluations are consistent in indicating $\alpha$ is larger than 1.17 and this supports the use of the index $\tilde{r}_T$. On the other hand, values of $\alpha$ larger than 1.17 seem less consistent with determining $V_{oi}$ from equation 2.4.

The values of $\tilde{r}_T$ reported in Table 3.4 are unusually low, especially those for the higher values of $\alpha$. The trends found did not seem consistent with the original conclusions of Zanazzi and Jona, and we wondered whether the tendency for low values of $\tilde{r}_T$ to be found for high $\alpha$ could be an artefact associated with the value of $\rho$ being fixed at 0.027 in the calculation of $(r_{T})_i$ in equation (2.40). According to Zanazzi and Jona [45], this value of $\rho$ was obtained by averaging $(r_{T})_i$ for matching random pairs of experimental and calculated I(E) curves. One uncertainty was whether "complexity of structure" was fully built into the scheme of Zanazzi and Jona. In general one would expect that an experimental I(E) curve that contains a lot of
Table 3.4: Conditions for best agreement between experimental I(E) curves at normal incidence for Rh(111) and curves calculated with the potential $v_{Rh}^{MJW}$ according to the reliability indices $\tilde{r}_r$ and $\tilde{r}_m$ for different values of $\alpha$.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$\Delta d%$ (%)</th>
<th>$V_{or}$ (eV)</th>
<th>$\tilde{r}_r$</th>
<th>$\tilde{r}_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.17</td>
<td>-1.6±0.8</td>
<td>-11.2±0.6</td>
<td>0.080</td>
<td>0.985</td>
</tr>
<tr>
<td>1.47</td>
<td>-2.5±0.5</td>
<td>-11.8±0.7</td>
<td>0.042</td>
<td>0.510</td>
</tr>
<tr>
<td>1.76</td>
<td>-2.3±0.6</td>
<td>-11.7±0.6</td>
<td>0.035</td>
<td>0.430</td>
</tr>
<tr>
<td>2.05</td>
<td>-2.3±0.5</td>
<td>-11.6±0.7</td>
<td>0.037</td>
<td>0.440</td>
</tr>
<tr>
<td>2.34</td>
<td>-2.0±0.6</td>
<td>-11.0±0.8</td>
<td>0.041</td>
<td>0.490</td>
</tr>
</tbody>
</table>
structure would be more difficult to match to calculated curves than one with less structure, and therefore in setting up a many-beam reliability-index perhaps the former should have a relatively greater weighting than the latter. One approach to this is to allow the value of $\rho$ to vary for each experimental curve. In order to make an initial assessment of whether such effects could be relevant to the trends of $\tilde{r}_r$ with $\alpha$ shown in Table 3.4, we replaced $\rho$ in equation (2.40) with a new quantity

$$r_{(\text{st.line,expt})} = \int_{E_1}^{E_2} \frac{|I''_{\text{obs}}|}{|I'_{\text{obs}}| + I_{\text{max}}'} \, dE \int_{E_1}^{E_2} I_{\text{obs}} \, dE \quad (3.1)$$

This quantity varies with each experimental $I(E)$ curve according to the amount of structure it involves. Equation (3.1) is obtained from equation (2.36) by comparing an experimental $I(E)$ curve with a straight line corresponding to $I_{i,\text{cal}} = I_{i,\text{cal}}' = I_{i,\text{cal}}'' = 0$. Using $r_{(\text{st.line,expt})}$ instead of $\rho$ in equation (2.40), we then set up a new overall reduced reliability index designated as $\tilde{r}_m$. The values of $\tilde{r}_m$ for the variation of $\alpha$ values are also summarized in Table 3.4. However, it turned out for the case considered here that minimizing $\tilde{r}_m$ gave identical values of $\Delta d\%$ and $V_{\text{or}}$ to those found by minimizing $\tilde{r}_r$; numerical values of the two indices are different, but to a good approximation corresponding values of $\tilde{r}_r$ can be obtained by dividing values of $\tilde{r}_m$ by 12.1. This observation does not support the possibility that the low values of $\tilde{r}_r$ found for high $\alpha$ (hence high $V_{\text{oi}}$) was associated with the constant value of $\rho$ used in equation (2.40).
Further investigation suggested that the high value of \( \alpha \) needed for better matching between calculated and experimental I(E) curves appears to be associated with the way that the experimental intensities were handled in the analysis. The initial value of \( \alpha = 1.17 \) was obtained by considering individually measured I(E) curves, whereas the experimental I(E) curves actually used in the comparisons with the calculated I(E) curves were averaged over appropriate sets of beams which are expected to be, and to a good approximation are, symmetrically equivalent. However, minor errors in the experiment \[107,108\] can lead to corresponding peak positions in "equivalent sets" of beams being shifted slightly (e.g. by 1 or 2 eV) from the mean values and this inevitably leads to some broadening of structure in the averaged I(E) curves. Upon investigating the averaged experimental I(E) curves, a choice of \( \alpha \) as suggested by equations (2.4) and (2.5) for the Rh(111) surface is 1.65. This value is in reasonable agreement with the conclusions noted above from the visual evaluation and the r-factor analysis.

These studies indicate the following conclusions:

1) Determined surface geometrical structure is insensitive to changes in \( V_{oi} \) values. This supports the usual approach of keeping \( V_{oi} \) fixed in the multiple scattering calculations, and of choosing suitable values of \( V_{oi} \) from equation (2.4).

2) The index \( \bar{r} \) proposed by Zanazzi and Jona is consistent with a visual analysis for identifying values of \( V_{oi} \) which optimize agreement between experimental and calculated I(E) curves.

3) Further improvements are needed in the experimental measurements for ensuring that I(E) curves from symmetrically-related beams really are equivalent.
3.3 (c) Reliability-Index and the Variation of Surface Debye Temperature

The effects of atomic vibrations are incorporated into multiple scattering calculations by means of temperature-dependent atomic scattering factors involving the Debye temperature ($\theta_D$) as indicated in equations (2.9)-(2.10). Strictly the atomic vibrations are expected to be layer dependent and to decrease into the bulk [114]. However, most LEED studies have used a single effective Debye temperature ($\theta_D^{\text{eff}}$) for all layers probed by the analysed electrons. In principle, a better, although still simple, possibility is to give the topmost layer a "surface value" ($\theta_D^{\text{surf}}$) and to assume the second and all deeper layers can be characterized by the bulk value ($\theta_D^{\text{bulk}}$) [56]. In the previous multiple scattering calculations made so far in this thesis, $\theta_D^{\text{bulk}}$ for rhodium was taken as 480 K [115] and $\theta_D^{\text{eff}}$ was estimated as $\sqrt{0.7} \theta_D^{\text{bulk}}$ [112]. Although this type of choice seems plausible, it is nevertheless made on intuitive, rather than rigorous, grounds; moreover for assessing further the choice of $\theta_D^{\text{surf}}$ it would seem helpful to determine the effect of its variation on the structural conclusions, as considered for variations of $V_{oi}$ in section 3.3 (b). For this investigation, multiple scattering calculations for the Rh(111) surface were made by varying $\theta_D^{\text{surf}}$ over the range of 200-600 K in 100 K steps, all other non-structural parameters being fixed at the values given in section 3.2(b) (except $a$ was restricted to 1.76).

Figures 3.9 and 3.10 show two different sets of contours of $\bar{r}_r$ plotted against $\theta_D^{\text{surf}}$. For both the contours are reasonably symmetrical about a horizontal line, and minimum values of $\bar{r}_r$ are closely indicated to correspond to the
Figure 3.9: Contour plot of $\bar{T}$ versus $\theta_{D,\text{surf}}$ and $V_{or}$ for normal incidence data from Rh(111) where the calculations use the potential $[V_{Rh}^{MJJW}]$ with $\alpha=1.76$ and $\theta_{D,\text{bulk}}=480$ K.
Figure 3.10: Contour plot of $\tilde{r}_T$ versus $\theta_{D,\text{surf}}$ and $\Delta d\%$ for normal incidence data from Rh(111) where the calculations use the potential $[V_{\text{Rh}}^{M}}W]$ with $\alpha=1.76$ and $\theta_{D,\text{bulk}}=480$ K.
values \( V = -11.5 \text{ eV} \) and \( \Delta d\% = -2\% \). These values are comparable with those reported previously in Tables 3.3 and 3.4 for a fixed value of \( \theta_D,\text{eff} \). An unexpected feature of these plots, however, is that they point to values of \( \theta_D,\text{surf} \) in the physically unreasonable range of being greater than \( \theta_D,\text{bulk} \) (i.e. 480 K for rhodium [115]).

Within the conventional procedure for including atomic vibrations in multiple-scattering calculations [24,65], the main effect of \( \theta_D \) is to modify overall intensities but without appreciably affecting structure in the calculated \( I(E) \) curves. This can be seen in figure 3.11 where \( I(E) \) curves calculated for the (01) beam of Rh(111) with \( \Delta d\% = -2.5\% \) are plotted for values of \( \theta_D,\text{surf} \) between 200 and 600 K. The most noticeable trend is that the lower values of \( \theta_D,\text{surf} \) especially give relatively lower calculated intensities at the higher energies. This contrasts with the trend observed in the experimental \( I(E) \) curves where relatively higher intensities are found at the higher energies. This suggests that the tendency to high values of \( \theta_D,\text{surf} \) picked out by the use of \( \tilde{r}_\text{r} \) is reflecting a real trend in the curves compared, although it is physically unreasonable for \( \theta_D,\text{surf} \) to be greater than \( \theta_D,\text{bulk} \). Our feeling is that the origin of this discrepancy may be associated with general problems in the data collecting processes. Changes both in grid transparency and in the solid angle presented to the camera as the spots move toward the centre of the screen for increasing energies can caused apparent variations in relative intensities. Legg et al. [117] made corrections for these factors and demonstrated a consequent lowering in relative beam intensities at the lower energies. In future LEED intensity
Figure 3.11: The experimental I(E) curve for the (01) beam at normal incidence from the Rh(111) surface compared with five corresponding curves calculated with the potential $V_{Rh}^{MJW}$, $\Delta d\% = -2.5\%$, and $a = 1.76$ for the parameter $\theta_{D,\text{surf}}$ varying from 200 to 600 K.
measurements we are planning to incorporate corrections for these effects; also it is possible that some refinement in the background correction could be needed at high energies when spots crowd together in the LEED screen. At present we feel that the source of discrepancy indicated by the untenable large value of $\theta_{D,\text{surf}}$ is associated with aspects of the experimental measurements, and although this has not yet been unambiguously confirmed, two conclusions do seem secure. The first is that the Zanazzi-Jona reliability index $T_R$ appears able to give a fair assessment of the relative intensities of I(E) curves when $\theta_{D,\text{surf}}$ is varied in the calculations (although an appreciable sensitivity in $T_R$ to relative intensities in successive sections of I(E) curves has not been recognized previously). Secondly, surface structural conclusions seem unaffected by variation of $\theta_{D,\text{surf}}$ in the calculations.

Although there would be advantages in refining the treatment of atomic vibrations in LEED intensity calculations [65], the evidence presented here does suggest that modifying values of $\theta_{D,\text{surf}}$ is not going to significantly affect conclusions about surface geometry. This suggestion is supported by an independent analysis of the Rh(111) surface with multiple-scattering calculations by Chan et al. [118]. Using $\theta_{D,\text{bulk}}$ as 300 K and $\theta_{D,\text{surf}}$ as 250 K, Chan et al. obtained $\Delta d\%$ for the topmost rhodium layer as 0±5%. Although these error limits seem rather large, nevertheless this conclusion is consistent with our determination of the Rh(111) surface (Table 3.2). Generally we feel, for the present stage of development of LEED crystallography, the multiple-scattering calculations might just as well continue to use $\theta_{D,\text{eff}}$ obtained from the experimental measurements [25] or alternatively $\theta_{D,\text{surf}}$ for the topmost layer specified as a certain fraction of $\theta_{D,\text{bulk}}$ [112].
3.4 Studies of Adsorption of some Gaseous Molecules on Rhodium surfaces

3.4 (a) Bibliography of Overlayer Structures on Rhodium Surfaces

The properties of well-defined surfaces of rhodium have been less extensively investigated than those of many other transition metals, even though rhodium shows a high degree of catalytic activity for many reactions [42]. Table 3.5 summarizes studies where general chemisorptive properties of rhodium have been investigated with LEED. Auger electron spectroscopy was not available for monitoring surface purity in the initial studies by Tucker [119-122] although this technique was available for all other studies reported in Table 3.5. Much of the work on rhodium that has emerged over the past several years has been concerned mainly with either LEED patterns or adsorption kinetics.

An important objective for part of the research reported in this thesis was to determine some detailed surface structures with LEED for adsorption on rhodium. The initial aim was to investigate some comparatively simple structures involving O or S adsorbed on low-index surfaces and to compare with similar systems already investigated with LEED crystallography, for example adsorption on nickel. The LEED analyses resulting from the adsorption of H₂S on the (100) and (110) surfaces of rhodium are described in chapters 4 and 5 respectively. The next section reviews observations for the adsorption of O₂ on Rh(100), a system that was originally planned to be investigated via analyses of LEED intensities.
Table 3.5: Surface structures reported for adsorption of small gaseous molecules on low index surfaces of rhodium.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Rh(100)</th>
<th>Rh(110)</th>
<th>Rh(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>surface structure</td>
<td>ref.</td>
<td>surface structure</td>
</tr>
<tr>
<td>O₂</td>
<td>p(2x2)-0</td>
<td>[a,b,f]</td>
<td>disorder</td>
</tr>
<tr>
<td></td>
<td>c(2x2)-0</td>
<td>[a,f]</td>
<td>c(2x4)-0</td>
</tr>
<tr>
<td></td>
<td>(3x1)-0</td>
<td>[b,f]</td>
<td>c(2x8)-0</td>
</tr>
<tr>
<td></td>
<td>c(2x8)-0</td>
<td>[b]</td>
<td>(2x2)-0</td>
</tr>
<tr>
<td>CO</td>
<td>c(2x2)-CO</td>
<td>[a]</td>
<td>(2x1)-CO</td>
</tr>
<tr>
<td></td>
<td>hexagonal overlayer</td>
<td>[a]</td>
<td>c(2x2)-C</td>
</tr>
<tr>
<td></td>
<td>(4x1)-CO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>c(2x2)-CO</td>
<td>[a]</td>
<td>---</td>
</tr>
<tr>
<td>NO</td>
<td>c(2x2)-NO</td>
<td>[a]</td>
<td>---</td>
</tr>
<tr>
<td>H₂S</td>
<td>p(2x2)-S</td>
<td>[f]</td>
<td>c(2x2)-S</td>
</tr>
<tr>
<td></td>
<td>c(2x2)-S</td>
<td>[f]</td>
<td></td>
</tr>
</tbody>
</table>

[a] Castner et al. [96]; [b] Tucker [119]; [c] Tucker [120,121]; [d] Marbrow and Lambert [97]; [e] Grant and Haas [102]; [f] This work [123,124]; [g] Weinberg et al. [127].
3.4 (b) Adsorption of $O_2$ on Rh(100)

The sample used in this study was cut from the single crystal provided by Tucker [94], and it was previously used by Watson et al. for a LEED analysis of the clean Rh(100) surface [108]. Prior to starting the adsorption work, the surface was repolished and checked to ensure that it was within $1^\circ/2$ of the (100) plane. After mounting and installing in the vacuum chamber, the sample was cleaned according to the procedures described in section 3.1, and annealed until the LEED pattern exhibited a sharp (1×1) pattern with low background intensities. The sample was heated to 300°C before high purity $O_2$ (99.99%, Matheson) was introduced into the vacuum chamber at a pressure of $10^{-7}$ torr. After 5 minutes a sharp (3×1) LEED pattern corresponding to two different domains was observed, and an Auger spectrum taken after the formation of this pattern failed to detect the presence of any impurities. The Auger peaks of oxygen at around 510 eV could not be detected. This effect has been observed previously for oxygen adsorption on some transition metals [125,126] and it appears to be associated with the low ionization cross-section for initiating the Auger process for adsorbed oxygen. A sharp (1×1) pattern characteristic of the clean Rh(100) surface can be restored (presumably by desorption of the oxygen [96,127]) upon heating at 1000°C for 10 minutes.

After returning to the base pressure the process could be repeated with a new dose of oxygen applied under the same conditions as indicated above. Sharp (3×1) patterns could always be obtained, although on different occasions variations were found in the domain structure. These ranged from two equally populated domains, to two unequally populated domains and even to the appearance
of a single domain (figure 3.12). From time to time faint half-order diffracted spots were observed superimposed on the (3×1) pattern, but the pattern never developed into a complete (2×2) pattern even though the crystal was exposed to O₂ for longer periods of time. Furthermore these spots could be removed by heating at 700°C for a few seconds; then after cooling to room temperature, the LEED pattern showed only the sharp (3×1) pattern.

A well-defined p(2×2) LEED pattern (figure 3.12) could be observed when the clean Rh(100) surface was exposed to O₂ at 10⁻⁶ torr for 5 minutes. An apparent, but incompletely developed, c(2×2) pattern could also be detected if the crystal was left in the constant atmosphere of O₂ at 10⁻⁶ torr for a further 30 minutes. This was observed as an increase in intensities of fractional-order spots of type (m/n), while the other fractional-order spots showed relative decreases in intensities.

These results for the adsorption of oxygen on Rh(100) agree partly with earlier work done by Tucker [119] and Castner et al. [96]. Tucker reported (2×2), (3×1) and (2×8) patterns for increasing oxygen exposures, but he did not observe the c(2×2) pattern. Castner et al. reported a p(2×2) pattern which transformed to the c(2×2) pattern at higher oxygen exposures, but no (3×1) pattern was detected in that work over a wide range of temperature and pressure. My observation of the p(2×2) pattern seems broadly in agreement with those observed in these other two studies. Also I had some evidence, through faint LEED patterns, for the transformation of a p(2×2) pattern into a c(2×2) pattern with oxygen exposure. One possibility for the discrepancies between these different studies could involve other gases (e.g. CO) being
Figure 3.12: Photographs of some p(2x2) and (3x1) LEED patterns observed at normal incidence from the adsorption of oxygen on a Rh(100) surface.
(a) Rh(100)-p(2x2)-0 at 70 eV,
(b) Rh(100)-(3x1)-0, single domain at 174 eV,
(c) Rh(100)-(3x1)-0, 2 equally populated domains at 100 eV,
(d) Rh(100)-(3x1)-0, 2 equally populated domains at 152 eV.
displaced from the walls of the vacuum chamber on admitting oxygen to the system. Unfortunately, the mass spectrometer did not function properly during these experiments and so we had no independent assessment of the gases in the chamber. However, no evidence was found for the build up of impurities on the surface on adding oxygen to the system, although it was again unfortunate that the retarding field analyzer as used at the time of this work was not sensitive enough to detect the oxygen. Nevertheless care was taken during the heat treatments to operate under conditions where carbon does not appreciably migrate from the bulk; the Auger spectra confirmed that carbon impurities remained at low levels during these experiments.

Two complete sets of photographs for the (3×1) patterns were taken on different occasions over the energy range 30-200 eV for normal incidence. The films were analysed to yield the I(E) curves shown in Appendices A1 and A2; the first is for two equally populated domains and the second is for a single domain type only. These I(E) curves have not yet been analysed with multiple-scattering calculations especially because we have no clues at present to the possible structure, and some geometrical models that should be tested are complex. An attack on the problem of the structure of the (3×1) surface would be aided by the availability of more detailed experimental data, for example on surface coverage (from AES with a cylindrical mirror analyzer) and on possible oxygen bonding sites from high-resolution electron energy loss spectroscopy [128].
CHAPTER 4

LEED Analysis of Rh(100)-p(2×2)-S Surface Structure
4.1 Introduction

Knowledge of the structures adopted by atomic and molecular species adsorbed on surfaces of rhodium is of importance for an understanding of the catalytic properties of this metal. This chapter reports an analysis with LEED for the (2×2) structure formed by adsorbing H₂S on the clean (100) surface [123]; this appears to represent the first such structural analysis for adsorption on rhodium. H₂S was chosen for this initial study since some structural information is available for sulphur adsorption (via H₂S) on other transition metal surfaces, thereby providing points of reference for assessing the structure of Rh(100)-p(2×2)-S. One immediate objective is to gain information about the chemical bonding at these surfaces.

4.2 Adsorption of H₂S on Rh(100)

A clean (100) surface of rhodium with a sharp (1×1) LEED pattern (obtained by the procedures described in section 3.1) was exposed to high purity H₂S (Matheson) at 10⁻⁸ torr for 1 min. After pumping excess gas, the surface was annealed at 300°C for 1 min. and a sharp p(2×2) LEED pattern obtained with good contrast (figure 4.1). Auger spectra (figure 4.2) taken after the formation of this pattern indicated S as the main foreign component with Auger peak height ratios 152eV(S)/302eV(Rh)≈2/3. Small traces of C could also be detected, but its proportions were minimized by the low temperature annealing.

We believe that H₂S dissociated on the Rh(100) surface, in part because we also obtained this p(2×2)-S LEED pattern by heating the metal such that sulphur impurity segregated to the surface from the bulk. Exactly similar
Figure 4.1: Photographs of LEED patterns observed at normal incidence from adsorption of S on Rh(100) surface.
(a) Rh(100)-c(2×2)-S at 80 eV,
(b) Rh(100)-p(2×2)-S at 72 eV,
(c) Rh(100)-p(2×2)-S at 114 eV,
(d) Rh(100)-p(2×2)-S at 168 eV.
Figure 4.2: Auger spectra of Rh(100) surfaces with 1.5 keV and 10 microamp beam at different stages during the preparation of Rh(100)-p(2×2)-S.
observations have been reported by Gauthier et al. [129] and Demuth et al. [130,131] in their preparations of Ni(100)-p(2x2)-S and Ni(100)-c(2x2)-S, and also by Castner et al. [96] in their studies of the Rh(100) surface. The I(E) curves measured from the Rh(100)-p(2x2)-S surface obtained by the migration of the bulk sulphur impurity agreed closely with those prepared by H$_2$S adsorption. This provided some tentative evidence that the adsorption of H$_2$S on this rhodium surface involves dissociative adsorption. Direct evidence for H$_2$S dissociating on a metal surface was provided by Keleman and Fischer's study on the Ru(100) surface with the additional techniques of uv photoemission and thermal desorption spectroscopy [132]. This work indicated that H$_2$S dissociated upon adsorption over the entire range of coverage.

In Rh(100)-p(2x2)-S, the adsorbed sulphur atoms are held strongly to the surface and could be removed only by extensive Ar$^+$ bombardment. After cleaning the Rh(100) surface, a c(2x2) pattern could also be formed on exposure to H$_2$S. This required heating the crystal at 400°C for 4 min. in the atmosphere of H$_2$S (1x10$^{-7}$ torr), and on cooling the LEED pattern of the surface exhibited a c(2x2)-S overlayer pattern (figure 4.1). Auger spectra for this surface gave a ratio of peak heights 152eV(S)/302eV(Rh)=4/3 which suggests that the S coverage for this structure is approximately twice that of the Rh(100)-p(2x2)-S structure.

I(E) curves were measured for Rh(100)-p(2x2)-S for normal incidence for the beams (01), (11), (02), (12), (0$\frac{1}{2}$), (1$\frac{1}{2}$), (11), (0$\frac{3}{2}$), and (1$\frac{3}{2}$), using the beam notation shown in figure 4.3. These measurements involved photographing the LEED screen at 2 eV intervals over the energy range 40-200 eV, and analyzing the photographic negatives with the computer-controlled Vidicon camera as described in section 3.1. Two independent sets of experimental data were collected.
Figure 4.3: Beam notation for the LEED pattern of Rh(100)-p(2×2)-S structure.
4.3 Computational Scheme

I(E) curves were calculated with the layer-doubling method [24], using a conventional muffin-tin-type potential, for some surface models in which only sulphur was present in an overlayer. The scatterings by the atomic potentials were described by eight phase-shifts. A band structure potential was used for the atomic regions in the substrate [110]. For the atomic regions in the sulphur overlayer, the superposition potential obtained by Demuth et al. [131] was used. This superposition potential was also used by Van Hove and Tong [146] in an analysis of surface structures formed by S on Ni(100).

The real part of the inner potential \( V \) was initially set at -12.0 eV (although this was refined later in the comparison with experimental data) for both the overlayer and the substrate, while the imaginary part \( V_{oi} \) was equated to \(-1.51E^{1/3}\) eV. The effective Debye temperatures were taken as 406 K for rhodium (as discussed in section 3.4) and 236 K for sulphur following Demuth et al. [131].

The geometrical models considered for Rh(100)-p(2x2)-S were simplified by fixing all interlayer spacings in the metal at the bulk value (1.9022 Å); this follows our previous conclusion for clean Rh(100) that this surface is not reconstructed and its topmost spacing is within 2.5% of the bulk value (section 3.2). Three types of structural model were tested, all corresponding to a quarter monolayer of S atoms. These models are shown in figure 2.8 and they are designated according to the number of nearest-neighbour metal atoms (as already described in section 2.7) as 4F, 1F and 2F. The packing of hard spheres, with radii given by Pauling [133], was used to guide the possible
values of topmost interlayer spacing for each model type; this analysis specifically considered spacings between 2.1 and 2.7 Å for the 1F model, between 1.4 and 2.2 Å for the 2F model and between 1.0 and 1.6 Å for the 4F model.

Symmetry could be used in the calculations at normal incidence and the number of beams used in the calculations are summarized in Table 2.1. For the 2F model it is necessary to average appropriate calculated beam intensities according to the possible symmetrically-equivalent domains.

4.4 Results

I(E) curves measured for normal incidence for the (01) and \(\frac{11}{22}\) sets of beams are shown in figure 4.4 for two independent experiments. Beams within each set should be symmetrically-equivalent, both with regard to peak positions and other structural features. The correspondences seen in the figure suggest that the experimental data are closely reproducible, and this supports their general reliability. The small variations which do occur must be attributed to experimental errors (involving such factors as uneven response of the screen, imperfections of the crystal surface, and some uncertainty in setting the angle of incidence); such errors, although small, do inevitably limit the level of agreement possible between calculation and experiment. To minimize any artefacts in the comparisons with the calculated intensities, measured I(E) curves for sets of beams which are theoretically equivalent were averaged and digitally smoothed (by two operations of the three-point smoothing filter) prior to comparing with the calculations.
Figure 4.4: Comparison for the \( \{11\}_{22} \) and \( (01) \) beams of \( I(E) \) curves from two different experiments measured at normal incidence.
Some comparisons of experimental and calculated I(E) curves for Rh(100)-p(2x2)-S are shown in figure 4.5. Visual comparisons of all data available points to the conclusion that the centre (4F) model gives a better overall correspondence to the experimental I(E) curves than the bridge (2F) and on-top (1F) models. For the integral-order beams alone, reasonable match-ups between experimental and calculated I(E) curves are found for the (01) and (02) beams with all the three models (i.e. 4F at 1.3 Å, 2F at 1.9 Å and 1F at 2.3 Å), but the 4F model also gives a good correspondence for the (11) beam whereas the 4F and 1F models fail in this regard. As expected, the fractional-order beams are generally more sensitive to the locations of the overlayer atoms, and the overall conclusion from a visual analysis of all data for the fractional order beams is that the 4F model gives the best account of the experimental I(E) curves with the Rh-S interlayer spacing close to 1.3 Å. However, the agreement is not complete, relative peak intensities are not properly accounted for and in a few instances the 4F model fails to reproduce features in the experimental I(E) curves. In particular, the calculated I(E) curve for the (0\frac{1}{2}) beam for the 4F model with the Rh-S interlayer spacing equal to 1.3 Å does not reproduce the peak present in the experimental curve at 110 eV; also for the (0\frac{3}{2}) beam the 4F model shows an extra small peak at 130 eV which could not be detected in the experimental curve.

For some fractional-order beams (especially (0\frac{5}{2}) and (\frac{13}{22})), calculated I(E) curves from the bridge (2F) model give reasonable agreement with the experimental I(E) curves for the topmost spacing of 1.9 Å, but this adsorption site is less favorable than the 4F site for the (0\frac{1}{2}) and (\frac{11}{22}) beams. The on-top (1F) model gives poor visual agreement between calculation and experiment.
Figure 4.5: Comparison of experimental I(E) curves for various integral- and fractional-order diffracted beams from Rh(100)-p(2×2)-S with the calculated curves for S adsorbed on the 4F, 2F and 1F sites at the topmost Rh-S interlayer spacing indicated for each curve.
for most beams, although some agreement is present for the $\frac{13}{22}$ beam for the topmost spacing of 2.7 Å. Illustrated in figure 4.6 are comparisons of experimental I(E) curves for the $\frac{1}{2}$ and $\frac{11}{22}$ beams with those calculated from the 4F model for various values of the topmost interlayer spacing ranging from 1.0 Å to 1.6 Å. Although the level of agreement is not complete, the best correspondence seems to occur with the S-Rh interlayer spacing between 1.2 and 1.3 Å.

The correspondence between the experimental and calculated I(E) curves for the Rh(100)-p(2×2)-S surface were also assessed by evaluating the reliability index ($\tilde{r}_T$) proposed by Zanazzi and Jona [45]. Figures 4.7(a)-4.7(c) give contour plots of $\tilde{r}_T$ as a function of the Rh-S spacing and $V_{or}$ for each of the three models when compared with one set of experimental data. Comparison with the other set of experimental data produced similar results, as summarized in Table 4.1. The analysis with $\tilde{r}_T$ unambiguously showed that the 4F model gives the best correspondence between the experimental and calculated I(E) curves. For this model, $\tilde{r}_T$ is minimized (figure 4.7(a)) with the Rh-S interlayer spacing equal to 1.30±0.03 Å and $V_{or}$ equal to -13.6±0.9 eV, when the uncertainties are given as $\pm\varepsilon_d$ and $\pm\varepsilon_v$ as indicated in section 2.8. The uncertainties correspond to 68% probabilities according to the analysis of Watson et al. [43]. The minimum value of $\tilde{r}_T$ for the 4F model is 0.26; this represents a moderate level of agreement and suggests that the structure is at least "probably" correct according to a criterion of Zanazzi and Jona [45]. The bridge (2F) model also gives a localized minimum, specifically at the Rh-S interlayer spacing of 1.94±0.08 Å and $V_{or}$ equal to -11.6±1.4 eV. The
Figure 4.6: Comparison of experimental I(E) curves for the \( \left( \frac{1}{2} \right) \) and \( \left( \frac{1}{2} \frac{1}{2} \right) \) beams from the Rh(100)-p(2x2)-S surface with those calculated for S adsorbed on the 4F site for a range of topmost Rh-S interlayer spacings.
Table 4.1: Conditions for minima of $r_T$ for different models of Rh(100)-p(2×2)-S.

<table>
<thead>
<tr>
<th>surface model</th>
<th>expt. no.</th>
<th>$\Delta E^\dagger$ (eV)</th>
<th>$d_{S-Rh}$ (Å)</th>
<th>$V_{or}$ (eV)</th>
<th>$r_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>centre site</td>
<td>1</td>
<td>856</td>
<td>1.30±0.03</td>
<td>-13.6±0.9</td>
<td>0.26</td>
</tr>
<tr>
<td>(4F)</td>
<td>2</td>
<td>932</td>
<td>1.31±0.03</td>
<td>-13.8±0.8</td>
<td>0.25</td>
</tr>
<tr>
<td>bridge site</td>
<td>1</td>
<td>856</td>
<td>1.94±0.08</td>
<td>-11.6±1.4</td>
<td>0.30</td>
</tr>
<tr>
<td>(2F)</td>
<td>2</td>
<td>932</td>
<td>1.94±0.08</td>
<td>-13.5±1.2</td>
<td>0.28</td>
</tr>
<tr>
<td>on-top site</td>
<td>1</td>
<td>856</td>
<td></td>
<td>no localized minimum</td>
<td></td>
</tr>
<tr>
<td>(1F)</td>
<td>2</td>
<td>932</td>
<td></td>
<td>no localized minimum</td>
<td></td>
</tr>
</tbody>
</table>

$^\dagger$total range of energy compared.
corresponding minimum value of $\bar{r}_T$ (0.30) is higher than that of the 4F model (0.26), although these $\bar{r}_T$ values are closer than expected on the basis of the visual analysis. Further suggestive support for the 4F model, from the reliability index analysis, is indicated by the larger uncertainties associated with the bridge model. The contour plot of $\bar{r}_T$ in figure 4.7 (c) does not indicate a localized minimum for the on-top (1F) model, also values of $\bar{r}_T$ are comparatively high over the complete ranges of $V_{or}$ and Rh-S interlayer spacing considered. However it was observed in separate calculations that the contour plots of $\bar{r}_T$ for the integral-order beams alone and for the fractional-order beams alone did show local minima corresponding to Rh-S interlayer spacings of 2.3 Å and 2.7 Å respectively; this indicates the reason why the calculated I(E) curves shown in figure 4.5 are for the spacings 2.3 and 2.7 Å.

4.5 Discussion

The evidence presented above indicates that the surface structure Rh(100)-p(2×2)-S has the sulphur atoms adsorbed on the four-fold (4F) sites of the Rh(100) surface at about 1.30 Å above the topmost rhodium layer. This corresponds to a nearest neighbour S-Rh distance equal to 2.30 Å. Evidence that this is a reasonable bond distance is suggested by the average values found by X-ray crystallography in $\text{Rh}_{13}S_{15}$ (2.33 Å) [134] and in $\text{Rh}_2S_3$ (2.37 Å) [135]; also Rh-S distances in unhindered coordination complexes generally range from 2.23 to 2.38 Å [136-138]. Often structures from LEED crystallography are discussed in terms of "effective radii" ($r_{eff}$) for the
Figure 4.7: Contour plots of $r^r_x$ for Rh(100)-p(2x2)-S versus $V_or$ and Rh-S interlayer spacing for (a) 4F model, (b) 2F model, and (c) 1F model. Error bars indicate standard errors as defined in chapter 2.
(b)

$\text{Rh}(100) - p(2 \times 2)S$

$2F$

$V_{or} (eV)$

$S$-$\text{Rh}$ DISTANCE ($\text{Å}$)
(c)

Rh(100)-P(2x2) S

1F
adsorbed species [139]. By considering Rh as being unchanged by adsorption so that it retains the metallic radius of 1.34 Å, an effective radius of S is obtained by subtracting the rhodium metallic radius from the Rh-S nearest-neighbour distance, and this gives the value of \( r_{\text{eff}} \) for S equal to 0.96 Å. This value can be compared with other \( r_{\text{eff}} \) values for S (Table 4.2) deduced with LEED crystallography for adsorption on metallic surfaces. From Table 4.2 it is clear that \( r_{\text{eff}} \) of S obtained in this work is similar to values obtained from some other studies, although it is probably not reasonable to expect \( r_{\text{eff}} \) of S to be constant in different bonding situations (involving for example, different metal atoms, different substrate dimension and especially different coordination sites).

Although hard sphere radii (e.g. \( r_{\text{eff}} \)) have often been used for interpretations of surface bond distances, it would clearly be preferable to relate such discussions more closely to the concepts of covalent bonding. That some M-X surface bond lengths correspond in a good approximation to single-bond values is established in Table 4.3 where some comparisons are given for M-X distances for the heavier chalcogens on (100) surfaces of fcc metals. Rationalizations of such correlations and their extensions to other surface systems, have been given by Mitchell [143,144] based on hybridization schemes for metals given by Altmann, Coulson and Hume-Rothery [145] and on relative valencies and the bond length - bond order relation given by Pauling [133]. The point of immediate interest, however, is that the Rh-S bond length found in the LEED analysis of Rh(100)-p(2×2)-S is within 0.01 Å of the single-bond value, thereby indicating a general consistency with surface bond lengths
Table 4.2: Effective radii of chemisorbed sulphur atoms on various metal surfaces.

<table>
<thead>
<tr>
<th>System</th>
<th>Overlayer surface structure</th>
<th>Bonding site</th>
<th>M-S bond distance (Å)</th>
<th>$r_{\text{eff}}$ of sulphur (Å)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>S/Ni(100)</td>
<td>c(2x2)</td>
<td>4F</td>
<td>2.18</td>
<td>0.94</td>
<td>131</td>
</tr>
<tr>
<td>S/Ni(100)</td>
<td>p(2x2)</td>
<td>4F</td>
<td>2.18</td>
<td>0.94</td>
<td>131</td>
</tr>
<tr>
<td>S/Ni(110)</td>
<td>p(2x2)</td>
<td>4F</td>
<td>2.17, 2.35$^+$</td>
<td>0.93</td>
<td>140</td>
</tr>
<tr>
<td>S/Ni(111)</td>
<td>p(2x2)</td>
<td>3F</td>
<td>2.02</td>
<td>0.78</td>
<td>140</td>
</tr>
<tr>
<td>S/Ir(111)</td>
<td>(√3x√3)R30°</td>
<td>3F</td>
<td>2.28</td>
<td>0.92</td>
<td>147</td>
</tr>
<tr>
<td>S/Rh(110)</td>
<td>c(2x2)</td>
<td>4F</td>
<td>2.12, 2.45$^+$</td>
<td>0.77</td>
<td>123</td>
</tr>
<tr>
<td>S/Rh(100)</td>
<td>p(2x2)</td>
<td>4F</td>
<td>2.30</td>
<td>0.96</td>
<td>124</td>
</tr>
<tr>
<td>S/Fe(100)</td>
<td>c(2x2)</td>
<td>4F</td>
<td>2.30</td>
<td>1.06</td>
<td>142</td>
</tr>
</tbody>
</table>

$^+$Each S atom is closer to a metal atom in the second layer than the atoms in the first layer.
Table 4.3: Comparisons of M-X bond distances for chalcogen atoms adsorbed on (100) surfaces of fcc metals with Pauling's single bond lengths [133].

<table>
<thead>
<tr>
<th>System</th>
<th>Overlay surface structure</th>
<th>Bonding site</th>
<th>M-X distance by LEED (Å)</th>
<th>M-X single bond length (Å)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>S/Ni(100)</td>
<td>c(2x2)</td>
<td>4F</td>
<td>2.18</td>
<td>2.19</td>
<td>131</td>
</tr>
<tr>
<td></td>
<td>p(2x2)</td>
<td>4F</td>
<td>2.18</td>
<td>2.19</td>
<td>131</td>
</tr>
<tr>
<td>Se/Ni(100)</td>
<td>c(2x2)</td>
<td>4F</td>
<td>2.28</td>
<td>2.32</td>
<td>131,140</td>
</tr>
<tr>
<td></td>
<td>p(2x2)</td>
<td>4F</td>
<td>2.32</td>
<td>2.32</td>
<td>131,140</td>
</tr>
<tr>
<td>Te/Ni(100)</td>
<td>c(2x2)</td>
<td>4F</td>
<td>2.59</td>
<td>2.52</td>
<td>131,140,149</td>
</tr>
<tr>
<td></td>
<td>p(2x2)</td>
<td>4F</td>
<td>2.52</td>
<td>2.52</td>
<td>131,140</td>
</tr>
<tr>
<td>Te/Cu(100)</td>
<td>p(2x2)</td>
<td>4F</td>
<td>2.48</td>
<td>2.54</td>
<td>148</td>
</tr>
<tr>
<td>S/Rh(100)</td>
<td>p(2x2)</td>
<td>4F</td>
<td>2.30</td>
<td>2.29</td>
<td>123</td>
</tr>
</tbody>
</table>
reported from other example of S, Se and Te adsorption on fcc (100) surface. This correlation had not been recognized at the time we initially published our LEED analysis for Rh(100)-p(2×2)-S [123].

Generally it is felt that the surface structure reported here for Rh(100)-p(2×2)-S gives bond dimensions which are broadly consistent with X-ray crystallographic data for S-Rh bond lengths and with LEED results for adsorption of S atoms on other surfaces. The level of agreement reached between the calculated and experimental I(E) curves is not complete, and the origins of the deficiencies are presently unknown. The number of model structures considered in the calculation for this work is limited; in principle more complicated models are possible, but since no conflict seems to be present with the principles of surface structural chemistry, as they are presently evolving, we do not feel that further multiple-scattering calculations on more complex surface models are required at this time. An inevitable problem with the trial-and-error approach in LEED crystallography is that, however good the correspondence may be between experimental and calculated I(E) curves for a given structure, there is no absolute way of ruling out the possibility that some other (untested) structures could give even better agreement. Although the origin of some discrepancies between the experimental and calculated intensities found here are not yet clear, we believe the results indicate that the structure most likely involves S atoms adsorbed at 1.3 Å above the four-fold sites of the Rh(100) surface.
CHAPTER 5

LEED Analysis of the Rh(110)-c(2×2)-S Surface Structure
5.1 Introduction

Having determined the surface geometry for sulphur adsorbed on the (100) surface of rhodium, we were interested in comparing with the situation for S adsorbed on the more open (110) surface. A second reason for making a LEED analysis of this additional structure was suggested by earlier reports that two different adsorption sites are indicated by LEED crystallography for atomic adsorption on (110) surfaces of face-centered cubic metals. Oxygen atoms are reported to adsorb on the short-bridge sites of both Ni(110) [59] and (impurity-stabilized) unreconstructed Ir(110) [151], whereas sulphur atoms adsorb on the centre (four-fold) sites of Ni(110) [140]. It is hoped that an investigation of the adsorption of S on the Rh(110) surface may give further insights into surface chemical bonding.

5.2 Experimental

The first part of this study involved obtaining a clean (110) surface of rhodium, and this followed closely the procedures described earlier in this thesis and in other work reported from our laboratory [109]. This study was performed on a single crystal slice cut from a rod of purity 99.99% purchased from Research Organic/Inorganic Chemical Corp. After pumping down in the vacuum chamber, the initial Auger spectrum indicated some contamination from phosphorus, sulphur and carbon. The S and P impurities could be removed from the surface by argon-ion bombardment (1 keV at 5 microamps for 20 minutes), but, as previously, a relative increase in the surface concentration of C was indicated. However, this impurity apparently diffused into the bulk on heating at 300°C. After several cycles of ion-bombardment and annealing, the surface
showed both an essentially-clean Auger spectrum (figure 5.1(a)) and a sharp (1×1) LEED pattern. This resulting Auger spectrum is similar to that obtained for the cleaned (100) surface of rhodium (figure 4.2).

After obtaining the well-defined LEED pattern characteristic of the clean Rh(110) surface, high purity H$_2$S (Matheson) was allowed to adsorb on the surface by the following procedures. First the sample was heated at 300°C for 1 minute and H$_2$S was let into the vacuum chamber at the pressure of $5 \times 10^{-7}$ torr for 1 minute. After pumping out the excess gas, LEED showed a diffuse ring pattern indicating that H$_2$S (or S) had adsorbed with only partial ordering on the surface. The sample was then heated at 300°C for 3 minutes and allowed to cool down. At this point LEED indicated that the ring pattern had been replaced by traces of ($m_n$/$22$) spots, characteristic of a c(2×2) pattern, but the spot intensities were weak. With further heating at 700°C for 2 minutes, LEED showed a stable and sharp c(2×2) pattern (figure 5.2) which could be removed only by argon ion bombardment. The Auger spectrum indicated no other detectable impurities and a ratio of the Auger peak heights S(152):Rh(302) approximately equal to 3:4 (figure 5.1(b)).

For the purposes of beam intensity measurements, two sets of photographs were taken: one at normal incidence over the energy range 22 to 220 eV and the other for off-normal incidence (specifically $\theta=10^\circ$, $\phi=135^\circ[100]$) from 22 to 160 eV. The photographic negatives were analyzed with the computer-controlled Vidicon camera as described in section 3.4. For normal incidence, I(E) curves were measured for 9 integral-order beams and for 5 fractional-order beams using the beam notation indicated in figure 5.3. These are
Figure 5.1: Auger spectra for a Rh(110) surface when cleaned and when containing a c(2x2) overlayer of sulphur.
Figure 5.2: Photographs of LEED patterns observed at normal incidence from adsorption of S on Rh(110) surface.
(a) Rh(110) at 144 eV,
(b) Rh(110)-c(2×2)-S at 78 eV,
(c) Rh(110)-c(2×2)-S at 102 eV,
(d) Rh(110)-c(2×2)-S at 150 eV.
Figure 5.3: Beam notation for the LEED pattern from the Rh(110)-c(2×2)-S surface structure.
The I(E) curves for the integral-order beams were found to be rather similar to those of the clean (110) surface; this suggested that the production of the Rh(110)-c(2x2)-S structure did not involve any appreciable changes in the positions of the Rh atoms from those in the clean surface. Typical experimental I(E) curves for normal incidence are shown in figure 5.4. The similarities for the beams which should be equivalent are not as close as those generally found from the Rh(100)-p(2x2)-S structure. This probably indicates larger deviations from normal incidence, although there may be extra degrees of roughness for the (110) surface. The complete sets of intensity data for both directions of incidence are collected in Appendices A5-A6.

5.3 Calculations

The simplest models for the c(2x2) translational symmetry associated with atoms adsorbed on an unreconstructed (110) surface of a face-centred cubic metal have already been shown in figure 1.8. These models are designated according to the sites of adsorption namely: centre or four-fold (4F) model, on-top or one-fold (1F) model, short-bridge (2SB) model and a long-bridge (2LB) model. I(E) curves for the various required diffracted beams were calculated using the layer-doubling method for all of these models. The computing times were reduced by exploiting the symmetry at normal incidence, and by adding the adsorbate layer separately to both the bottom and
Figure 5.4: Experimental I(E) curves for two sets of beams which are expected to be equivalent for the Rh(110)-c(2x2)-S structure.
the top of the substrate stack, after the reflection and transmission matrices have converged for the substrate alone (this typically requires 8 to 16 layers), to give diffracted beam intensities from the 4F and 1F models from a single set of multiple-scattering calculations (similarly the 2LB and 2SB models could be treated together). All four structural models considered have two perpendicular mirror planes; 49 symmetrically inequivalent beams were included in the calculation to ensure convergence.

The same non-structural parameters were used in the multiple-scattering calculations on Rh(110)-c(2×2)-S as for the analysis of the Rh(100)-p(2×2)-S structure. Specifically the Rh potential was characterized by phase shifts (to \( \varepsilon = 7 \)) derived from a band structure calculation [110]; the real part of the constant potential \( (V_{\text{or}}) \) between the atomic spheres was set initially at -12.0 eV; a superposition potential [131] was used for S; the surface Debye temperatures were taken as 406 and 236 K for Rh and S respectively, while the imaginary part \( (V_{\text{oi}}) \) of the constant potential between all spheres was equated to \(-1.51E^{1/3}\) eV. The structural parameters for the Rh(110)-c(2×2)-S surface were simplified by fixing all interlayer spacings for Rh(110) at the bulk value (1.345 Å); this follows our previous observations that the clean Rh(110) surface is not reconstructed and that the topmost interlayer spacing is contracted by only 3% from the bulk value [109,150]. The Rh-S spacings were varied over the following ranges: 0.65 - 1.25 Å for the 4F model, 2.0 - 2.6 Å for the 1F model, 1.1 - 1.7 Å for the 2LB model and 1.6 - 2.2 Å for the 2SB model.
Preliminary attempts were made to calculate the diffracted beam intensities for the conditions measured in the experiment for off-normal incidence ($\theta=10^\circ$, $\phi=135^\circ$). Symmetry could not now be exploited and hence the total number of beams needed in the calculation is greatly increased over that for normal incidence. Around 175 beams would be required at 200 eV, and we found that the consequent computational requirements were too expensive for us to proceed with these calculations. The experimental data for off-normal incidence has however been collected in the appendix.

5.4 Results

Some comparisons of experimental and calculated $I(E)$ curves are given in figures 5.5 and 5.6. Figures 5.5(a)-5.5(c) compare experimental $I(E)$ curves for the $(10)$, $(01)$ and $(\frac{31}{22})$ beams with those calculated for the 4F, 1F, 2SB and 2LB models for various Rh-S interlayer spacings. Visual comparisons show poor agreement for the short-bridge (2SB) and long bridge (2LB) models, and while the on-top (1F) model produced a reasonable correspondence for the $(10)$ beam, there was little agreement for other beams. Visual comparisons over the complete range of data unambiguously indicated that the best correspondence between the experimental and calculated $I(E)$ curves is provided by the 4F model with the Rh-S interlayer spacing in the range 0.75 to 0.85 Å (figure 5.6). Discrepancies are apparent, especially for some relative peak heights, although at the present stage of development of LEED crystallography the general correspondence can (we believe) be classified as "good".
Figure 5.5: Comparison of some experimental I(E) curves from Rh(110)-c(2×2)-S with those calculated for the four structural models over a range of topmost interlayer spacings: (a) (01) beam, (b) (10) beam, and (c) $(\frac{31}{22})$ beam.
Figure 5.6: Comparison of experimental I(E) curves for some integral- and fractional-order beams from Rh(110)-c(2×2)-S with those calculated for the 4F model with sulphur either 0.75 or 0.85 Å above the topmost rhodium layer.
Figure 5.7: Contour plots of $\bar{r}_r$ for Rh(110)-c(2x2)-S versus $V_o$ and Rh-S interlayer spacing for four different structural models.
The comparisons between experimental and calculated I(E) curves were also assessed by evaluating the reliability index proposed by Zanazzi and Jona [45]. Figure 5.7 gives contour plots of $\tilde{r}_r$ as a function of Rh-S spacing and $V_{or}$ for each of the four models considered here. Again there is clear evidence that the centre (4F) model gives the best correspondence between the experimental and calculated intensities. The minimum value of $\tilde{r}_r$ (0.165) represents a good level of agreement [45], and it corresponds to $V_{or} = -12.2\pm0.8$ eV and a Rh-S interlayer spacing of $0.77\pm0.04$ Å. For the other models, $\tilde{r}_r$ was always sufficiently large ($>0.35$) to indicate a poor correspondence between the experimental and calculated I(E) curves.

5.5 Discussion

The evidence just presented indicates that the Rh(110)-c(2x2)-S structure has the sulphur atoms adsorbed on the centre (4F) sites of the Rh(110) surface at about 0.77 Å above the topmost rhodium layer. The multiple-scattering calculations made here assumed that all metal-metal distances correspond to the normal bulk values. Tentative evidence in support is provided by an additional analysis with the reliability index $\tilde{r}_r$; we used this index to assess the level of correspondence between the experimental I(E) curves for the beams (10), (01), (11) and (12) for the overlayer structure and those calculated for the clean surface. For these conditions, we found $\tilde{r}_r$ was minimized at the value of 0.22 with the topmost interlayer spacing of rhodium being expanded by just 1% over the bulk value.
Figure 5.8 indicates interatomic distances in the vicinity of adsorbed sulphur atoms in the Rh(110)-c(2×2)-S structure assuming there is no relaxation for the rhodium structure. It is apparent that the four-fold hole in the Rh(110) surface is sufficiently large that the sulphur atom can penetrate quite deeply; in fact sulphur becomes considerably closer to the rhodium atom directly below in the second metal layer than to the four neighbouring rhodium atoms in the first layer. The respective distances are

\[ \text{Rh}_{\text{II}}-\text{S} = 2.12 \text{ Å} \text{ and } \text{Rh}_{\text{I}}-\text{S} = 2.45 \text{ Å}. \]

Similar observations have also been made from LEED crystallographic analyses for S adsorbed on the Ni(110) surface [140], for which the corresponding distances are

\[ \text{Ni}_{\text{II}}-\text{S} = 2.17 \text{ Å} \text{ and } \text{Ni}_{\text{I}}-\text{S} = 2.35 \text{ Å}, \]

and for O adsorbed on the Fe(100) surface (figure 5.9) for which [153]

\[ \text{Fe}_{\text{II}}-\text{O} = 2.02 \text{ Å} \text{ and } \text{Fe}_{\text{I}}-\text{S} = 2.08 \text{ Å}. \]

By contrast, adsorption of S on the Fe(100) surface does not involve significant interaction of S to the second layer Fe atom [142]. In this case, S is too large to sink deeply into the four-fold hole of the Fe(100) surface. The differences between O and S chemisorbed on fcc(110) surfaces can plausibly be associated with size effects. O appears too small to adsorb on the centre (4F) site and interact with metal orbitals directed at this site in terms of hybridization model of Altmann, Coulson and Hume-Rothery [145]. Bonding possibilities for O seem better on the short-bridge sites [143].
Figure 5.8: Schematic specification of interatomic distances in the vicinity of an overlayer sulphur atom in the surface structure Rh(110)-c(2×2)-S. Distances in Ångstroms.

Figure 5.9: Interatomic distances for the specification of hard sphere radii in the neighbourhood of an oxygen atom in the Fe(100)-(1×1)-O structure. Distances in Ångstroms. (After Legg et al. [153]).
The most significant comparison for the new results for S on Rh(110) is with the structure formed by adsorption of the same species on Ni(110). Mitchell [143] has offered a tentative analysis of these structures, and indicated a tendency for S to form a single covalent bond to the metal atom directly below in the second layer and four $3/4$ order bonds to the neighbouring metal atoms in the topmost layer. An interesting point is that while the distances found from LEED for S on Ni(110) are broadly consistent with this, it is physical impossible for the corresponding distances to be simultaneously satisfied for S on Rh(110), and this is a direct consequence of the longer Rh-Rh distance compared with the Ni-Ni distance. Mitchell concluded that this results in S being held at that height above the Rh(110) surface where the combined strengths of the five bonds are optimized, and this requires some "squeezing" of the Rh$_{II}^-S$ distance from the single bond value (2.29 Å) in order to get reasonable interactions to the four Rh atoms in the first layer. An important aspect of this discussion is that it represents a start on utilizing covalent bonding concepts for chemisorption. Most analyses so far have emphasized hard sphere radii. The effective radius indicated for S on Rh(110) is 0.77 Å; this can be compared with other values reported from LEED crystallography varying from 0.78 Å to 1.04 Å as noted in section 4.5.
CHAPTER 6

Studies with the Quasidynamical Method
6.1 Introduction

Reliable surface structures so far reported by LEED crystallography have come from studies which used the trial-and-error approach wherein experimental I(E) curves are compared with those calculated for a range of possible surface models and a selection is made of the geometrical model that gives the best overall correspondence. Generally the calculations have used multiple-scattering methods which are either formally exact (e.g. the T-matrix or Bloch-wave methods) or involve good iterative approximations to the full multiple-scattering methods (e.g. layer-doubling or RFS methods). This provides the only generally-accepted approach to LEED crystallography at the present time. Aside from limitations still present in the experimental measurements, and limitations introduced into the calculations through the model assumed for the potential and lattice vibrations, the accuracy of the present approach to LEED crystallography is limited especially by computation time and core storage. A serious problem for surface structural chemistry concerns the limitations set on this approach for complex surface structures, for which multiple-scattering calculations inevitably become prohibitively expensive. This opens the need to search for new calculation schemes which maintain reliability while reducing the computational burden.

In principle the simplest LEED calculation involves the kinematical method [49] in which scattering by ion-cores is assumed to be weak so that only single scattering events are included. The discussion in section 2.1 establishes that this method is inadequate for describing the actual features observed in the scattering of low-energy electrons by a solid surface. Attempts
have been made to make the kinematical theory usable for LEED by processing experimental data such that the multiple-scattering contributions are averaged out and the residual intensities can then be analyzed with the kinematic theory. These data processing procedures include the "constant momentum transfer averaging" method introduced by Lagally et al. [25], the "energy averaging" method introduced by Tucker and Duke [154], and the "Fourier transform" method [157]. Although attractive in principle, these methods cannot yet be considered well-established for determining unknown surface structures involving adsorption.

A new approximate multiple-scattering scheme for calculating LEED intensities is the quasidynamical method [46]. In this method, only single scattering is included within an atomic layer, while the interlayer scattering is calculated properly, for example by the RFS method. The original authors proposed that this approach should be most reliable for surface systems involving light atoms in relatively open structures, where the neglect of intralayer multiple-scattering is expected to be less serious. Initial analyses for the unreconstructed model of GaAs(110) and for reconstructed Si(100) gave promising agreement with full multiple-scattering calculations [155] and with experimental data [46,47] respectively. Such tests indicated that the quasidynamical method can give reasonable accounts of the positions of the main peaks in experimental I(E) curves, as well as much of the secondary structure, although the absolute intensities and the relative intensities of neighbouring peaks are often not predicted reliably.

The purpose of the present study is to investigate further the quasidynamical method by comparing with experimental and calculated I(E) curves
already reported in this thesis, especially for the adsorption systems Rh(100)-p(2×2)-S and Rh(110)-c(2×2)-S. A particular objective is to assess whether this method can identify certain surface models as giving sufficiently poor correspondences with the experimental I(E) curves that these models need not be considered in the refinement stages of LEED crystallographic analyses. Analyses for the corresponding clean surfaces of rhodium are made, and they provide convenient reference points for the adsorption systems.

6.2 Calculations

A fundamental part of calculations of LEED intensities involves evaluation of the layer diffraction matrices $M^{++}$ (equation 2.30) for each atomic plane; then the planes are stacked in order to determine the scattering from a crystal slab (of either finite or semi-infinite extent). Generally the evaluation of $M^{++}$ is the most time consuming part of this whole process, specifically because it involves calculating $[I - X]^{-1}$ which describes all multiple-scattering events within an atomic layer (equation 2.30). The quasidynamical scheme makes use of a commonly-found observation, that interlayer multiple scattering is much stronger than intralayer multiple-scattering [46], by equating the planar scattering matrix $X$ to zero. This assumption gives substantial reductions in computation times. The important question now concerns whether the gain in computational convenience is offset, or not, by too great a loss of accuracy in the calculated I(E) curves.

The present tests with the quasidynamical method use the same types of surface models as those considered in the previous studies with the full
multiple-scattering calculations [123,124,150]. Thus only the regular face-centred cubic registries were considered here for the clean surfaces, but relaxations of the topmost interlayer spacings were allowed. Different models for the S overlayer are designated as in figures 1.8 and 2.8; all Rh-Rh distances are fixed at the appropriate bulk values. Unless otherwise indicated here the same non-structural parameters were used in the quasidynamical calculations as in the corresponding multiple-scattering calculations described previously (chapters 3-5). The only modifications made in this regard were to the constant potentials between the spherically-symmetric atomic potentials. The imaginary part \( V_{\text{oi}} \) of this potential was fixed at -6.8 eV for the 1F, 2SB and 2LB models of Rh(110)-c(2×2)-S whereas the energy dependent form

\[
V_{\text{oi}} = -1.76E^{1/3} \text{ eV}
\]

was used for all other surfaces considered, except clean Rh(110) for which \( V_{\text{oi}} \) was represented by \(-2.05E^{1/3} \text{ eV}\). The real part of this potential \( V_{\text{or}} \) was fixed at -12 eV for all calculations, although this value was effectively refined during comparisons with experimental I(E) curves for each system.

Quasidynamical calculations were made for normal incidence over the energy range 40 to 208 eV for clean Rh(100) and over the range 50 to 178 eV for all other systems considered here. The RFS method was used for stacking atomic planes, these calculations were made with 91 beams and electrons were allowed to travel through upto 12 layers in the crystal. For the 4F model of Rh(110)-c(2×2)-S, it was necessary to combine the sulphur layer and the topmost rhodium layer as a composite layer because of their close spacing.
6.3 Results and Discussion

6.3 (a) Rh(110) and Rh(110)-c(2×2)-S

Experimental I(E) curves for normal incidence on the clean Rh(110) surface are compared with those from quasidynamical calculations for Ad% = 0 and -10% in figure 6.1. General correspondences in peak positions are apparent for every pair of curves, although relative intensities are often not satisfactory. Comparisons between quasidynamical (QD) and multiple-scattering (MS) calculated I(E) curves are also shown in the same figure; again major peak positions match, although the relative intensities have changed in the quasidynamical case. The experimental and calculated I(E) curves were also assessed with the reliability index \( \tilde{r}_T \) [45], and Table 6.1 lists the conditions for best correspondence (i.e. minimum \( \tilde{r}_T \)) between experimental and calculated I(E) curves (from both multiple-scattering and quasidynamical calculations) for the various surfaces considered. The previous multiple-scattering calculations on clean Rh(110) indicated that the best correspondence is with the topmost interlayer spacing contracted by 3.3% from the bulk value. The corresponding analysis with the quasidynamical method points to a contraction of 10.8%, however detailed studies of the individual I(E) curves suggested that the index \( \tilde{r}_T \) may be less helpful for this particular purpose. This conclusion depends on \( \tilde{r}_T \) being quite sensitive to relative intensities over successive portions of individual I(E) curves [150], and the fact (as seen from figure 6.1 and noted above for GaAs(110) and Si(100) [46]) that the quasidynamical method is often unreliable for peak magnitudes within each I(E) curve.
Table 6.1: Comparisons of conditions for minimum $\bar{r}_r$ for various surface structures obtained from evaluating experimental $I(E)$ curves with corresponding curves from multiple-scattering calculations and from quasidynamical calculations.

<table>
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<th>Multiple-scattering calculations</th>
<th>Quasidynamical calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta d%$</td>
<td>$d_{Rh-S} (\AA)$</td>
</tr>
<tr>
<td>Rh(110)</td>
<td>-3.3</td>
<td>--</td>
</tr>
<tr>
<td>Rh(100)</td>
<td>1.0</td>
<td>--</td>
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</tr>
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<td>Rh(100)-p(2x2)-S</td>
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<td>1.30</td>
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<tr>
<td>(4F model)</td>
<td>--</td>
<td></td>
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</tbody>
</table>
Figure 6.1: Comparison of experimental I(E) curves for normal incidence on Rh(110) with those calculated with the quasidynamical method and the full multiple-scattering method when the topmost interlayer spacing equals the bulk value (0%) and when it is contracted by 10%.
I(E) curves for different models of the Rh(110)-c(2×2)-S surface calculated by the quasidynamical (QD) method were compared, by direct observation, with the experimental I(E) curves and also with the corresponding curves calculated with the multiple-scattering (MS) method for the 4F model with the topmost Rh-S interlayer spacing (d_{Rh-S}) equal to 0.75 Å. Overall it was difficult to pin-point the structural model from the quasidynamical calculation which gives the best agreement with the experimental curves; in part this was because of the effects of errors in relative intensities for successive portions of the calculated I(E) curves. Also there are systematic shifts in peak positions for the quasidynamically-calculated I(E) curves. However it did seem possible to conclude, from the visual analysis, that the best match with the I(E) curves from the full multiple-scattering calculations occurred for the 4F model in the quasidynamical calculations with d_{Rh-S} = 1.15 Å.

Conclusions on conditions for correspondence between quasidynamically-calculated and experimental I(E) curves were aided with the reliability index of Zanazzi and Jona. Two-dimensional contour plots of $\tilde{r}_T$ versus $d_{Rh-S}$ and $V_{or}$, for each structural model, are shown in figure 6.2. Comparisons of contour plots suggest that the 4F model gives the lowest $\tilde{r}_T$ value (0.23). No local minima are found for the 2SB model whereas, for the 2LB and 1F models, minima in $\tilde{r}_T$ occur with rather high values (>0.42) which suggests that these models are less probable. The contour plots of $\tilde{r}_T$ for the 4F and 2LB models show the common feature of exhibiting more than one local minimum (figure 6.2). For the 4F model, the first minimum (with $\tilde{r}_T$ = 0.23) occurs for $d_{Rh-S}$ = 0.83 Å and $V_{or}$ = -24.4 eV, the second (with a slightly higher value of $\tilde{r}_T$, viz. 0.28)
Figure 6.2: Contour plots of $\bar{r}_r$ for Rh(110)-c(2×2)-S versus $V_{Or}$ and the Rh-S interlayer spacing for four different structural models calculated with the quasidynamical method.
occurs with \( d_{\text{Rh-S}} = 1.02 \, \text{Å} \) and \( V_{\text{or}} = -18.0 \, \text{eV} \) and the third \( (\bar{r}_r = 0.30) \) occurs at \( d_{\text{Rh-S}} = 0.72 \, \text{Å} \) and \( V_{\text{or}} = -16.4 \, \text{eV} \) (Table 6.1). This situation is to be compared with a single minimum for the corresponding contour plot of \( \bar{r}_r \) for the same system when the calculations utilize the full multiple-scattering procedures (figure 5.7); in this case \( d_{\text{Rh-S}} = 0.77 \, \text{Å}, V_{\text{or}} = -12.2 \, \text{eV} \) and \( \bar{r}_r = 0.17 \) (Table 6.1).

In principle the existence of more than one local minimum could relate to multiple-coincidences in adsorbate-substrate spacings as discussed by Andersson and Pendry [156]. However, against this possibility are the following observations:

i) no such effect was detected in the previous analysis with the multiple-scattering calculation (figure 5.7), and

ii) visual analysis of the individual \( I(E) \) curves calculated with the quasidynamical method for the spacings 0.75, 0.85 and 1.05 Å are on balance less satisfactory than those calculated for 1.15 Å.

Two effects seem to be involved here. The first concerns the incomplete nature of the quasidynamical method, and the second appears to be associated with the reliability-index analysis being less reliable for assessing interlayer spacings when the relative intensities of successive portions of individual \( I(E) \) curves are not calculated correctly, even though a reasonable match in positions of structure may still be recognized between the experimental and calculated \( I(E) \) curves.
For quasidynamical calculations for the 4F model, minima in \( \vec{r}_\tau \) are associated with values of \( V_{or} \) in the range -16.4 to -24.4 eV. These values are substantially changed from the value of -12.2 eV reported from the multiple-scattering calculations. This shows up in the visual analysis of the individual \( I(E) \) curves; features from the quasidynamical calculations occur on average at about 6 eV lower in energy than do the corresponding features from the multiple-scattering calculations. This need for a systematic shift in the \( I(E) \) curves must be associated with the neglect of intralayer multiple-scattering in the quasidynamical calculations. Similar changes in \( V_{or} \) have also been observed for the quasidynamical calculations of Rh(110) (Table 6.1) and of Si(100) [47].

Figure 6.3 compares experimental \( I(E) \) curves for the (01) and \( (\frac{33}{22}) \) diffracted beams with the corresponding quasidynamically-calculated \( I(E) \) curves for particular geometries of the four different structural models. Also shown are the corresponding \( I(E) \) curves calculated by the multiple-scattering method for \( d_{\text{Rh-S}} = 0.75 \, \text{Å} \). For these two representative beams, quasidynamical calculation for the 2SB and 2LB models do not show any agreement with the experimental \( I(E) \) curves. Significant levels of agreement are apparent for both beams for the 4F model, whereas for the 1F model the quasidynamical calculation gives some reasonable agreement for the \( (\frac{33}{22}) \) beam but little agreement for the (01) beam. These comparisons emphasize the matching of peak positions; when all available data from the quasidynamical calculations are considered the 4F model appears to give the best correspondence with \( I(E) \) curves from both experiment and from the reference multiple-scattering calculations.
Figure 6.3: Comparison of I(E) curves measured for the (01) and \( \frac{33}{22} \) diffracted beams for normal incidence on Rh(110)-c(2x2)-S with those calculated by the quasidynamical method and by the full multiple-scattering method for the four structural models described in text.
Table 6.2: A demonstration of the correspondence between peak positions in I(E) curves calculated with the quasidynamical method for the four models of Rh(110)-c(2×2)-S at the specified S-Rh interlayer spacing and those given by experiment and by the corresponding full multiple-scattering calculations. In the entries for each beam, the denominator specifies the number of significant peaks in the relevant I(E) curve from experiment or from the full multiple-scattering calculations, and the numerator gives the number of those peaks that are matched to within 7 eV by the quasidynamical calculations.

<table>
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<th>4F Expt</th>
<th>Full MS</th>
<th>1F Expt</th>
<th>Full MS</th>
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Figure 6.4: Comparisons of some experimental I(E) curves for fractional-order beams for normal incidence on Rh(110)-c(2×2)-S and Rh(100)-p(2×2)-S with those calculated for the centre adsorption sites with the quasidynamical method and with the full multiple-scattering method. The topmost Rh-S interlayer spacings in the quasidynamical calculations are 1.15 Å and 1.3 Å for Rh(110)-c(2×2)-S and Rh(100)-p(2×2)-S respectively; the corresponding values for the multiple-scattering calculations are 0.75 Å and 1.3 Å.
Electron energy (eV) vs. Intensity (arbitrary units) for Rh(110)-c(2x2)-S and Rh(100)-p(2x2)-S with different beam orientations.
Evidence is provided in Table 6.2, where the details in matching of peak positions for each beam and for each model are summarized. A spread in peak positions of up to 7 eV was allowed in this matching in order to accommodate variations of $V_{or}$ for the different surface models.

From the comparisons indicated in Table 6.2, it appears for the 4F model that the level of agreement, between the quasidynamical calculations and either experiment or full multiple-scattering calculations, is better for the fractional-order beams than for the integral-order beams. A similar observation was also reported by Tong and Maldonado for the Si(100) surface [47]. Figure 6.4 (a) details some specific I(E) curves for the fractional-order beams calculated with the quasidynamical method for Rh(110)-c(2x2)-S, and compares with those from experiment and from multiple-scattering calculations.

6.3 (b) Rh(100) and Rh(100)-p(2x2)-S

The previous analysis of LEED intensities from Rh(100), based on multiple-scattering calculations and the use of the reliability-index $r_r$, indicated that the topmost interlayer spacing is very close to the bulk value, there being a surface layer contraction of about 1% [43,150]. A similar analysis made here with beam intensities calculated with the quasidynamical method also suggests a small contraction, this time by 3% (Table 6.1). Figure 6.5 indicates for clean unreconstructed Rh(100) appreciable correspondence between peaks in I(E) curves calculated with the quasidynamical method and those from either experiment or multiple-scattering calculations. In matching with the experimental I(E) curves, the quasidynamically-calculated I(E) curves needed shifting to lower energy by approximately 6 eV. This is consistent with $r_r$ being minimized at $V_{or} = -18.0$ eV.
Figure 6.5: Comparisons of some experimental I(E) curves for normal incidence on Rh(100) with those calculated with the quasidynamical method and with the full multiple-scattering method.
For Rh(100)-p(2x2)-S, previous analysis with the multiple-scattering calculations (section 4.4) pointed to the conclusion that the 4F model with \(d_{\text{Rh-S}} = 1.30 \, \text{\AA}\) gives the best correspondence with the experimental \(I(E)\) curves (Table 6.1). In this earlier analysis we noted that the 2F model also produced a minimum \(\ddot{r}_{\text{T}}\) which is comparable with that from the 4F model. Similar analyses here with the quasidynamical calculations highlight corresponding features; both 4F and 2F models give local minima with comparable \(\ddot{r}_{\text{T}}\) values (figure 6.6a) although no minimum is found for the 1F model. With quasidynamical calculations, \(\ddot{r}_{\text{T}}\) is minimized at \(d_{\text{Rh-S}} = 1.32 \, \text{\AA}\) and \(V_{\text{or}} = -21.0\) eV for the 4F model, whereas for the 2F model the corresponding values are 1.70 \(\text{\AA}\) and -12.2 eV respectively.

To assess this further we made a visual evaluation of the individual \(I(E)\) curves and evaluated \(\ddot{r}_{\text{T}}\) just for the fractional-order beams. The latter beams are expected to be especially associated with the adsorbate layer and Table 6.2 notes for Rh(110)-c(2x2)-S that the quasidynamical method appears to work better for the fractional-order beams than for the integral-order beams. Figure 6.6(b) shows contour plots of \(\ddot{r}_{\text{T}}\) for Rh(100)-p(2x2)-S, from quasidynamical calculations, where only the fractional order beams are included in the comparison with experiment. Both the 4F and 2F models give definite minima in the contour plots, although the minimum value of \(\ddot{r}_{\text{T}}\) for the 4F model (with \(d_{\text{Rh-S}} = 1.34 \, \text{\AA},\ V_{\text{or}} = -21.0\) eV) is now clearly better than that from the 2F model (with \(d_{\text{Rh-S}} = 1.91 \, \text{\AA}\) and \(V_{\text{or}} = -27.2\) eV). Support for the 4F model from the quasidynamical calculation is provided by the observation that the values of \(d_{\text{Rh-S}}\) and \(V_{\text{or}}\) which give minimum \(\ddot{r}_{\text{T}}\) from the fractional-order
Figure 6.6: Contour plots of $r_r$ for Rh(100)-p(2×2)-S versus $V_{or}$ and the Rh-S interlayer spacing for the 4F and 2F structural models calculated by the quasidynamical method: (a) comparisons with all integral- and fractional-order beams; (b) comparisons with fractional-order beams only.
Rh(100)-p(2x2)-S: Quasidynamical calculation

(a) integral + fractional

(b) fractional only
Figure 6.7: Comparisons of I(E) curves measured for the (01) and \( \frac{13}{22} \) diffracted beams for normal incidence on Rh(100)-p(2×2)-S with those calculated by the quasidynamical method and by the full multiple-scattering method for three possible structural models.
Table 6.3: A demonstration of the correspondence between peak positions in I(E) curves calculated with the quasidynamical method for the four models of Rh(100) - p(2x2) - S at the specified S-Rh interlayer spacing and those given by experiment and by the corresponding full multiple-scattering calculations. In the entries for each beam, the denominator specifies the number of significant peaks in the relevant I(E) curve from experiment or from the full multiple-scattering calculations, and the numerator gives the number of those peaks that are matched to within 7 eV by the quasidynamical calculations.

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<th>Beam</th>
<th>4F Expt</th>
<th>S-Rh=1.3A Expt</th>
<th>S-Rh=1.3A Full MS</th>
<th>S-Rh=2.2A Expt</th>
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beams alone are very similar to those from the combination of fractional-order and integral-order beams. By contrast, the conditions for minimum \( \bar{r}_T \) are very different in these two situations from the 2F model. Overall, then, we believe that the quasidynamical calculation indicates that the 4F model gives the best correspondence with experimental I(E) curves for Rh(100)-p(2×2)-S with \( d_{\text{Rh-S}} = 1.32 \text{ Å} \) and \( V_{\text{or}} = -21.0 \text{ eV} \).

Figure 6.7 compares quasidynamically-calculated I(E) curves for the (01) and (\( \frac{13}{22} \)) beams of Rh(100)-p(2×2)-S with those from experiment and from multiple-scattering calculations. Correspondences in peak positions are apparent for all models with the (11) beam, but the 4F model shows the best match for the (\( \frac{13}{22} \)) beam. Details of comparisons of individual I(E) curves are summarized in Table 6.3. Again this table shows that the best matching for the fractional-order beams is provided by the 4F model. (Some actual I(E) curves are illustrated in figure 6.4(b)).

6.4 Concluding Remarks

The results presented in Table 6.2 and 6.3 for the quasidynamical method indicate that adsorption occurs in the 4F sites for both Rh(110)-c(2×2)-S and Rh(100)-p(2×2)-S; comfortingly these are just the adsorption sites indicated by the full multiple-scattering calculations. For Rh(100)-p(2×2)-S the quasidynamical calculation, in conjunction with the Zanazzi-Jona reliability-index \( \bar{r}_T \), indicates a topmost interlayer spacing of 1.32 Å, in very close agreement with that (1.30 Å) from the multiple-scattering calculation (Table 6.1); however the significance of this close correspondence must be
tempered by the appreciable discrepancies found for both clean Rh(110) and Rh(110)-c(2×2)-S. In general, the index \( r_T \) seems less reliable for assessing interlayer spacings and \( V_{oi} \) from the quasidynamical calculations, especially since this method can be erroneous for calculating relative peak intensities over successive portions of \( I(E) \) curves.

Comparisons in figure 6.4 show that some peaks in experimental \( I(E) \) curves are either absent in the quasidynamically-calculated curves or are represented only by shoulders. In part the latter may represent a consequence of the relatively large values of \( V_{oi} \) that are needed in our quasidynamical calculations to avoid occasional difficulties in convergence.

Although the quasidynamical method clearly is not exact, we are nevertheless encouraged by our observations for Rh(110)-c(2×2)-S and Rh(100)-p(2×2)-S that it is able to select the correct adsorption sites as providing the most likely models for these surfaces. Moreover the calculations here were made for a metal which is a relatively strong scatterer and therefore does not correspond to the situations for which the quasidynamical method was initially judged to be most helpful. These observations support the possibility of using the quasidynamical method for making preliminary assessments of those trial models that need more detailed analyses with full multiple-scattering methods, although further tests are needed to delineate the ranges of scattering strengths and geometrical types for which this conclusion may be applicable. If such ranges can be obtained, then this would clearly provide a most significant role for the quasidynamical method in LEED crystallography. In any event this method should have value in making preliminary assessments
of adsorption systems which involve weakly-scattering adsorbates at low coverage, particularly where the number of fractional-order beams is large and the conventional multiple-scattering procedures rapidly become intractable.
REFERENCES


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Appendices

The following appendices contain all the experimental data from rhodium surfaces collected during this work. In all cases, the data is as collected and has not been smoothed.

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<th>Appendix</th>
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Rh(100)(3×1)-O, \( \theta = 0, \phi = 0 \)

2 equal domains
Rh(110) - (3x1) - O

1 domain only

A2

energy (eV)
A3
Rht(100)-P(2x2)S

expt. 1, θ = 0, φ = 0

energy (eV)
A4
Rh(100) - \( p(2 \times 2) S \)

expt. 2, \( \theta = 0, \phi = 0 \)
A5
Rh(110)-c(2x2)S

expt. 1, \( \theta = 0, \phi = 0 \)