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Abstract

The work in this thesis involved assessments and applications of procedures used for determining surface geometrical structures with low energy electron diffraction (LEED), a subject that is now often referred to as LEED crystallography. Specific studies were made for the (311) surfaces of copper and nickel, and for the (0001) surface of zirconium. These surfaces were cut from high purity single crystal samples, studied under conditions of ultra-high vacuum, and characterized by LEED and Auger electron spectroscopy. The LEED crystallographic studies of the (311) surfaces of face-centered cubic metals represent the first investigations of stepped surfaces which employed multiple scattering calculations. In general, in this thesis, the multiple scattering calculations used the renormalized forward scattering and the layer doubling methods, and the experimental intensity versus energy curves for the diffracted electron beams were measured with our combined vidicon-photographic method.

In these studies, many of the procedures currently employed in LEED crystallography were investigated, particularly in regard to their effects on surface geometry determinations. These procedures included smoothing raw experimental data, averaging beams that are expected to be equivalent from symmetry considerations, correcting measured intensities for effects of non-uniform grid transparency, and setting appropriate values for the suppressor grid voltage. In addition, consideration was given to investigating ways of dealing with numerical instabilities, which sometimes occur in the perturbative methods.
used for calculating LEED intensities, and assessments were made of the reliability index recently proposed by Pendry. The latter gives numerical values for the 'goodness of fit' between experimental and calculated intensity curves, and was compared especially with the index proposed previously by Zanazzi and Jona. Some consideration was also given to the question of assessing uncertainties in structural analyses based on the use of reliability indices.

The topmost interlayer spacing in the (311) surfaces of copper and nickel are indicated to be contracted by about 5% and 14.5% respectively from the bulk spacings. Possible reasons for this difference are discussed in the thesis. By contrast, the (0001) surface of zirconium has a topmost spacing which is very close to the bulk value. Experimental intensity versus energy curves have also been measured for three surfaces involving oxygen adsorption on Zr(0001); one of these surfaces is designated Zr(0001)-(2x2)-O while the other two are both designated Zr(0001)-(1x1)-O. For the latter, one is believed to involve a monolayer coverage of oxygen atoms while the other probably involves oxygen incorporation into the surface region. The LEED intensity data for these oxygen structures, once they have been analyzed with multiple scattering calculations, should provide a basis for detailing structural aspects of the initial stages of the oxidation of Zr(0001).
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CHAPTER 1

SURFACE SCIENCE AND LOW ENERGY ELECTRON DIFFRACTION
1.1 INTRODUCTION

Many important industrial processes depend upon the properties of solid surfaces, for example the fields of heterogeneous catalysis, friction and wear, corrosion, and semiconductor technology. Fundamental to a thorough understanding of these areas is knowledge of the surface processes which occur at the atomic level, information that has been only slowly becoming available. Historically, chemical research on surfaces emphasized the study of materials with high surface/volume ratios and measurements were made on surfaces with uncertain distributions of exposed crystallographic planes and impurity and defect populations. Although useful empirical relationships were derived from these traditional studies, they did not provide a detailed understanding of the events that were occurring on the atomic scale. In the 1960's, with the development of the means for routinely producing ultra-high vacuum (UHV), an alternative 'clean-surface' approach became possible. This approach studied surfaces that could be well-characterized (i.e. high purity single crystals cut to expose a single crystallographic plane) and an emphasis was placed on investigations that would provide knowledge of the basic processes (adsorption, desorption, diffusion, dissociation, etc.) which take place at such solid surfaces.

The necessity of ultra-high vacuum for studies of well defined surfaces follows from the kinetic theory of gases which predicts that a monolayer of molecules can be adsorbed in about one second at a pressure of $10^{-6}$ torr. The formation of monolayer coverage assumes that each molecule-surface collision
results in adsorption (i.e. a sticking probability of unity). UHV is generally defined as pressures less than $1 \times 10^{-9}$ torr ($1$ torr = $133$ pascal), and it is evident that such pressures are essential to produce a clean surface and to carry out controlled experiments on it. At the present time a range of techniques are available for surface characterization within the 'clean surface approach'. These techniques generally involve studying the interaction of the sample with photons, electrons, or ions through the measurement of the angular and/or energy distributions of the emitted particles. Some of these experimental methods are low energy electron diffraction[1,2] (LEED), Auger electron spectroscopy[3,4] (AES), electron energy loss spectroscopy[5], photoelectron spectroscopy[6], field ion microscopy[7], molecular beam scattering[8], and ion neutralization spectroscopy[9]. Various general reviews are available describing the numerous techniques used in modern surface studies under UHV conditions[10-14]. The work in this thesis involves the use of two of these techniques, LEED and AES, in the determination of surface geometries.

The first LEED experiment was performed by Davisson and Germer[15] in 1927. They observed that the angular distribution of elastically backscattered electrons from an annealed nickel sample was highly anisotropic, and they correctly interpreted the backscattered electron distribution as resulting from diffraction by the periodic array of surface atoms. Initially the importance of this experiment resulted from its confirmation of the wave-like nature of electrons according to De Broglie's hypothesis, although Davisson and Germer did recognize the
potential of this technique for determining surface structures. Equation 1.1 shows the relationship between the wavelength ($\lambda$ in Å) and energy ($E$ in eV) for non-relativistic electrons.

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

A typical LEED experiment involves electrons with energies around 100eV and therefore wavelengths of the order of an angstrom. Such electrons are well suited as probes of the interatomic and interlayer separations in solids.

A distinction is made between LEED and other electron diffraction experiments such as reflection high energy electron diffraction RHEED[16], and inelastic low energy electron diffraction ILEED[17]. The LEED experiment involves directing an incident electron beam of well-defined energy and direction at a well-characterized surface and studying electrons which are elastically backscattered from the surface. The RHEED experiment, which in practice especially probes the surface topography, directs a beam of high energy (10-100keV) electrons at grazing angles of incidence on to a surface and observes the elastically scattered electrons. ILEED uses incident electrons with energies similar to those in LEED and it involves the study of the inelastically backscattered electrons where both energy loss and diffraction processes have occurred. ILEED could become a useful technique for studying aspects of the surface valence electronic structure (e.g. surface plasmon dispersion relations).

Even though the first LEED experiment was performed over 50
years ago, difficulties in the control and characterization of surfaces hindered its application to surface studies. In the 1960's, when UHV and Auger electron spectroscopy facilities became readily available, there occurred a renewed interest in LEED. To date LEED has emerged as the principal method for surface structure determination. Other surface techniques that can give this type of information include angle-resolved photoemission[18], ion scattering[19], and extended X-ray absorption fine structure[20] experiments. These alternative techniques have not yet been able to produce enough results to assess their full usefulness for surface structure determinations. A recent compilation of LEED structure determinations for both clean and absorbate covered surfaces is given by Van Hove and Tong[21].

Auger electrons were first observed in a cloud chamber in 1925 by Pierre Auger[22], and following a suggestion of Lander[23] in 1953, Auger electrons are now used to give information about the elemental composition of surfaces. Auger electrons are emitted during the relaxation of an initial core hole state which is usually produced by bombarding the sample with electrons. Figure 1.1 shows schematically the emission of Auger electrons from aluminum. In the late 1960's Auger electron spectroscopy (AES) became an essential part of 'clean surface' studies with the development of convenient ways for taking Auger spectra[24,25]. More details of the theoretical and experimental aspects of Auger electron spectroscopy are given in Chapter 3 of this thesis.
Fig. 1.1 Energy level diagram of aluminum illustrating the production of $L_{2,3}VV$ Auger electrons. The energy levels were obtained from xray studies and are given relative to the Fermi level.
1.2. SOME SURFACE NOMENCLATURE

The term 'surface' is somewhat ambiguous insofar as its meaning depends on the type of experimental probe being used. In LEED, the top 2-5 atomic layers are typically probed; this thickness is determined by the mean free path length of the electrons (Section 1.3.1). The sensitivities of other surface methods such as field ion microscopy or ion neutralization spectroscopy are not governed by the electron mean free path length, and in consequence these techniques probe different aspects of a surface.

Figure 1.2a suggests that LEED electrons often probe regions where the triperiodicity of the solid is established. The surface region studied is conveniently divided into a 'substrate' which possesses the triperiodicity of the bulk and diperiodic 'overlayers'. The diperiodicity of the 'surface region' studied involves a superposition of the diperiodic overlayer with an effectively diperiodic substrate. Assuming the superposition of the substrate and overlayer periodicities is coherent, the diperiodicity of the surface region can be represented by a two-dimensional net with unit vectors $\mathbf{S}_1$ and $\mathbf{S}_2$, such that all equivalent points in the surface region can be generated by the translation vectors $\mathbf{T}$.

$$\mathbf{T} = n\mathbf{S}_1 + m\mathbf{S}_2$$ where $n, m$ are integers \hspace{1cm} (1.2)

There are 5 diperiodic surface nets analogous to the 14 Bravais lattices used in triperiodic crystallography. These are shown in Figure 1.2b with the corresponding reciprocal nets. The
Fig. 1.2a Schematic illustration of the 'surface region' probed by a LEED experiment showing overlayer and substrate, both of which are diperiodic in the x,y direction.

Fig.1.2b Diperiodic surface nets and the corresponding nets in reciprocal space.
reciprocal net vector \( g(h,k) \) is defined in equation 1.3 where \( \mathbf{S}_1^* \) and \( \mathbf{S}_2^* \), the reciprocal unit vectors, are related to the real net vectors \( \mathbf{S}_1, \mathbf{S}_2 \) by equation 1.4.

\[
g(h,k) = h\mathbf{S}_1^* + k\mathbf{S}_2^* \quad \text{where } h, k \text{ are integers} \tag{1.3}
\]

\[
\mathbf{S}_1^* = 2\pi(\mathbf{S}_2 \times \mathbf{Z})/(\mathbf{S}_1 \cdot \mathbf{S}_2 \times \mathbf{Z}) \\
\mathbf{S}_2^* = 2\pi(\mathbf{S}_1 \times \mathbf{Z})/(\mathbf{S}_2 \cdot \mathbf{S}_1 \times \mathbf{Z}) \tag{1.4}
\]

Here \( \mathbf{Z} \) is a unit vector perpendicular to the plane defined by \( \mathbf{S}_1 \) and \( \mathbf{S}_2 \). As in other diffraction phenomena, the reciprocal net construction provides a convenient means of designating diffracted beams and is useful in the description of the scattering of electrons from the surface. The diffraction patterns observed from incommensurate surface structures, where the superpositions of overlayer and substrate are incoherent, have been discussed by Estrup and McRae[1].

Crystallographically well-defined surfaces are naturally identified with the Miller indices \((hkl)\) of the plane that is parallel to the surface (e.g. the \((100),(110), \) and \((111)\) surfaces of face-centered cubic solids). Low-index surfaces of metals often have the structure expected from the truncation of the bulk except for an expansion or contraction of the topmost interlayer spacing. In contrast, surfaces where covalent bonds are involved commonly 'reconstruct' (e.g. \( \text{Si}(111) \)). Reconstruction refers to the rearrangement of the atoms in the top few layers. 'Adsorbate' structures (e.g. \( \text{Zr}(0001)-(2\times2)-0 \)) consist of a substrate and one or more adsorbed overlayers.
Adsorbate and reconstructed surface structures are usually named with reference to the substrate net vectors. The most simple surface structures involve vectors which are parallel to those of the substrate and have lengths which are integral multiples of the substrate vector lengths; such a structure is commonly identified as a nxm structure, where n,m are the ratios of the lengths of the surface to substrate vectors. Further discussions of surface crystallography have been given by Wood[26], and for more general situations, Park and Madden[27] have introduced a matrix notation.

1.3 LOW ENERGY ELECTRON DIFFRACTION

1.3.1 Electron Scattering in Solids

When a monoenergetic beam of electrons impinges on a solid surface the energy distribution of the backscattered electrons is like that shown in Figure 1.3a. The energy distribution of the emitted electrons is conveniently divided into three regions;

a) the elastic peak
b) the intermediate energy range
c) the low energy secondary peak

The elastic peak is comprised of the electrons of interest in a LEED experiment. This peak, which corresponds to approximately 1-5% of the incident current at 100eV[28], involves electrons that have been truly elastically scattered as well as those electrons that have suffered small energy losses due to phonon scattering (the quasi-elastic electrons); the latter are not resolved from the elastically scattered electrons.
in a typical LEED experiment.

The reason that the electrons studied in LEED are sensitive to the surface region of the solid is illustrated by Figure 1.3b which shows the mean free path length $L$, as a function of electron energy. The mean free path length is defined by

$$I(l) = I_0 \exp\left(-\frac{l}{L}\right)$$

(1.5)

where $I_0$ is the incident intensity at a particular energy attenuated to $I(l)$ after propagating a distance $l$. Since the mean free path length for electrons with typical LEED energies in the 30-300eV range corresponds to just a few atomic layers, then it follows that the electrons that comprise the elastic peak must have been turned around by the top few layers. The comparatively short mean path length in solids, for the electron energies used in LEED, reflects the existence of strong inelastic scattering. Above 10eV the major loss mechanism is the excitation of plasmons[29] which can be envisaged as the quantized oscillations of the 'electron gas' in the solid. Specific peaks corresponding to plasmon losses are indicated in Figure 1.3a at energies 10-20eV below the elastic peak.

The intermediate energy range of the backscattered electron distribution in Figure 1.3 shows peaks corresponding to Auger electrons and characteristic energy losses resulting from ionizations and excitations of the valence and core electrons. The peaks due to Auger electrons can be distinguished from other loss peaks since their energy is independent of the incident beam energy. The large low energy secondary peak results from
Fig. 1.3a) Energy distribution of electrons backscattered from a surface for an incident beam energy $E_0$.

Fig. 1.3b) Mean free path length $L(\text{Å})$ of electrons in a metallic solid as a function of electron energy (eV).
cascade processes[4] where the incident electron excites a number of secondaries through interactions with electrons in the solid. The secondary electrons can interact with other electrons and produce tertiaries etc.; all of which contribute to the intensity of the 'secondary' peak.

1.3.2 The LEED Experiment

The electron energy analyser of a typical LEED experiment is shown in Figure 1.4a. The electron gun directs a beam of nearly monoenergetic electrons towards the sample. The full width at half maximum (FWHM) of the energy distribution of the incident electrons is determined primarily by the temperature of the emitting filament; it is about 0.5eV for a tungsten emitter at 2000°C. The electrons that are elastically backscattered from the sample pass through the four hemispherical grids (the LEED optics) and are accelerated towards a phosphor coated screen which glows where the electrons strike it. The inner grid (G1) is grounded and keeps the region surrounding the sample field free. Electrons with energies greater than the retarding voltage on the double grid (G2,G3) can pass through these grids and then through another grounded grid (G4) to be displayed on the phosphor screen. The use of a double grid for the retarding grids is to reduce the effects of field inhomogenities and thus improve the instrument's energy resolution; this is particularly important when the LEED optics are used for taking Auger electron spectra. G4 is grounded to prevent the high voltage on the screen (about 5kV) from penetrating the region of the double grids.
Fig. 1.4a) Schematic diagram of the LEED experiment.

Fig. 1.4b) Schematic diagram showing how the conservation conditions determine a diffracted beam's direction. The (0,0) beam results from specular reflection.
In the conventional experimental arrangement, the fluorescent screen can be viewed through a window from outside the vacuum chamber and thus an electron diffraction pattern can be observed directly. When the incident electrons are elastically scattered from a well-ordered surface, the LEED pattern is seen to be a regular array of spots of differing intensities. The objective of quantitative LEED experiments is to measure, at a known direction of incidence, the intensities of these diffracted beams over a range of incident beam energy and thereby produce intensity versus energy spectra or I(E) curves. An alternative, but less common, approach is to vary the angle of incidence at a fixed beam energy and produce intensity versus angle profiles. Examples of some I(E) curves are shown in Figure 1.5 for diffracted beam intensities measured at normal incidence from the Cu(311) surface compared with calculated I(E) curves for different topmost interlayer spacings.

1.3.3 The LEED Diffraction Pattern

The incident and diffracted electrons in a LEED experiment travel in free space and, to a good approximation, can be represented by plane waves of type;

\[ \Psi = e^{i \mathbf{k} \cdot \mathbf{r}} \]

where \( \mathbf{k} \) is the wavevector with appropriate direction and with magnitude equal to \( 2\pi/\lambda \). The wavevector and energy are related by;

\[ E = \hbar^2 |k^2| / 2m \quad (1.6) \]

The diffraction of the electrons into discrete beams by a
Fig. 1.5 Leed I(E) curves for normal incidence data from a clean Cu(311) surface compared with I(E) curves calculated for different topmost interlayer spacings.
well ordered surface is a direct consequence of the diperiodic translational symmetry which necessitates the conservation of momentum condition illustrated by equation 1.7. The elastically scattered electrons that are analyzed in a LEED experiment also satisfy energy conservation as given by equation 1.8.

\[
\begin{align*}
\vec{k}_g - \vec{k}_o &= \vec{g}(h, k) \\
|\vec{k}_g|^2 &= |\vec{k}_o|^2
\end{align*}
\]

Here \( \vec{g}(h, k) \) is the reciprocal net vector as defined in equation 1.2, and \( \vec{k}_o \) and \( \vec{k}_g \) are the parallel wavevectors of the incident and diffracted electron waves respectively. Figure 1.4b shows how the direction of a diffracted beam (wavevector \( \vec{k}_g \)), depends on the value of \( \vec{g}(h, k) \) and \( E \).

The conservation of parallel momentum arises from the condition that the phases of waves scattered at equivalent sites in the surface region must differ by \( 2\pi n \) \( (n \text{ integer}) \) for constructive interference. The limited penetration of the elastically scattered electrons precludes substantial constructive interference associated with the periodicity normal to the surface. Nevertheless, intensities of the diffracted beams are sometimes large near the energies that satisfy;

\[
\vec{k}_g - \vec{k}_o = \vec{g}(hkl)
\]

where \( \vec{g}(hkl) \) is a triperiodic reciprocal lattice vector. The peaks in the \( I(E) \) curves which correspond to this condition are called Bragg peaks.

The low energy electrons studied by LEED interact with the
solid surface much more strongly than do X-rays. Elastic
cross-sections for 100eV electrons are of the order of $10^2\,\text{Å}^2[30]$ and are therefore about $10^7$ times greater than typical cross-sections for X-ray diffraction[31]. Associated with this strong interaction, extra structure occurs in the I(E) curves because many electrons undergo more than one scattering event. These 'multiple scattering' peaks are often more intense than the Bragg peaks. Clearly, the single-scattering (kinemtical) theories of X-ray diffraction are inadequate for LEED and 'multiple scattering' theories are required (Chapter 2).

1.3.4 LEED Crystallography

The presently employed method of surface structure
determination with LEED is to propose a trial structure and then calculate I(E) curves for the electron beams diffracted from this structure. The proposed structure is then altered until the calculated and experimental I(E) curves show the closest correspondence. The comparison of the experimental and calculated I(E) curves has often been done visually by matching the energies and shapes of all the peaks in the I(E) curves. Figure 1.5 shows the comparison of two experimental I(E) curves with calculated I(E) curves for various topmost interlayer spacings. Normally, 10 or more I(E) curves are measured, and often for more than one angle of incidence. The large amount of data involved when there are many possible structures, and many experimental I(E) curves, has made the visual assessment approach extremely cumbersome. Recently, numerical 'reliability indices' have been proposed which purport to quantify levels of
correspondence. The work is this thesis uses the reliability index approach to LEED crystallography and examines many of the procedures that are followed in structural determinations.

Alternative methods to derive structural information from the experimental LEED data are being investigated. These methods include the constant momentum transfer averaging approach[32] (CMTA), and Fourier transform techniques[33]. The CMTA method averages large sets of experimental intensity data at constant momentum transfer to the surface, with the hope of reducing the multiple scattering contributions so that comparisons can be made with kinematic calculations for different proposed surface models. The Fourier transform techniques attempt to provide 'direct' approaches to structural information, analogous with the Patterson function method of X-ray crystallography. Both of these approaches avoid complex multiple scattering calculations, but so far they have not yet provided generally applicable procedures for determining surface structures.

1.4 INSTRUMENTAL RESPONSE, DOMAINS AND DISORDER

The LEED electron gun usually produces a beam that is about 1 mm in diameter and so intersects an area on the top surface layer that contains about $10^{13}$ atoms. However, the incident beam possesses angular and energy deviations associated with the finite size and high temperature of the source, and these factors define an instrumental response function which yields a characteristic dimension, the transfer width $W$, over which the instrument is sensitive as a probe of the surface periodicity[34]. The LEED instrument can only resolve angular
distributions of electrons which result from diffraction by features on the surface with periodicities smaller than W, or alternatively, the instrument obscures information about surface structures with periodicities greater than the transfer width. Park et al.[34] found that typical transfer widths ranged from 20 to 100 Å. The restriction of the areas that contribute to LEED intensities is significant since it ensures that the observed diffraction pattern is the sum of a very large number of individual diffraction patterns; each from a region on the order of 10^4 Å².

An interesting observation for (0001) surfaces of hcp metals is provided by their LEED patterns which show 6-fold symmetry rather than the 3-fold symmetry expected for the perfect truncation of the bulk. The conventional explanation can be indicated with reference to Figure 1.6. This shows the presence of two different 'domains' or islands with surface net vectors related by a 180° rotation. These domains result from the presence of monoatomic steps on the surface. For domains that are larger than the area associated with the instrumental transfer width and are smaller than the electron beam width, the observed diffraction patterns involve a summation over patterns from the different domains. When the populations of the two sets of domains are approximately equal, 6-fold symmetry results for the 'domain-averaged' LEED pattern. For overlayer systems, LEED patterns usually show the rotational symmetry of the substrate, even though each domain may have lower symmetry. This can introduce ambiguities in interpretation. For example, the same LEED patterns are produced from (2x2) overlayers on a hcp(0001)
Fig. 1.6 Structure of the hcp(0001) surface showing the two possible domains that result from the truncation of the bulk structure. Larger circles represent atoms in the topmost atomic layer, full and open circles atoms in layers A and B respectively. The two domains are related to each other by a 180° rotation. Axes selection and unit cell vectors after Van Hove [21].
Fig.1.7 Three 120° related domains of (2x1) overlayer structures on a hcp(0001) surface. X's represent atoms in the topmost layer of the hcp(0001) substrate and dark circles represent the atoms in the overlayer.
surface, as from three (2x1) domains related by 120° rotations as indicated in Figure 1.7. An analysis of beam intensities is necessary in order to distinguish between these possibilities.

The discussion of the formation of LEED patterns assumed diffraction from perfectly ordered surfaces. Real surfaces inevitably have imperfections; the presence of steps, kinks, and dislocations is well-known[35]. It is important to know what effects such features can have on LEED patterns and beam intensities.

The LEED pattern is not always sensitive to the presence of surface disorder. Studies of Si(111) surfaces[36] have shown that up to 20% of the Si atoms on the surface can be randomly distributed without causing any observable changes in the LEED pattern. The presence of regular steps, faceting, and domains with dimensions less than the transfer width, leads to the splitting or broadening of the LEED diffraction spots. Information about the distribution of domain sizes can be obtained by studies of the angular profiles of the diffracted beams[37]. Generally, the main effect of the disordered areas is to reduce the absolute beam intensities and to produce a smoothly varying background. However, there is evidence that disorder may also alter relative peak intensities[38] and this possibility should be considered when taking intensity measurements. Disorder resulting from the thermal vibrations of the atoms is normally accounted for when calculating the diffracted beam intensities (Chapter 2).
1.5 THIS WORK

The work described in this thesis represents a contribution to the development of the subject of LEED crystallography. Specific studies have been made for clean (311) surfaces of the face-centered cubic (fcc) metals copper and nickel, and for (0001) surfaces of zirconium both when clean and when containing adsorbed oxygen. The (311) surfaces were studied as comparatively simple examples of stepped surfaces, and this work was the first LEED study of a stepped surface that employed multiple scattering calculations to determine the surface geometry. Stepped surfaces are of interest to chemists as they have been shown to possess different reactivities (e.g. for catalytic reactions) from the flat low index surfaces of the same metal[39,40]. These (311) surfaces were amenable to detailed LEED analyses because they can be represented by a primitive lattice which is sufficiently small for multiple scattering calculations to be practical. As part of the study of Ni(311), a comparison was made of two reliability indices that have been proposed for use in LEED crystallography[41,42].

Studies on Zr(0001) were initiated for several reasons. No quantitative LEED work has been done on this metal, although Ti(0001) shows some interesting features in its surface structural chemistry[43,44]. It was hoped that some comparisons could be made with Ti(0001) by studying the adsorption of oxygen on Zr(0001). Zirconium is also a special challenge because it is highly reactive and because it undergoes a phase transition to the body centered cubic form at around 865°C[45]; both these factors complicate the procedures for cleaning surfaces of this
Briefly the outline of this thesis is as follows. Chapter 2 outlines multiple scattering theories of low energy electron diffraction and describes the salient features of the computer programs used here for calculating diffracted beam intensities. Chapter 3 includes an examination of the experimental aspects of LEED/Auger studies, as well as describing the reliability index routines used in the comparisons of the experimental and calculated I(E) curves. Chapter 4 details the work on the (311) surfaces of copper and nickel and its implications to broader aspects of LEED crystallography, especially with regard to the use of reliability indices. Finally, Chapter 5 describes studies on the (0001) surface of zirconium, both when clean and when containing adsorbed oxygen.
CHAPTER 2

LEED INTENSITY CALCULATIONS
This chapter will briefly describe the theoretical approach to the problem of electrons scattered by a solid surface. The emphasis is on the physical nature of the scattering process and on the utilization of the computer programs that were available for our LEED crystallographic studies.

2.1 INTRODUCTION

The first attempts at developing realistic multiple scattering calculations took place in the late 1960's[46,47]. Significant advances were the inclusion of an imaginary self-energy to account for absorption due to inelastic scattering[48] and improved models for the scattering potential[49]. Various schemes of calculation have been developed to calculate LEED I(E) curves and detailed statements have been given in the reviews by Duke[50], Tong[51], and Pendry[52]. The computations made in this work are based on programs supplied by M. A. Van Hove; these are described in the monograph by Van Hove and Tong[21].

Within a crystal, two different representations of the scattered wavefield are normally used, and they are suggested by two aspects of the overall scattering problem. In the K-space, or beam, representation the wavefield is represented by plane waves, which are the natural functions for electrons moving in regions of constant potential. The L-space, or spherical wave, representation is natural for considering the wavefield in the region of an atom, where a spherical potential provides a useful approximation. In general plane waves can be described in terms of a series expansion of spherical waves[53], and vice versa,
but for particular aspects of the overall scattering problem one of these representations may be more convenient[54,55].

Most methods for calculating LEED intensities break down the whole scattering problem into simpler units, which start by calculating scattering amplitudes from individual atoms, which are assumed to be spherically symmetric. Next the scattering within whole layers of atoms parallel to the surface is calculated, and then the different layers are stacked and the interlayer scattering is calculated. Finally, the wavefield outside the crystal is matched to the wavefield inside the crystal at the solid-vacuum interface[47]. The wavefield outside the crystal takes the form

$$\Psi(r) = \exp(ik_0\cdot r) + \sum_g C_g \exp(ik_g\cdot r)$$

The objective of a LEED calculation is to compute the beam reflectivities,

$$R_g = \frac{|kg|}{|k_0|} |C_g|^2$$

which relate to the relative intensities of the measured I(E) curves.

2.2 PHYSICAL PARAMETERS FOR LEED CALCULATIONS

As well as a structural model, various non-geometrical parameters are required for the computation of I(E) curves; the latter specifically involve the atomic scattering factors, scattering by the electron gas of the solid, and the effects of the atomic vibrational motions. A discussion of these parameters is included in this section.
2.2.1 The Ion Core Potential

A helpful model for the crystal potential is that conventionally used in band structure calculations. This model is called the muffin tin approximation, and is illustrated in Figure 2.1[56]. The largest possible non-overlapping spheres are drawn about each atom center. A spherically symmetric potential is used inside each sphere and the potential between the spheres is taken to be constant. In LEED, electrons are especially backscattered by the ion core potentials (where the effective nuclear potential is strong).

The wavefunction of an electron inside a muffin tin sphere is calculated by solving the Schrodinger equation

\[ (-\hbar^2 \nabla^2 / 2m + V) \Psi = E \Psi, \tag{2.3} \]

where \( V \) is the sum of the coulombic part of the ion core potential and a contribution for exchange. In LEED calculations, the atomic potentials used are often self-consistent band structure potentials, examples of which are given by Moruzzi et al[57], but potentials calculated for cluster models are also used[58]. The latter could be important for adsorption systems where the appropriate band structure potential may not be available. The exchange term in the potential is often related to the charge density \( \rho(r) \) by Slater's expression

\[ V_{\text{exc}} = -6A[3\rho(r) / 8\pi]^{1/3}, \tag{2.4} \]

with values of \( A \) tabulated by Schwarz[59,60]. It has been suggested that (2.4) includes some correction for correlation.
For the multiple scattering calculations for the Cu(111) surface, Tear et al[61] varied $A$ to give the best fit between the calculated and experimental $I(E)$ curves.

The asymptotic form of the solution to equation (2.3), that is at a long distance from the atom where $V=0$, is

$$\Psi \sim A[\exp(ik\cdot r) + f(\theta^S, E) r^{-1} \exp(i\kappa \cdot r)] \quad (2.5)$$

where $f(\theta^S, E)$, the structure factor, can be expanded in terms of spherical waves

$$f(\theta^S, E) = 1/2ik \sum_{\ell} (2\ell + 1) \sin(\delta^\ell) \exp(i\delta^\ell) P_\ell(\cos(\theta^S)) \quad (2.6)$$

In (2.6), the $\delta^\ell$ are called phase shifts, the $P_\ell(\cos(\theta^S))$ are Legendre polynomials, and $\theta^S$ is the angle through which the electron is scattered. The phase shifts can be evaluated by matching the derivatives of the solution of (2.3), for the appropriate ion core potential, with the asymptotic form in equation (2.5) at the muffin tin radius. The phase shifts are dependent on electron energy, as well as the particular atom, and in principle the expansion for $f(\theta^S, E)$ involves an infinite number of $\ell$ values. However, in practice convergence is sufficiently rapid that only a comparatively small number of phase shifts are required.
Figure 2.1 Model for potential of an adsorbate covered surface.

Region (after Marcus [65])
2.2.2 The Constant Potential $V_0$

The constant potential between the muffin tin spheres changes the energy of the electrons inside the crystal. The energy inside the crystal can be related to the electron energy in vacuum by

$$E_{\text{inside}} = E_{\text{vacuum}} - V_0 \quad (2.7)$$

where $V_0$ is, in general, constructed of a real part ($V_{\text{or}}$) and an imaginary part ($V_{\text{oi}}$)

$$V_0 = V_{\text{or}} + iV_{\text{oi}} \quad (2.8)$$

i) $V_{\text{or}}$

The real part of the constant potential ($V_{\text{or}}$) accommodates the increase in energy as a result of the attractive potential experienced by an electron inside the crystal. $V_{\text{or}}$ usually has a value between $-5$ and $-15$ eV. The value of $|V_{\text{or}}|$ is approximately equal to $\phi + E_f$ where $\phi$ is the work function and $E_f$ is the Fermi energy. In principle exchange and correlation effects give $V_{\text{or}}$ an energy dependence[62], but nevertheless it is often an adequate approximation to treat $V_{\text{or}}$ as constant. Increasing $|V_{\text{or}}|$ shifts the peaks in the calculated $I(E)$ curves to lower values of $E_{\text{vacuum}}$. In the present work, a plausible value of $V_{\text{or}}$ is used for the multiple scattering calculations and then, during the comparison between the experimental and calculated data, the calculated $I(E)$ curves are given a constant shift to provide the best agreement with the experimental $I(E)$ curves. This procedure effectively refines the value of $V_{\text{or}}$, which is therefore an empirical parameter. In this thesis, $V_{\text{or}}$ is often called the inner potential.
ii) Voi

The importance of inelastic scattering to LEED was established in Section 1.3.1; this is included phenomenologically in the calculations by an imaginary contribution (Voi) to the constant potential between the muffin tin spheres. The effect of Voi is to introduce an imaginary component into the wavevectors for electrons inside the crystal, and in turn this results in absorption. For the general time dependence

\[ \Psi(r, t) = \mathcal{P}(r) \exp(-iEt/\hbar), \]

the intensity \( |\Psi|^2 \) is damped, after propagating for time \( t \), by the factor \( \exp(2Voi/t) \) when Voi is a negative quantity. This sets a minimum width of \( 2|Voi| \) on peaks in the calculated \( I(E) \) curves. The dependence of peak width on Voi is a consequence of the Heisenberg uncertainty principle and the finite lifetime of the decaying wave\[2\]. For LEED energies in the range 30 to 300eV, values of Voi from -2 to -8eV are typical, with Voi generally being a slowly varying function of energy. A suitable value for Voi in the calculations is normally obtained by reference to peak widths observed in the experimental \( I(E) \) curves. Emphasis is on peaks which appear essentially kinematical; care is needed because multiple scattering results in broadening due to the presence of overlapping peaks. Jepsen et al\[63\] proposed the functional form

\[ Voi = -BE^{1/3} \quad (2.9) \]

for silver. This energy dependence is assumed in the present
work, and has been fairly widely used for metals. The parameter B is determined from an examination of the narrowest peaks in the experimental I(E) curves.

2.2.3 Atomic Motions

The atomic motions associated with a vibrating lattice cause many electrons to be scattered incoherently. The intensities of the diffracted electron beams are thus reduced and the background intensity increases compared with the case of a rigid ideal solid. Since the time an incident electron interacts with an atom is much shorter than the period of an atomic vibration, the LEED experiment measures the average atomic positions by sampling over the 'snap shot' positions of many atoms. The intensities are further averaged since the period of data acquisition is relatively long (on the order of a second).

For kinematic calculations, a diffracted beam intensity I from a vibrating lattice is reduced from that (Io) for a rigid lattice by

\[
I = Io \exp[-2M] \tag{2.10a}
\]

\[
M = 3 \left( \frac{Kg^- - Ko^+}{\Theta_D} \right)^2 \frac{T}{2mk_B} \tag{2.10b}
\]

and \( \exp[-M] \) is often referred to as the Debye Waller factor. In (2.10b), \( k_B \) is the Boltzmann constant, m is the atomic mass, and \( \Theta_D \) is the Debye temperature. The dependence on \( Kg^- - Ko^+ \) results in a greater reduction in intensity for higher electron energies. \( \Theta_D \) has the units of temperature and is inversely related to the atomic vibration amplitudes. In the high
temperature limit \((T \gg \Theta_p)\),

\[ \Theta_p^2 = \frac{9T}{mk_b \langle (\Delta r)^2 \rangle}, \quad (2.11) \]

where \(\langle (\Delta r)^2 \rangle\) is the mean square vibration amplitude. With multiple scattering, only the amplitudes strictly follow a Debye-Waller type dependence, although in practice, expressions such as (2.10a) often provide a good approximation.

Averaged Debye temperatures for the surface region have often been determined by measuring LEED intensities as a function of temperature[64,65]. Surface values are generally lower than bulk Debye temperatures from X-ray diffraction studies; this reflects the enhanced vibrational amplitudes of atoms in the topmost atomic layers.

For isotropic scatterers, and neglecting correlations between the motions of neighbouring atoms, the effects of thermal vibrations can be included in multiple scattering calculations by modifying the phase shifts appropriate for the rigid lattice according to

\[ f(\tilde{\Theta},T) = f(\tilde{\Theta}) \exp[-M] \quad (2.12) \]

This has the effect of making the temperature dependent phase shifts complex; also an increased number of phase shifts are required for convergence at any given energy compared with the rigid lattice. For energies up to 200eV, eight phase shifts \((l=0\) to 7\) are usually adequate for multiple scattering calculations of \(I(E)\) curves.
2.2.4 The Solid-Vacuum Interface

Both Vor and Voi tend to zero in vacuum at a long distance from the solid. However, the detailed scattering of incident electrons by the crystal must depend on the specific variations of Vor and Voi through the solid-vacuum interface. A particular situation is illustrated in Figure 2.1. Often it turns out to be adequate to ignore this effect and to set both Vor and Voi equal to zero at a step at the outermost extent of the top atomic layer. This approximation is only inadequate for shallow angles of incidence or for low energies (<40eV) where narrow extra structure can be observed in experimental I(E) curves[66]. This structure is attributed to a resonance phenomenon, which involves evanescent electron waves being trapped between the surface potential barrier and the substrate prior to scattering into diffracted beams that can emerge from the crystal[67]. Such features are usually seen in I(E) curves at energies just below that for emergence of another diffracted beam.

Refraction of electrons at the solid-vacuum interface is accommodated in the multiple scattering calculations by Vor. At normal incidence refraction only occurs when the diffracted beams emerge from the crystal, and so the scattering paths within the crystal are not affected. For off-normal incidence, an incident beam refracts upon entering a crystal. The inclusion of refraction in the multiple scattering calculations is therefore more important for incident angles well away from the normal.

The calculations made in this work include the effects of refraction, but neglect scattering by the surface barrier at the
solid-vacuum interface. It would be possible to include such effects by including an additional 'overlayer' with reflection and transmission matrices appropriate for a model potential of the surface barrier. (Section 2.3)

2.3 MULTIPLE SCATTERING METHODS

The first step in the calculation of beam reflectivities is the computation of the scattering amplitudes of the individual atoms. This requires a suitable ion core potential and a value for the Debye temperature, in order to determine the temperature dependent phase shifts[2]. The next step is the calculation of the layer diffraction matrices $M$. The particular element $Mg'g$ gives the amplitude of the plane wave with wavevector $kg'$ which is scattered from a layer for an incident plane wave of unit amplitude and wavevector $kg$. Superscript signs are also added to indicate the plane wave directions; specifically, a + sign for propagation into the crystal and a - sign for propagation out of the crystal. Figure 2.2a schematically illustrates this situation. The general expression[2] for $Mg'g$ is

$$Mg'g = \frac{8\pi^2i}{\Delta\omega} \sum_{L} \sum_{\ell} \bar{Y}_L(kg')[1-X]^{-1} Y_L(kg)exp(i\delta')\sin(\delta') \quad (2.12)$$

where $Y_L(kg)$ are spherical harmonics of the angle between $kg$ and the surface normal, the $L$ notation implies a sum over all $\ell$ and the associated $m$ values, and the matrix $X$ describes the multiple scattering within the layer[2].

The exact Bloch wave method (exact within the muffin tin
approximation) expands the interlayer wavefield in terms of plane waves. It is convenient to consider local interlayer origins at the midpoints between neighbouring atomic planes. For the planes \( n \) and \( n+1 \), the wavefield at the local origin can be expressed

\[
\Psi(r) = \sum_{g} C_{rg} \exp(ikg \cdot r) + C_{n \rightarrow g} \exp(ikg \cdot r) \tag{2.13}
\]

The matrix elements which describe transmission \( T^{++} \), \( T^{--} \) and reflection \( R^{+-}, R^{-+} \) with propagation between interlayer origins are

\[
T_{g'}g^{++} = P_{g'}^{+} (Ig'g + Mg'g^{++})P_{g'}^{+} \tag{2.14a}
\]
\[
T_{g'}g^{--} = P_{g'}^{-} (Ig'g + Mg'g^{--})P_{g'}^{-} \tag{2.14b}
\]
\[
R_{g'}g^{+-} = P_{g'}^{+} Mg'g^{+-}P_{g'}^{-} \tag{2.14c}
\]
\[
R_{g'}g^{-+} = P_{g'}^{-} Mg'g^{-+}P_{g'}^{+} \tag{2.14d}
\]

where, for example, \( P_{g'} = \exp[ikg' \cdot \frac{d}{2}] \) represents propagation through one half of an interlayer spacing \( d \). In equations 2.14, \( Ig'g \) is an element of the unit matrix and represents the unscattered plane wave. A schematic representation of the transmission and reflection matrices is shown in Figure 2.2b. Using the appropriate transmission and reflection matrices the relation between waves propagating between layers \( n \) and \( n+1 \) can be expressed as

\[
C_{n+1}^{++} = T_{n}^{++} C_{n}^{+} + R_{n}^{+-} C_{n+1}^{-} \tag{2.15c}
\]
\[
C_{n}^{-} = T_{n}^{-+} C_{n+1}^{+} + R_{n}^{++} C_{n}^{+} \tag{2.15b}
\]
\[ \sum_{g} b_{g}^{+} \exp(i k_{g}^{+} \cdot r) \quad \sum \sum_{g} M_{g g}^{\pm} b_{g}^{+} \exp(i k_{g}^{\pm} \cdot r) \]

Fig. 2.2a Schematic representation of a set of plane waves \((k_g)\) incident from the left and multiply scattered by an atomic layer into outgoing waves \((k'_g)\).

Fig. 2.2b Schematic diagram illustrating the transmission and reflection of waves at the \(n\)th atomic layer. Dashed lines represent the midpoints between the \(n\)th plane and the \(n-1\) and \(n+1\) atomic layers.
where, for example, the elements of column matrix $C_{n+1}^+$ are the values of $C^{g}_{n+1}$ between layers $n$ and $n+1$. The values of $C^{g}_{n+1}$ in equation (2.2) are found by matching the wavefunctions at the solid-vacuum interface. Details of this procedure are given by Jepsen et al[62] for the calculation of LEED intensities from the Al(001) surface. This calculation employed the Bloch wave method and treated intralayer scattering using the 'layer KKR' method from band structure calculations.

Another exact method, the T-matrix method, works in angular momentum space. The reflectivity of an $N$-layer slab is found by solving $N$ equations, each with matrices of dimensions $(l_{\text{max}}+1)^2 \times (l_{\text{max}}+1)^2$, where $l_{\text{max}}$ is the number of phase shifts needed (typically 8 for energies less than 200eV). For information on the T-matrix method, the interested reader is referred to the review by Tong[51].

2.4 PERTURBATIVE METHODS

Both the Bloch wave and T-matrix methods have formidable computing time and storage space (about 0.4-1 Mb) requirements[51], and, in the development of LEED for practical surface structure determinations, there are consequently considerable pressures for developing faster methods with less severe storage requirements.

As detailed in Section 1.3.1, inelastic losses result in a short mean free path length and this may limit the order of multiple scatterings that will be important for determining beam reflectivities. The K-space methods described below, renormalized forward scattering (RFS) and layer doubling,
utilize this by approximating the final reflectivity by the sum over terms with progressively higher order of multiple scattering.

2.4.1 Renormalized Forward Scattering

The renormalized forward scattering (RFS) method was developed by Pendry[55]. The RFS procedure is an iterative method which evaluates the forward scattering to all orders. As schematically illustrated in Figure 2.3, the computation proceeds layer by layer until the sum of the amplitudes of the forward scattered beams is less than some predetermined fraction of the amplitude incident on the first layer (e.g. 0.2%). Inelastic losses limit the penetration and hence the number of atomic layers required to represent the crystal in this context. The amplitudes of waves propagating from the nth to the n+1th layer can be represented by a column vector $a^{(i)}_{n+1}$ where i is the iteration order. Then

$$a^{(1)}_{n+1} = \begin{bmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{bmatrix}$$ represents the incident beam and (2.16a)

$$\tilde{a}^{(1)}_{n+1} = T^{\ast \ast n} \tilde{a}^{(1)}_{n}$$ (2.16b)

gives the amplitudes incident on the n+1th layer. Proceeding from the deepest layer towards the topmost layer, the backscattered amplitudes for each layer are summed with the transmitted flux to calculate the amplitudes of beams on the way out of the crystal.
Fig. 2.3 Schematic illustration of the computation procedure of Renormalized Forward Scattering (RFS). The triplets of arrows represent the entire set of propagating plane waves.

a) RFS procedure for three iterations
b) Propagation of inward moving waves
c) Propagation of outward moving waves

(after Van Hove and Tong)
\[ b_0^{-n} = R_0^{-n}a_0^{-n} + T_0^{-n}b_0^{-n} \]  

(2.17)

The calculation proceeds layer by layer until the topmost layer is reached and yields \( b_0^{-n} \), the first approximation to the reflected amplitudes. The process is iterated to give \( a_{-n}^{(2)} \) values by proceeding back into the bulk using the backscattered amplitudes \( R_0^{-n}b_0^{-n} \). The procedure is repeated until the reflected amplitudes converge; usually after 3-5 iterations.

2.4.2 Layer Doubling

The layer doubling method, schematically illustrated in Figure 2.4, begins with the computation of \( M \). The calculation then proceeds by evaluating the transmission and reflection matrices for a two-layer slab \( c \), composed of atomic layers \( a \) and \( b \).

\[
T_c^{++} = T_b^{++}(I-R_a^{--}R_b^{--})^{-1}T_a^{++} \tag{2.18a}
\]

\[
T_c^{--} = T_a^{--}(I-R_b^{--}R_a^{--})^{-1}T_b^{--} \tag{2.18b}
\]

\[
R_c^{--} = R_a^{--} + T_a^{--}R_b^{--}(I-R_a^{--}R_b^{--})^{-1}T_a^{++} \tag{2.18c}
\]

\[
R_c^{++} = R_b^{++} + T_b^{++}R_a^{--}(I-R_b^{--}R_a^{++})^{-1}T_b^{--} \tag{2.18d}
\]

The two layer slabs are stacked together and the diffraction matrices are calculated, again using equations (2.18a-d). This procedure is repeated for 8,16.. layer slabs until the calculated reflectivities converge. The layer doubling method involves the inversion and multiplication of matrices of order \( n_b \), where \( n_b \) is the number of beams required in the calculation (see below).
Fig. 2.4 Illustration of the layer doubling procedure of stacking layers. Layers A and B are stacked together and the transmission and reflection matrices are calculated. The double layer C is then stacked together to form a 4-layer slab and the diffraction matrices are again calculated. (after Tong[56])
2.4.3 Comparison of Methods

Computing times for the layer doubling and RFS methods scale as $n_b^3 \log(L)$ and $n_b^2 L$ respectively, where $L$ is the number of layers. However, the RFS method can fail to converge for small interlayer spacings (approximately 1 Å or less), and in such cases the layer doubling method is a useful alternative. An attractive feature of the layer doubling method is that once the layer diffraction matrix $M$ has been computed for the substrate it can be stored and the LEED intensities for different overlayer sites can be calculated, whereas using the RFS procedure each overlayer model must be calculated starting from the one-layer values of Mg'g.

Some limitations on multiple scattering computations are set by possible numerical errors. Within the K-space methods, numerical instabilities can be especially troublesome when the number of beams required in a calculation is large[68], and this is always the case for small interlayer spacings. The relationship between number of beams required for the K-space calculations and the interlayer spacing $d$ has been estimated by Van Hove and Tong[21] as

\[ n_b = A/4\pi \left[ 2(E-V_0) + \log(t)/d \right]^2 \]  \hspace{0.5cm} (2.19)

where $A$ is the area of the unit cell and $t$ is the fraction of the original amplitude of a diffracted beam after propagating through the interlayer spacing $d$. In the computing programs used here in the calculations for the (311) surfaces of copper and nickel, $t$ was set to 0.002.
In cases where \( n_b \) is required to be of the order of 100 or more the computing requirements of all the K-space methods (including the layer doubling method) become unfavorable compared with L-space methods. This has encouraged the use of 'combined space' methods[21] where the L-space representation is used for the scattering by planes of atoms with small interlayer spacings (composite layers) and then the K-space representation is used to calculate the interlayer scattering between the composite layers and the other layers. A perturbative approach developed within the L-space formalism, the reverse scattering perturbation method[69], is useful when interlayer spacings are small.

To illustrate the number of beams required in this work for the multiple scattering calculations for Ni(311), Figure 2.5 shows a map of reciprocal half-space with circles A, B, and C which enclose the numbers of beams used in the calculation, those that emerge from the crystal, and those that appear on the LEED screen for an incident energy of 200eV. It can be seen that a much larger number of beams are required for the multiple scattering calculations than are available for direct measurement.

2.5 PROGRAM FLOW AND THE USE OF SYMMETRY

Computational requirements can be greatly reduced when the direction of incidence coincides with a symmetry axis or symmetry plane[70]. In the K-space representation, the wavefunctions for symmetrically related beams are replaced by a symmetrized linear combination of plane waves. This results in a
Fig. 2.5 A map of reciprocal half-space for nickel(311) with circles A, B, C, which enclose:
A-the number of beams used in the calculation
B-the number of beams that emerge from the crystal
C-the number of beams that appear on the LEED screen for an incident energy of 200eV.
reduction in the number of wavefunctions required for the diffraction matrices, and substantial reductions in computation times can occur (e.g. by a factor of 10 or more).

A flowchart indicating the general procedures followed by the LEED programs used here is shown in Figure 2.6. The beam set and symmetry labels, values for the physical parameters, and the geometry of the proposed structural model are input to the program and beam intensities are calculated for one energy. For the purpose of economy, the energy increments are chosen as the widest possible spacing that does not result in a significant loss of information about peak and trough positions in the $I(E)$ curves. For the values of Voi used in this work (viz. Voi=-4 or -5eV at 100ev incident energy and varied with energy as in equation 2.9), the multiple scattering intensities were calculated at 2eV spacings for energies less than 100ev and 4eV spacings above. The calculated $I(E)$ curves are then interpolated to the same energy grid as the experimental data (2eV) in preparation for the r-factor analysis (Chapter 3).
Fig. 2.6 Flowchart of the LEED programs[21] used to calculate diffracted beam intensities as a function of energy using the layer doubling or RFS methods.
CHAPTER 3

EXPERIMENTAL METHODS
LEED crystallographic studies require theoretical and experimental $I(E)$ curves for comparison. The theoretical $I(E)$ curves for different proposed surface models are generated via the LEED computer programs described in the previous chapter. The experimental curves are obtained from surfaces that have been specially prepared and characterized. This chapter reviews the general techniques of sample preparation and characterization, and the collection of $I(E)$ data. A description is then given of the $r$-factor programs that are used to find the best fit between the two sets of $I(E)$ curves.

3.1 SAMPLE PREPARATION

Sample preparation, before entering the UHV chamber, starts by cutting a high purity single crystal rod to expose the desired surface. This involves mounting the crystal on an aluminum block with a conductive mixture of aluminum powder and plastic cement, and then fixing to a goniometer which allows the orientation to be adjusted. The crystal is oriented to the desired crystallographic plane using back reflection Laue X-ray diffractography\cite{71}. Slices about 1mm thick are cut from the rod using spark erosion ('Agietron', Agie, Switzerland) and the crystal discs are then mounted in an acrylic resin ('Quickmount', Fulton Metallurgical Products). The crystal is polished using a planetary lapping system (DU 172, Canadian Thin Films Ltd.) that uses a polishing jig\cite{72} with alignment micrometers that allow the sample orientation to be adjusted without removing it from the jig. The whole assembly can be mounted on the X-ray diffractometer and thus the crystal
orientation can be readjusted to compensate for errors in alignment introduced during the cutting and polishing stages. Crystals are mechanically polished with progressively finer grades of diamond paste, finishing with either 0.05 micron alumina or 1 micron diamond paste. After polishing, the optical face is aligned by back reflection of a Ne/He laser fixed on an optical bench to less than 1/2° from normal. The assembly is then moved to the X-ray diffractometer, and a Laue picture is taken to ensure that the desired crystallographic plane and the optical face are aligned within ±1/2°. An oriented surface is often acid etched to remove foreign material incorporated into the surface during the polishing process. Finally the sample is ultrasonically rinsed in deionized water, acetone and methanol.

3.2 THE UHV CHAMBER

Ultrahigh vacuum (UHV), required to control the conditions of a surface during an experiment, involves a number of techniques that are illustrated by Figure 3.1. Two vacuum chambers (Varian 240 and FC12 models) were used in this work. Both chambers are constructed of stainless steel and have seals made by compressing OFHC copper gaskets between knife-edge (Conflat) flanges. The initial stage of pumpdown from atmospheric pressure involves the use of a mechanical pump or sorption pumps containing molecular sieve. Sorption pumping is preferable because of oil-free operation, and pressures of about 1 micron (10⁻³ torr) are achieved after chilling the pumps with liquid nitrogen. This initial pumping reduces pressures into the range where ion pumps and titanium sublimation pumps can be
Fig. 3.1  (a) Schematic diagram of the FC12 UHV chamber
(b) Diagrammatic representation of the pumping system:
IP = ion pump
TSP = titanium sublimation pump
SP = sorption pump
started; the latter yield pressures around \(1 \times 10^{-10}\) torr after baking the chamber for about 12 hours at 200-250°C and degassing all the filaments. Ion pumps depend on a discharge to produce ions, and these ions are trapped by magnetic fields and directed on to reactive 'getter' plates (often titanium) which remove the gases either by the formation of stable solid compounds (e.g. as oxides, hydrides or nitrides), or by burial for the noble gases. A titanium sublimation pump simply evaporates films of titanium which have very high pumping rates for reactive gases. More detailed information about UHV equipment and techniques is given by Holland et al[73]; aspects of the handling and selection of materials for UHV are discussed by Rosebury[74].

The following facilities were available in both UHV chambers: a set of LEED optics (Varian 981-0127), a glass viewport to observe the fluorescent LEED screen, an ion gun for cleaning by ion bombardment, a nude ion gauge to monitor the pressure, a sample holder with heating stage, a manipulator which allowed \(x, y, z\) linear translation and two degrees of rotational freedom, a quadrupole mass spectrometer (EAI 150A) to analyze the system gas composition, and a variable leak valve and capillary to admit gases for cleaning or adsorption experiments. The FC12 system was also equipped with a single-pass cylindrical mirror analyzer (Varian 981-2607) and a glancing incidence electron gun for Auger electron spectroscopy. The manipulator used on the Varian 240 chamber has the crystal sample on the rotation axis (Varian 981-0523). The FC12 chamber is built for multi-technique analysis and therefore uses a manipulator (Varian 981-2530) with the sample 2 1/2" off-axis.
On both chambers, the variable leak valve is connected to a gas manifold which has 3 gas bottles attached. Each manifold is pumped by a 20 ℓ/s ion pump.

Magnetic fields in the laboratory are annulled as far as possible by three orthogonal sets of square 'Helmholtz coils'[75] using a Hall probe to set zero field at the sample position. For all experimental data reported in this thesis, the residual field was reduced sufficiently that movement of the specular beam was not detected at energies as low as 10eV. The reduction of the magnetic fields seemed adequate for LEED studies since symmetrically related beams showed the expected equivalence even at low energies.

3.3 AUGER ELECTRON SPECTROSCOPY

Auger electron spectroscopy is an essential technique for characterizing surfaces in modern surface science. The basic process for the emission of Auger electrons is indicated in Figure 1.1. The competing processes associated with relaxation of an initial core hole are photon emission or ejection of an Auger electron, but for core level binding energies less than 2keV the Auger process is the dominant one[76]. The initial core holes are usually formed by electron bombardment, but X-ray or ion beams can also be used. Auger transitions are classified by the three energy levels of the electrons involved in the relaxation. A WXY transition refers to an original core hole in level W being filled by an electron from level X, while the Auger electron is emitted from level Y to leave a doubly positively charged ion. In solids the X and Y levels may be in
the valence band in which case the transition is designated WVV.

The use of AES for quantitative analysis, band structure
determination, and for chemical shift information has been
reviewed by Chang[3]. For the studies in this thesis, AES is
used especially for qualitative surface analysis; the assignment
of observed Auger energies is made by reference to a
handbook[77] which catalogues experimental Auger spectra for the
various elements.

When the excitation source is an electron beam, Auger
electrons produce very small peaks on a slowly varying
background. The ratio of the Auger signal to background in the
intermediate region of Figure 1.3a is approximately 1/10 [3],
and the features in the spectrum are normally enhanced by
electronic differentiation[78]. This can be done using the
conventional LEED optics as a retarding field analyzer, as shown
in Figure 3.2. Taking an Auger spectrum involves ramping the
retarding voltage on grids G2 and G3 (Figure 1.4a) and
collecting the electrons reaching the fluorescent screen.
Derivative spectra are obtained by adding a small modulation
(1kHz) voltage to the ramp applied to the retarding grids and
monitoring the 2kHz component of the output with a lock-in
amplifier (PAR HR8). The screen to grid capacitance, which has
already been substantially reduced by the use of the grounding
grid between the retarding grids and the fluorescent screen
collector, generates a large 1kHz signal at the collector. This
signal must be reduced to avoid saturation of the lock-in
amplifier. The neutralization capacitor between the modulation
transformer and the collector feeds back an out of phase signal
Fig. 3.2  Schematic diagram of LEED optics used as a retarding field analyzer for Auger electron spectroscopy: MCA=multichannel analyzer (Fabritek 1062)
which further reduces the capacitively coupled grid-collector signal. The voltage ramp is controlled by a multi-channel analyzer (Fabritek 1062) linked to a programmable power supply (Kepco OPS2000). The output from the lock-in amplifier is stored in the Fabritek and signal averaged until the S/N ratio is acceptable. The tuned preamplifier is based on the design by Nathan and Hopkins[79]. The circuit is biased at +300V to facilitate the collection of the electrons. Modulation voltages from 3 to 10V (peak to peak) are used with typical primary beam currents (Ip) of 20μA for primary beam energies (Ep) of 2000eV. An Auger spectrum for the energy range 50-550eV can be obtained in 3-5 minutes; it is finally plotted on an X-Y recorder (Hewlett-Packard 7004b).

The existence of a cylindrical mirror analyzer (CMA) on the FC12 system allows a much more sensitive analysis. This arises because the restricted energy range of collected electrons obtained with a CMA reduces the shot noise that limits the sensitivity of retarding field analyzers (LEED optics)[13]. The experimental arrangement for using the CMA is shown in Figure 3.3. The modulation on the outer cylinder is about 3V(peak to peak) at 5-10kHz and a preamplifier is used to isolate the high voltage (2-2.5kV) on the collector of the channel electron multiplier[80]. The front end of the channeltron is usually grounded, but is held at +300V when electrons of less than 50eV are to be detected. The glancing incidence gun increases the surface/bulk sensitivity[81]. The incident beam typically has an energy of 2-3keV, a current of 100-200 μA, and a cross-sectional area <1mm². The CMA is a dispersive analyzer, and as a
Fig. 3.3 Schematic diagram of the experimental set up on the Varian FC12 vacuum chamber using the cylindrical mirror analyzer and glancing incidence electron gun to take Auger spectra.
consequence derivative spectra are obtained by setting the lock-in amplifier at the modulation frequency applied to the outer cylinder[13]. Spectra superior to those obtained with the retarding field LEED optics can be taken in less than 30 seconds with the CMA; moreover they can be displayed directly on an oscilloscope. The latter is convenient for quick monitoring of the composition of different areas of a crystal.

3.4 CLEANING THE SAMPLE

The general method for cleaning crystal specimens under UHV involves Ar+ bombardment, followed by annealing to relieve the bombardment damage. It is generally preferable to start by bombarding the sample at room temperature, and then only heating the sample after Auger spectra show the surface is essentially clean. This avoids contaminating the bulk with impurities introduced during sample preparation, and so hinders the formation of compounds (e.g. metallic carbides) which can be difficult to remove. During Ar+ bombardment, the titanium sublimation pump is used to pump impurity gases (this pump has negligible pumping speed for argon). After a few hours of ion bombarding, the argon is pumped away by the ion pumps, and a new supply of argon introduced via the variable leak valve. When Ar+ bombarding, the system is typically in the 10⁻⁵ to 10⁻⁶ torr range and partial pressures of impurities are usually <1x10⁻⁸ torr. Argon ions with energies in the range 300 to 3000 eV are used for bombarding, although ions with energies at the lower end of this range are preferable when the sample becomes cleaner in order to reduce the bombardment damage. Ion currents are
measured using a Keithley electrometer (DCVTVM 200B) and currents around 1-10μA are typically used.

For annealing, and heating of samples to drive out impurities from the bulk, samples are mounted on resistive heaters (Varian 981-2058) with tantalum clips. The sample temperature is monitored either with a 0.005" alumel-chromel thermocouple spot-welded to the crystal, or with an optical pyrometer (Hartmann and Braun, Frankfurt). The procedures that result in clean, well-ordered surfaces have to be discovered by trial and error. This involves varying the Ar+ bombardment and heating conditions, and using AES and LEED to monitor the surface composition and surface order respectively. Further details for the specific crystals studied here are discussed in the experimental sections of Chapters 4 and 5.

3.5 LEED INTENSITY ANALYSIS

An important parameter for LEED intensity measurements is the direction of incidence. This is controlled here by Varian manipulators which have reproducible motions to better than 1°. A LEED analogue of the X-ray Laue technique is used to determine normal incidence. Polaroid film is exposed by the light from the LEED screen as the incident electron energy is varied from 40 to 250 eV. The sample is then translated (with rotational motions locked) so that a further exposure of the light from the filament of the electron gun can be made. The resulting picture indicates tracks from the movement of the diffracted beams as the energy increases. Normal incidence is indicated when the beam paths intersect at the center of the electron gun. This
condition can be determined to within 1/2° (limitations being set by the finite aperture of the electron gun and the uncertainties in aligning the camera). This procedure is also useful as a method of indicating stray fields which cause curvature in the paths of the diffracted beams. A common method for determining normal incidence involves measuring I(E) curves for symmetrically equivalent beams; this approach is not applicable with the photographic method, where the I(E) curves are only available after developing and analyzing the film.

A description of the LEED optics was given in Chapter 1; here consideration is given to the measurement of diffracted beam intensities. One standard approach involves an internal Faraday cup[82] which can intercept individual diffracted beams, so providing a direct measurement of beam currents. With knowledge of incident beam currents, they can be converted to absolute beam intensities (diffracted beam current divided by the incident beam current), which are related to the calculated reflectivities defined in equation (2.2). The Faraday cup is especially convenient for measurements of the specular beam, since the beam direction does not change with energy (provided the electrons move in field-free space). However, it is less convenient for the non-specular beams whose directions change with energy. Another standard method of LEED data collection involves the use of an external spot photometer[83] to measure the light from the fluorescent screen, but this method also suffers from an inability to measure all beams quickly. Since the multiple scattering calculations automatically give intensities for all diffracted beams, it is advantageous to
employ data collection techniques which can simultaneously measure all the diffracted beam intensities. Also speed of measurement is important in order to avoid changing surface conditions while the measurements are being made. Newer developments in LEED data acquisition methods include the photographic method of Stair et al[84], and most recently the use of low light level TV cameras[85] and the use of multichannel plates. With the latter, sufficient amplification of diffracted beam currents can be obtained so that LEED patterns can be displayed with incident electron beam currents on the order of a nanoampere[86].

The method for intensity measurements used here involves a combined vidicon-photographic procedure[87]. Photographs of the LEED screen are taken through the viewport with a Nikon F2 camera, using Kodak Tri-X 35mm black/white film, with the lens (85mm-f1.8 with K2 extension ring) normally set for 1 second exposures and an aperture of f1.8 or f2.8. A set of photographs from 30 to 300eV in 2eV intervals can be taken in about 4 minutes. As the energy is varied the incident beam current is recorded for normalization of the intensity data. After taking a set of photographs an Auger spectrum is always recorded to assess the degree of surface cleanliness.

Film is developed in a tank using Acufine developer for 5-10 minutes at 75-80°C with gentle agitation. After fixing (Kodak Rapid Fixer-5 minutes) a permanent record of the diffraction patterns as a function of energy is available for determining I(E) curves. The analysis follows the procedures described by Frost et al[87]. Photographic negatives are scanned
by a vidicon camera; each region around a diffraction spot is
digitized (vidicon and digitizer, Spatial Data Systems, Galena,
California) and the density values are integrated subject to a
background subtraction to yield one intensity value per
diffracted spot per energy. It is assumed here that the density
of the film is directly proportional to the luminance of the
screen, which in turn is assumed to be proportional to the
impinging electron current. Further, the linearity of the
integrated digitized output with film density is assumed so that
the vidicon output is a measure of the relative intensity of a
diffracted beam. The relative intensities are stored on cassette
tape and can be transferred via paper tape to the University
Computing Centre (IBM 370/168 later replaced by Amdahl 470 V8)
for comparison with the calculated I(E) curves.

3.6 THE R-FACTOR PROGRAMS

The procedure of selecting the best model for the surface
graph was originally done by visual comparison of the
experimental and calculated I(E) curves. However, with 10 or
more experimental beams and often at least 20 geometries to be
considered, the visual method is inevitably unwieldy. This is
particularly true since the inner potential, Vor, used in the
calculations, also needs some refinement. Such considerations
point to the advantages of numerical indices which signify the
levels of agreement between two sets of I(E) curves; such
indices may also indicate measures of the 'reliability' of a
determination. Several reliability indices, or r-factors, have
been proposed[88]. Many compare the energies and/or shapes of
peaks and troughs in the calculated and experimental I(E) curves, without regard to the absolute values of the intensities. Two r-factors are used and discussed here; namely those proposed by Zanazzi and Jona[41], and by Pendry[42].

For later reference it is useful to distinguish here between an r-factor \((r_i)\) for an individual (the ith) beam and an overall r-factor, \(R\), built up from a set of \(r_i\). One useful parameter for describing the geometry of a clean surface is the topmost interlayer spacing \((d)\) which may vary significantly from that of the bulk value \((d_0)\), even though the second and successive spacings essentially equal \(d_0\). The changes in the topmost spacing are often expressed as percentage changes, namely as

\[
\Delta d\% = 100 (d-d_0)/d_0
\]

For the analysis involved in assessing uncertainties in the determined surface geometry, \(gmin_i\) is used to indicate the value of \(\Delta d\%\) where \(r_i\) is minimized, while \(Gmin\) indicates the topmost spacing corresponding to the minimum in \(R\).

An r-factor comparison normally allows for variation in Vor by shifting the energy scale for one set of I(E) curves relative to the other. A convenient way of presenting this comparison is with contours of \(R\) values plotted as functions of Vor and \(\Delta d\%\) (e.g. Figures 4.8 and 4.16).
3.6.1 The Reliability Index of Zanazzi and Jona

The Zanazzi and Jona index for an individual beam takes the shapes of the experimental and calculated \( I(E) \) curves into account by comparing first and second derivatives. The specific expression used for the reduced \( r^{(i)} \) value is

\[
\begin{align*}
  r^{(i)} &= \sum w(E) |C_{th}-I_{exp}| dE / \int 0.027 I_{exp} dE \\
  C &= \sum I_{exp} dE / \int I_{th} dE \\
  w(E) &= |C_{th}-I_{exp}| / (|I_{exp}| + X)
\end{align*}
\]  

(3.2)  
(3.3)  
(3.4)

Here \( I_{exp} \) and \( I_{th} \) are the experimental and theoretical intensities, a single prime represents the first derivative with respect to energy, a double prime represents the second derivative. The \( I_{exp} \) value in the expression for \( w(E) \) increases the weights, in the comparison, of maxima and minima in the experimental curves; \( X \) is chosen as the maximum absolute value of \( I_{exp} \), namely

\[
X = |I_{exp}|_{\text{max}}
\]  

(3.5)

to prevent the denominator in (3.4) from equalling zero. The coefficient \( 0.027 \) in (3.2) is a normalization factor determined by matching random sets of data[41].

To apply to many-beam analyses, a multi-beam index (\( \bar{r}_r \) in notation of Zanazzi and Jona) is calculated by weighting the contributions of the individual beams by their energy range

\[
R_{zj} = \sum_{i=1}^{M} r^{(i)} E^{(i)} / \sum_{i=1}^{M} E^{(i)}
\]  

(3.6)
where $E(L)$ is the energy range of available $I(E)$ data for the $i$th beam. Zanazzi and Jona introduced another quantity $R$ which was dependent on the number of beams used in the analysis. However, provided a reasonable number of beams (e.g., $>8$) is used, $R$ seems not to have any advantages over the use of $R_{zj}$.

Clearly, the better the level of correspondence between a set of experimental and calculated $I(E)$ curves, the lower the value of $R_{zj}$. Zanazzi and Jona proposed that values of $R_{zj}<0.2$ indicate that the structural model used in the calculations is probably correct, whereas values of $R_{zj}>0.5$ indicate poor agreement and that the proposed model is probably incorrect.

3.6.2 The Pendry R-factor

Pendry has constructed an $r$-factor that uses only first derivatives and therefore involves less computation than the Zanazzi and Jona $r$-factor. Pendry's multi-beam index is

$$R_p = \sum \frac{(Y_{ith}-Y_{iexp})^2 dE}{\sum (Y_{ith}^2 + Y_{iexp}^2) dE} \quad (3.8)$$

$$Y = \frac{L^{-1}}{(L^{-2} + V_{oi}^2)} \quad (3.9)$$

$$L = \frac{I'}{I} \quad (3.10)$$

where, for example, $Y_{ith}$ is the logarithmic function for the $i$th calculated beam. The value of $V_{oi}$ used for both $Y_{ith}$ and $Y_{iexp}$ in (3.9) is the same value that is used in the multiple scattering calculations of the $I(E)$ curves. The Pendry $r$-factor is most sensitive to the positions of peaks and troughs in the $I(E)$ curves and, because of the logarithmic derivatives involved, it gives all the maxima and minima approximately equal
weights in the comparisons. Rp values of zero indicate that all corresponding experimental and calculated I(E) curves are identical; values of Rp close to 1.0 implies there is no correlation between the calculated and experimental curves.

3.6.3 R-factors and Error Estimation

An important objective of the reliability index approach is to provide an estimate of the uncertainty in the value of an interlayer spacing found for a minimum R value. We have examined three approaches for estimating these uncertainties; all being based on standard errors[89]. In the discussions that follows, Vor is assumed to be fixed at the value which minimizes R.

The first method for estimating uncertainties involves calculating the standard error from the \( r^{(l)} \) values at minimum R, and then relating this to an uncertainty in geometry by using the specific dependence of R on \( \Delta d_\% \). For a comparison involving N experimental I(E) curves

\[
U\{1\}R = \sqrt{\frac{\sum W^{(l)} (R_{min} - r^{(l)})^2}{(N-1)}}
\]

(3.11)
gives the standard error in R. In (3.11), \( W^{(l)} \) is the weight of an individual beam (detailed further below). Figure 3.4b shows how \( U\{1\}G \), the corresponding uncertainty in geometry, can be determined from \( U\{1\}R \).

Difficulties with \( U\{1\}R \) for estimating uncertainties can arise because of an implication that the set of \( r^{(l)} \) values fit a normal distribution (i.e. implies that deviations in \( r^{(l)} \) from their mean are the result of random errors). In principle, it is
possible that all $r^{(i)}$ values could go through minima at the same $\Delta d\%$ but show large differences in the absolute value of $r^{(i)}$[90]. Furthermore, the multi-beam $R_{zj}$ vs. $\Delta d\%$ curves are in practice rather smoother than would be expected from the comparatively large uncertainties indicated by $U(1)R$, while the $g_{\text{min}}^{(i)}$ values for the individual beams can all be grouped well within the range of $\Delta d\%$ corresponding to $U(1)R$ (ie. $U(1)G$). This is illustrated in Figure 3.4b for a model situation involving the comparison of two pairs of experimental and calculated $I(E)$ curves (and hence two single beam indices $r^{(1)}$ and $r^{(2)}$), where both comparisons show best agreement at the same value of $\Delta d\%$, but the absolute values of $r^{(1)}$ and $r^{(2)}$ are quite different. For such a situation the differences in $r^{(i)}$ values may not be due to random errors, but rather to systematic experimental uncertainties (e.g. associated with surface roughness or errors in angles of incidence) which affect some beams more than others. For example, beams furthest from the surface normal are likely to be more affected by protuberances in the surface.

Another difficulty with the use of $U(1)$ occurs in a situation where there is considerable scatter in the individual beam minima, but it is still possible to obtain small errors in $R$. Figure 3.4a shows a model situation where two beams indicate very different topmost interlayer spacings ($g_{\text{min}}^{(1)}, g_{\text{min}}^{(2)}$), and yet $U(1)$ would be negligible since the $r^{(i)}$ values are equal at the minimum in $R$.

A second method for estimating uncertainties calculates the standard error of the weighted mean of the $g_{\text{min}}^{(i)}$ values[90]
Fig. 3.4 Model r-factor versus geometry plots for two situations involving two different beams. Top illustration suggests a possible failure of $U(1)$ to represent the difference in 'best fit' geometries ($g_{\text{min}}^{(1)}$, $g_{\text{min}}^{(2)}$) found for the individual beams. Bottom diagram shows the large $U(1)$ value that can be found because of the differences in the absolute $\Delta r^{(i)}$ values even when both beams show their best agreement with the same structural model.
\[ U(2)G = \sqrt{\frac{\sum_i W^{(i)} (g_{\text{min}}^{(i)} - G',\text{min})^2}{(N-1)}} \]  

(3.12)

where \( G',\text{min} \) is the weighted mean of the individual \( g_{\text{min}}^{(i)} \) values

\[ G',\text{min} = \frac{\sum_i W^{(i)} g_{\text{min}}^{(i)}}{\sum_i W^{(i)}} \]

\( U(2)G \) has been used for assessing uncertainties in much of this work, although it has a potential weakness insofar as it does not take into account the 'shapes' of the individual \( r^{(i)} \) vs. geometry curves. Often some of these curves do not show a strong structural dependence, and therefore do not significantly influence the overall structural determination. It is suggested here that such flat curves should not contribute substantially to error estimates, although this is not the case for \( U(2)G \). A third approach, which does take curve shape into account, is

\[ U(3)R = \sqrt{\frac{\sum_i W^{(i)} (\Delta r^{(i)})^2}{(N-1)}} \]  

(3.13)

where the \( \Delta r^{(i)} \) values are the differences between \( r^{(i)} \) values at \( G_{\text{min}} \) and \( r^{(i)\text{min}} \) at \( g_{\text{min}}^{(i)} \). \( \Delta r^{(1)} \) and \( \Delta r^{(2)} \) are shown in Figure 3.4a. Error estimates using \( U(3)R \) give the greatest weighting to the sharpest \( r^{(i)} \) vs. geometry curves. For the situation in Figure 3.4a, beam 1 would be given a larger weighting in the calculation of \( U(3)R \) than beam 2 since \( \Delta r^{(1)} \) is larger than \( \Delta r^{(2)} \).

These calculations of uncertainties require a weighting factor \( W^{(i)} \) for each beam. In the multibeam reliability index of
Zanazzi and Jona[40] this is taken as

\[ W(L) = \frac{E^{(i)}}{\sum E^{(i)}} \]  

(3.14)

and the same weighting factors are used in equations (3.11)-(3.13) for analyses involving the Zanazzi and Jona index. However, the calculation of the multibeam index of Rp involves a weighting factor for each individual beam depending on the value of \( Y_{2i}^{\text{exp}} + Y_{2i}^{\text{th}} \). To provide an overall consistency, calculations of uncertainties based on Rp values use the weight of an individual beam given by

\[ W^{(i)} = \frac{\int (Y_{2i}^{\text{exp}} + Y_{2i}^{\text{th}}) dE}{\sum \int (Y_{2i}^{\text{exp}} + Y_{2i}^{\text{th}}) dE} \]  

(3.15)

The three methods noted for estimating uncertainties treat each experimental I(E) curve as an independent measurement; this is indicated by division by \((N-1)\) where \(N\) is the number of non-equivalent beams. However, the energy ranges over which intensities for individual beams can be measured are often quite different since the higher index beams appear on the fluorescent screen only at higher energies. This opens the question of whether the unit of intensity information, here identified with a whole I(E) curve of an individual beam, should be defined in some alternative way, for example by a fixed energy range, or by a certain amount of structure (e.g. number of peaks, troughs, shoulders) in the I(E) data. However, such possibilities have not yet been analyzed.

It must be assumed that these analyses are applicable to situations where the best-obtainable agreement between
experimental and calculated I(E) curves has been reached through the variation of both geometrical and non-geometrical parameters (e.g. phase shifts, Vor, Voi, and Debye temperature) in the multiple scattering calculations. The question being considered in this subsection concerns the uncertainty in geometry associated with the residual discrepancy, as shown by the non-zero values of Rp or Rzj. The value of the methods indicated here for estimating uncertainties can only be assessed through their application to data for many different surfaces.
CHAPTER 4

STUDIES OF THE (311) SURFACES OF COPPER AND NICKEL
4.1 INTRODUCTION

The clean, principal low-index surfaces of copper and nickel have been studied previously by the methods of LEED crystallography [91-94]. The work presented here represents the first studies of stepped surfaces which employ dynamical calculations to determine surface geometries.

The surface net vectors of a fcc (311) surface are shown in Figure 4.1; a diagram of the corresponding reciprocal net vectors is in Figure 4.2. According to the conventions of the International Tables of X-ray Crystallography[95], the (311) surface belongs to the cm two-dimensional space group and can be represented by a centered-rectangular net. The intensities of the (h,k) beams are zero when h+k is odd. The (311) surface of a fcc metal is a stepped surface consisting of (111) terraces and (100) steps of monoatomic height and would be designated \{2(111)x(100)\} following the notation of Lang, Joyner and Somorjai[96]. It can also be represented by a primitive mesh of comparatively small area, which makes it a suitable candidate for multiple-scattering calculations.

The study of the (311) surface of copper is presented first. The determination of the Ni(311) surface geometry follows, and this Chapter also includes an examination of the sensitivity of the r-factor analysis to some of the experimental and data handling methods commonly employed in LEED crystallography.
Fig. 4.1 Illustration of the centered-rectangular net that describes a fcc(311) surface.
Fig. 4.2 Reciprocal net vectors and beam labels corresponding to the surface net shown in Fig. 4.1.
4.2 COPPER (311)

4.2.1 Experimental

Data for the Cu(311) surface were obtained in the Varian 240 chamber described in Chapter 3. The copper specimens were cut by spark erosion from a 99.999% purity crystal rod. The crystal slice was prepared following the procedure given in Section 3.1 except that a saturated solution of CuCl in HCl was used in the last polishing stage with the one micron diamond paste[97]. The sample was mounted on a standard Varian resistive heater and a chromel-alumel thermocouple was attached. After bakeout, large amounts of carbon and sulphur as well as some phosphorus, and either boron or chlorine, were seen in the Auger spectra taken using the LEED optics. The sample was cleaned by cycles of Ar+ bombardment (1-2μA, 300-400eV) and annealing at 400-700°C. With this method, all contaminants except carbon could be removed to below the detection limit of the retarding field analyzer. Most of the residual carbon could be removed by heating the sample for 15-20 minutes in 1x10⁻⁶ torr of oxygen, followed by a further Ar+ bombard and a final anneal for 10 minutes at 400-500°C. Surfaces could be obtained with carbon Auger peak heights reduced to less than 1/100 of that for the 63eV peak of copper. The detectable limit for Auger signals was about 1/200 of the Cu(63eV) peak height. Using the relative sensitivities of the Auger signals for carbon and copper from the spectra given by Palmberg[77], the residual carbon contamination appears to correspond to less than 5% of a monolayer. From the values of S(150eV)/Cu(63eV) peak ratios given by Argile and Rhead[98], the minimum detectable sulphur
contamination would be about 1-2% of a monolayer. An Auger spectrum of a cleaned surface is shown in Figure 4.3b with the spectrum of a contaminated surface shown for comparison in Figure 4.3a.

No evidence of faceting or reconstruction of the surface was indicated from observations of the LEED diffraction patterns. Adsorbed overlayers of both oxygen and sulphur did not produce any well-ordered LEED patterns, but often showed streaks that correspond to partial ordering along the steps on the (311) surface.

Photographs of the normal incidence diffraction pattern displayed on the LEED fluorescent screen were taken at 2eV intervals from 50 to 230eV. A second independent set of data was taken to check for the reproducibility of the experimental I(E) curves. The photographs were analyzed using the vidicon camera-digitizer system and data for 17 beams, including 4 equivalent pairs, were output on paper tape for subsequent comparison with the theoretical calculations.
Fig. 4.3a) Auger spectrum of a contaminated Cu(311) surface taken using the LEED optics as an energy analyzer (Ep=1500eV, Ip=20μA).

Fig. 4.3b) Auger spectrum of the cleaned Cu(311) surface.
4.2.2 Calculations and R-factor Results

Due to the relatively close bulk interlayer spacing, (1.09Å), the layer doubling method was chosen for the calculations. Eight phase shifts were used, and they were obtained from the potential of Burdick and Chodorow[99]. The vibrational amplitudes for both the top layer and the bulk layers were set equal using the surface Debye temperature ($\Theta_p=270^\circ K$) measured for the Cu(111) surface[100]. The maximum number of beams made available for the calculation of the diffraction matrices was 67 and this resulted in CPU times of about 100s for each energy point on the IBM 370/168 computer.

An initial value of -9.5eV (best value found for Cu(111) by Watson et al[90]) was chosen for $\nu_0$ in the multiple-scattering calculations; this value was then refined during the r-factor comparison with the experimental I(E) curves by rigidly shifting the energy scale. After examining the narrowest peaks in the experimental data, $\nu_0$ was set to -4.5eV at 100eV energy and was given the $1/3$ power energy dependence in equation (2.9). The top layer spacing was the only geometrical parameter which was allowed to vary; calculations were made for nine $\Delta d\%$ values from $+5.0\%$ to $-15.0\%$. Figures 4.4-4.7 compare some of the experimental I(E) curves with those from the calculations for different topmost layer spacings. The remaining experimental I(E) curves are presented in Appendix 1.

The r-factor analysis of Zanazzi and Jona was used in the comparison between the calculated and experimental I(E) curves and a minimum value of $R_{\text{ZJ}}=0.088$ was found with the corresponding $\Delta d\%$ equal to $-5.0\pm1.5\%$. A contour plot of the
multi-beam Rzj values for various Vor and topmost interlayer spacings is shown in Figure 4.8. The experimental I(E) curves used in the comparison were smoothed once with a three-point smoothing routine using 1:2:1 weights. The error limits on the final determination are given by U{2}G (eqn.3.12).
Fig. 4.4 (0,-2) beam measured at normal incidence from Cu(311) compared with calculated I(E) curves for various topmost interlayer spacings.
Fig. 4.5 (1,-3) and (-1,-3) beams measured at normal incidence from Cu(311) compared with calculated I(E) curves for various topmost interlayer spacings.
Fig. 4.6 (1,5) beam measured at normal incidence from Cu(311) compared with calculated I(E) curves for various topmost interlayer spacings.
Fig. 4.7 (1,1) and (-1,1) beams measured at normal incidence from Cu(311) compared with calculated I(E) curves for various topmost interlayer spacings.
Fig. 4.8 A contour plot of the multi-beam Rzj values for the copper(311) normal incidence data as a function of Vor and Ad%. 
4.3 NICKEL(311)

The study of the structure of the (311) surface of nickel was more extensive than that for the corresponding surface of copper insofar as it included an investigation of many of the procedures that are used in LEED crystallography. This work represents a continuation of studies already done by this group in assessing the sensitivity of the r-factor analysis to the values of the non-structural parameters involved in the theoretical calculations[101]. These studies were done to find guidelines for procedures that will allow more definitive results to be obtained from the comparison of the calculated and experimental I(E) curves.

4.3.1 Experimental

The (311) faces used in these experiments were cut by spark erosion from a 99.999% purity, 1/4" diameter single crystal nickel rod oriented using Laue photographs to within 1/2° of the (311) direction. Each sample was then mechanically polished (0.05 micron alumina), mounted on a Varian heater assembly, and a 0.005" chromel-alumel thermocouple was spot-welded to the crystal edge. The specimen was introduced into the Varian FC12 UHV chamber where the surface was cleaned and ordered by cycles of Ar+ bombardment (500-2000eV, 1-10μA) and heating at 700°C. Sulphur and carbon were the principal contaminants and sulphur proved very troublesome since it diffused to the surface quickly at temperatures above 600°C. After many hours of alternating Ar+ bombardment and annealing, the sulphur contamination could be reduced to minimal levels provided the anneal after argon
bombarding did not exceed 1/2 hour at 600°C. Photographs of the LEED pattern at normal incidence were taken at 2eV intervals over the energy range 50 to 230eV; this was repeated for an independently cleaned and aligned sample, and yet again for a slightly contaminated surface which had been allowed to 'soak' for about 3 hours at 2x10^{-10} torr. Figures 4.9a,b show Auger spectra of the contaminated and cleaned surfaces. Using the relative Auger peak heights S(150eV)/Ni(865eV), for sulphur adsorbed on nickel surfaces given by Demuth[102], the sulphur impurity level for our cleaned Ni(311) surfaces corresponds to less than 2% of a monolayer.

The LEED patterns indicated that contaminants on the Ni(311) surface often ordered; (1x2), (2x5), (2x1), and (2x3) patterns were observed for sulphur diffused from the bulk. Oxygen and carbon impurities produced streaks in the S2* direction, with indications of a partially ordered (1x2) structure. No measurements of I(E) curves were made for these overlayer structures.
Fig. 4.9a Auger spectrum of a contaminated Ni(311) surface taken using the CMA on the FC12 vacuum system with $E_p=2500\text{eV}$, $I_p=100\mu\text{A}$.

Fig. 4.9b) Auger spectrum of a cleaned Ni(311) surface.
4.3.2 Calculations and R-factor results

The layer doubling method used for the multiple scattering calculations on Cu(311) was also used for Ni(311) in conjunction with the following values for the non-structural parameters; \( V_{or} = -10.0 \text{eV}, \ V_{oi} = -0.9E^{1/3}\text{eV (E in eV)}, \ \Theta_D = 380^\circ\text{K} \). The value for \( V_{oi} \) was obtained with equation 2.9 after measuring the widths of the narrowest peaks in the experimental \( I(E) \) curves. The value used for the Debye temperature was obtained by averaging the vibrational amplitudes determined by Clark et al\[103\] for the first five layers, with weighting 0.38, 0.26, 0.17, 0.12, 0.07 suggested by the attenuation of 100eV electrons propagating between the layers with \( V_{oi} = -4 \text{ev} \). These non-structural parameters are reasonably similar to those used by Demuth et al\[94\] for studies of the low index surfaces of nickel. The multiple scattering calculations for Ni(311) used eight energy dependent phase shifts derived from Wakoh's band structure potential\[104\], and were run for the energy range 50 to 200eV, for nine topmost interlayer spacings (\(-24 \leq \Delta d \% \leq 0\)). The range of contractions considered was determined after a preliminary calculation had indicated a contraction of 12\% or greater. Up to 51 non-equivalent beams were included in the calculations of the bulk diffraction matrices.

The \( I(E) \) curves so calculated showed unphysical spikes or 'crashes' at some particular energies and geometries. Such numerical instabilities have been observed by others\[105\], and they proved particularly troublesome at higher energies. In order to facilitate the development of automatic assessments of experimental and calculated \( I(E) \) curves, it is important that
such irregular features can be readily identified. Often their existence is obvious, however, since this is not always the case, methods are needed for detecting and correcting any intensities that have been so affected.

In this study it was found that a plot of the sum of the reflected intensities vs. $\Delta d\%$ for particular energies provided a convenient and effective way of detecting the incorrectly calculated data points (which appear displaced from an otherwise smooth curve), even when there were no obvious indications in the I(E) curves that an error had occurred. An example of this procedure is detailed in Figures 4.10a,b,c. When errors were found, the intensities were recalculated for different numbers of beams. The 'crashed' diffracted intensities were replaced by intensities calculated for the largest number of beams that could be used before any numerical errors became apparent. The success of this approach is illustrated by Figures 4.10a-d which show plots of intensity vs. geometry for calculations using different number of diffracted beams. For calculations at energies that did not show any numerical errors the intensities obtained using 42 beams were usually changed by less than 5% from those obtained from calculations involving 51 beams. Figure 4.10d shows a plot, for different numbers of beams, of the sum of reflected amplitudes (RA) of the diffracted beams.

$$RA=\sum_{i} |R_i^-(\text{real})| + |R_i^-(\text{imaginary})| \quad (4.1)$$

where $R^-_i$ is the reflected amplitude for the $i$th beam in the $-z$ direction. RA values were obtained from the subroutine which
Fig. 4.10 a) Sum of emergent beam intensities vs. $\Delta \delta$% at 200eV. 
b), c) Reflected intensity vs. $\Delta \delta$% at 200eV for (0,0) and (1,3) beams. 
The calculations with 42 or 51 beams yield the same intensities (on this scale) except at $\Delta \delta$% = -18 where the calculation with 51 beams fails to converge.) 
d) RA (equation 4.1) plotted as a function of the number of beams used in the calculation of the bulk diffraction matrices at 200eV.
calculates the diffraction matrices for the bulk layers.

The assessments of the experimental and calculated \( I(E) \) curves using the reliability index of Zanazzi and Jona yielded optimal agreement when \( \Delta d\% = -14.7 \pm 2.6 \) (\( R_{zj} = 0.12 \)), while that of Pendry gave \( \Delta d\% = -14.4 \pm 2.2 \), (\( R_p = 0.32 \)). The uncertainties quoted are the values of \( U(2)G \) (eqn 3.12). Examples of \( I(E) \) curves for Ni(311) are shown in Figures 4.11-4.15. Here each experimental curve is plotted above the set of curves calculated for \( \Delta d\% \) values ranging from -24 to 0. Contour plots of \( R_{zj} \) and \( R_p \) versus \( \Delta d\% \) and \( V_{or} \) are shown in Figures 4.16 and 4.17 respectively. Appendix 1 contains further \( I(E) \) curves measured for normal incidence on Ni(311).
Fig. 4.11 (0,4) beam measured at normal incidence from Ni(311) compared with I(E) curves calculated for \( \Delta d \) from -24 (0.80Å) to 0 (1.06Å).
Fig. 4.12  $(0,2)$ beam measured at normal incidence from Ni(311) compared with $I(E)$ curves calculated for $\Delta d_\parallel$ from -24 (0.80Å) to 0 (1.06Å).
Fig. 4.13 (0,-2) beam measured at normal incidence from Ni(311) compared with I(E) curves calculated for Δδ% from -24 (0.80Å) to 0 (1.06Å).
Fig 4.14 (0,-4) beam measured at normal incidence from Ni(311) compared with I(E) curves calculated for $\Delta d%$ from -24 (0.80Å) to 0 (1.06Å).
Fig. 4.15 (1,-1) beam measured at normal incidence from Ni(311) compared with $I(E)$ curves calculated for $\delta_d$ from $-24$ to 0 ($1.06\%$).
Fig. 4.16 Contour plot of values of multi-beam index \( R_{zj} \) for \( I(E) \) curves measured at normal incidence from a Ni(311) surface as a function of inner potential (\( V_{or} \)) and percentage change in the topmost interlayer spacing (\( \Delta d\% \)).
Fig. 4.17 Contour plot of values of multi-beam index $R_p$ for $I(E)$ curves measured at normal incidence from a Ni(311) surface as a function of inner potential ($V_{or}$) and percentage change in the topmost interlayer spacing ($\Delta d\%$).
4.4 THE R-FACTOR AND THE NICKEL EXPERIMENTAL DATA

Since the determination of surface geometry involves the comparison of experimental and calculated I(E) curves, it is important to know whether the results derived from such comparisons are sensitive to changes in the mode of treatment of the experimental data. An investigation was made here of the effects on Rp and Rzj of smoothing the experimental data, of averaging experimental I(E) curves that should be symmetrically equivalent, and of correcting the measured intensities for differences in grid transparency. Reliability index comparisons were also made between experimental beams which should be equivalent at normal incidence, and between corresponding beams in independently measured sets of data.

4.4.1 Effects of Grid Transparency

When a LEED pattern is observed through the window of the vacuum chamber, the hemispherical grids have different transparencies for light coming from different parts of the screen. For the experimental set up shown in Figure 4.18, Legg et al[106] have corrected for the variation in grid transparency with a treatment which assumes that the light is emitted from the phosphor according to the cosine law (expected for a rough surface). From simple geometry for a four-grid system, an actual intensity I is changed to an apparent intensity I' by I' = T(w)I, where T(w) has the form

\[ T(w) = t^4(1 - d/s)^4 \sin(w) \]  \hspace{2cm} (4.2)
Fig.4.18 Experimental arrangement for LEED intensity measurements showing the angles and distances relevant to equation 4.2 which corrects for the differences in grid transmission as a function of beam position on the LEED screen (all dimensions in mm).
where \( t = 1 - \frac{d}{s \sin(w)} \), \( d \) is the diameter of the grid wires and \( s \) their separation.

Figure 4.19 shows an example of the effect of this correction on a particular experimental I(E) curve. The effect of the transparency correction is to increase the beam intensities for lower energies. A question of importance to the present study concerns whether surface structural determinations are affected by this correction. The effects of this procedure for data from Ni(311) for the reliability indices \( R_{zj} \) and \( R_p \) were found to be rather small. The \( R \) values were reduced slightly with the correction (specifically \( R_{p\text{min}} = 0.33 \) uncorrected, \( R_{p\text{min}} = 0.32 \) corrected, \( R_{zj\text{min}} = 0.14 \) uncorrected, \( R_{zj\text{min}} = 0.12 \) corrected), but changes in \( G_{\text{min}} \) turned out to be less than 1% (0.01Å).

4.4.2 Smoothing

Some smoothing of experimental I(E) curves is generally necessary to remove noise and thereby avoid extraneous structure which can affect the values of the derivatives required for the r-factor calculations. Figure 4.20 shows a plot of \( R_p \) vs. \( \Delta d \% \) for the comparison of calculated I(E) curves with experimental curves that have undergone up to three smoothing operations. A single operation of smoothing was done according to

\[
I(E) = \frac{[Ir(E-e) + 2Ir(E) + Ir(E+e)]}{4} \quad (4.3)
\]

where the \( Ir \) indicate raw or input intensities, and \( e \) is the spacing of the energy grid for the experimental intensities.
Fig. 4.19 The (0, -4) beam measured at normal incidence from Ni(311) before and after correcting for the differing transmission of the LEED grids as a function of energy. Largest changes occur at the lowest energies.
4.20 Multi-beam index $R_p$ plotted as a function of $\Delta d\%$. The $R_p$ values are from the comparison of $I(E)$ curves measured at normal incidence from Ni(311), that have been smoothed up to 3 times, with calculated $I(E)$ curves for changes in the topmost interlayer spacings in the range from -24% to 0%.
Figure 4.20 indicates that a limited amount of smoothing gives a reduction of $R_p$ values, although after excessive smoothing values of $R_p$ increase. $R_{p_{min}}, G_{min}$ and associated uncertainties are listed in Table 4.1 for the comparison of $I(E)$ curves calculated for $\Delta d_\%$ values in the range $-24$ to $0$ with experimental data that has been smoothed $0, 1, 2, 3$ times. The uncertainty in the structural determination is largest for unsmoothed data and there are only small differences in the values of $G_{min}$ obtained for data that has undergone different amounts of smoothing.

4.4.3 Averaging Symmetrical Beams

At normal incidence the mirror plane present in the (311) surface results in the equivalence of the $(h,k)$ and $(-h,k)$ diffracted beams. The experimental data available for Ni(311) consisted of 14 individual beams, including 4 pairs of symmetrically equivalent beams. $R$-factor comparisons were made for the data in two ways: (i) for all 14 beams, and (ii) for 10 beams where pairs of $I(E)$ curves which are expected to be equivalent are averaged. In this analysis, every beam was treated as a separate measurement for the multi-beam $R_p$ values and the uncertainties. The Pendry $r$-factor determinations give for (i) $\Delta d_\% = -14.4 \pm 2.2$ at $R_{p_{min}} = 0.315$, and for (ii) $\Delta d_\% = -13.8 \pm 2.0$ at $R_{p_{min}} = 0.323$. The change in $G_{min}$ and the increased $R_{p_{min}}$ value are associated with the equivalent beams being given a smaller weighting in (ii) compared with (i). There is a reduction in $U_{\{1,2,3\}}$ values for the averaged set and the $r^{(i)}$ values for an averaged beam were always slightly smaller than the average $r^{(i)}$. 
Table 4.1 Pendry R-factor, A d%, and uncertainty values where Rp is minimized, for the comparison of calculated I(E) curves for Ni(311) with experimental data that has been smoothed 0, 1, 2, 3 times. These values were obtained for Vor=-10eV.

<table>
<thead>
<tr>
<th>Rp_{min}</th>
<th>G_{min}</th>
<th>U(1)G</th>
<th>U(2)G</th>
<th>U(3)G</th>
</tr>
</thead>
<tbody>
<tr>
<td>RAW DATA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.378</td>
<td>-14.1</td>
<td>±2.6</td>
<td>±2.1</td>
<td>±2.9</td>
</tr>
<tr>
<td>SMOOTHED ONE TIME</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.332</td>
<td>-14.1</td>
<td>±2.4</td>
<td>±1.9</td>
<td>±2.8</td>
</tr>
<tr>
<td>SMOOTHED TWO TIMES</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.320</td>
<td>-14.4</td>
<td>±2.5</td>
<td>±1.9</td>
<td>±2.6</td>
</tr>
<tr>
<td>SMOOTHED THREE TIMES</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.329</td>
<td>-14.4</td>
<td>±2.8</td>
<td>±2.0</td>
<td>±2.5</td>
</tr>
</tbody>
</table>
value of the two equivalent beams. It may be that averaging simulates a correction for deviations in the angle of incidence. For deviations from normal incidence, one of the set of equivalent beams propagates so that interlayer spacings are slightly smaller than those experienced at normal incidence and the symmetrical beam experiences slightly longer interlayer spacings. Generally, this would result in the peaks in the I(E) curves shifting to higher and lower energies respectively, and thus it is not unreasonable that the averaged data can have peaks at positions which are closer to expectation for normal incidence. Figure 4.21 shows the experimental I(E) curves for a pair of beams which are expected to be equivalent in the ideal situation, as well as their average.

4.4.4 Comparison of two sets of experimental data

Single beam r-factor comparisons were made for two independent sets of experimental I(E) curves, and values from both Zanazzi and Jona's and Pendry's reliability index calculations are listed in Table 4.3. Table 4.2 includes data on the r-factor comparison of symmetrically related beams from the same experiment. Comparisons of I(E) curves between corresponding beams in the two experiments, or for equivalent beams within a single experiment, always yielded lower single beam r-factors than those determined for one experimental I(E) curve compared with the calculated I(E) curve which gives best agreement. Figures 4.22 and 4.23 show some examples of the experimental I(E) curves involved in the comparisons in Table 4.2.
Fig. 4.21. (1,-1) and (-1,-1) beams and their average from data measured at normal incidence for the Ni(311) surface.
Table 4.2 Single beam r-factor values for the comparison of pairs of nominally symmetric beams measured at normal incidence from Ni(311).

<table>
<thead>
<tr>
<th>BEAMS</th>
<th>ZANAZZI AND JONA</th>
<th>PENDRY</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,1) (-1,1)</td>
<td>0.028</td>
<td>0.041</td>
</tr>
<tr>
<td>(1,-1) (-1,-1)</td>
<td>0.042</td>
<td>0.125</td>
</tr>
<tr>
<td>(1,-3) (-1,-3)</td>
<td>0.030</td>
<td>0.180</td>
</tr>
<tr>
<td>(1,3) (-1,3)</td>
<td>0.039</td>
<td>0.064</td>
</tr>
</tbody>
</table>

Table 4.3 Single beam r-factor values for the comparison of corresponding beams measured at normal incidence from Ni(311) from two independent experiments. Superscripts on beam labels indicate the source of the I(E) curve (i.e. either experiment 1 or 2).

<table>
<thead>
<tr>
<th>BEAMS</th>
<th>ZANAZZI AND JONA</th>
<th>PENDRY</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,-4)¹ (0,-4)²</td>
<td>0.056</td>
<td>0.045</td>
</tr>
<tr>
<td>(0,-2)¹ (0,-2)²</td>
<td>0.028</td>
<td>0.041</td>
</tr>
<tr>
<td>(0,2)¹ (0,2)²</td>
<td>0.034</td>
<td>0.040</td>
</tr>
<tr>
<td>(0,4)¹ (0,4)²</td>
<td>0.045</td>
<td>0.091</td>
</tr>
<tr>
<td>(1,-1)¹ (1,-1)²</td>
<td>0.104</td>
<td>0.119</td>
</tr>
<tr>
<td>(1,1)¹ (1,1)²</td>
<td>0.050</td>
<td>0.104</td>
</tr>
<tr>
<td>(1,-3)¹ (1,-3)²</td>
<td>0.048</td>
<td>0.061</td>
</tr>
<tr>
<td>(1,3)¹ (1,3)²</td>
<td>0.056</td>
<td>0.109</td>
</tr>
<tr>
<td>(0,-3)¹ (0,-3)²</td>
<td>0.140</td>
<td>0.098</td>
</tr>
</tbody>
</table>
Fig. 4.22. $(1,-3)$ and $(-1,-3)$ beams measured for normal incidence on Ni(311). Upper pair of $I(E)$ curves are for symmetrically related beams from one experiment, and lower pair of curves are from an independent experiment.
Fig. 4.23. (1,1) and (-1,1) beams measured for normal incidence on Ni(311). Upper pair of I(E) curves are for symmetrically related beams from one experiment, and lower pair of curves are from an independent experiment.
4.4.5 Variable Inner Potential

The multiple scattering calculations for Ni(311) used a constant value of Vor equal to -10eV. From LEED investigations of the nickel (100), (110) and (111) surfaces, Demuth et al[94] provided evidence that it could be advantageous to make Vor energy dependent, particularly so its value becomes less negative with increasing energy. The values of Vor tabulated by Demuth et al were used here to alter the energy scale of the calculated intensities, and new intensity values were then determined by interpolation to the original energy grid. An r-factor comparison of the experimental data with these I(E) curves resulted in a poorer fit (Rp=0.36) and a shift in Gmin towards a less contracted topmost layer spacing (Δd%= -10). The direction of the shift in Gmin is consistent with the form of the Vor dependence, since, as noted by Demuth et al, the observed Vor dependence and top layer contractions shift peaks in the I(E) curves in the same direction. An energy-independent Vor is favored by the present analysis; it is possible that the Vor dependence suggested by Demuth et al arises in part from slight underestimates of the topmost layer contractions for the nickel (100), (111), and (110) surfaces.

4.5 CALIBRATION

The calibration of the vidicon-digitizer system has been previously checked for linearity[87] by analyzing a set of photographs of a step density wedge. It was shown that the digitizer output vs. optical density (O.D.) is approximately linear over a range of about 1.6 O.D. units. In the present
work, testing of the phosphor-film-vidicon system was accomplished from a series of photographs taken at a fixed incident beam voltage (175eV) for different incident beam currents. The curve A in Figure 4.24 is the result of a calibration involving the digitizer output vs. incident beam current. This curve was constructed using several of the diffracted beams available at 175eV so that the range of diffracted beam currents (from weakest beam at lowest incident current to the most intense beam at the highest incident current) is not dependent on the accurate measurement of small values (less than 0.2μA) of incident beam current. The ratio of the digitized intensities was considered to be an accurate measure of the ratio of the relative beam currents in the 'linear range' of the data (i.e. digitized intensities in the range 25 to 275). The calibration curve A shown in Figure 4.24 corresponds to the f-stop (f2.8) of the vidicon camera which gave the largest linear response for the range of film densities encountered. This aperture setting was also used for the measurement of the LEED I(E) curves for Ni(311). A saturation effect is evident at higher intensities; the output actually decreases with increasing incident beam currents in the high range of the latter. This effect is in part due to the broadening of the diffracted beam profile on the photographic film. It can be partially compensated, as shown in curve C of Figure 4.24, by making the array size that samples the spot intensity on the digitizer sufficiently large to include the entire cross-section of the beam.

The use of smaller apertures (f4.0) on the vidicon camera
Fig. 4.24. Digitized intensities of diffracted beams measured at 175eV for normal incidence from a Ni(311) surface plotted as a function of diffracted beam current. A Vidicon camera aperture set at f2.8 B Vidicon camera aperture set at f2.0 C Vidicon camera aperture set at f2.8 and camera moved away from the film so that the entire diffracted beam profile is included in the integration.
causes an even more severe saturation of the curve at higher beam currents. This is because the black level (maximum digitized value) occurs at smaller O.D. values on the film, and thus the usable intensity range is reduced. The effect of a larger aperture (f2.0) for the vidicon camera is shown in Figure 4.24, curve C. There is evidently less saturation at the same film density as in curve A, but there is a significant non-linearity at lower values of beam current.

The largest diffracted beam currents encountered in the study of the Ni(311) surface correspond roughly to the start of saturation in the calibration curve A of Fig.4.24 (about 300 units of digitized intensity). This means that the intensities of the strongest peaks in the measured I(E) curves are actually smaller than they should be. The linear range of digitized film intensity versus incident current appears to be adequate for r-factor comparisons that are not too sensitive to peak shape. Modifying the I(E) curves measured from the Ni(311) surface using the results of the measured intensity vs. diffracted beam current (curve A in Fig.4.24) did not significantly alter the values of Rp obtained for the comparison with the calculated I(E) curves (i.e. changes in Rpmin and Gmin were much less than 1%).

It is apparent from this study that more thought will have to be given to the selection of various camera settings (vidicon and Nikon) and photographic processing methods in order to ensure that the measurements fall within the restricted linear range of digitized intensities. In this regard, a real-time data analysis system would be advantageous as it would allow direct
calibration of the LEED experiment for the non-linear response of the phosphor and TV camera.

4.6 SUPPRESSOR GRID VOLTAGE

The retarding or suppressor grids (G2,G3 in Figure 1.4a) are used to filter out the inelastically backscattered electrons from the elastic electrons which are of interest in the LEED experiment. The voltage on these grids, the suppressor grid voltage, determines the energies of the electrons that will be transmitted through to the screen. Suppressor grid voltages are chosen so that only the elastically scattered electrons and those electrons that have undergone small energy losses (e.g. a few eV) can reach the collector. Figure 4.25 shows a plot of the intensity ratios for two pairs of diffracted beams vs. suppressor grid voltage. Ideally the curves would be horizontal lines. However, the intensities are dependent on the suppressor voltage due to effects such as variations in the work function on different parts of the retarding grids (as a result of uneven accumulation of deposited material during heating and bombarding operations). If the energy window set by the suppressor voltage is too restrictive, then the transmission 'cutoff' will occur on the highly-sloped elastic peak. For these values of suppressor voltage, small work function changes on different parts of the grids can lead to appreciable changes in transmitted current.

To lessen the effects of such variations, the data reported in this thesis was collected with grid suppressor voltages 3-6eV more positive than the incident energy. This allows the
Fig. 4.25. Digitized diffracted beam intensity ratios for two pairs of diffracted beams measured at 175eV for normal incidence from a Ni(311) surface plotted as a function of the suppressor grid voltage. The greatest changes occur for suppressor grid voltages of less than 3 volts.
collection of the entire elastic peak (resolution of analyzer is about 1%, i.e. 2eV for 200eV electrons) and also those electrons which contribute to the flat region in the energy distribution between the elastic peak and the energy loss peaks due to plasmons in Figure 1.3a. The selection of this range of suppressor grid voltages (i.e. 3-6eV) is consistent with the results in Figure 4.25. The plots are reasonably flat above the lower limit of 3eV, and the 6eV upper limit should restrict the energies of the collected electrons so that no electrons that have undergone energy losses due to plasmons will be collected.

To alleviate work function variations for future work, we intend to cover the LEED optics with a protective shutter when the sample is being heated or Ar+ bombarded to prevent material from being deposited on to the grids.

4.7 DIRTY NI(311)

A set of I(E) curves was measured from a Ni(311) surface which was exposed for about three hours to the residual gases comprising the background at 1x10^{-10} torr. The photographs of the LEED pattern showed faint streaks and overlayer spots at some particular energies. An Auger spectrum showed the presence of some carbon and sulphur; using the relative sensitivities given by Demuth et al[102], coverages of about 0.20 of a monolayer C, and about 0.25 of a monolayer S were indicated. A reliability index comparison between the experimental I(E) curves for this contaminated surface and the I(E) curves calculated for the clean Ni(311) surface gave best agreement of Rp=0.49 at Δd%=−8.7. The level of agreement was not as good as
for the clean Ni(311) data (Rp=0.32), but this study illustrates the possibility that a significant relaxation of the top layer spacing may occur in the presence of adsorbed impurities (Δd% (cleaned surface)=-14.5)). Alternatively, it is possible that this relaxation is not real, but rather associated with the different phase shifts introduced by the contaminating overlayer. Figure 4.26 shows a contour plot of Rp as a function of Vor and Δd%.
Fig. 4.26 Contour plot of values of multi-beam index $R_{zj}$ for $I(E)$ curves measured at normal incidence from a contaminated Ni(311) surface as a function of inner potential ($V_{or}$) and percentage change in the topmost interlayer spacing ($\Delta d\%$).
4.8 CONCLUSION

Values of $\Delta d\%$ found in these studies (viz. -5% for Cu, -14.5% for Ni) can be compared with $\Delta d\%$ values reported for fcc(110) surfaces. This comparison is reasonable since fcc(110) surfaces are more like the stepped (311) surfaces than the flat fcc (100) and (111) surfaces. $\Delta d\%$ values reported for fcc(110) surfaces are listed below:

Ni = -5% [94]
Al = -9 to -15% [107, 108]
Ag = -6 to -10% [109, 110]
Rh = -3% [111]

A 14.5% contraction for the topmost interlayer spacing of Ni(311) represents a Ni-Ni bond length contraction of only 0.075 Å (3%). The contraction found for Ni(311) is rather larger than the 5% contraction found for the topmost interlayer spacing of Ni(110), where the bond length contraction is only 1.5%[94]. The possibility that the large percentage contraction indicated for Ni(311) is associated with surface roughness, as suggested previously for Al(110)[107] and Ag(110)[110], seems unlikely. The sharp LEED pattern, the overall agreement between the theoretical and experimental sets of $I(E)$ curves, as well as the agreement between independent experimental sets of data tend to argue against such a problem for Ni(311). Also, there was no evidence of spot splitting or streaking in the observed LEED patterns that could have indicated appreciable amounts of surface roughness existed.

The overall contraction of 5% found for the Cu(311) topmost interlayer spacing is significantly smaller than the 14.5% value
found for nickel. This difference may be real, although unexplained, or it could be associated with the presence of disordered oxygen that was not detected in the Auger spectra. It has been noted previously that there are difficulties in detecting the Auger signal of oxygen at 510eV when oxygen is adsorbed on copper surfaces[93,98]. The presence of the oxygen could cause an actual relaxation of the top layer of copper atoms towards the bulk layer spacing, or an apparent relaxation due to the different phase shifts introduced by the overlayer. This possibility is supported by the conclusion of Section 4.7 where a significantly smaller contraction was found for the toplayer spacing of a contaminated Ni(311) surface compared with the clean surface.

It is comforting that the effects of smoothing, averaging and correcting experimental intensities for variations in grid transparency produced only very small changes in the final structure determination. The larger change observed with the inclusion of a variable inner potential is of more concern, but it also may be a useful means of determining the dependence of Vor on electron energy. The investigation of other experimental parameters, such as suppressor grid voltage and the calibration of the LEED intensity measurements helps establish guidelines for future work and may also yield information that will be important when updating our present LEED system to permit real-time analysis.

An initial evaluation of the reliability index of Pendry[42], compared with Zanazzi and Jona's index, is presented here, based on the limited use of these r-factors for the
comparison of I(E) curves in this thesis. Generally, the main advantage of the Pendry r-factor over that of Zanazzi and Jona is the significant reduction in computing costs. For computations on the Amdahl 470 V6 (a large main-frame computer), the cost of computations for the Pendry r-factors were about 8 to 10 times less than the corresponding calculations for the Zanazzi and Jona programs. The Pendry r-factors were appreciably more sensitive to a variation in Vor, and were somewhat more sensitive to changes in Ad% (as evidenced by the smaller uncertainties). The multibeam r-factors from both procedures generally yielded the same structural conclusions. However, there was a significant difference between the values of Vor and Ad%, found in the two r-factor analyses, that gave the best agreement for an individual experimental I(E) curve.

Although there are no apparent advantages to using the more expensive Zanazzi and Jona r-factor program, it is probably useful to continue with the practice of comparing the results of both r-factors until a wide range of surfaces have been investigated.
CHAPTER 5

STUDIES ON THE (0001) SURFACE OF ZIRCONIUM
Although zirconium has important technological uses (e.g. nuclear reactor material, getter for electronic tubes), zirconium surfaces have not so far been widely studied by the 'clean surface' methods in ultra-high vacuum. In part, this may be attributed to the difficulties of obtaining well-characterized surfaces, due especially to their high reactivities and to the bulk phase change (hcp to bcc at around 865°C).

The (0001) surface of an hcp metal (often referred to as the basal plane) has two possible terminations; with the hexagonal layers stacked in order A,B,A,B..., either A or B may be the topmost layer. These terminations are illustrated in Figure 1.6. The LEED experiment averages over the two terminations (see Section 1.5) and thus the diffracted beams display 6-fold symmetry at normal incidence. In the present work, I(E) curves have been measured for both the clean Zr(0001) surface and for Zr(0001) surfaces containing adsorbed oxygen. A complete LEED crystallographic analysis has been made for the clean surface.
5.1 THE CLEANED (0001) SURFACE OF ZIRCONIUM

5.1.1 Experimental

Specimens were cut by spark erosion from 1/4", 99.9% purity single crystal rods (prepared by A. Akhtar, Department of Metallurgy, University of British Columbia). After cutting, the samples were mechanically polished (1μ diamond paste) and then polished chemically in acid solution (45% HNO₃, 50%water, 5%HF by volume)[112]. This procedure resulted in a shiny surface with an 'orange-peel' appearance when viewed with a 10X magnifier. The crystal slices were mounted on a Varian resistive heater and a chromel-alumel thermocouple was spotwelded to the sample edge.

Figure 5.1a shows an Auger spectrum measured with the cylindrical mirror analyzer from a Zr(0001) surface on entering the FC12 chamber. Large quantities of carbon and oxygen were indicated, and clearly the sample was initially strongly contaminated. Argon ion bombardment (1-2keV, 5μA) was then carried out at room temperature until carbon was the only detectable contaminant; but it proved impossible to reduce the carbon contamination below detectable limits. The total bombardment time at room temperature was greater than 50 hours. The lowest levels of contamination corresponded to Auger peak height ratios C(272eV)/Zr(174eV) of around 0.05 to 0.10. Such ratios are believed to correspond to coverages of less than 3% of a monolayer; this estimate is based on the results of experiments that measured the Auger peak heights as a function of CO exposure(Section 5.2.1). Well-ordered surfaces, cleaned to the level of minimum carbon contamination, were produced by cycles of Ar+ bombardment(400-600eV) and annealing at 600°C. An
Auger spectrum of such a cleaned surface is shown in Figure 5.1b.

Annealing at temperatures above 600°C resulted in the accumulation of sulphur on the surface. The sulphur coverage was difficult to quantify since the S(150eV) and Zr(147eV) peaks could not be resolved even when using modulation voltages less than 1Vpp. To monitor the presence of sulphur it was necessary to measure the relative peak heights of the zirconium Auger peaks at 92, 116, 124, 147, and 174eV. Since surface order also affected the relative peak heights, an increase in sulphur contamination was only unambiguously indicated when the Auger peak at around 150eV increased relative to all the other peaks associated with zirconium.

The LEED pattern could also be changed by the presence of sulphur. Low coverages produced an increased background and a faint 3x3 pattern. Higher sulphur coverages resulted in a very faint and complicated LEED pattern that possibly indicated the formation of zirconium sulphide.

For the cleaned Zr(0001) surface, two independent sets of I(E) curves were measured for normal incidence, and a further set was measured for off-normal incidence (θ=9°, φ=13°) following the procedures of Section 3.5. Figure 5.2 shows how the azimuthal angle φ is specified following the convention of Zanazzi et al[113].
Fig. 5.1a Auger spectrum of a contaminated Zr(0001) surface measured using the CMA on the FC12 vacuum chamber (Ep=2500eV, Ip=100μA).

Fig. 5.1b Auger spectrum of a cleaned Zr(0001) surface.
Fig. 5.2 Diagram showing how the azimuthal angle is specified for the off-normal incidence experiment on Zr(0001). The azimuth is defined following the convention of Zanazzi et al. [113] for the selection of substrate axes illustrated.
5.1.2 Calculations

$I(E)$ curves were calculated using the renormalized forward scattering (RFS) method with the following non-structural parameters: $V_{or}=-10\text{eV}$, $V_{oi}=-1.08E^{1/3}\text{eV}$ (where $E$ is vacuum energy in eV), $\theta_0=270^\circ\text{K}$. Eight phase shifts were obtained from the band structure potential of Moruzzi et al[57]. The value of $\theta_0$ was an average value from a compilation by Schneidner[114]; $V_{oi}$ was estimated from an examination of the narrowest peaks in the experimental $I(E)$ curves, and was fitted to the energy dependence expressed in equation 2.9.

The effect of domains due to the two terminations was considered. At normal incidence this involved averaging the $I(E)$ curves for beams related by a $180^\circ$ rotation. For the off-normal incidence calculations, $I(E)$ curves were calculated for the two possible terminations and then averaged. A possible surface reconstruction, hcp to hcp+fcc top layer (ABABA... to CBABA...), was also investigated. RFS calculations for this reconstructed surface, again allowing for the two terminations, were also made for normal incidence and for $\theta=9^\circ$, $\phi=13^\circ$. The two sets of calculations were made for $\Delta \%$ values in the range $-7.5$ to $+7.5$, and for energies at $2\text{eV}$ intervals in the range $50$ to $100\text{eV}$, and at $4\text{eV}$ intervals from $100$ to $230\text{eV}$. The maximum number of beams available for the calculation was 61. Figure 5.3 compares some $I(E)$ curves measured at normal incidence with calculated curves for the hcp and hcp+fcc top layer surface models that showed closest agreement. Figures 5.4-5.7 show $I(E)$ curves measured at $\theta=9^\circ$, $\phi=13^\circ$ compared with curves calculated for the hcp model with $\Delta \%$ values ranging from $-7.5$ to $7.5$. Visual assessments of
the curves indicated that the calculated I(E) curves for the two surface models are very similar, and that the comparison with experiment seemed perhaps to favour the unreconstructed model.

5.1.3. R-factor Results

Table 5.1 lists the single beam r-factor values for the comparison of experimental I(E) curves with both the unreconstructed and the hcp+fcc top layer surface models. The $r^{(i)}$ values in Table 5.1 are the minimum values found for the ranges of Vor and $\Delta d\%$ values investigated. The reliability index approach was unambiguous in all cases with the best agreement (smallest $r^{(i)}$) always found for the unreconstructed surface model. The minimum multi-beam Rzj values for the unreconstructed surface model were 0.086 at $\Delta d\%=0.2\pm1.0$ for the normal incidence data and 0.132 at $\Delta d\%=-2.4\pm0.8$ for the experiment with $\theta=9^\circ$, $\phi=13^\circ$. The corresponding values for the hcp+fcc top layer surface model were 0.150 at $\Delta d\%=3.0\pm1.7$ and 0.254 at $\Delta d\%=-2.6\pm1.5$, respectively. The quoted uncertainties in $\Delta d\%$ are $U(2)$ values (equation 3.12). The magnitudes of both the uncertainty and Rzj values also indicated that the unreconstructed surface model was favored over the hcp+fcc top layer model. A contour plot of the multibeam Rzj values as a function of Vor and $\Delta d\%$ for the normal incidence data is shown in Figure 5.8 for the unreconstructed surface model; the Rzj contours for comparison with the hcp+fcc top layer model are plotted in Figure 5.9. Contour plots for the off-normal incidence data for both surface models are shown in Figures 5.10a and 5.10b.
Fig. 5.3 (1,0) and (1,1) beams measured at normal incidence from the (0001) surface of zirconium compared with the calculated I(E) curves which gave the lowest single beam r-factors for the hcp and hcp+fcc top layer surface models.
Fig. 5.4 (0,0) beam measured for off-normal incidence ($\theta=9^\circ$, $\phi=13^\circ$) from the cleaned Zr(0001) surface, and compared with calculated $I(E)$ curves for $\Delta d\%$ values ranging from -7.5 to 7.5.
Fig. 5.5 (0,1) beam measured for off-normal incidence (θ=9°, φ=13°) from the cleaned Zr(0001) surface, and compared with calculated I(E) curves for Δd% values ranging from -7.5 to 7.5.
Fig. 5.6  (-2,1) beam measured for off-normal incidence (θ=9°, φ=13°) from the cleaned Zr(0001) surface, and compared with calculated I(E) curves for Δd% values ranging from -7.5 to 7.5.
Fig. 5.7 (-1,1) beam measured for off-normal incidence (\(\theta = 9^\circ\), \(\phi = 13^\circ\)) from the cleaned Zr(0001) surface, and compared with calculated I(E) curves for \(\Delta d\%\) values ranging from -7.5 to 7.5.
Table 5.1 Single beam Zanazzi and Jona r-factors for the comparison of I(E) curves measured from the (0001) surface of zirconium with calculated I(E) curves for the unreconstructed (hcp) and reconstructed (hcp+fcc top layer) surface models.

<table>
<thead>
<tr>
<th>BEAM LABEL</th>
<th>HCP MODEL</th>
<th>HCP+FCC TOP LAYER</th>
</tr>
</thead>
<tbody>
<tr>
<td>THETA=0°</td>
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<td></td>
</tr>
<tr>
<td>(1,0)</td>
<td>0.045</td>
<td>0.066</td>
</tr>
<tr>
<td>(1,1)</td>
<td>0.055</td>
<td>0.102</td>
</tr>
<tr>
<td>(2,0)</td>
<td>0.123</td>
<td>0.146</td>
</tr>
<tr>
<td>(2,1)</td>
<td>0.062</td>
<td>0.084</td>
</tr>
<tr>
<td>THETA=9°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0,0)</td>
<td>0.021</td>
<td>0.085</td>
</tr>
<tr>
<td>(1,-1)</td>
<td>0.038</td>
<td>0.080</td>
</tr>
<tr>
<td>(1,0)</td>
<td>0.249</td>
<td>0.373</td>
</tr>
<tr>
<td>(0,1)</td>
<td>0.149</td>
<td>0.168</td>
</tr>
<tr>
<td>(-1,0)</td>
<td>0.051</td>
<td>0.059</td>
</tr>
<tr>
<td>(-1,1)</td>
<td>0.080</td>
<td>0.160</td>
</tr>
<tr>
<td>(-2,0)</td>
<td>0.207</td>
<td>0.270</td>
</tr>
<tr>
<td>(-2,1)</td>
<td>0.096</td>
<td>0.151</td>
</tr>
</tbody>
</table>
Fig. 5.8 Contour plot of the multi-beam Rzj values as a function of $V_{or}$ and $\Delta d\%$ for the comparison of I(E) curves measured at normal incidence from the Zr(0001) surface with calculated I(E) curves for an unreconstructed (hcp) surface with $\Delta d\%$ values ranging from -7.5 to 7.5.
Fig. 5.9 Contour plot of the multi-beam $R_{zj}$ values as a function of $V_{or}$ and $\Delta d\%$ for the comparison of $I(E)$ curves measured at normal incidence from the Zr(0001) surface with calculated $I(E)$ curves for a reconstructed (hcp+fcc top layer) surface with $\Delta d\%$ values ranging from -7.5 to 7.5.
Fig. 5.10 Contour plots of the Rzj values as a function of Vor and Ad% for the comparison of I(E) curves measured for off-normal incidence (θ=9°, φ=13°) from the Zr(0001) surface with calculated I(E) curves for Ad% values ranging from -7.5 to 7.5:

a) an unreconstructed (hcp) surface,
b) a reconstructed (hcp+fcc top layer) surface.
5.1.4 Comparison With Other Work

The comparison of the normal and off-normal incidence experimental data with I(E) curves calculated for the two surface models suggests that the (0001) surface is unreconstructed and has a topmost interlayer spacing that is close to the bulk value. An overall contraction of $-1\pm2\%$ seems reasonable to cover the slight discrepancy between the normal and off-normal incidence experiments.

Similar conclusions have been reached by LEED for the (0001) surfaces of other hexagonal close packed metals. Corresponding values of $\Delta d\%$ reported in the literature are:

\[
\begin{align*}
\text{Be} & \ 0\% \ [115] \quad \text{Cd} \ 0\% \ [116] \quad \text{Co} \ 0\% \ [117] \\
\text{Ti} & \ -2\% \ [43] \quad \text{Zn} \ -2\% \ [118]
\end{align*}
\]

The most complete studies are those for titanium and cobalt, and it is comforting that those structural results are in very close agreement with that found here for zirconium. The other studies are less complete. For example, the study for zinc relied on averaging methods to determine the structure, the data for the Be(0001) surface were taken without any means of chemical analyses, and the study for cadmium involved a four-layer deposition on Ti(0001). Nevertheless, there does seem to be a general conclusion that (0001) surfaces of hcp metals are unreconstructed with a topmost interlayer spacing very close to the bulk value.
5.2 OXYGEN ADSORPTION ON THE (0001) SURFACE OF ZIRCONIUM

Initial exposure of a cleaned Zr(0001) surface to oxygen at room temperature yielded a faint (2x2) LEED pattern with diffuse diffraction spots, after an exposure of about 1 L; however, the spots became brighter and sharper when the sample was annealed at approximately 250°C. Annealing at temperatures above 400°C for a few minutes resulted in a depletion of oxygen, presumably due to diffusion into the bulk. With increasing oxygen exposure, the (2x2) pattern became fainter and eventually a (1x1) pattern appeared with I(E) curves different from those of the cleaned surface. For even greater oxygen exposures, the LEED pattern remained (1x1) but became more diffuse with an increased background.

Because the oxygen adsorption structures necessarily contained some carbon which could not be completely removed in the cleaning process, it seemed appropriate to expose a Zr(0001) surface to carbon monoxide in order to have a means for calibrating the relative Auger peak heights of the C(272eV) and O(510eV) peaks. CO adsorption yielded initially a bright (2x2) pattern, which converted at higher coverages to a (1x1) pattern. This latter pattern was sharp and bright and, unlike the oxygen structure, it did not rapidly degrade with increasing CO exposure. Generally, the LEED patterns of the CO structures were sharper and brighter than the patterns of the oxygen structures. These observations are consistent with those of Shih et al[119-121] for studies of oxygen and carbon monoxide adsorption on the (0001) surface of titanium.

A difference between titanium and zirconium, which may be
significant to the question of oxygen adsorption on the (0001) surface, is that zirconium forms only one bulk oxide (ZrO$_2$)[122], while both TiO and TiO$_2$ are stable compounds of titanium. It is therefore plausible that the structure formed for the highest oxygen exposures on zirconium will be ZrO$_2$, whereas for titanium, the oxide formed upon exposure to oxygen at room temperature is reported to be TiO[119].

A question of interest in the study of oxygen adsorption on the Zr(0001) surface is whether the adsorbed oxygen is an overlayer or an underlayer (i.e. between the two topmost layers of zirconium). Shih et al[44] provided evidence that an ordered underlayer of nitrogen was formed on the Ti(0001) surface at room temperature. This underlayer structure precedes the formation of any overlayers. The probability of underlayer formation was also mentioned in a LEED investigation of the structure of CO adsorbed on Ti(0001)[121]. Because of the marked similarity between titanium and zirconium, it seems possible that underlayers may play a part in the adsorption of oxygen on the (0001) surface of zirconium.

5.2.1 Experimental

The introduction of oxygen into the FC12 vacuum chamber always resulted in the production of CO and CO$_2$, as well as smaller quantities of CH$_4$ and H$_2$O, from displacement processes and from reactions of the oxygen with the walls, hot filaments and the ion pumps. The gas composition was monitored with the EAI150 quadrupole mass spectrometer. Matheson UHP grade (99.95% purity) and research grade (99.99% purity) oxygen was used in
these studies; no detectable changes were observed in the mass spectra or in the surface contamination levels, as indicated by Auger electron spectroscopy, for the different gas purities. The cleanest oxygen-covered surfaces were obtained by leaking oxygen into the chamber with both the titanium sublimination pump and the main ion pump operating. The CO partial pressure was further reduced using the following two procedures:

i) 'conditioning' the inlet system and chamber by flowing oxygen through at $10^{-6}$ torr, and then subsequently cleaning the sample and repeating the adsorption experiment;

ii) positioning the sample directly in front of the capillary gas inlet and adjusting the leak valve for the minimum detectable leak.

For ii) the leak rate did not increase the system pressure of about $2 \times 10^{-10}$ torr (i.e. no observable increase of the ionization gauge reading), but it could be detected with the CMA by monitoring an increase in the oxygen Auger peak at 510 eV, relative to the carbon peak at 272 eV and the zirconium peaks at 92, 116, 124, 147, and 174 eV.

Figure 5.11 shows plots of the Auger peak height ratio $O(510eV)/Zr(174eV)$ as a function of oxygen exposure. There were no apparent breaks for the range of coverages that correspond to the (2x2) LEED pattern, although the slope decreases at higher oxygen coverages; nevertheless the oxygen to zirconium Auger ratio continues to increase slowly with further exposures. This ratio is expected to level off when the oxide layer becomes thicker than the escape depth of the emitted Auger electrons.

To quantify the coverage of carbon observed during oxygen
Fig. 5.11 Auger peak height ratio $O(510\text{eV})/Zr(174\text{eV})$ plotted as a function of oxygen exposure for two independent experiments (large and small circles). The Auger peak height ratios have been divided by 2.8 to yield approximations to the fractional monolayer coverage.
adsorption, carbon monoxide was introduced into the vacuum system. Figure 5.12 shows a plot of the Auger peak height ratios $C(272\text{eV})/Zr(174\text{eV})$ and $O(510\text{eV})/Zr(174\text{eV})$ as a function of CO exposure. The $C(272\text{eV})/O(510\text{eV})$ Auger peak height ratio was found to be approximately 1.5 for all CO coverages. Unlike the oxygen exposure experiment, the adsorption of CO has a sharp break at saturation coverage (which presumably corresponds to half monolayer coverage for C and half monolayer coverage for O). The saturation ratios are $C(272\text{eV})/Zr(174\text{eV})=2.1$ and $O(510\text{eV})/Zr(174\text{eV})=1.4$. The CO (2x2) LEED pattern was observed for total C+O coverages ranging from 0.2 to 0.6 of a monolayer. These ratios are consistent with the conclusions of Shih et al[121], that the (2x2) CO structure on Ti(0001) corresponds to 1/4 monolayer coverage each for C and O.

Using the information about relative Auger peak heights from the CO adsorption experiments, the coverages for the oxygen on Zr(0001) structures were estimated. The oxygen (2x2) pattern was observed for oxygen coverages between 0.25 and 0.6 of a monolayer, while a (1x1) pattern occurred for oxygen coverages from 0.6 to greater than monolayer coverage. The (2x2) oxygen pattern is thought to correspond to a (2x1) structure of 1/2 monolayer coverage. The presence of symmetrically equivalent domains would generate the observed (2x2) LEED pattern (Figure 1.7). For coverages greater than a monolayer, the linear extrapolation of the oxygen to zirconium Auger peak height ratio is expected to give a less reliable indication of coverage if some of the oxygen is incorporated between the layers of zirconium atoms.
Fig. 5.12 Auger peak height ratios for C(272eV)/Zr(174eV) and O(510eV)/Zr(174eV) plotted as a function of exposure for the adsorption of CO on a (0001) surface of zirconium.
A third adsorption experiment is illustrated by the Auger peak ratio versus exposure profiles in Figure 5.13. After adsorbing oxygen until a (2x2) LEED pattern was observed, the surface was exposed to carbon monoxide. The final Auger peak height ratios indicated coverages of 0.38 of a monolayer of carbon and 0.65 of a monolayer of oxygen; again demonstrating a saturation coverage of one monolayer.

For measurements of I(E) curves, two sets of LEED photographs were taken for independent preparations of the oxygen (2x2) pattern. Further sets of the (1x1) oxygen patterns were taken for oxygen coverages that were thought to be near monolayer coverage and for much higher oxygen coverages. The carbon contamination of the oxygen (2x2) structure was estimated to be about 5% of a monolayer, and about 10% of a monolayer for the (1x1) oxygen structures.
Fig. 5.13 Auger peak height ratios for C(272eV)/Zr(174eV) and O(510eV)/Zr(174eV) plotted as a function of CO exposure on a Zr(0001) surface that contained adsorbed oxygen and which showed a (2x2) diffraction pattern.
5.2.2 Results

Some examples from the two sets of I(E) curves measured for the (2x2) oxygen pattern are shown in Figures 5.14 and 5.15. An r-factor analysis of corresponding beams from the two data sets yielded the single beam $r^{(i)}$ values in Table 5.2. Generally, the correspondence is quite good, especially for the integral order beams. Each I(E) curve in the comparison is the result of averaging the symmetrically equivalent beams within an experimental set and the average was then smoothed once with a three point triangular smooth (equation 4.3). The I(E) curves from the saturation (1x1) oxygen structure are given in Appendix 1. These curves are different from the I(E) curves measured for the clean surface and are also different from curves measured for the lower coverage (1x1) pattern. The latter data are included in Appendix 1.
Fig. 5.14 I(E) curves for (1,0) beams at normal incidence from two independent measurements for the Zr(0001)-(2x2)-O structure. The curves illustrated are formed by averaging symmetrically equivalent I(E) curves within each set, and each average has been smoothed once (equation 4.3).
Fig. 5.15 I(E) curves for (0,3/2) beams at normal incidence from two independent measurements for the Zr(0001)-(2x2)-O structure. The curves illustrated are formed by averaging symmetrically equivalent I(E) curves within each set, and each average has been smoothed once (equation 4.3).
Table 5.2 Single beam Pendry r-factors for the comparison of corresponding beams from two independent measurements of beams from the Zr(0001)-(2x2)-O structure. Within an experimental set, symmetrically equivalent beams were averaged and smoothed once (equation 4.3).

<table>
<thead>
<tr>
<th>BEAM LABEL</th>
<th>R-FACTOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,1/2)</td>
<td>0.081</td>
</tr>
<tr>
<td>(1/2,1/2)</td>
<td>0.158</td>
</tr>
<tr>
<td>(1,0)</td>
<td>0.043</td>
</tr>
<tr>
<td>(1,1)</td>
<td>0.066</td>
</tr>
<tr>
<td>(0,3/2)</td>
<td>0.126</td>
</tr>
<tr>
<td>(1,3/2)</td>
<td>0.128</td>
</tr>
</tbody>
</table>
5.2.3 Future Work

Sets of I(E) curves for a large number of possible sites, each with a range of interplanar spacings, would have to be calculated with the multiple scattering methods in order to establish the best models for the (2x2) and (1x1) oxygen adsorbate structures. Such studies are to be undertaken, but it is being hoped that these investigations can be guided with high resolution electron energy loss spectroscopy (HREELS). This technique gives vibrational frequencies, which in principle can be interpreted in terms of adsorption site (including symmetry and type). A HREELS spectrometer, based on the design of Carette[123], has been constructed in our laboratory, and it is currently being evaluated. Initial studies have indicated the spectrometer design is workable, and the recent addition of magnetic shielding should allow us to achieve sufficient sensitivity with the required resolution (less than 20meV).

Another planned development is the modification of the LEED analysis system using a more sensitive vidicon camera. This modification would enable us to record I(E) curves while the adsorption experiment is in progress and a particular surface structure could be investigated with optimization of the experimental conditions. This development should be particularly helpful for distinguishing between the two possible (1x1) structures. Currently, it is not possible to obtain LEED I(E) curves until after the photographic film has been developed and the spot intensities have been digitized.

Further modifications to the FC12 vacuum chamber have been proposed to allow us to carry out studies on adsorption systems
more effectively. These include moving the inlet gas doser so that the sample can be left at the focus of the CMA while the gas is leaked into the system, and the addition of a separate inlet gas-line and leak valve to be dedicated to handling the argon required for ion bombardment cleaning. This latter modification would facilitate the cleaning operations after an adsorption experiment. Currently, the adsorbing gas must be pumped away in the gas-line before it can be refilled with the argon necessary for ion bombarding. This pumpdown involves a significant 'turn-around' time as well as a possibility of contaminating the argon.
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APPENDIX
COPPER (311) EXPERIMENT
COPPER(311): EXPERIMENT

Intensity (arbitrary units)

Energy (eV)

(15)

(06)

(06)

(15)
COPPER(311): EXPERIMENT

INTENSITY (ARB. UNITS)

INTENSITY (ARB. UNITS)

ENERGY (eV)

80
120
200
240

(i)

(13)
NICKEL(311): CLEAN SURFACE

\[
\begin{align*}
\text{ENERGY (eV)} & \\
120 & 160 & 200 & 240
\end{align*}
\]

\[
\begin{align*}
\text{INTENSITY (ARB. UNITS)} & \\
\text{(0,3)} & \\
\text{(0,3)} & \\
\text{(0,3)} & \\
\text{(0,3)} & \\
\end{align*}
\]
(1,3)

NICKEL(311): CLEAN SURFACE

ENERGY (eV)

INTENSITY (ARB. UNITS)
NICKEL(311)

CONTAMINATED SURFACE

INTEGRITY (ARB. UNITS)

ENERGY (eV)

(1,1)

(0,4)

(1,3)
NICKEL(311): CONTAMINATED SURFACE

(0,4)  (1,1)
(0,5)  (1,3)

ENERGY (eV)  ENERGY (eV)
Zr(0001)–(2x2)–O
EQUIVALENT BEAMS AVERAGED
1ST AND 2ND EXPERIMENTS
Zr(0001)-(1x1)-O

Low Coverage Structure

Equivalent Beams Averaged
Zr(0001) - (1x1) - O
HIGH COVERAGE STRUCTURE

EQUIVALENT BEAMS AVERAGED