LEED CRYSTALLOGRAPHIC STUDIES FOR CHEMISORPTION ON THE Cu(100) SURFACE

by

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The work in this thesis includes LEED crystallographic studies with low-energy electron diffraction (LEED) for the surface structures designated Cu(100)-(2x2)-S, Cu(100)-c(2x2)-N, Cu(100)-(√2x√2)45°-O and Cu(100)-(2√2x√2)45°-O formed by chemisorption on the (100) surface of copper. In each case the intensity-versus-energy curves (I(E) curves) were measured with a video LEED analyser for a set of independent diffracted beams, and comparisons were made with the results of multiple-scattering calculations for various structural models. Levels of correspondence between experimental and calculated I(E) curves were assessed with visual comparisons as well as with the reliability indices introduced by Zanazzi and Jona and by Pendry. Surface structures were determined by the conditions for the best correspondence between the measured and calculated I(E) curves, and were analysed with bond length-bond order relationships to check chemical reasonableness.

The Cu(100)-(2x2)-S surface structure was obtained by the adsorption and presumed dissociation of H$_2$S on the (100) surface of the copper. An initial LEED intensity analysis which assumed the metal atoms remain in their regular bulk positions was made for 16 diffracted beams measured at normal incidence and at one off-normal incidence direction. This study indicated that S atoms adsorb 1.32 Å above the "expected" four-fold adsorption sites, which corresponds to a nearest-neighbour S-Cu bond distance equal to 2.24 Å. The second LEED crystallographic study used data measured for the 5 beams at normal incidence to investigate the lateral and vertical relaxations experienced by the four Cu atoms which bond to S. It was found these atoms relax outwards by about 0.04 Å, a result that contrasts with a report from a recent analysis with the angle-resolved-photoemission extended-fine-structure (ARPEFS) method, which indicated an inward relaxation by 0.05 Å for this surface structure. The
interlayer spacing between S and the first copper layer obtained by this work differs substantially from that by ARPEFS (1.29 Å and 1.42 Å respectively). Further LEED observations were performed for the S on Cu(100) system to address some beam splitting phenomena observed at higher sulphur coverage. In addition investigations were made to study the constancy of I(E) curves for corresponding beams with varying coverages of sulphur. This can be used to simplify some calculations, and to check the polar angle for a LEED analysis at off-normal incidence.

The Cu(100)-c(2x2)-N structure was prepared by the adsorption of nitrogen activated by an ion gun. The structural conclusions from LEED intensity studies differ markedly from those in two earlier reports in the literature. An initial intensity analysis with ten independent beams (at normal and off-normal incidences) showed that this surface structure involves N atoms incorporated deeply into the expected four-fold sites to become closely coplanar with the topmost copper layer. Each N atom then becomes 5-fold coordinated with bonding to the atom directly below in the second copper layer. A further analysis investigated the adsorbate induced relaxations. This indicated that the N atoms adsorb about 0.06 Å above the topmost copper layer, the Cu-Cu interlayer spacing between the first and the second metal layers increases by 0.04 Å from the bulk value (1.81 Å), and those Cu atoms in the second metal layer directly below N relax downward by about 0.09 Å.

A range of geometrical models have been considered for the oxygen on Cu(100) system. A LEED multiple-scattering analysis with ten independent diffracted beams for the Cu(100)-(\(\sqrt{2}\times\sqrt{2}) 45^\circ\)-O surface indicates for chemisorption of O atoms on the four-fold hollow sites that the agreement is slightly better for coplanar adsorption than for adsorption about 0.75 Å above the topmost copper layer as reported by earlier ARPEFS and SEXAFS studies. A new model proposed here for the Cu(100)-(2\(\sqrt{2}\times\sqrt{2}) 45^\circ\)-O
surface has missing rows of copper atoms parallel to the [010] direction. Several versions of this model were considered in a LEED analysis which used 6 diffracted beams for normal incidence. This analysis indicated the O atoms adsorb at 0.5 monolayer coverage in sites adjacent to the missing rows (these sites would correspond to four-fold sites in the regular surface). O is held at close to 0.15 Å above the topmost copper layer, while the topmost Cu-Cu interlayer spacing increases to 2.02 Å; each oxygen atom then bonds to four neighbouring copper atoms with an average O-Cu bond length of 1.91 Å.
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CHAPTER 1
SURFACE SCIENCE AND SURFACE STRUCTURE

1.1 Surface Science

Surface science has been in a stage of rapid development during the last two decades. This progress is due, in part, to the application of an array of powerful instruments that can reveal the structural and chemical composition of surfaces on a submicroscopic scale [1,2]. The instrumentation has been stimulated, as well, by a wide range of technological problems which require an increased understanding of the properties of surfaces.

A surface is the transition region between bulk material and either vacuum or a gas phase. For a triperiodic crystal, a regular surface can be visualised by imagining a cleavage along a crystallographic plane of the bulk. At the surface, the atoms have unsatisfied bonding capacity because the neighbouring atoms are missing on one side. As a result, these surface atoms show a strong tendency for lowering the free energy via the formation of surface chemical bonding or undergoing some surface relaxation or reconstruction. Surface scientists are not just interested in the topmost "surface layer". In general they are interested in the whole region of special physical and chemical behavior, which may cover any adsorbate or thin film and the top few layers of the bulk material.

Surface science spans the traditional boundary between chemistry and physics and has developed from a phenomenological to a fundamental science and from there to an applied science. The main interest of basic surface science is concentrated on the investigation of structural, chemical, electronic and vibrational properties of surfaces. These fundamental studies have become a very active frontier and have had significant
impact on corrosion science [3,4], heterogeneous catalysis [5], adhesion [6] and friction, as well as for producing and analysing new surfaces and interfaces with novel and useful electronic properties [7].

1.2 Determination of Surface Structure

In the past, progress in our understanding of the properties of surfaces has been hampered by a lack of knowledge of their structures. To start these fundamental studies, low-Miller-index unreconstructed surfaces of metallic single crystals have been commonly chosen to test low energy electron diffraction (LEED) theories because they are simple and stable. The (100), (110), and (111) surfaces of face-centred cubic (fcc) crystals have frequently been the subjects of structural determination; a smaller number of studies have been done on body-centred cubic (bcc) solids and very few on hexagonal close-packed (hcp) crystals [8,9]. Studies of the structures of adsorbed species on these surfaces are required to develop understanding of a variety of surface phenomena. Knowledge concerning adsorption sites and bond lengths is relevant to understanding the complex phenomenon of heterogeneous catalysis [10]. For example, metallic surfaces may be stepped, with terraces several atoms wide and separated by atomic steps; these steps are often of monoatomic height but they may also contain atomic kinks. Atoms at these ledges are even more exposed, and can therefore become more reactive. Such chemically significant irregularities can be identified by several techniques including LEED, ARXPS, UPS (see Table 1.1) [11-13]. The precise knowledge of atomic arrangements at or near surfaces becomes a key ingredient to understanding surface physics and chemistry, and it is the starting point for advancing knowledge on other properties of surfaces [14].
<table>
<thead>
<tr>
<th>Surface Technique</th>
<th>Acronym</th>
<th>Probe with</th>
<th>Physical Basis</th>
<th>Information Provided</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scanning Tunneling Microscopy</td>
<td>STM</td>
<td>Electrons</td>
<td>Tunneling effects of surface electrons</td>
<td>Surface structure, electronic structure</td>
<td>[17,18]</td>
</tr>
<tr>
<td>Auger Electron Spectroscopy</td>
<td>AES</td>
<td>Electrons</td>
<td>Electron emission from excited surface atom</td>
<td>Surface composition</td>
<td>[21]</td>
</tr>
<tr>
<td>Secondary Ion Mass Spectroscopy</td>
<td>SIMS</td>
<td>Ions</td>
<td>Induced ejection of surface atoms as ions</td>
<td>Surface composition</td>
<td>[22,23]</td>
</tr>
<tr>
<td>Ion Scattering Spectroscopy</td>
<td>ISS</td>
<td>Inert gas ions</td>
<td>Ion scattering</td>
<td>Atomic structure, composition</td>
<td>[24]</td>
</tr>
</tbody>
</table>

Table 1.1 Techniques for surface structure study.
<table>
<thead>
<tr>
<th>Method</th>
<th>Technique</th>
<th>Radiation</th>
<th>Analysis</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Extended X-ray Absorption Fine Structure</td>
<td>SEXAFS</td>
<td>X-ray</td>
<td>Interference effects in photo-emitted electrons</td>
<td>Bond lengths</td>
</tr>
<tr>
<td>Angle-Resolved-Photoemission Extended-Fine-Structure</td>
<td>ARPEFS</td>
<td>X-ray</td>
<td>Photoelectron scattering</td>
<td>Bond lengths</td>
</tr>
<tr>
<td>X-ray Photoelectron Spectroscopy</td>
<td>XPS</td>
<td>X-ray</td>
<td>Electron emission from inner shells</td>
<td>Surface composition, surface oxidation states</td>
</tr>
<tr>
<td></td>
<td>ESCA</td>
<td>X-ray</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-ray Diffraction</td>
<td>XD</td>
<td>X-ray</td>
<td>Diffracted X-ray</td>
<td>Surface structure</td>
</tr>
<tr>
<td>UV Photoelectron Spectroscopy</td>
<td>UPS</td>
<td>UV</td>
<td>Electron emission from valence shells</td>
<td>Valence structure</td>
</tr>
<tr>
<td>Thermal Desorption</td>
<td>TDS</td>
<td>Heat</td>
<td>Thermally induced desorption, decomposition</td>
<td>Desorption energy, surface chemistry</td>
</tr>
<tr>
<td>Infrared Spectroscopy</td>
<td>IRS</td>
<td>IR light</td>
<td>Vibrational excitation by absorption</td>
<td>Molecular identity, orientation, surface bonding of adsorbate</td>
</tr>
</tbody>
</table>

Table 1.1 Continued.
There are a variety of techniques that can provide information on surface structure at this time. The various techniques probe a surface with particles or photons. Among the particles that have been used are electrons, ions, neutral atoms, neutrons, positrons, and electronically excited atoms. In contrast, photon probes, extending from the X-ray region to the infrared, can be effective when the surface is in contact with a gas or a liquid, as in real surface catalyst situations. Table 1.1 lists representative surface techniques that are used at the present time. The table is categorised according to the types of the information provided.

Surface science entered the era of structural determination [8] around the early 1970s, particularly through developments in low energy electron diffraction (LEED). This technique is still a dominant one for the determination of surface structures. LEED can be applied not only to clean metal surfaces, but also to atomic overlayers, to semiconductors, to ionic compounds, and even to adsorbed molecules on surfaces [9]. However, each technique listed in Table 1.1 may have its own particular advantages, even though most of these techniques are only in their initial development stage. For surface-structure determinations, a combination of two or more techniques are often more effective than any one technique alone. For this reason, a "multi-technique strategy" is usually required in structural determination [16].

Two major techniques, LEED and AES, are used in this thesis to determine the structure and composition of surfaces and they will be described in the next two sections. Other techniques which give closely related information, such as SEXAFS, ARPEFS, ISS and HREELS can be reviewed from the references quoted in Table 1.1.
1.3 Low Energy Electron Diffraction

1.3.1 Scattering process

The initial observation of LEED was made by Davisson and Germer in 1927 [35]. It took nearly 50 years from its discovery until LEED could be used to determine atomic positions. The role of LEED in determining structure in surface science is in principle similar to that played by X-ray diffraction in the structural determination of bulk crystals [36,37].

In its diffraction, X-rays are scattered relatively weakly by matter and therefore they can penetrate deeply into the bulk and probe the triperiodic translational symmetry in an ordered solid. Accordingly X-ray crystallographic studies traditionally give bulk structural information, although recent developments with synchrotron radiation at grazing incidence can provide surface structural information [30]. By comparison, low energy electrons interact strongly with matter, and with strong attenuation the elastically scattered electrons provide specifically surface information. The surface region probed in LEED can be thought of as an arrangement of nuclei surrounded by the localised core electrons (to form the "atomic cores") as well as the less localised valence and conduction electrons [15]. The inelastic scattering mechanisms experienced by electrons as they interact with a solid involve especially plasmon excitations, but also phonon [38,39] and electronic excitations (including secondary-electron emission). Such inelastic scatterings give a loss of flux for the initial energy; the average distance travelled by an electron in a solid before it loses energy defines a mean free path $\lambda_e$ [15,40]. Electrons with energies above the plasmon threshold, to around $10^3$ eV, are ideally suited for surface investigations, since their mean free paths in solids are of the order of only a few atomic layers. Electron mean free paths as a function of energy generally follow the form shown in Figure 1.1. Differences for different materials are quite small, so that this is often
Figure 1.1 Variation in mean free path with increasing electron energy.
called a universal curve. For the typical energy range in LEED of 30 to 250 eV, elastically scattered electrons can penetrate only around 10 Å below the surface due to the high probabilities for inelastic scattering. Furthermore, for this energy range the wavelengths of the electrons are comparable to the atomic spacing.

### 1.3.2 Diffraction conditions

When electrons of a given direction and energy in the LEED range are incident on a surface, a small fraction of them (typically 1 to 5 %) will be scattered elastically. The incident electron beam can be represented in field free space by a plane wave

$$
\psi_i(r) = \exp(ik_i \cdot r),
$$

(1.1)

where the magnitude of the wavevector $|k_i|$ equals $\frac{(2mE)^{1/2}}{\hbar}$, $m$ is the electron mass and $E$ is the electron energy. Similarly, a diffracted beam can be written as

$$
\psi_d(r) = \exp(ik_d \cdot r).
$$

(1.2)

The general expression of the differential scattering cross section has the form

$$
\frac{d\sigma}{d\Omega} = \frac{m}{2\pi\hbar^2} \langle k_d T | k_i \rangle^2,
$$

(1.3)

where $T$ is the appropriate transition operator, which gives a complete description of the diffraction [41,42].

For an ordered surface, for which the surface structure is invariant under a symmetry operation $S$, Messiah [41] showed that
With Equation (1.4) we can consider the effect of different symmetry operations of a diperiodic net [43]. For example, the effect of a diperiodic translation operation on a plane wave is

\[ |\text{S}k\rangle = e^{ik\cdot t}|k\rangle, \]

where \( t \) is a surface net vector, and (1.4) can be rewritten as

\[ |\text{k}d\{T|k\rangle = \exp[i(k_i-k_d)\cdot t]|k_d\{T|k\rangle. \]

This equation immediately shows that either \( |k_d\{T|k\rangle = 0 \), or \( \exp[i(k_i-k_d)\cdot t] = 1 \). The latter equation requires that

\[ (k_i-k_d)\cdot t = 2p\pi \]

for \( p \) integral. With \( s_1 \) and \( s_2 \) as the basis vectors of the unit mesh for the surface region, \( t \) in real space can be written as

\[ t = ms_1 + ns_2, \]

where \( m \) and \( n \) are integers. The corresponding net vector \( g \) in reciprocal space [16] is

\[ g = hs_1^* + ks_2^* \]

where the unit vectors \( s_1^* \) and \( s_2^* \) in reciprocal space are defined by the relations:

\[ s_1^* \cdot s_1 = s_2^* \cdot s_2 = 2\pi \]

(1.10)
The condition in Equation (1.7) is satisfied for

\[ s_1 \cdot s_2^* = s_2^* \cdot s_1^* = 0 \]  \hspace{1cm} (1.11)

where \( s_1^* \) and \( s_2^* \) are the wave vectors of the incident and diffracted electrons, respectively. This defines a diffraction condition in LEED as a result of momentum conservation parallel to the surface. For elastic scattering, energy conservation requires that wave vectors of the incident and diffracted electrons have the same magnitude:

\[ |k_g^-|^2 = |k_1^+|^2 \]  \hspace{1cm} (1.13)

where \( k_g^- \) represents the particular \( k_d \) associated with the reciprocal space vector \( g \) according to Equation (1.12). The superscripts used here indicate the wavevector directions into(+) or out(-) of the crystal. The above discussion can be visualised by adopting the diperiodic Ewald-sphere [44] construction shown in Figure 1.2. The intersections of this sphere with the reciprocal net rods define the conditions under which both the parallel momentum conservation condition and the conservation of beam energy are satisfied simultaneously.

1.3.3 Interpretation of LEED patterns

According to the analysis in 1.3.2, the plane waves with the wave vectors \( k_g^- \) can form well-defined diffracted beams that may emanate from the crystal and travel toward a detector. In particular, if a luminescent screen is used, the two-dimensional reciprocal net may be seen directly on the screen. Each beam is labeled by a particular set
Figure 1.2 The Ewald-sphere construction for LEED. The Ewald-sphere is shown at two energies for the same incident direction (view parallel to the surface).
of integers \((h,k)\) in Equation (1.9). Relations between real surface nets and the corresponding reciprocal nets for the five dipedipic Bravais [45] nets are shown explicitly in Figure 1.3.

Let two basis vectors \(a_1\) and \(a_2\) describe the primitive unit mesh of the substrate layers, and let \(s_1\) and \(s_2\) be the corresponding basis vectors for a surface region containing an overlayer (either adlayer or reconstructed layer). The relationship of the surface region to substrate can be represented quite generally as:

\[
s_1 = m_{11}a_1 + m_{12}a_2, \quad (1.14)
\]

\[
s_2 = m_{21}a_1 + m_{22}a_2, \quad (1.15)
\]
or in matrix notation:

\[
\begin{bmatrix}
  s_1 \\
  s_2 \\
\end{bmatrix} =
\begin{bmatrix}
  m_{11} & m_{12} \\
  m_{21} & m_{22} \\
\end{bmatrix}
\begin{bmatrix}
  a_1 \\
  a_2 \\
\end{bmatrix}
\]

or

\[
s = M \cdot a \\
\]

Similarly, the corresponding reciprocal basis vectors may be defined as

\[
s^* = M^* \cdot a^* \\
\]
i.e.

\[
\begin{bmatrix}
  s_1^* \\
  s_2^* \\
\end{bmatrix} =
\begin{bmatrix}
  m_{11}^* & m_{12}^* \\
  m_{21}^* & m_{22}^* \\
\end{bmatrix}
\begin{bmatrix}
  a_1^* \\
  a_2^* \\
\end{bmatrix}
\]

\[
M = (M^* \cdot 1)^T \\
\]

where \((M^* \cdot 1)^T\) is the inverse transpose of the matrix \(M^*\) [46] and in principle, Equation (1.20) allows the real surface mesh to be derived from the corresponding reciprocal net.
Figure 1.3 Five diperiodic Bravais nets and corresponding reciprocal nets.
observed on a LEED screen, although the presence of rotationally-related domains may make the analysis less clear-cut.

Two notations are commonly used to describe surface structures. The first one [46,47] is

\[ S(hkl) - M - \eta A \]  

(1.21)

where (hkl) specifies the Miller indices [44] of the substrate surface identified by the chemical symbol S, M is defined in Equation (1.17), A denotes the chemical formula of the adsorbate, and \( \eta \) is the number of adspecies in the substrate unit mesh. The second notation [48] is the simple variant

\[ S(hkl) - \left[ \frac{s_1}{a_1} \times \frac{s_2}{a_2} \right] \alpha - \eta A \]  

(1.22)

which applies when the angle of rotation \( \alpha \) between \( a_1 \) and \( s_1 \) is the same as that between \( a_2 \) and \( s_2 \). Some examples of surface structures used in this thesis are shown in Figure 1.4 for both notations.

LEED patterns by themselves help identify the size and shape of the unit mesh, associated with the diperiodicity of the surface region probed by the LEED electrons. This information can be utilised to examine order-disorder phase transitions [16,49,50] at surfaces, to monitor chemical reactions [51] at surfaces and to study the formation of islands at low coverage [16]. In addition, interpretations of beam splitting [51], systematically missing beams and glide-plane extinctions [52] can provide extra indications for certain details of the actual surface structures. Some aspects of these applications will be presented later.
<table>
<thead>
<tr>
<th>Surface</th>
<th>Wood Notation</th>
<th>Matrix Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1x1)</td>
<td>[1 0]</td>
</tr>
<tr>
<td></td>
<td>c(2x2) or (sqrt(2)xsqrt(2))R45°</td>
<td>[1 -1]</td>
</tr>
<tr>
<td></td>
<td>(2x1)</td>
<td>[2 0]</td>
</tr>
<tr>
<td></td>
<td>(1x2)</td>
<td>[1 0]</td>
</tr>
<tr>
<td></td>
<td>(2x2)</td>
<td>[2 0]</td>
</tr>
<tr>
<td></td>
<td>(2sqrt(2)x2sqrt(2))R45°</td>
<td>[2 -2]</td>
</tr>
</tbody>
</table>

Figure 1.4 Some superstructures studied in this work in both Wood and matrix notations.
1.3.4 Surface crystallography by LEED

For the purpose of structural determination, the intensity in each diffracted beam relative to the incident beam intensity is commonly recorded as a function of energy [15] giving rise to the LEED spectrum (I(E) curve) or intensity profile as shown by an example in Figure 1.5. Typically a LEED I(E) curve has a series of broad peaks and dips with characteristic structure, which overall is very different from the situation in X-ray diffraction. In LEED, the electrons are scattered much more strongly by matter, including the strong inelastic scattering. The strong elastic scattering gives multiple-scattering and hence a more complex spectrum than would be the case from the single-scattering theory applicable in X-ray diffraction.

The current approach for LEED crystallography follows a "trial and error" methodology [53]. This involves postulating a surface structure model that conforms with the symmetry properties revealed by the diffraction pattern, and then calculating the theoretical I(E) curves with multiple scattering methods according to the model proposed. Surface crystallography by LEED depends heavily on evaluating levels of correspondence between experimental and calculated I(E) curves. R-factors [54] have been applied to satisfy this need in LEED, in some analogy with their application in X-ray crystallography [55], although considerable checking by a visual comparison is still required. If calculated I(E) curves agree roughly with those from experiment, the postulated model may appear as possibly reasonable and the further refinement can be done by modifying certain parameters [52].

1.4 Auger Electron Spectroscopy

The radiationless deexcitation of ionised atoms was predicted from theoretical considerations by Rosseland [56] in 1923. At about the same time, Auger [57,58]
Figure 1.5 Schematic diagram of an incident electron beam (with energy E and direction \((\theta, \phi)\)) and specular diffracted beam (whose intensity is recorded in the form of an I(E) curve).
discovered the Auger process in a study of the photoelectric effect using hard X-ray radiation. In 1953 Lander [59] observed small characteristic Auger peaks in his study of the energy distribution of secondary electrons emitted from solid samples irradiated with slow electrons. He also pointed out that these electrons might be used as a tool for surface analysis, but it was not until 1967 that the expectation was followed up [60-62]. The application of Auger electron spectroscopy (AES) to surface analysis effectively started with these studies.

In principle any type of radiation which is able to ionise an inner atomic shell of atoms can be used to excite Auger electrons [58]. But most often, in combination with LEED, the most convenient means is an electron beam, which has now become more or less the standard source of excitation. When a "hole" is created in an inner level of an atom, the ionised atom may relax to its electronic ground state via one of the following competing processes (Figure 1.6):

a) X-ray emission — An electron from a higher level may drop down into the core hole with emission of a quantum of characteristic X-radiation.

b) Auger electron emission — The inner hole is again filled by an outer electron, while the available energy is transmitted in a radiationless process to a second electron, which leaves the double positive charged atom with a characteristic kinetic energy.

Auger electrons are classified by referring to the three energy levels involved, and an example of a KL₁L₃ transition is illustrated in Figure 1.6. The kinetic energy of the Auger electron is determined by the energy states involved; also for energies that give short electron escape depths (Figure 1.1) information is obtained from the surface region. Specifically surface chemical analysis can be achieved in Auger electron spectra by assigning peaks to a particular element, in practice the assignment are helped by comparing the energies of observed Auger peaks with listed Auger energies [63] and with
Figure 1.6 Processes for de-excitation of atomic core holes. a) X-ray emission; b) Auger electron emission.
representative spectra [64]. The lower limit of detection for contaminations such as C, N, and O, is around 1% of a monolayer when using a cylindrical mirror analyser [65]. Auger electron signals generally appear as small features superimposed on the large background of secondary electrons; accordingly it is often helpful to show the spectra in derivative form to emphasise the small peaks on a high background. In this mode, by convention, the peak position is taken as the most negative part of the derivative peak. An example of this is shown in Figure 1.7 for a Cu(100) crystal surface before cleaning by Ar⁺ bombardment.

1.5 Bond Length - Bond Order Relationship

Surface structural information is being accumulated by a range of surface sensitive techniques for well-defined single crystal chemisorption systems. Ultimately, it is worthy to unify these individual efforts into more generalised theoretical concepts which underlies a major motivation for all of them. For surface systems involving a chemisorbed species X on a metal surface M, the bond length X-M can be related to simple chemical bonding concepts as discussed by Mitchell [66,67] and others [68]. Guidance can be obtained from analyses of bulk structures, where Brown and Altermatt [69] have recently used the expression:

\[ r = r_0 - 0.85 \log s \]  \hspace{1cm} (1.23)

which derives from results of Pauling [70]. In Equation (1.23), \( r \) is the X-M bond length for the particular bond valence \( s \), and \( r_0 \) is the corresponding distance for a bond of unit valence. Mitchell has applied this relation to chemisorption bonding, and in particular has expressed the bond valence as [71]
Figure 1.7 Auger spectrum of the contaminated Cu(100) surface before cleaning.
where \( v \) is the atomic valence of \( X \) and \( n \) is the number of neighbouring \( M \) atoms. The value of \( r_0 \) can be estimated from the known coordination number of \( X \), and the corresponding \( X-M \) neighbouring interatomic distances in a reference solid [71]. Equations (1.23) and (1.24) have been used to assess the general reasonableness of structural results in this thesis, and will be discussed further in later chapters.

### 1.6 Current Status of Structural Studies for Chemisorption on the Cu(100) Surface

The clean (100) surface of copper has been a well-studied system for testing methodologies, reproducibility, and evaluation of structural parameters in the LEED technique [72-75]. The result of those structural studies demonstrates for the clean surface that the first interlayer spacing compresses by about -1\%, while the second expands by about +1\%.

However, when chemisorption occurs on the (100) surface of copper, the structural information is much less clear, even though these surfaces are usually regarded as "simple" systems. Some structural determinations concerning N, O, and S atomic adsorption on Cu(100) are listed in Table 1.2. The range of proposals in the current literature immediately suggests that these structures are far from having been convincingly solved. Further structural studies on these chemisorbed systems are therefore needed, and that provides the main subjects of this thesis. In addition this work should help evaluate the reliability of different surface structural techniques for chemisorbed systems.
<table>
<thead>
<tr>
<th>Surface</th>
<th>Adsorbate</th>
<th>Pattern</th>
<th>Adsite</th>
<th>Interlayer Spacings</th>
<th>Bond Lengths</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(100) N</td>
<td>c(2x2)</td>
<td>4F</td>
<td>d_i=1.45Å</td>
<td>d_N-Cu=2.32Å</td>
<td>LEED [76]</td>
<td></td>
</tr>
<tr>
<td>Cu(100) N</td>
<td>c(2x2)</td>
<td>4F</td>
<td>d_i=0.6Å</td>
<td>d_N-Cu=1.91Å</td>
<td>HREELS [77]</td>
<td></td>
</tr>
<tr>
<td>Cu(100) O</td>
<td>c(2x2)</td>
<td>4f</td>
<td>d_i=1.2-1.5Å</td>
<td>r_O-Cu=2.17-2.35Å</td>
<td>ARSIMS [78]</td>
<td></td>
</tr>
<tr>
<td>Cu(100) O</td>
<td>c(2x2)</td>
<td>2f</td>
<td>d_i=1.4Å</td>
<td>r_O-Cu=1.90Å</td>
<td>LEED [79]</td>
<td></td>
</tr>
<tr>
<td>Cu(100) O</td>
<td>c(2x2)</td>
<td>2f &amp; 4f</td>
<td>d_i=1.4Å, 0.0Å</td>
<td>r_O-Cu=1.90Å, 1.81Å</td>
<td>LEED [80]</td>
<td></td>
</tr>
<tr>
<td>Cu(100) O</td>
<td>c(2x2)</td>
<td>4f</td>
<td>d_i=0.0Å</td>
<td>r_O-Cu=1.81Å</td>
<td>LEED [81]</td>
<td></td>
</tr>
<tr>
<td>Cu(100) O</td>
<td>c(2x2)</td>
<td>4f</td>
<td>d_i=0.0Å</td>
<td>r_O-Cu=1.81Å</td>
<td>LEED [81]</td>
<td></td>
</tr>
<tr>
<td>Cu(100) O</td>
<td>c(2x2)</td>
<td>4f</td>
<td>d_i=0.7Å</td>
<td>r_O-Cu=1.94Å</td>
<td>SEXAFS [82]</td>
<td></td>
</tr>
<tr>
<td>Cu(100) O</td>
<td>c(2x2)</td>
<td>4f</td>
<td>d_i=0.8Å</td>
<td>r_O-Cu=1.97Å</td>
<td>ARPEFS [83]</td>
<td></td>
</tr>
<tr>
<td>Cu(100) O</td>
<td>c(2x2)</td>
<td>4f</td>
<td>d_i=0.0Å</td>
<td>r_O-Cu=1.81Å</td>
<td>XPS [84]</td>
<td></td>
</tr>
<tr>
<td>Cu(100) O</td>
<td>2√2x√2</td>
<td>4f &amp; 2f</td>
<td>no c(2x2)</td>
<td></td>
<td>LEED [85]</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.2 Previous structural results for N, O, and S chemisorptions on the Cu(100) surface.
† O replaces half Cu atoms in toplayer.
<table>
<thead>
<tr>
<th>System</th>
<th>Monolayer</th>
<th>Surface Structure</th>
<th>d$_{S1}$</th>
<th>r$_{S-Cu}$</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(100)</td>
<td>S</td>
<td>(2x2) 4f</td>
<td>1.39 Å</td>
<td>2.28 Å</td>
<td>ARPEFS [86]</td>
</tr>
<tr>
<td>Cu(100)</td>
<td>S</td>
<td>(2x2) 4f</td>
<td>1.39 Å</td>
<td>2.28 Å</td>
<td>HREELS [87]</td>
</tr>
<tr>
<td>Cu(100)</td>
<td>S</td>
<td>(2x2) 4f</td>
<td>1.42 Å</td>
<td>2.26 Å; relaxation</td>
<td>ARPEFS [88]</td>
</tr>
</tbody>
</table>

Table 1.2 Continued.
1.7 Outline of Thesis

An outline of the other chapters in this thesis is highlighted as follows:

Chapter 2 describes the multiple-scattering theoretical basis for LEED crystallography, including the layer doubling (LD) method, renormalized forward scattering (RFS) methods as well as the combined space (CS) approach used in the calculations. Some discussions of the physical parameters to be included in LEED calculations is also given, as well as the evaluations with R factors of the correspondences between experimental and calculated I(E) curves.

Chapter 3 is devoted to a description of the experimental apparatus and methods used by the research described. The emphasis is on the methods and instrumentation for LEED and AES including procedures for sample preparation and measurement of intensities.

Chapter 4 reports LEED crystallographic analyses for the Cu(100)-(2x2)-S surface structure. A series of relaxation models are investigated to clarify the interesting relaxation model proposed recently by the ARPEFS method [88]. Some further LEED observations related to this surface structure are discussed. In particular some approximate multiple scattering calculations are applied to this system, and consideration is also given to some beam splitting phenomena which are observed at higher coverages.

Chapter 5 focuses on LEED crystallographic analyses for the Cu(100)-c(2x2)-N surface structure. Discussions are included on the use of bond length - bond order relations to identify chemically reasonable surface structures, on comparisons between the LD and CS methods, as well as on approaches to refinement of this surface structure. Further LEED crystallographic studies are performed for some N-induced surface relaxation models.
Chapter 6 concentrates on LEED crystallographic studies for the chemisorption of oxygen on the Cu(100) surface. A series of models designed for a $(\sqrt{2}\times\sqrt{2})45^\circ$-O surface structure are investigated to reveal the relationship between the $(\sqrt{2}\times\sqrt{2})45^\circ$-O and $(2\sqrt{2}\times\sqrt{2})45^\circ$-O structures and to provide a starting point for the $(2\sqrt{2}\times\sqrt{2})45^\circ$-O investigation. A systematic study of some missing row models for the $(2\sqrt{2}\times\sqrt{2})45^\circ$-O structure is included.

Chapter 7 considers some further research directions for refining our knowledge of the surface structures considered in this thesis.
CHAPTER 2
MULTIPLE-SCATTERING CALCULATIONS OF LEED INTENSITIES

2.1 Introduction

Even at the time of the first LEED experiment, Davisson and Germer [89] found that this technique could not be described quantitatively by the single-scattering theory used in the X-ray diffraction analysis [90]. However, the multiple-scattering theory of LEED only developed during the late 1960s and early 1970s. The origins of LEED multiple-scattering calculations may be traced to band-structure theories [91]. In 1968, a self-consistent formalism that describes the backscattering of electrons from a crystal using the L-space representation was presented by Beeby [92]. In the same year, McRae [93] used a different approach which incorporated the Bloch-waves within the crystal which were matched across the solid-vacuum interface to the plane waves outside the crystal. Neither method in its initial form provided a satisfactory description of measured LEED intensities, because of exclusion of inelastic scattering, but soon afterwards that defect was overcome by the incorporation of a complex component into the constant part of the muffin-tin potential. This was first done by Duke and Tucker within the L-space method [94,95], but the most convincing agreement for calculated intensity curves was obtained by Jepsen, Marcus and Jona with their layer-KKR technique [96,97], a Bloch-wave method. Other developments which have had profound impact in the area of surface-structure determination include the formulation of perturbative methods [98-102]. Very recent proposals include the diffuse-LEED method for determining local structure in disordered surfaces [206a], and tensor-LEED, a "direct method", for efficient assessment of complex reconstructed surfaces [206b].
Most current LEED multiple-scattering calculations are based on layer models. The approach is two-tier: first the multiple-scattering by a single layer is calculated, and this is followed by the stacking of layers into the complete surface region. Two different mathematical approaches [100] are commonly used in the scattering theory, and this permits multiple-scattering calculations to be divided into two categories. In one category, the scattering is described in terms of spherical waves (the L-space representation); this is a natural basis insofar as the electrons are scattered by spherically symmetric ion cores. The other category describes the scattering within the crystal in terms of plane waves and is commonly known as the momentum (or K-space) representation; this is natural insofar as plane waves provide eigenfunctions for electrons travelling in a region of constant potential. Of the two approaches, the K-space representation is perhaps the easier to visualise since the scattering is described directly in terms of diffracted beams, and symmetry can be utilised [53] to reduce the number of plane waves in practice. The mathematical transformation between the plane and spherical representations has been discussed in detail by Marcus [103]. The scattering amplitude for a single layer is normally calculated in the angular momentum (L-space) representation using spherical waves [53,103]. The calculation of the multiple-scattering between these layers can be performed either in the L- or K-representations. The advantage of the former is that the complexity of the calculation does not depend on interlayer spacing, and in particular very small interlayer spacings can be handled (including different kinds of surface atoms in a single plane). However it requires very large matrices when the number of atomic layers is large [53,103]. Use of the K-representation has the advantage that the scattering of an assembly of parallel layers can be simply described by a product of the scattering matrices of the single atomic layers involved, but there is the disadvantage that only a finite number of beams can be taken
into account in a practical calculation (matrix dimensions increase directly with the number of beams required) [53,104].

In multiple-scattering calculations, the total wave function outside the solid-vacuum interface can be written as

$$\Psi_{\text{out}}(r) = e^{i k_o \cdot r} + \sum_g c_g e^{i k_g \cdot r}$$

(2.1)

where $e^{i k_o \cdot r}$ and $e^{i k_g \cdot r}$ represent the incident plane wave and diffracted plane waves respectively (the superscripts "+/−" specify into-the-crystal/out-of-the-crystal directions). The coefficients $c_g$ represent the scattered amplitude of a plane wave traveling in the direction $k_g$. The beam intensity (or reflectivity) of the $g$th diffracted beam can be expressed as

$$R_g = \left( \frac{k_-}{k^+_{o \perp}} \right) |c_g|^2$$

(2.2)

where $k^+_{g \perp}$ and $k^+_{o \perp}$ are the perpendicular components of the diffracted beam and the incident beam, and they are measured outside the crystal [105].

This chapter summarises some salient features of the multiple-scattering and intensity evaluation methods used in this thesis. All the multiple-scattering calculations made here were done with the computer programs of Van Hove and Tong. More detailed information is provided in their book [53] and in other reviews of the subject [15,100,103,105]. Expressions in this chapter are given in atomic units where $\hbar = e = m = 1$. 

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2.2 Physical Parameters in Multiple-Scattering Calculations

The parameters required in LEED multiple-scattering calculations divide into two groups: (i) geometrical (or structural) parameters which include all distances between atoms and between atomic layers; (ii) the other physical parameters which are not directly related to structure and are called "non-structural" parameters. In the following subsections, these "non-structural" parameters will be discussed along with their selection criteria.

2.2.1 Muffin-tin potential

In LEED the electrons are scattered by the solid's potential. A convenient model, for a regular diperiodic surface region, is provided by the "muffin-tin" approximation which is well established in band structure calculations [106]. Figure 2.1 illustrates a potential of this type. In this approximation, it is assumed that each atom of the surface region is represented by a perfectly spherical potential within a muffin-tin sphere, while the potential between the atomic spheres is constant. For LEED it is assumed that each sphere does not overlap the neighbouring atomic spheres. In relatively close-packed materials, the interstitial regions of the ion-core have potential variations that are small compared to LEED energies, namely at most a few eV in worst case [104]. It is then reasonable to assume a constant value of the potential (muffin-tin constant) in those regions. The great advantage of this simplification is derived from the fact that electron waves propagating in these regions have simple forms. Also much basic information is available from the use of the muffin-tin approximation in band structure studies.

In LEED multiple-scattering calculations, the muffin-tin constant is referenced to the zero-energy level in vacuum; it determines the amount by which an electron is speeded up on entering the crystal, a concept that has traditionally been covered by the term "inner
Figure 2.1 Muffin-tin approximation: a) potential contour plot through an atomic layer; b) variation of potential through a single row of ion cores along xx' ($V_0$ is the constant intersphere potential).
potential" [15]. In practice, in LEED the muffin-tin constant is expressed as a complex number

\[ V_0 = V_{or} + iV_{oi} \]  

(2.3)

For clean metals, the real component \( V_{or} \) may be estimated from the sum of the Fermi energy and the work function [15,107]. Generally, \( V_{or} \) takes values between -5 to -15 eV, and it is not normally a strong function of incident electron energy in the range studied by LEED. In this work it has always been taken as a constant which is chosen by the best fit of experimental and calculated intensity curves (I(E) curves)[15]. The imaginary component \( V_{oi} \) can be determined by the width in energy of dominant peaks in experimental I(E) curves:

\[ \Delta E \geq 2 |V_{oi}| \]  

(2.4)

Most LEED intensity calculations have used a constant value for \( V_{oi} \) between -3 and -5 eV throughout the whole energy range, although sometimes a weak energy-dependence has been included [108,109] such as

\[ V_{oi} = -BE^{1/3} \]  

(2.5)

In principle, different values of \( V_{or} \) and \( V_{oi} \) may be chosen for the top surface (or adsorbed) layer and for layers below, but most often — as in this work — single values are chosen for the whole surface region [110].
2.2.2 Phase shifts

The scattering of a plane wave of wave vector $k_0$ by a spherical potential has the following asymptotic form [53]:

$$e^{ik_0 \cdot r} + i\frac{k_0 r}{r}$$

where $t(\theta)$ is the atomic scattering amplitude and $\theta$ is the scattering angle; $k_0 = |k_0|$. The scattering amplitude may be expanded in Legendre polynomials $P_l$:

$$t(\theta) = 4\pi \sum_{l=0}^{\infty} (2l+1) t_l \sin \theta$$

where

$$t_l = \frac{\exp(2i\delta_l) - 1}{4ik_0} = \frac{\exp(i\delta_l) \sin \delta_l}{2k_0}$$

and the $\delta_l$ are the phase shifts for angular momentum values ($l = 0, 1, 2, \ldots$) [111]. The phase shifts are obtained by integrating the radial Schrodinger equation for the LEED electron in the presence of the ion core potential [15]. Phase shifts are characteristic of the particular ion core potential used and also depend on the incident electron energy; the elastic scattering process may be described fully by a set of phase shifts, one for each possible angular momentum value $l$. Equation (2.7) appears as an infinite sum, although for LEED to around 200 eV from a nonvibrating lattice, the summation can generally be truncated to about 5 or 6 terms, and it may even be less for weakly scattering atoms. More terms are needed the higher the energy and the stronger the atomic scattering.
However with a vibrating lattice, required for describing temperature effects, the number of required $l$ values needs to be increased by about 2 over that for stationary atoms [16]. In practice in LEED for energies to about 220 eV, the inclusion of eight phase shifts (i.e. to $l = 7$) is satisfactory [16].

The calculation of atomic potentials from band structures has been described in detail by Loucks [112] and a commonly used scheme for calculating the constant potential between the atomic spheres has been detailed by Mattheiss [113]. The phase shifts for both the copper substrate and adsorbates studied in this work were calculated from appropriate atomic potentials using the computer programmes of the CAVLEED package [15,114]. In outline, the atomic potential for copper was derived from a band structure calculation made by Moruzzi et al. [115]. In addition, an alternative potential for copper was deduced from a superposition of copper charge densities which are distributed at atomic sites on a FCC lattice with the regular lattice constant of 3.165 Å. This calculation assumed the Slater approximation for the local exchange term [116], and the copper phase shifts (to $l = 7$) were calculated using the standard RKM method of numerical integration [15]. However it turned out that both sets of copper phase shifts are almost identical.

For the non-metallic adsorbates (sulphur, nitrogen, and oxygen) the atomic potentials were also calculated by the superposition of atomic charge densities which are distributed over some model lattices as detailed in Table 2.1 and Figure 2.2. The individual atomic charges were determined from atomic wave function information [117-119]. Ultimately, the suitability of a potential can only be judged by its success in allowing close agreement between theoretical and experimental LEED beam intensities [120].
<table>
<thead>
<tr>
<th>Phase Shifts</th>
<th>Lattice</th>
<th>Element(s)</th>
<th>$a_0$</th>
<th>$r_{MT}$</th>
<th>Derived by</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHSH1</td>
<td>bcc</td>
<td>S</td>
<td>2.49 Å</td>
<td>1.08 Å</td>
<td>Demuth et al. [161]</td>
</tr>
<tr>
<td>PHSH2</td>
<td>bcc</td>
<td>S</td>
<td>2.24 Å</td>
<td>0.97 Å</td>
<td>This work</td>
</tr>
<tr>
<td>PHSH3</td>
<td>bcc</td>
<td>N</td>
<td>1.64 Å</td>
<td>0.70 Å</td>
<td>Moritz et al. [182]</td>
</tr>
<tr>
<td>PHSH4</td>
<td>bcc</td>
<td>N</td>
<td>1.60 Å</td>
<td>0.69 Å</td>
<td>This work</td>
</tr>
<tr>
<td>PHSH5</td>
<td>bcc</td>
<td>O</td>
<td>1.73 Å</td>
<td>0.75 Å</td>
<td>Demuth et al. [161]</td>
</tr>
<tr>
<td>PHSH6</td>
<td>sc</td>
<td>O</td>
<td>2.56 Å</td>
<td>0.57 Å</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sc</td>
<td>Cu</td>
<td>2.56 Å</td>
<td>1.28 Å</td>
<td>This work</td>
</tr>
<tr>
<td>PHSH7</td>
<td>bcc</td>
<td>O</td>
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<td>1.08 Å</td>
<td>This work</td>
</tr>
<tr>
<td>PHSH8</td>
<td>sc</td>
<td>O</td>
<td>2.56 Å</td>
<td>1.08 Å</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table 2.1 Adsorbate phase shifts used in the LEED multiple scattering calculations; $a_0$ is lattice constant and $r_{MT}$ the muffin-tin radius.
Figure 2.2. Unit cells for hypothetical CuO crystal lattice (a), body-centred cubic oxygen lattice (b) and simple cubic oxygen lattice (c). Open circles: Cu atoms; dark filled circles: oxygen atoms.
2.2.3 The Debye-Waller factor

Temperature has a number of effects on LEED. First, the momentary vibrational displacements of surface atoms from perfect periodicity will lead to incoherent scattering, reducing the intensities of diffracted spots and increasing the background intensity. Secondly, the diffracted spots may be broadened because of the momentum exchange with phonons. Finally, the lattice will expand with increasing temperature, so shifting Bragg peaks slightly towards lower energies.

The effect of thermal vibrations in LEED for the purposes of surface structure determination can be included by multiplying the atomic scattering amplitudes $t(\theta)$ with a Debye-Waller factor $e^{-M}$:

$$t^T(\theta) = e^{-M} t(\theta)$$  \hspace{1cm} (2.9)

where

$$M = \frac{1}{2} \langle (\Delta k - \Delta r)^2 \rangle_T = \frac{1}{6} \Delta k^2 \langle (\Delta r)^2 \rangle_T$$  \hspace{1cm} (2.10)

In Equation (2.10), $\Delta k$ is the momentum transfer and $\langle \Delta r^2 \rangle$ is the mean square vibration amplitude for the atoms which are assumed all equivalent. This equation assumes the harmonic approximation for the lattice vibrations [121]. Then, in the high-temperature limit the factor $M$ is

$$M = \frac{3(\Delta k)^2 T}{2mk_B \theta_D^2}$$  \hspace{1cm} (2.11)

where the atomic mass $m$ is expressed in units of the electron mass, $k_B$ is Boltzmann's constant ($3.17 \times 10^{-6}$ Hartree / Kelvin), and the actual and Debye temperatures, $T$ and $\theta_D$...
are in Kelvins. The Debye temperature $\theta_D$ is a parameter which describes the rigidity of the lattice with respect to vibrations; the higher $\theta_D$ the stronger the bonding in the solid \[10,121\].

Jepsen, Marcus, and Jona incorporated the Debye-Waller factor into atomic scattering and showed how to derive temperature-dependent phase shifts \[97\] assuming isotropic atomic vibrations. The temperature-dependent phase shifts $\delta^T_i$ are the basic atomic parameters to be input into multiple-scattering calculations.

### 2.3 Layer Diffraction Matrices

The previous section outlined several basic ingredients to be included in multiple-scattering calculations of LEED intensities. The next stage is to put these ingredients together and to describe the scattering of an incident plane wave from the vacuum side of the crystal surface. In principle, we can construct a crystal by stacking individual diperiodic layers, while a layer can be understood to consist of one or more atomic planes parallel to the surface. The scattering of any plane wave $k_g^\pm$, not just the primary incident beam $k_0$, incident onto either side of such a layer can be described by the layer diffraction matrix $M^{\pm\pm}$.

A single diperiodic plane of identical atoms that extends to infinity in all directions defines a Bravais-lattice layer. The scattering by such a layer is represented by the layer diffraction matrix, where the particular element $M_{g'g}^{\pm\pm}$ specifies the amplitude of the diffracted plane wave $k_g^\pm$ due to an incident wave $k_g^\pm$ \[16\]:

$$M_{g'g}^{\pm\pm} = \frac{16\pi^2}{\cal A k} \sum_{LL'} Y_L^*(k_g^\pm) \tau_{LL'}(k_0) Y_{L'}(k_g^\pm)$$  \(2.12\)
where $A$ is the area of the layer unit mesh. $L$ and $L'$ represent the pairs of angular momentum quantum numbers $(l, m)$ and $(l', m')$ respectively. The $Y_L(k)$ are spherical harmonics for the angle between the $k$ and the surface normal ('*' indicates complex conjugation). $\tau_{LL'}(k_0)$ is the $LL'$ element of the planar scattering matrix $\tau(k_0)$ and can be expressed as:

$$\tau(k_0) = t(k_0)[I - X]^{-1} \quad (2.13)$$

where $t(k_0)$ is the diagonal ion core $t$-matrix whose non-zero element has been presented by Equation (2.8). $I$ is the unit matrix and the matrix $X$ describes multiple-scattering within the atomic layer in angular momentum space [98]:

$$X = G(k_0^+)t(k_0) \quad (2.14)$$

where $G$ is a structural factor which describes the intraplanar propagators (in $L$-space) and is dependent on damping and the structural arrangement of the ion cores but is independent of the scattering properties of the ion cores.

The planar scattering matrix $M^{\pm \pm}$ distinguishes between reflected and transmitted plane waves, and the following notation can be used to represent the layer reflection and transmission matrices [53]:

$$r^{+ -} = M^{+ -}, \quad r^{+ +} = M^{+ +}, \quad t^{+ +} = M^{+ +} + I, \quad t^{- -} = M^{- -} + I \quad (2.15)$$

where $I$ is the unit matrix for representing the unscattered plane wave when it is transmitted without change of direction through the layer. The superscripts "+/−" specify
into-the-crystal / out-of-the-crystal directions and they follow the right-to-left logical order. The above discussion is depicted in Figure 2.3.

2.4 Diffraction by a Stack of Layers

Once the individual layer diffraction matrices calculated by exact methods are known, the next step is to determine the scattering by a stack of such layers. There are two popular iterative approaches to this problem. One is called the layer doubling method (LD) [15,98], and the other is the renormalised forward scattering (RFS) method [98]. These are both K-space methods, but they do not work well when there are small interlayer spacings present (e.g. 0.5 Å or less). Then the number of plane waves, and correspondingly the dimension of the matrices involved, is too large for numerical reliability [104]. When some interlayer spacings are small while others are large, it is effective to combine the K- and L-representations for calculating the multiple-scattering between layers. This defines the "combined space (CS) method" [122,123] which basically uses an L-space calculation for the close layers (≤ 0.5 Å) and a K-space calculation (e.g. RFS) for the relatively large interlayer spacings (≥1.0Å). Intermediate cases can be handled with the LD method.

2.4.1 Layer doubling method

Given the reflection and transmission matrices for two diffracting layers (referred as layer A and layer B), Pendry [15,98] showed how to determine the corresponding matrices for the combined system A+B. The infinite summation over all orders of multiple-scattering occurring between these layers gives a geometrical series which is easily evaluated to give the compact expressions:
Figure 2.3  a) Schematic diagram of transmission (t) and reflection (r) matrices at nth layer. The dashed lines are midway between consecutive layers. b) Multiple-scattering of a set of plane waves by a layer of ion cores with diffraction matrices $M^{\pm\pm}$ as indicated in a).
\[ R^{++} = r_A^{++} + t_A P_B^{++} (I - r_A^{-+} P_B^{+-})^{-1} t_A^{++}, \]
\[ T^{++} = t_B^{++} P_B^{++} (I - r_A^{-+} P_B^{+-})^{-1} t_A^{++}, \]
\[ R^{+-} = r_B^{+-} + t_B^{+-} P_A^{++} r_B^{-+} P_B^{-+} (I - r_B^{+-} P_A^{++})^{-1} t_B^{-+}, \]
\[ T^{+-} = t_A^{-+} P_A^{++} (I - r_B^{+-} P_A^{++})^{-1} t_B^{-+}, \]
\[ (2.16) \]

with
\[ P_g^\pm = e^{\pm i k_g r_{BA}} \]
\[ (2.17) \]

Here the \( P_g^\pm \) are plane wave propagators for every \( g \) between layers A and B, and the vector \( r_{BA} \) relates the two reference points in the layers.

Equation (2.16) gives a set of diffraction matrices which describe the effect of scattering from the double layer. The iteration procedure for the layer-doubling method is depicted in Figure 2.4. First, layers A and B are combined into a slab. Then two identical slabs from the first step are stacked into a 4-layer slab (this just requires substituting the results on the left-hand side of Equation (2.16) into the right-hand side). For a stack of 8 layers, 3 iterations are required. After \( n \) such iterations, \( 2^n \) layers have been stacked. The diffraction matrices of the growing stack will converge due to the limited mean free path of electrons. Typically, about 4 iterations produce satisfactory numerical convergence [15].

### 2.4.2 Renormalised-forward-scattering method

For LEED energies forward scattering is normally stronger than backward scattering, and this guided the renormalisation of the interlayer perturbation theory introduced by Pendry [15]. Generally, transmission through a layer is not just described
Figure 2.4 Schematic diagram of the doubling procedure for a 8 layer slab. A and B represent layers A and B with different layer registries.
by unperturbed plane waves, but rather by plane waves modified by forward scattering through that layer together with all other plane waves transmitted at various scattering angles. Figure 2.5 illustrates the iterative procedure treated in the RFS method. The first-order calculation contains all paths that have been reflected (backscattered) only once, but transmitted from layer to layer until they are sufficiently attenuated. The second-order of perturbation is obtained by reflecting the emerging plane waves from the first-order result back into the crystal and collecting the additional reflections from the emerging waves at each layer. As in the first-order calculation, the newly emerging plane waves also collect the reflections from the forward scattered waves at each layer as they are propagated into the surface. The second-order result is then added to the first-order results, and the iteration is carried on for higher-orders until the reflected amplitudes converge.

The plane wave amplitudes $a_{(1)g}$ in the $i$th interlayer spacing are computed iteratively with:

$$
a^\text{new}_{(i)g} = \sum_{g'} (t^+ P^+(i-1)_{g'g} a_{(i-1)g'} + r^+ P^+(i)_{g'g} a_{(i)g'})
$$

(2.18)

for penetration and

$$
a^\text{new}_{(i)g} = \sum_{g'} (t^- P^-(i+1)_{g'g} a_{(i+1)g'} + r^- P^-(i)_{g'g} a_{(i)g'})
$$

(2.19)

for emergence, where $P^\pm(i)$ are plane wave propagators between successive layers. For the surface plane, $i = 1$ and the initial values for the iteration procedure can be written as
Figure 2.5: a) Illustration of the renormalised forward scattering method. Horizontal lines represent layers, and $i$ represents $i$th interlayer spacing. b) Propagation steps for penetration waves. c) Propagation steps for emergence waves.
\[ a_{(i)g} = 0 \quad \text{for all } i \text{ and } g, \text{ except} \]

\[ a_{(1)0} = 1 \quad \text{(2.20)} \]

Typically, the RFS scheme uses 12 to 15 layers and 3 to 4 orders of iteration for convergence, and this enables it to require relatively small amounts of computing time. However, RFS fails to converge well either when multiple-scattering between layers is very strong or when the electron damping is small.

### 2.4.3 Combined space method

When atomic layers are closely spaced, the K-space methods (e.g. Bloch wave, LD, and RFS) cannot provide convergence with a manageable number of plane waves. For small-adsorbate chemisorption systems, the interlayer spacings between adsorbate and the first substrate layer are often relatively small. Also, the topmost substrate layer may undergo relaxations or reconstructions which require it to be divided into different atomic planes. Such an atomic layer with more than one atomic plane (or more than one atom per unit mesh) parallel to the surface defines a composite layer. Such composite layers dealt with in this thesis were treated with the combined space (CS) method [122,123].

The combined space method combines representations in linear momentum K-space and in angular momentum L-space. The interlayer multiple-scattering between the atomic layers is most efficiently calculated with K-space methods, although the diffraction matrix for the entire composite layer is expressed in L-space:
Here $g$ and $g'$ are reciprocal lattice vectors of the surface with an unit mesh area $A$. The index $i$ labels the $N$ "subplanes" of the layer, each of which is defined by one of the atoms in the unit mesh, also

$$R_{g}^{i\pm} = e^{\pm k_{g}^\pm \cdot r_{i}} \quad (2.22)$$

where $r_{i}$ is the position for the $i$th atom. The element $T_{LL'}^{i}$ in (2.21) gives the self-consistent amplitude of an outgoing spherical wave $Y_{L}$ leaving the atom $i$ due to an incident spherical wave $Y_{L}^{*}$, incident on all atoms of the layer. Beeby [92] showed that the matrices $T^{i}$ can be calculated by solving a set of linear equations:

$$T = A^{-1} \tau \quad (2.23)$$

where $T$ and $\tau$ are column matrices formed from $T^{i}$ and $\tau^{i}$ respectively, and $\tau^{i}$ represents the scattering matrix containing all scattering paths within the subplane $i$. However, the matrix $A^{-1}$ can be transformed to yield

$$T = A^{-1} \tau = D_{g}^{-1} A^{-1} D_{g} \tau \quad (2.24)$$

where $A^{-1}$ does not depend on $g$ and $D_{g}$ is a diagonal matrix with the simple diagonal element $R_{g}^{i\pm}$ [122,123]. Hence, the time-consuming matrix inversion step in (2.24) needs to be done only once.
Another calculation scheme originated by Zimmer and Holland for a composite layer is the reverse-scattering perturbation (RSP) method [124] which works along similar lines to RFS, but in the L-space representation. Figure 2.6 illustrates the scattering process for the case of a layer with 4 subplanes. The thin lines represent the incident plane waves and the thick lines indicate the scattered spherical waves. The multiple-scattering within each subplane of a layer to be treated by RSP is assumed to have been obtained as the matrices $\tau^i$ noted above. The subplanes are ordered according to increasing distance from the vacuum (1-4). The iterations involve an "in - and - out pass" procedure as depicted in Figure 2.6. Convergence provides the quantities $T^i$ of Equation (2.23) and the problem is solved [122]. However, every perturbation method has its limits of validity. When the atoms of a composite layer scatter too strongly for proper convergence of the RSP method, matrix inversion may be necessary. If a composite layer is composed of some strong scatterer subplanes and some weaker scatterer subplanes, a combined matrix-inversion / RSP treatment may be appropriate [122,123]. The reflection and transmission matrices for a composite layer can also be defined by Equation (2.15).

2.5 Reliability Factors and Result Evaluations

In LEED crystallography, a structural model is considered correct if the calculated $I(E)$ curves correspond very well with those from experiment. It follows that the evaluation of a structural model is done by examining curve shapes, peak positions, relative peak intensities, and the existence or absence of shoulders. Traditionally, this evaluation has been made by visual inspection and comparison of calculated and experimental $I(E)$ curves. Although there are some advantages for this approach, it can become subjective and unwieldy when the data base is large. Therefore it is desirable to
Figure 2.6 Diagram of the reverse-scattering perturbation scheme for the case of a composite layer with four subplanes (1-4).
have quantitative reliability factors, in some analogy with their use in X-ray crystallography [55]. R-factors are mathematical indices (simple numbers) which summarise the level of correspondence between sets of curves. They are all defined so an R-factor is zero when identical curves are compared, but their upper limits can vary. For structural determination, an R-factor should be especially sensitive to structural parameters and relatively insensitive to non-structural parameters. In addition, an R-factor can provide a basis for a search strategy for structural optimisation [125]. Ideally, an R-factor would also allow crystallographers to evaluate the quality of different structural determinations in an objective manner. A number of different R-factors have been proposed for LEED [54]. However, the question of which R-factor is "best" can only be answered by a subjective choice. Two main R-factors used extensively in LEED crystallography will be described in the following.

To take into quantitative account all features in a comparison between experimental and calculated I(E) curves, Zanazzi and Jona [126] proposed a single-beam reliability factor $r_{ZJ}$ which is defined as:

$$r_{ZJ} = A \int \frac{|I_e'' - cI_c''| |I_e' - cI_c'|}{|I_e'| + \max |I_e'|} dE$$

(2.25)

The single and double primes in (2.25) indicate the first and second derivatives of the intensity with respect to the energy; $I_e$ and $I_c$ are the experimental and calculated intensities respectively. $A$ is a reducing constant

$$A = \frac{1}{0.027 \int I_e dE}$$

(2.26)

and $c$ is a scaling constant
Zanazzi and Jona showed that the reduction factor 0.027 is a typical average value from a set of random curves. In addition, this factor makes $r_{ZJ}$ dimensionless. Van Hove and Koestner [54] modified the reducing constant

$$A_M = \frac{1}{\int |I_e| dE}$$

(2.28)

and accordingly defined a modified $r$-factor

$$r_{MZJ} = A_M \int \frac{|I_e - |cI| | |I_e - |cI| dE}{|I_e| + \max |cI|}$$

(2.29)

in which $\max |cI|$ replaces $\max |I|$ of (2.25). This modification avoids a normalisation problem that can occur by an unusually large $|I|$ dominating the integrand. For comparing $I(E)$ curves from several diffracted beams, the multi-beam $R$-factor proposed by Zanazzi and Jona is

$$R_{ZJ} = \frac{\sum_i \Delta E_i r_{ZJ}^i}{\sum_i \Delta E_i}$$

(2.30)

where $i$ indicates each individual beam. $R_{ZJ}$ represents an average of $r$ values, weighted according to the energy range over which the comparison with experiment has been
made. Similarly, the modified multi-beam R-factor given by Van Hove and Koestner [54] is

\[ R_{MZJ} = \frac{\sum \Delta E^i r_{MZJ}^i}{\sum \Delta E^i} \]  

(2.31)

Pendry has constructed a reliability factor [127] that avoids the second derivatives used in \( R_{ZJ} \) and thus reduces computing times. This R-factor is chiefly sensitive to peak and valley positions, although it plays some attention to relative intensities. It emphasises the simple logarithmic derivative \( L(E) \) of the \( I(E) \) curves

\[ L = \frac{I'}{I} \]  

(2.32)

and the function

\[ Y = \frac{L}{(1 + L^2 V_{0i})} \]  

(2.33)

where \( V_{0i} \) is the imaginary part of the constant potential used in the calculations. Pendry's multi-beam R-factor is defined in terms of the \( Y \) functions:

\[ R_p = \frac{\sum \int (Y_{ei} - Y_{ci})^2 \, dE}{\sum \int \left[ (Y_{ei})^2 + (Y_{ci})^2 \right] \, dE} \]  

(2.34)

where again the summations are over the different beams \( i \) and the subscripts \( e \) and \( c \) refer to experiment and calculation respectively. The denominator in (2.34) normalises \( R_p \) to
unity when there is no correlation between calculation and experiment. Van Hove and Koestner [54] compared many different R-factors for LEED, and introduced appropriate normalisation constants to ensure that all the different indices generally range between 0 and 1 in practice. One of these normalised R-factors used in this work is

\[ R_p' = \frac{1}{2} R_p \]

(2.35)

where 1/2 is the normalisation constant given by Van Hove and Koestner for Rp.
CHAPTER 3
EXPERIMENTAL METHODS

3.1 The UHV Facilities

Ultra-high vacuum (UHV) technology [128] is an essential requirement for a LEED/AES experiment. There are two main reasons for this. First, UHV is needed to achieve a surface that is free from unwanted adsorbed species and therefore to maintain the desired surface phases during the experiment. Second, LEED/AES experiments probe a surface with electrons which need a long mean free path for the region between source and detector without many collisions with gas-phase molecules. A vacuum pressure level in the $10^{-10}$ Torr range or below is required for detailed studies on well-defined surfaces. Figure 3.1 shows the basic experimental arrangement used in this work. The UHV chamber (Varian 240) is constructed of non-magnetic stainless steel and is connected to a series of pumps, pressure gauges, and other facilities. Vacuum seals between flanges are made using copper gaskets pinched between steel knife-edges. Pressures in the low $10^{-10}$ Torr range could be achieved by the following pumping sequence (Figure 3.2):

a) An initial roughing by the adsorption pump reduces the pressure of the chamber from the atmospheric value to $\sim 10^{-3}$ Torr. Adsorption pumps work by physically adsorbing gases from the chamber on to surfaces of molecular sieves (zeolites) which are cooled by liquid nitrogen.

b) The system is then pumped with an oil diffusion pump (Varian M2). The non-volatile oil (polyphenyl ether) serving as pump fluid is vaporised from the boiler by electrical heating. The pump fluid vapour streams through the chimneys and emerges with high speed from a three-stage nozzle. The vapour later condenses on a water-cooled
Figure 3.1 Schematic diagram of the Varian 240 UHV chamber and associated experimental arrangement.
Figure 3.2 Pumping system for UHV experimental chamber (Varian 240) and gas line. TCG: thermocouple gauge; IG: ion gauge.
wall and returns to the boiler, while the gases are pumped away by a rotary pump. The system can be pumped easily down to around $10^{-7}\ \text{Torr}$ within 10 minutes.

c) When the pressure is in the $10^{-7}\ \text{Torr}$ range, the main sputter-ion pump (2001 s$^{-1}$) connected at the bottom of the chamber can be turned on. In a sputter-ion pump, cylindrical anodes are closely arranged between parallel cathodes made of titanium, whose axes are perpendicular to the cathodes. The cathodes are at negative potential (a few kV below the anodes), and the whole electrode system is maintained in a strong, homogeneous magnetic field. The pumping action is initiated by a discharge at the anode to produce ions from the gas to be pumped. These ions are then trapped by the strong homogeneous magnetic field, and sputter the titanium cathode surface. The primary pumping mechanism is gettering by the titanium film which is continuously replenished via sputtering of the cathodes. All gaseous molecules can be pumped by these processes, although at different speeds. With the ion-pump operating, the pressure of the system would normally be reduced quickly to the $10^{-8}\ \text{Torr}$ range.

d) The whole system is then baked out for ~12 hours at ~200°C to remove adsorbed gases from the walls of the chamber. Soon after the baking, all filaments used in the system are degassed thoroughly while the system is still at ~100°C. A titanium sublimation pump is also available to provide extra pumping capacity during both the degassing and normal operations. Titanium is used as the getter material, which is evaporated from a resistance-heated wire consisting of an alloy with a high titanium content. The baking and degassing procedures may be repeated until a pressure in the $10^{-10}\ \text{Torr}$ range or below is attained.

The gas-line pressure is monitored by two thermocouple gauges (Varian 972-0006) and the gauge on the small ion pump. The experimental chamber and the oil diffusion pump are equipped with ionisation gauges (Varian 971-0003) respectively for pressure measurement (see Figure 3.2). The crystal sample is attached to a molybdenum
sample cup which is equipped with a resistive heater (Varian 981-2058) to allow heating. Crystal temperature is measured with a 0.005" chromel-alumel thermocouple which is in contact with the sample cup. The manipulator (Varian 981-2528) has translational motions (x,y,z) and two rotations (azimuthal and flip). The azimuthal rotation allows the sample to be directed to either the LEED/AES optics or the ion-bombardment gun (Varian 981-2043) used for cleaning the surface. Argon and gases for chemisorption studies are introduced into the chamber through a variable leak valve from a gas inlet manifold. This gas line is equipped with its own small ion pump (20 l s⁻¹, Varian 981-0200), and it can be baked out separately from the main chamber.

3.2 Instrumentation

3.2.1 LEED

The LEED optics used in this work is of the conventional "display" type, for which the diffraction pattern is made visible on a fluorescent screen. Figure 3.3 gives a simplified indication of such a LEED system. Some of its essential elements are described below. The LEED electron gun (Varian 981-2148) consists of a directly heated cathode (~2000°C) made of tungsten, an extraction electrode, a deflector, an array of focusing electrodes, and a field-free drift tube. The cathode is surrounded by a Wehnelt cylinder [129] except for the beam extraction aperture. The electrons emitted from the cathode are collimated by the deflector and focusing lens system, and finally leave the drift tube with an energy determined by the accelerating voltage. The drift tube is earthed so that electrons move in a field-free region between gun and sample. The typical electron beam has a diameter of less than 1 mm at the sample surface and an energy spread of about 0.5 eV (FWHM) determined by the thermal energy distribution [130]. In the normal constant-current mode, the incident current is directly read from the digital
Figure 3.3 Schematic diagram of the electron gun and 4-grid detection system used for the LEED experiment.
panel meter. Typically the current is of the order of 1 µA for energies above 100 eV, but below 100 eV the current decreases linearly with decreasing energy.

The diffracted electrons are analysed by the detection system which comprises of a hemispherical fluorescent screen and four hemispherical nested grids just before the screen. The screen is biased at about 5 kV positive potential, so that approaching electrons are accelerated rapidly onto the phosphor coating and create a glow proportional to the beam current. The efficiency of the phosphor in converting electrons to photons depends on the phosphor particle size, the size distribution, and the thickness of the coating [129]. The first grid is earthed so that it provides a field-free region around the sample. The second and third grids are linked together and act as an energy selector (filter) [131]. These grids are maintained at a negative potential just a few eV below the accelerating voltage. The objective is to get sharp spots while admitting only a very restricted number of inelastically scattered electrons [129]. The fourth grid is earthed to isolate the fluorescent screen potential from the energy-selection potential at retarding grids 2 and 3. A series of LEED patterns corresponding to different energies can be displayed on the screen by systematically modifying the primary beam energy and simultaneously the potential applied to the retarding grids.

3.2.2 Auger electron spectroscopy

The electron gun noted above was also used for the AES experiments with a typical primary beam energy around 1500 eV[132]. The Auger electrons were detected in this work by using the four-grid LEED optics as a retarding field analyser (RFA) [131], as shown schematically in Figure 3.4. The first and fourth grids of the optics are again earthed, but the repeller grids (grids 2 and 3) are treated differently. The negative potential $V_r$ applied will repel all electrons with kinetic energies less than $kV_r$, so
Figure 3.4 The AES experimental set-up using the LEED optics as a retarding field analyser (RFA) for detection of Auger electrons.
preventing those electrons from reaching the collector (fluorescent screen). Two repeller grids are needed to improve the energy-selection resolution in AES (one of these grids would be sufficient for LEED alone). In order to extract the Auger electrons, the repeller grids are modulated by a small voltage $k\sin\omega t$ ($k$ in the range of 1~10 V) about the ramped $V_r$ through a transformer in the preamplifier unit. The fourth grid between repeller and collector reduces the capacitance between them and prevents any AC modulation voltage applied to the repeller from being passed directly to the collector. The capacitance between collector and repeller grids is compensated by adding a capacitor bridge circuit in the preamplifier [133]. The voltage ramp unit consists of a multichannel analyser (Fabritek 1062) and a programmable power supply (Kepco OPS 2000). The collected electrons are detected with a lock-in amplifier (PAR 128), and the Auger spectrum (in $dN(E)/dE$ versus $E$ form) is obtained by synchronously detecting the collector current at the second harmonic of the modulation frequency ($2\omega$) [134]. The output of the lock-in amplifier is stored in the multichannel analyser, and the data are averaged to improve signal to noise ratio. Finally, the spectrum may be displayed on an oscilloscope or X-Y plotter (HP 7004B). Typically, to display a spectrum between 50-1000 eV, only a few minutes is needed using a primary beam of about 15-20 $\mu$A and a primary energy of 1.5-2.0 kV.

3.3 Sample Preparation and Cleaning

3.3.1 Preparation procedures

The Cu(100) surface used in this work was prepared from a 99.999% purity single crystal rod grown in the Metallurgy Department, UBC. To prepare the surface, the copper crystal rod was mounted on a goniometer with plastic cement and aluminum powder and oriented to the (100) crystallographic plane by using back reflection Laue X-ray diffractometry [135]. After orientation, a slice about 1 mm thick was cut from the rod
by spark erosion ('Agietron', Agie, Switzerland), and the sample disc was then fixed in an acrylic resin ('Quickmount', Fulton Metallurgical Products Corp., USA) and mounted to a polishing assembly equipped with alignment micrometers. These allow the sample orientation to be checked and readjusted by Laue X-ray diffraction so that any errors resulting from the later polishing steps could be eliminated. The subsequent surface polishing used a planetary lapping system (DU172, Canadian Thin Film Ltd.) with progressively finer grades of diamond paste (from 9 to 3 micron). Final polishing with either 0.05 micron alumina or 1 micron diamond paste was done by hand on a flat glass plate covered with deer skin (Microcloth, Buehler 40-7218). After the final polishing, an optical face alignment is done by back reflection of a Ne/He laser fixed on an optical bench as shown in Figure 3.5. Once the reflected laser beam makes an angle less than 0.5° from the normal, the result is considered satisfactory. The assembly is then moved back to the X-ray diffractometer to ensure that the optical face is parallel to the (100) plane to within 0.5°. These procedures gave a flat, scratch-free Cu(100) surface of several mm² in area. Finally, the assembly is dismounted and the sample is immersed in acetone to dissolve the acrylic resin. After washing and degreasing (trichloroethylene, acetone, methanol and distilled water), the sample is ready for cleaning inside the UHV chamber.

3.3.2 Cleaning procedures

For the purpose of LEED crystallography, the surface to be studied must not only be clean but also well crystallised. This can be achieved by the following procedures.

After sample transfer into the UHV chamber and pump down, the whole UHV system is baked out thoroughly to attain an acceptable base pressure (low 10⁻¹⁰ Torr
Figure 3.5 Arrangement of laser alignment method to check the coincidence of the optical face and desired crystallographic plane; $\theta = r / 2R$ (rads) for large $R$. 
range) after cooling. All filaments to be heated are also outgassed before starting to clean the sample surface.

Auger electron spectroscopy is used to assess the chemical state of the surface at frequent stages during the cleaning process. The common impurities after bakeout at the Cu(100) surface are sulphur and chlorine, as well as carbon, and this can be seen in Figure 1.7.

The surface cleaning and ordering operations consist of Ar$^+$ bombardment (around 40 hours in total) alternated with annealing treatments. For the initial stage of the cleaning, the current and the energy of the bombarding Ar$^+$ ions are set at low values (1.0 $\mu$A cm$^{-2}$ and 400 eV) [120]. The sample and sample holder are then outgassed at about 300°C for 10 minutes, while the chamber pressure remains in the $10^{-10}$ Torr range with the sample hot. This treatment eliminates most of the impurities that may have been left on the surface from the sample preparation at atmospheric pressure, and which may otherwise diffuse into the surface during the first annealing treatment. After a few cycles of the bombarding and annealing, all contaminants except sulphur could be removed to below the detectable limits of the retarding field analyser. The sulphur contaminant comes mainly from the bulk crystal. To remove the contaminants, while getting a well-ordered surface, it is important to study their behaviors as a function of temperature [120]. A well chosen annealing temperature is the key to obtaining a well-ordered surface while preventing impurity segregation. Figure 3.6 shows four Auger spectra taken at a series of annealing temperatures, and it is clear from the magnitudes that sulphur segregation [136] occurs more freely as the temperature increases. At this stage annealing temperatures of between 550 and 650°C were adopted to deplete the sulphur from below the surface region. For the next stage of ion bombardment, the Ar pressure was held in the $10^{-5}$ Torr range, and the Ar$^+$ current and energy were increased to 2.0 $\mu$A.
Figure 3.6 Auger spectra of the Cu(100) surface after heating for fixed times at different temperatures.
cm$^{-2}$, 600 V to speed up the bombarding operation (600 V was the maximum voltage for the ion gun we had available). During the Ar$^+$ bombardment, the titanium sublimation pump is used to pump all chemisorbing gases. After each cycle of Ar$^+$ bombardment and annealing, different regions of the surface were monitored by Auger electron spectroscopy and LEED since the distribution of sulphur can vary over the surface. This is illustrated in Figure 3.7 by four Auger spectra measured for different surface regions (a,b,c, and d) of the same sample with corresponding LEED patterns (which were either of the (1x1) or (2x2) types). For each cleaning cycle, a new supply of Ar is introduced via the variable leak valve. The bombarding and annealing operations are continued until AES indicates no detectable impurity signals and LEED shows a sharp (1x1) spot pattern with low background; then the sample is considered to be sufficiently clean and well crystallised for further study.

After each chemisorption experiment, a clean and well-ordered Cu(100) surface can be obtained with just 3–4 hours of Ar$^+$ bombardment (2.0 μA, 400 V) followed by annealing at 550 °C for 15 minutes.

3.4 Measurement of LEED Intensities

3.4.1 Angles of incidence

The orientation of the incident electron beam on the surface is described by the two angles, $\theta$ and $\phi$. The polar angle $\theta$ is defined as the angle between the incident plane wave $\mathbf{k}$ and the inward-pointing normal to the surface; it is always positive. Defining a left-handed coordinate system with $x$- and $y$-axes within the surface plane and the $z$-axis into the surface, the azimuthal angle is the angle between $k_\parallel$, the projection on the surface plane of the incident wavevector $\mathbf{k}$, and the $x$-axis [137]. Conventionally the $x$-axis is chosen to be along one of the surface basis vectors (the longer of the two); for the
Figure 3.7 Auger spectra indicating different amounts of S on different regions (a-d) of the Cu(100) surface with their corresponding LEED patterns.
Cu(100) surface this corresponds to the $s_1$ axis in Figure 1.5. Particular values of $\phi$ may be favoured in practice. In one sense, non-symmetrical values of $\phi$ may have an apparent advantage insofar as all degeneracies are then split; hence all $I(E)$ curves are different and more experimental data can be obtained. However, if the symmetrical $\phi$ values are chosen, the computer time and complications of the multiple-scattering calculations can be reduced. Additionally, more reliable experimental data can be obtained after suitable averaging of the related $I(E)$ curves [138]. For the Cu(100) surface, represented by a square net, it is convenient to select $\phi = 0^\circ$; then the off-normal incidence direction coincides with a symmetry plane in the surface region, and correspondingly there is a symmetry plane in the LEED patterns.

3.4.2 Video LEED analyser

The measurement of experimental $I(E)$ curves is the first step in LEED crystallography. Earlier techniques which are still used today are the Faraday cup and spot photometer methods [129,139]. However, they are slow and relatively inconvenient for many purposes. An initial attempt to reduce the time that the electron beam hits on a surface was made by Stair et al. [140], but more recently various attempts have been made to improve measuring speed by introducing computerised measuring systems. These range from a moving Faraday cup to the use of channel plates and Vidicon cameras [129,141,142]. The favoured approach depends on the applications [143], but for LEED crystallography TV measuring systems have been quite common [144-146]. Rapid data acquisition is particularly important to minimise the build up of contamination levels, as well as the effects of the electron-beam during an experiment.

The computerised data acquisition system used in this work is based on a commercial video LEED analyser (VLA, Data-Quire Corp., Stony Brook, N.Y.), which
is shown schematically in Figure 3.8. The analyser consists of a microcomputer unit, a TV camera, a video monitor, and a terminal (Teletype model 43). The microcomputer with a 32 K microprocessor (Motorola 6800) is the heart of the system and it is connected to each peripheral unit by means of appropriate cables. The TV camera (COHU 4410/ISIT) is positioned in front of the window of the LEED chamber in full view of the fluorescent screen. This camera consists of a photocathode tube and a silicon target. When light passes through the camera lens on to the photocathode tube, electrons are generated. Unlike the earlier Vidicon cameras, these electrons are further accelerated on to the silicon target, and therefore more secondary electrons are produced so giving better sensitivity. The incident beam current can be kept at around 1 μA to minimise any heating or electron-beam induced desorption [147-149].

3.4.3 Measurement of I(E) curves

In a VLA measurement, the picture of a LEED pattern shown on the video monitor screen defines a frame which consists of 256x256 picture elements (or pixels). The scan of a frame starts at the upper left corner and moves left to right first along the topmost horizontal line (one pixel wide), and then continues down to scan all 256 horizontal lines in order. A single scan of a frame is completed in 1/60 second. However, the digitisation is done columnwise; i.e. only one of the 256 pixels on the same horizontal line is digitised in a single scan. In the digitisation process, a frame can be viewed as being made up of 256 pixel columns, and the complete digitisation of a single frame requires 256/60 seconds.

In this work, the intensity of a LEED spot is defined as the summation of the digitised intensities of the 10x10 pixels in the window which completely covers the spot as shown in Figure 3.9(a), and this is the area which is digitised. The VLA system
Figure 3.8 Block diagram of the video LEED analyser (VLA, Data-Quire) used in the measurement of LEED intensities.
provides up to 49 isolated user-selected windows for different LEED pattern digitisations. The present software (approximately 30 subroutines written in machine code) allows each window to be matched automatically to the new spot position for the next digitisation process. In practice for adsorbed systems, the intensities of integral order (IO) beams are often stronger than those of the fractional order (FO) beams; then separate measurements are advantageous with different gain level settings. Typically for 100 energy points, 6 independent beams can be measured in 15 minutes.

The raw intensities collected in this way must be normalised to the incident electron current since it increases with the accelerating voltage [150]. An absolute diffracted beam intensity is defined by:

\[ I = \frac{i}{i_0} \]  

(3.1)

where \( i \) and \( i_0 \) are raw diffracted and incident currents respectively. The measurement of I(E) curves with the our VLA system can only give relative intensities. The summed measurement of spot brightness has to be divided by the measured incident beam current at each energy. After this normalisation, some symmetrically related I(E) curves are subsequently averaged. Davis and Noonan have shown that this can help minimise any further small experimental uncertainties [138]. Finally, the resulting averaged I(E) curves are treated with two cubic spline smoothing routines to give the experimental I(E) curves which are actually used for later comparison with calculated I(E) curves.

3.4.4 Spot profile measurement

Chemisorbed layer growth may occur at different points on a surface and antiphase domains may form [46,151]. If the mean domain diameter exceeds the transfer width \( t_w \) of the instrument [152], the LEED pattern is formed by a superposition of the
Figure 3.9 Measurement of beam intensities: (a) a diffracted spot is digitised within a user-selected window (10x10 pixels); (b) (x,y) defines the location of each pixel, while intensity of the pixel is recorded as z; (c) a three dimensional intensity distribution or spot profile z(x,y).
Figure 3.9 Continued.
diffracted intensities from the individual domains and the diffracted spots appear as sharp as possible for the particular measurement system. However if the average domain diameter is smaller than $t_w$, the superposition of the beam amplitudes may affect the intensity distributions and in particular cause broadening or other structure in the spot profiles [46,153].

Spot profile analysis in LEED can provide valuable information about domain structure, step distributions, chemisorption island sizes and related effects [11,154]. As well as allowing a relative measurement of LEED spot intensity, the pixel mode in the VLA system has been designed for an additional measurement of intensity distribution within a LEED spot. Usually, the measurement of such profiles is done at a fixed energy and direction of the incident beam, but while varying other parameters (like surface coverage, time, temperature). Figure 3.9(b) illustrates 10 profiles which are the cross-sections along the y direction of the window for 10 values of the x coordinate for the 10x10 window. The intensities are recorded as the z coordinate and therefore each pixel can be described as $z(x,y)$. This allows us to display an intensity profile for each spot in cross section, for example, by joining up the maxima in Figure 3.9(b). For detailing the splitting directions, a spot can also be shown as a three dimensional distribution as given in Figure 3.9(c).
CHAPTER 4
LEED CRYSTALLOGRAPHIC ANALYSES
AND RELATED STUDIES OF
THE Cu(100)-(2x2)-S SURFACE STRUCTURE

4.1 Introduction

Studies of the adsorption of sulphur, and of sulphur-containing molecules, on surfaces of transition metals are of interest from several perspectives. These include the general curiosity to probe the fundamental aspects of the initial chemisorption steps, as well as, at the other extreme of S exposure, the continuing technological need to investigate such processes as S poisoning in catalysis and sulphidisation [155,156]. In all cases it is important to assess consistency, for example by comparing information provided by different experimental techniques, and by relating such information to current models of electronic structure and chemical bonding.

A particularly fundamental property of chemisorption systems is geometrical structure. Knowledge and understanding of this property is basic for developing models of other properties including chemical reactivity. The initial surface crystallographic information for atoms from the groups 16 and 17 adsorbed on well-characterised surfaces of metals has recently been related to models which are established from bulk crystallography [67,71], but much further testing and refinement is needed since the subject of surface crystallography is still relatively in its infancy. As part of this continuing project, investigations with LEED for the chemisorption of sulphur on the (100) surface of copper are reported in this chapter. This topic is also of interest to provide an assessment of structural conclusions reached by the alternative technique of photoelectron diffraction, since two analyses with this technique have recently been reported for the Cu(100)-(2x2)-S
surface structure by Barton et al. [86] and by Bahr et al. [88]. The latter study reported a surface structure with considerable relaxations for copper. This was not considered in our first LEED crystallographic analysis (Section 4.3), and therefore a refined LEED crystallographic analysis (Section 4.4) was undertaken to give another assessment of the lateral and vertical relaxations for the Cu(100)-(2x2)-S surface structure.

In addition to the surface crystallographic analyses, a closer look at this surface system is useful in order to obtain the maximum background information for this apparently simple chemisorption system and to compare with other related contrasting surfaces. For example, a discussion by Richter and Gerhardt [157] contrasted the shapes in cross section of diffracted beams in LEED from the c(2x2) surface formed by oxygen adsorbed on the (100) surface of nickel and copper under conditions where antiphase scattering from neighbouring domains is significant. In particular these authors suggested that the spot profiles indicate that oxygen adsorbs on bridge sites of Cu(100) but on sites with 4-fold symmetry on Ni(100). The former result appears consistent with some reports [80], although it contrasts with structural conclusions from SEXAFS [82] and photoelectron diffraction [83].

The chemisorption of sulphur on Cu(100) also contrasts with that for oxygen chemisorption on the same surface insofar as the c(2x2) surface structure for 0.50 monolayer (ML, i.e. ratio of number of S atoms to number of Cu atoms in the top layer for the ideal metal surface) coverage is not observed for the former, although a more complex surface structure is observed which appears to arise from a coincidence-site superposition structure designated as \( \left( \frac{4}{1} - \frac{1}{4} \right) \) with respect to the substrate [158]. No quantitative analyses have yet been undertaken for the latter structure, which would be a particularly challenging one at the current stage of development of LEED crystallography, although the basic LEED pattern does suggest a top layer of alternating S and Cu atoms [156].
To provide a background for investigations of other surface structures formed by sulphur on the Cu(100) surface, a LEED spot profile study has been made for some coverages greater than that applying in the LEED crystallographic studies (i.e. where the sharpest and best defined (2x2) LEED patterns are found). In addition, some further observations that extend the LEED crystallographic analyses are also reported in Section 4.5. In particular, the multiple scattering calculations required in the structural studies provide a helpful base for numerical investigations of the stability of I(E) curves for diffracted beams when the sulphur coverage is varied for constant adsorption site and constant S-Cu interlayer spacings in the calculations [81,159]. This part of the study broadens an earlier investigation from this laboratory for adsorption on the (0001) surfaces of titanium and zirconium [160] insofar as we now cover off-normal angles of incidence. Further, reliability-index studies of the comparisons associated with the Cu(100)-(2x2)-S surface enable an efficient reassessment of the polar angle of the incidence used for some intensity data in the LEED crystallographic investigation, as well as a consequent estimate of the effect of error in this angle on the surface structural analysis.

4.2 Experimental

The sample preparation and cleaning procedures, as well as the analysis chamber used in this work, have been detailed in Chapter 3. The cleaned and ordered Cu(100) surface, which showed a sharp (1x1) LEED pattern, was exposed at room temperature to high purity H₂S (Matheson Research Grade) at around 2×10⁻⁸ Torr. The surface was continuously monitored by LEED until weak, broad half-order beams were observed, at which point the leak valve was closed. Annealing of this surface for a few minutes at 280°C resulted in a good (2x2) pattern.

Figure 4.1 shows a typical sulphur uptake curve measured by
Figure 4.1 Auger peak height ratio S(152 eV)/Cu(920 eV) plotted as a function of time of exposure to H$_2$S at 4x10$^{-7}$ Torr. The insert compares individual peak heights for the high-coverage complex pattern referred to in the text.
(4.1)

\[ R = \frac{A_{152}}{A_{920}} \]

(i.e. the ratio of the Auger peak-to-peak height for S at 152 eV to that of Cu at 920 eV) as a function of exposure. The best (2x2) patterns were observed for values of R close to, but less than, 2.2 (i.e. at values just below the region at which the curve assumes a constant and low slope). Increased exposures into the constant-slope portion of the uptake curve at 2\times10^{-8} \text{Torr} did not result in any new structures, but rather the (2x2) LEED pattern persisted although with increasing background and streakiness in the fractional beams. At considerably increased exposures (e.g. with H_2S pressure increased to 5\times10^{-6} \text{Torr}) a more complex LEED pattern was observed, which sharpened on annealing at 560°C. This pattern was first reported by Domage and Oudar [158], and it was best developed for conditions where the Auger ratio R is approximately double that found for the sharpest (2x2) pattern.

4.3 Structure Analysis

4.3.1 Experimental data set

Intensity-versus-energy (I(E)) curves for diffracted beams from the Cu(100)-(2x2)-S surface structure were measured with the video LEED analyser system described in Chapter 3. Integrated relative beam intensities were measured over the approximate energy range 50 to 220 eV with a constant increment of 2 eV. Each spot on each frame was scanned three times, and the multiply-summed integrated intensities were normalised to the incident beam current. Incidence settings were fine-tuned on-line to check for the symmetrical equivalences expected for normal incidence. In the final processing, I(E) curves measured for symmetrically-related beams were averaged to minimise any small
experimental uncertainties [138], and the resulting curves were smoothed with two cubic spline operations. A total of 16 independent I(E) curves were so measured for the beams

\[(1, 0), (1, 1), (1/2, 0), (1/2, 1), (1/2, 1/2)\] at normal incidence \((\theta = 0^\circ, \phi = 0^\circ)\),

\[(0, 0), (0, 1), (-1, 1), (0, 1/2), (1/2, 0), (-1/2, 0), (1/2, 1/2), (-1/2, 1/2), (1/2, 1), (-1/2, 1),
\]

\[(-1, 1/2)\] at off-normal incidence \((\theta = 14^\circ, \phi = 0^\circ)\)

where the beam notation and designation of the angles for the incident beam follow the convention proposed by Zanazzi et al. [137]. Figure 4.2 shows the beam notation used for this surface system, and the symmetry plane through \(k_x\) axis for the off-normal incidence experiment.

4.3.2 Calculations and results

The simplest models for the \((2x2)\) structure have S atoms adsorbed on the unreconstructed (100) surface of copper (which has a face-centered cubic (fcc) structure), and they are conveniently designated according to the coordination number at the site of adsorption. I(E) curves for the various diffracted beams were calculated using the renormalised forward scattering method (Section 2.4.2), with inclusion of symmetry, for models with adsorption on the "expected" sites of four-fold coordination (4f sites), as well as on the on-top (1f) sites and the bridge (2f) sites. A maximum of 71 inequivalent beams were used for calculations at normal incidence, and a maximum of 91 beams at \(\theta = 14^\circ\). For the 2f model, calculated beam intensities require the appropriate averaging to account for the expected presence of domains related by 90° rotations.

The structural parameters in these calculations for Cu(100)-(2x2)-S were input by fixing all interlayer spacings for Cu at the bulk value (1.81 Å), while the S-Cu interlayer spacings were varied over the ranges: 1.20 - 1.60 Å for the 4f model, 1.45 - 2.05 Å for
Figure 4.2 Beam notations for a LEED pattern from the Cu(100)-(2x2)-S structure.
the 2f model and 1.70 - 2.30 Å for the 1f model. The non-structural parameters used are detailed as follows. The atomic potential in the substrate was characterised by phase shifts (up to \( l = 7 \)) derived from a band structure potential for copper (Section 2.2.2), and the real part of the constant potential \( (V_{or}) \) between the spheres was set initially at -11.2 eV for both the surface layer and the bulk. The sulphur phase shifts used in this work were obtained from Demuth et al.[161] (PHSH1, Table 2.1) which were calculated from a superposition potential associated with a hypothetical bcc sulphur lattice. The Debye temperatures were taken as 343 K [162] and 335 K [163] for copper and sulphur respectively, while the imaginary part \( (V_{oi}) \) of the potential between all atomic spheres was equated to \(-0.85E^{1/3}\) eV.

Both a visual comparison of the calculated and experimental I(E) curves, as well as an analysis with reliability indices, show that the best correspondence is for the expected 4f adsorption site with the S-Cu interlayer spacing in the vicinity of 1.30 to 1.40 Å. Relevant comparisons are shown in Figures 4.3 and 4.4 for these structures, and Figure 4.5 includes the contour plots for the reliability index \( R_p' \) (Section 2.5) as a function of overlayer spacing and \( V_{or} \). The plots in Figure 4.5 are made for the 16 diffracted beams measured, and they emphasise that the lowest values of \( R_p' \) are clearly for the 4f adsorption site. The minimum value of \( R_p' \) (0.306) corresponds to a S-Cu interlayer spacing of 1.32 Å and \( V_{or} \) equal to -5.4 eV; further the contour plot indicates an uncertainty in the S-Cu interlayer spacing equal to ±0.04 Å according to the compromise measure of uncertainty detailed by Moore et al.[164]. Overall the level of agreement between experiment and calculation reached in this part of the study corresponds to a "moderate" level.

4.3.3 Discussion

The evidence reported above suggests that the Cu(100)-(2x2)-S structure has the S atoms adsorbed on the "expected" 4f sites of the Cu(100) surface at 1.32±0.04 Å above the
Figure 4.3 Comparison of experimental I(E) curves for diffracted beams from Cu(100)-(2x2)-S at normal incidence with those calculated for the 4f model with S either 1.30 or 1.40 Å above the topmost copper layer.
Figure 4.4 As for Figure 4.3 except I(E) curves are now for $\theta = 14^\circ$. 

$\theta = 14^\circ, \phi = 0^\circ$

A: --- 1.300 Å
B: ----- expt
C: --- 1.400 Å
Figure 4.4 Continued.
Figure 4.5 Contour plots for the surface Cu(100)-(2x2)-S of Rp' versus \( V_{or} \) and the Cu-S interlayer spacing for 16 beams and three different structural models.
topmost copper layer. If no relaxations are experienced by the metal atoms, each S atom is then bonded to four neighbouring Cu atoms at a distance of $2.24\pm0.02\ \text{Å}$. This value appears in reasonable agreement with the value of $2.28\pm0.03\ \text{Å}$ reported by Barton et al. [86] with the first photoelectron diffraction study. Also the value determined by LEED agrees closely with the value ($2.25\ \text{Å}$) predicted from a bond length-bond order relation (Section 1.5) parametrised by the bulk structure of CuS [71]. However making comparisons with S-Cu bond lengths reported in the copper sulphides is not simple because of the tendency for the bulk structures to be relatively complex [165]. Indeed it is possible that the latter may carry over to the surface structure, particularly since, as noted previously [158], the half monolayer coverage gives a complex LEED pattern.

The fact that a simple c(2x2) LEED pattern is not observed at the higher coverages of S on the Cu(100) surface contrasts with the situation for the adsorption on many other fcc (100) surfaces of transition metals. At coverages beyond the rapid change in slope in the sulphur uptake curve in Figure 4.1, and hence beyond 0.25 ML associated with the ideal Cu(100)-(2x2)-S structure, the LEED pattern shows broader spots and streaks which are characteristic of antiphase domains; ultimately a complex pattern becomes established. Our general observations support the conclusion of Domange and Oudar [158] that this latter pattern corresponds to the formation of a coincidence site superposition structure designated as $\begin{pmatrix} 4 & -1 \\ 1 & 4 \end{pmatrix}$ with respect to the substrate in terms of the notation of Park and Madden [47].

4.4 Surface Relaxations

4.4.1 Adsorbate induced metal relaxations

The majority of studies so far for chemisorption on low-index metal surfaces have assumed that the basic metallic structure is maintained, even though reconstructions are sometimes apparent from LEED patterns [166]. The quantification of adsorbate-induced
changes to metallic surface structures is important for developing detailed accounts of surface electronic structure and ultimately other properties, including chemical reactivity. Most of the limited data available so far has come from LEED crystallographic studies with full multiple scattering calculations, although an exception has been the most recent evaluation for the Cu(100)-(2x2)-S surface using the photoelectron diffraction method by Bahr et al. [88]. In this latter work, the technique is called angle-resolved-photoemission extended-fine-structure (ARPEFS) [27], and it was used to determine lateral and vertical relaxations induced in the (100) surface of copper by S atoms chemisorbed according to the (2x2) surface translational symmetry.

The structural studies by ARPEFS [86,88] as well as by LEED, discussed in Section 4.3, have agreed that S chemisorbs above the 4-coordinate hollow sites of the unreconstructed Cu(100) surface with the Cu-S bond distance around 2.26 Å and therefore in close correspondence with chemical predictions [71]. However the details from different studies vary. For example Bahr et al. [88] reported that the topmost S-Cu interlayer spacing is 1.42 Å, whereas the value from LEED which assumed no relaxation in the metal structure indicated a S-Cu interlayer spacing of about 1.32 Å. Further LEED crystallographic studies on this chemisorption system are therefore needed, both to check the details of the ARPEFS result, and to assess the ability of LEED to identify lateral and vertical relaxations.

4.4.2 New experimental data set

The structural refinement in LEED crystallography, as in any other technique, depends on the existence of very reliable experimental data. Therefore it seemed advantageous to produce new independent measurements. One refinement over the previous experiment was to select different gain level settings in the VLA system for the
integral-order beams and fractional-order beams. Five I(E) curves at normal incidence and
seven at off-normal incidence (θ = 7.5°) were thus obtained with a lower background than
in the initial measurements.

Since the theoretical calculations for surface relaxations are much more complicated
than those in the previous LEED analysis, the treatment here is restricted to the analysis of
I(E) curves measured at normal incidence (θ = 0°, φ = 0°) as labelled in the following:

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

4.4.3 Optimisation strategy

In a LEED structural refinement, the optimisation is performed by searching for a
minimum of a reliability index [54] as some parameters are changed, and using the initially
obtained optimised parameters to start the next calculation. Two methods were applied in
the present study. The first used by Adams et al. [125] is an iterative procedure that aims
to obtain convergence of the variable parameters by minimising each parameter value
individually and successively. It can involve a rather large number of surface model
calculations. The second method is unconstrained optimisation [167] which aims to find a
minimum efficiently by changing several parameter values simultaneously. The
optimisation procedure in this study is outlined as below.

1) Choose an initial model
2) Set up ranges and step sizes of parameters to be varied and do the calculations
3) Use reliability index analysis to identify new directions towards better parameter
   values
4) Go to 2) until the reliability index ceases to reduce within the constraints of the
   model chosen
5) Acceptable model? If no, go to 1)  
6) Stop

4.4.4 Calculations

Structural parameters appropriate to the Cu(100)-(2x2)-S system when surface relaxations occur down to the second metal layer are indicated in Figure 4.6, and the ranges of the structural parameters investigated are detailed in Table 4.1. Additionally, an independent calculation was performed for the model proposed by ARPEFS [88] to assess the structural information derived by this technique.

The full multiple scattering calculations performed here have been described previously in Section 4.3. Briefly, the diffraction matrices for the relaxed copper layers were calculated by the combined-space method (Section 2.4.3), with up to four atoms per unit mesh, and layer stacking was done with the layer doubling method (Section 2.4.1). The real part of the constant muffin-tin potential (V₀) was set at -11.2 eV for the initial calculations, but its value was refined during the comparison of experimental and calculated beam intensities by searching for minima in contour plots of R₂J made as a function of V₀ and geometrical parameters [54,126]. The later calculations started with a value of -5.1 eV for V₀, which was similarly refined during the evaluation. The imaginary part of the constant muffin-tin potential was fixed throughout at -5.0 eV for the surface and bulk regions. A new set of phase shifts for sulphur (PHSH2, Table 2.1) was tested in the final stage of the refinement. All other non-structural parameters were unchanged from those in Section 4.3.
Figure 4.6 Notation used for the Cu(100)-(2x2)-S surface structure. The model is viewed from above in (a), and from the side in (b) along the cross section marked by the diagonal line in (a). S atoms are represented by dark circles and Cu atoms by the larger open circles. The dashed circles are for Cu atoms in the second layer which are designated as of types A, C or O following ref.88. Lateral displacements for atoms in the first Cu layer are fixed by a parameter $\Delta$ whose magnitude corresponds to the displacement from the regular bulk positions and whose sense is positive when the displacements are in the directions of the arrows shown.
<table>
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<tr>
<th>Stage</th>
<th>(d_{S1})</th>
<th>(\Delta)</th>
<th>(d_{1C})</th>
<th>(d_{1O})</th>
<th>(d_{1A})</th>
<th>(d_{C3})</th>
<th>(d_{O3})</th>
<th>(d_{A3})</th>
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<td>1.81</td>
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<td>-0.10(0.05)0.10</td>
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<td>1.81</td>
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<tr>
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<td>1.82</td>
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<tr>
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<td>1.81</td>
<td>1.81</td>
<td>1.82</td>
<td>1.84</td>
</tr>
</tbody>
</table>

Table 4.1 Ranges of structural parameters considered for the relaxation model of the Cu(100)-(2x2)-S surface.
4.4.5 Comparison of the results from ARPEFS and LEED

Figure 4.7 includes I(E) curves measured for five beams from Cu(100)-(2x2)-S and compared with the corresponding curves calculated for the specific model described by Bahr et al.[88] (see Table 4.2). The level of correspondence between the experimental curves in Figure 4.7 and those calculated for the model of ARPEFS [88] is much less than ideal, and therefore this structural model does not pass the 'LEED test'. Accordingly the experimental I(E) curves in Figure 4.7 have been compared with those calculated for a range of structural variables as in Figure 4.6 and Table 4.1, and after the iterative optimisation procedure, the specific parameters which minimise $R_Z/J$ are included in Table 4.2. The corresponding calculated I(E) curves are also shown in Figure 4.7, and it is clear that these curves give a superior match to the experimental curves compared with the curves calculated for the model from ARPEFS. For the LEED structure, the correspondence is least good for the (1 1/2) beam, apparently as a result of this beam being weak and the consequent inclusion of relatively more disorder contributions in the measurement.

The Cu-S bond lengths proposed by the ARPEFS and the LEED studies agree at 2.26 Å, although other details differ considerably (Table 4.2). While the ARPEFS analysis indicates that the four Cu atoms which bond to S relax laterally inwards by 0.05 Å, LEED indicates an outward relaxation by 0.04 Å. There are also significant differences in the topmost S-Cu interlayer separation (1.42 Å from ARPEFS, 1.29 Å from LEED) and in the associated Cu-S-Cu bond angle (102.2° from ARPEFS, 110.2° from LEED). Basically, ARPEFS indicates that the neighbouring Cu atoms relax vertically and laterally toward S, while LEED indicates the reverse. In the second copper layer, LEED shows only small changes from the bulk situation, although the Cu atoms in this layer which are directly below S are displaced downwards by 0.03 Å compared with the other Cu atoms in the layer. By contrast, ARPEFS indicates that these Cu atoms relax in the opposite sense,
Figure 4.7 Comparisons of experimental I(E) curves (dashed) for five diffracted beams from the Cu(100)-(2x2)-S surface structure at normal incidence with those calculated for the models specified by the headings ARPEFS and LEED in Table 4.2.
Figure 4.7 Continued.
Table 4.2 Values of displacements and interlayer spacings in Å for the Cu(100)-(2x2)-S surface structure as indicated in Figure 4.6 and as given by the ARPEFS study in ref. 88 and by the LEED study reported here.

<table>
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<tr>
<th>Parameters</th>
<th>ARPEFS Model</th>
<th>LEED Model</th>
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</tr>
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</tr>
<tr>
<td>d1O</td>
<td>1.65</td>
<td>1.83</td>
</tr>
<tr>
<td>d1A</td>
<td>1.74</td>
<td>1.81</td>
</tr>
<tr>
<td>dC3</td>
<td>1.93</td>
<td>1.81</td>
</tr>
<tr>
<td>dO3</td>
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<td>1.82</td>
</tr>
<tr>
<td>dA3</td>
<td>1.81</td>
<td>1.84</td>
</tr>
</tbody>
</table>
while the total vertical separation within the second metal layer has the surprisingly large value of 0.12 Å.

This LEED analysis found that $R_{ZJ}$ equals 0.168 for the LEED structure and 0.499 for the structure given by ARPEFS. Incidentally the latter is much larger than the value of 0.203 for the case where $d_{S1}$ is optimised but all Cu atoms are held at their bulk positions. It is clear from these numbers, and from the comparisons in Figure 4.7, that the structural model from LEED gives a much better account of the measured I(E) curves than does the structural model from ARPEFS proposed by Bahr et al. [88]. It is believed that the Cu(100)-(2x2)-S surface may provide a good system for testing the abilities of different structural methods for extracting important adsorbate induced relaxations in metal surfaces.

4.5 Related Observations and Studies

4.5.1 Spot profile analysis

Earlier, Domange et al. [156] proposed that for low exposures of H$_2$S on the (100) surface of copper, a (2x2) chemisorption structure is formed, with the Cu atoms held essentially in the regular bulk positions, but that for exposures at higher pressures of H$_2$S, an irreversible sulphidisation process occurs with the formation of a surface compound (this gives the $\left( \begin{array}{c} 4 \\ 1 \\ 4 \end{array} \right)$ structure noted earlier). There is a general agreement between results from $^{35}$S measurements [156] and from the measurement with Auger electron spectroscopy (Section 4.2) that the first chemisorption structure corresponds to around 0.25 ML of S, while the S coverage associated with sulphide formation is approximately twice as great. Consistently with this evolution of structures, the LEED spot profile analysis reported here indicates that there is no recognisable tendency for local regions of 0.5 monolayer coverage to form at antiphase boundaries between neighbouring (2x2) domains (whereas S on the Ni(100) surface successively forms (2x2) and c(2x2)
structures. The experimental part of this work followed procedures described in Section 4.2. The uptake curve in Figure 4.1 shows two main regions for which $R$ increases almost linearly with exposure of sulphur. At the lower exposures, the slope is high (i.e., rapid uptake); at the higher exposures, the slope becomes close to zero. The sharpest (2x2) LEED patterns, with least background, were obtained with an exposure of about 70 Langmuir ($1\text{ Langmuir} = 10^{-6}\text{ Torr} \cdot \text{s}$) followed by a 10 min anneal at 300°C; this surface is characterised by $R$ equal to 2.1, and on the uptake curve this point is in the intermediate region (i.e., just below where the slope of $R$ vs. exposure flattens out). With an exposure of around 100 L, the adsorption system is characterised with $R = 2.2$. At this exposure, a (2x2) LEED pattern is still observed after heating, although some diffraction spots elongate and there is associated streaking. These tendencies are developed more strongly at $R = 2.4$ (which is in the essentially flat region of the uptake curve).

Figure 4.8 indicates diffracted spot profiles measured with the VLA system for three beams at coverages corresponding to $R = 2.2$ and 2.4. As $R$ increases, all diffracted spots tend to lose intensity to the streaking; for example, the (0 1/2) beam elongates in the $k_x$ direction (similarly, the (1/2 0) beam elongates in the $k_y$ direction), the (1/2 1/2) beam elongates in both the $k_x$ and $k_y$ directions, but the (1 0) beam (as well as all other integral beams) basically maintains its circular shape. These tendencies suggest the existence of antiphase scattering from neighbouring regions (domains) whose dimensions are less than the instrumental transfer width (around 100 Å) [168], but the loss of intensity is most marked for the (1/2 1/2) beam. Two main types of antiphase boundaries can, in principle, be involved, assuming the S atoms continue to adsorb on the hollow sites of fourfold coordination (these different boundaries are designated I and II in Figure 4.9). The beams which are split by the antiphase scattering, and hence lead to streaking (elongation) when a statistical average is taken, are determined by the vector $d = d_x a_x + d_y a_y$, which links
Figure 4.8 LEED profiles for the (0 1/2), (1/2 1/2) and (1 0) beams measured at 90 eV for R = 2.2 and R = 2.4.
Figure 4.8 Continued.

Figure 4.9 Two types of antiphase boundaries (I and II) and their corresponding vectors $d_I$ and $d_{II}$ considered between (2x2) domains. The open circles indicate top-layer Cu atoms, while the filled circles indicate adsorbed S atoms.
adsorbed atoms across the domain boundary [46]. Specifically, the \((h,k)\) beam is so elongated, in the direction perpendicular to the domain boundary, whenever

\[
hd_x + kd_y = \frac{1}{2} (2n + 1)
\]  

(4.2)

for \(n\) integral.

Schematic indications of the beam elongations expected in LEED patterns from surfaces with antiphase boundaries of types I and II are shown in Figure 4.10 (in both cases, equivalent vertical and horizontal boundaries are assumed to have equal weightings). The LEED patterns actually observed for \(R > 2.1\) correspond to the situation in II and not that in I. This allows the following conclusions for S on a Cu(100) adsorption system.

(i) Microregions corresponding to local \(1/2\) monolayer coverage of S atoms in the c(2x2) orientation do not appear to form on the Cu(100) surface. This contrasts with the corresponding situation for S adsorption on Ni(100), which readily forms a c(2x2) structure after (2x2) [169]. Apparently, the next nearest neighbour S-S interactions are more repulsive on Cu(100) than on Ni(100); in general though, it is recognised that these interactions are dominated by indirect "through substrate" contributions [170].

(ii) The LEED patterns for \(R = 2.1\) used in the structural analysis correspond to an overall coverage of just less than 0.25 ML.

(iii) The existence of local regions connected by the antiphase boundary vector \(d_{\Pi}\) suggests that the fourth nearest neighbour interactions are comparable to the third nearest neighbour interactions. This in turn highlights the possibility that regions of c(4x2) translational symmetries (Figure 4.11) may coexist with (2x2) on the real surface.

That regions with different translational symmetries can be simultaneously present on a single surface is not new, although we are not aware of previous suggestions that local
Figure 4.10 Schematic indications of beam elongations expected in (2x2) LEED patterns from surfaces with antiphase boundaries I and II.
Figure 4.11 The c(4x2) structure and expected LEED pattern from a surface composed of both domain orientations with antiphase boundaries corresponding to the local (2x2) structure. The lines in the diffraction pattern schematically indicate elongated beams.
regions of c(4x2) ordering may occur for S on the Cu(100) surface. Figure 4.11 includes schematically the beam elongations expected in a LEED pattern from domains of this type, but with antiphase boundaries corresponding to \( d = 2a_x \) or \( 2a_y \) (i.e., boundaries where neighbouring arrangements correspond to the local (2x2) structure). At the resolution of our standard four-grid Varian LEED optics system, the elongation expected for the (1/4 1/2) beam would accentuate the elongation (and streaking) in the \( k_x \) direction noted in Figure 4.8 for the (0 1/2) beam. Also, because the c(4x2) beam does not contribute intensity to the (1/2 1/2) beam, the fact that the intensity of this beam falls very quickly, as \( R \) increases beyond 2.2, is consistent with local c(4x2) regions becoming more significant at larger values of \( R \). Incidentally, Joyner et al. [171], in an earlier study, failed to observe the (1/2 1/2) beam for this system, and they concluded that their streaked patterns corresponded to a disordered surface with domains of the (2x1) type. Nevertheless, it is proposed in this section that the elongations in the spot profiles observed for S on Cu(100) relate to microregions of the c(4x2) type forming in the approach to 0.25 ML coverage. Whether or not a reasonably ordered c(4x2) surface can be formed with suitable preparation conditions remains unknown. Observations of different surface treatments yielding differences in ordering emphasise a general need to characterise better the surface disorder, for example with the high-resolution spot profile analysis LEED technique (SPA-LEED) [11]. Further LEED studies at high resolution would be helpful to probe the details of S lateral interactions on this surface in the approach to maximum chemisorption and beyond to the onset of sulphidisation.

4.5.2 Stability of I(E) Curves

A serious bottleneck to the undertaking of LEED crystallographic analyses for surfaces with larger unit meshes is the computational effort involved with the required
multiple scattering calculations [15]. Therefore, it is important to assess approximation schemes. When the I(E) curves of fractional-order diffracted beams are closely independent of coverage, for a constant local geometry of adsorbed species, there is an implied insensitivity of the LEED technique to surface coverage. In part that may appear as a disadvantage, but equally, insofar as the fractional beams are independent of the unit mesh area, useful multiple scattering calculations can be made with restricted beam sets appropriate to less than the actual unit mesh area. This latter point can help ease the computational burden associated with LEED intensity calculations for surfaces with long repeat distances [159]. A recent study treated a variety of atomic scattering strengths for overlayer atoms adsorbed on (0001) surfaces of titanium and zirconium [160], and showed that high levels of stability in corresponding I(E) curves can be obtained at normal incidence. For actual LEED crystallographic analyses, measurements are generally needed also at off-normal directions of incidence, especially for around 10 - 15°, so that the specular beam can be measured without obstruction. Yang et al. [81] argued earlier that stability in the fractional-order I(E) curves with changing coverage requires a constant structural environment around each adsorbed atom, as well as negligible scattering between the adsorbed atoms. Plausibly, the intralayer scattering between the adsorbed species could become more prominent as the angle of incidence varies from the normal, although this point does not appear to have been assessed previously.

In this subsection further consideration is given to the stability of LEED I(E) curves as the overlayer coverage and/or translational symmetry are changed while maintaining some fractional-order diffracted beams in common. Multiple scattering calculations (Chapter 2) for model situations involving S atoms adsorbed on hollow sites of fourfold coordination on the Cu(100) surface have been made for (2x2), (2x1) and c(2x2) translational symmetries with the S-Cu interlayer spacing varying as 1.20(0.10)1.60 Å,
and the polar angle of incidence varying as 4(10)34°. The calculated I(E) curves for the beams in common, but with different translational symmetries, are very similar. Calculated I(E) curves for sets of beams in common, for a pair of translational symmetries, have also been compared with the many-beam reliability index $R_{ZJ}$. Comparisons between the c(2x2) and (2x2) structures, and between the (2x1) and (2x2) structures, are summarised in Figure 4.12 for integral and fractional beams separately. The total energy range considered, and the extent of structural features in pairs of I(E) curves being compared, varies with conditions, but in general the corresponding I(E) curves for the calculations from different translational symmetries match well, as is emphasised by all calculated $R_{ZJ}$ values being less than 0.10. Nevertheless, differences do tend to increase with the polar angle of incidence, $\theta$; that is highlighted both by increases in the absolute values of $R_{ZJ}$ and by increases in differences between $R_{ZJ}$ values for the (2x2)-c(2x2) and the (2x2)-(2x1) comparisons. In this subsection, the stability of I(E) curves to changing coverage of S on Cu(100) is established for these polar angles of incidence. Indeed, in combination with the observations reported previously for normal incidence [160], this result can likely be extended, especially to less strongly scattering overlayer atoms but probably also to some heavier atoms. Where applicable, that could create simplifications in multiple scattering calculations of beam intensities, both for making structural analyses and for providing independent checks of the off-normal directions of incidence estimated from the positions of diffraction spots on a screen. Consistency with the latter also provides a helpful check against any deleterious effects on a structural analysis resulting from stray fields. In practice, their influences are often less readily assessed at off-normal directions, compared with normal incidence where the appropriate equivalences can be checked in I(E) curves measured from diffracted beams that are expected to be systematically related.
Figure 4.12 R_{ZJ} versus Cu-S interlayer spacing for the c(2x2)-(2x2) and (2x1)-(2x2) comparisons at θ = 4(10)34°: (a) fractional-order beams, (b) integral-order beams.
Figure 4.12 Continued.
4.5.3 Polar angle of incidence

The LEED crystallographic analysis for the Cu(100)-(2x2)-S surface structure used intensities measured both for normal incidence and for $\theta = 14^\circ$ (see Section 4.3). In this work, conditions for normal incidence can be well set by ensuring the existence of appropriate equivalences between I(E) curves measured for symmetrically related beams [172], but the off-normal polar angles have to be deduced directly from the observed positions of the specular beam on the LEED screen [16]. Even with the absence of stray fields, some errors in experimental settings [173] can lead to uncertainties in the measurement of nonzero values of $\theta$, and that opens consideration of the degree to which these uncertainties lead to error in the deduced structure. One approach to limit this source of error in the analysis involves making the multiple scattering calculations for several polar angles [174] and refining the previously estimated value by optimising the correspondence between experimental and calculated I(E) curves. However, that approach can lead to considerably increased computing costs, especially for adsorption systems with long repeat distances. On the other hand, the study in Section 4.5.2 offers a helpful simplification when the I(E) curves are reasonably stable with respect to changing coverage; for Cu(100)-(2x2)-S, the comparisons in Figure 4.12 show that this stability holds well with $\theta$ in the vicinity of 14°.

New multiple scattering calculations of LEED I(E) curves have been made for S adsorbed on the four-coordinate hollow sites of Cu(100) with the (2x1) translational symmetry for $\theta = 10(2)16^\circ$, and these intensities have been compared with the appropriate curves in the experimental data (see Section 4.3). The use of a (2x1) unit mesh rather than (2x2) reduces the computation time by a factor of about 4. The comparisons between the experimental intensities and those calculated for (2x1) models show that $R_{ZJ}$ varies smoothly with $\theta$ and is minimised at $\theta = 13^\circ$. The corresponding S-Cu interlayer spacing is
found to equal 1.33 Å, a value that is just 0.01 Å longer than that reported previously in Section 4.3 for the study that fixed the polar angle of incidence at 14°. Indeed, this small change in the S-Cu interlayer spacing does not significantly affect the S-Cu bond length, which still equals 2.24 Å provided the surface Cu atoms do not relax from their normal bulk positions (Section 4.3).

4.6 Summary

In this chapter, an intensity analysis with low-energy electron diffraction is reported for the (2x2) surface structure obtained by the adsorption and presumed dissociation of H₂S on the (100) surface of copper. I(E) curves were measured with the VLA for five diffracted beams at normal incidence and for eleven beams at an off-normal direction with a polar angle of incidence equal to 14°. Comparisons were made with intensity curves calculated with the renormalised forward scattering method for three types of structural models in which the metal atoms remain in their regular bulk positions. The best correspondence between experimental and calculated intensities occurs with sulphur atoms adsorbed in the "expected" 4-coordinate adsorption sites. The Rp' is minimised with S atoms 1.32 Å above the topmost metal layer; this corresponds to nearest-neighbour S-Cu bond distances equal to 2.24 Å. This value appears broadly consistent with the measurement by photoelectron diffraction [86], as well as from model predictions [71].

The second crystallographic analysis has been undertaken to assess the lateral and vertical relaxations for the Cu(100)-(2x2)-S surface structure. It is found that the surface structure given by ARPEFS [88] does not account well for the measured LEED intensity curves, although these curves can be reasonably accommodated by a structural model with components of relaxation in some opposite senses to those previously reported. For example, while the ARPEFS analysis shows that four Cu atoms which bond to S relax
laterally inward by 0.05 Å, LEED indicates an outward relaxation by 0.04 Å. The interlayer spacing between S and the first copper layer obtained by ARPEFS is also different from that by LEED (1.42 Å from ARPEFS and 1.29 Å from LEED), although S-Cu bond lengths derived by them are almost identical. In addition, LEED shows only a small degree of change from the bulk structure for the copper positions in the second layer (by 0.03 Å), whereas ARPEFS indicates changes as large as 0.12 Å. The differences reported by ARPEFS and LEED suggest that the Cu(100)-(2x2)-S surface may provide a good system for testing the abilities of different surface techniques for detecting small adsorbate-induced relaxations.

LEED spot profile investigations for the higher coverages of S, where antiphase scattering occurs, suggest that domain boundaries do not correspond to microregions with local c(2x2) structure, but rather that the beam elongations observed are consistent with local regions of the c(4x2) type in the approach to 0.25 ML coverage. Diffracted I(E) curves calculated for the (2x2), c(2x2) and (2x1) translational symmetries, for fixed adsorption sites and S-Cu interlayer spacings, show that the intensity curves of corresponding beams can remain closely independent of actual symmetry and coverage for polar angles of incidence in the range \( \theta = 4(10)^{\circ}34^\circ \). This observation may help simplify calculations of LEED intensities from surfaces with larger unit meshes; it can also provide an economical route for checking values of \( \theta \) estimated from the positions of diffraction spots on conventional LEED screens. A test of the latter with the off-normal intensity data used in our previous analysis of the Cu(100)-(2x2)-S surface structure, indicated \( \theta \) to be modified by 1° from the previously estimated value, but that does not significantly affect the determined S-Cu nearest-neighbour bond length.
5.1 Introduction

The chemisorption of N atoms by the (100) surface of copper has long been known to yield a surface structure with the c(2x2) translational symmetry [175], although published information for the structural details is conflicting. An analysis of LEED intensities with the (quasikinematical) constant-momentum-transfer averaging scheme indicated that N atoms adsorb in hollow sites of four-fold coordination with the topmost interlayer spacing equal to 1.45 Å [76]. This adsorption site is consistent with a very recent analysis of surface phonon dispersion curves, although the latter study suggests that the N atoms are held at about 0.6 Å above the surface [77]. These results can be compared with reports for surfaces of the same overall translational symmetry formed by O atoms chemisorbed on Cu(100), although a variety of structural conclusions have been reported for this system also as discussed in Chapter 6.

The present chapter describes a new analysis with LEED for the Cu(100)-c(2x2)-N surface structure prepared by annealing after exposing a clean Cu(100) surface to nitrogen gas which has been activated by electron impact. This follows the preparation procedure first described by Lee and Farnsworth [175], although it cannot be confirmed at this time that the c(2x2) structure formed in this work is exactly equivalent to that prepared by Franchy et al. [77]. These latter authors adsorbed NH₃ at 100 K and then heated to give both molecular dissociation and N ordering. Nevertheless the present study has the significant purpose of making the first LEED crystallographic analysis using multiple
scattering calculations for a Cu(100)-c(2x2)-N surface. In addition to LEED structural analysis, some emphasis is given to the N-induced relaxation at this surface.

Detailed structural information for nitrogen chemisorbed on well-characterised surfaces of transition metals remains sparse so far, although for oxygen chemisorption appreciable adsorbate-induced relaxations and reconstructions have been identified [176,177]. A recent report by Heskett et al. pointed to the possibility of a N-induced reconstruction at the (110) surface of copper, with the formation of a surface layer of copper nitride [178]. The earlier investigation of phonon spectra from the c(2x2) surface formed by N chemisorbed on Cu(100) suggested a structure related to that of bulk Cu$_3$N [77], although the subsequent LEED analysis reported in Section 5.3 also noted some significant difference from this bulk structure [179]. For example, in Cu$_3$N each N atom is surrounded octahedrally by six Cu atoms [179], whereas at the Cu(100) surface N atoms apparently chemisorb with essentially 5-coordination (Section 5.3). To a first approximation, the Cu(100) surface presents a rigid array of adsorption sites to a chemisorbing N atom, although with chemisorption relaxations in the metallic structure could occur, particularly since the energy associated with the chemisorption interaction is large compared with that in the individual Cu···Cu interactions. Indeed using thermodynamic data for bulk copper and copper nitride as a rough guide [180], the former can be estimated to exceed the latter by a factor which is greater than 40.

5.2 Experimental

The sample preparation, cleaning procedures and analysis chamber used in this work were the same as those detailed in Chapter 3. The cleaned and ordered Cu(100) surface, which showed a sharp (1x1) LEED pattern after cleaning and annealing, was exposed at room temperature for 50 minutes to high purity nitrogen gas at 5x10$^{-5}$ Torr
which was activated by electron impact in the ion gun. The gun was operated at 200 V, and the surface was then annealed for 10 minutes at around 270°C to give an ordered Cu(100)-c(2x2)-N LEED pattern as reported by others [175,181].

I(E) curves for diffracted beams from the Cu(100)-c(2x2)-N surface structure were measured with the VLA system (Section 3.4) and a total of 10 independent I(E) curves were measured over the approximate energy range 50-220 eV, with a constant increment of 2 eV, for the beams

(1 0), (1 1), (1/2 1/2) at normal incidence and

(0 0), (0 1), (-1 0), (-1 1), (-1/2 -1/2), (-1/2 1/2), (-1/2 3/2) at an off-normal direction where the polar angle is 15° and the azimuthal direction is [001] with respect to crystal axes (i.e. the LEED pattern shows reflection symmetry about the [11] line). The raw data treatments for these beams correspond to the descriptions in Chapter 3.

5.3 Structural Analysis

5.3.1 Initial calculations

The structures considered for the initial LEED calculations emphasised models in which N atoms are held above the topmost copper layer in symmetrically-coordinated adsorption sites, specifically in the "expected" sites of four-fold coordination (the 4f sites), as well as in the two "unexpected" sites which are designated as on-top (1f) sites and bridge (2f) sites. For these initial LEED calculations all Cu-Cu interlayer spacings were kept at the bulk value (1.81 Å) and the topmost N-Cu interlayer spacings were varied over the ranges: 1.05 to 1.65 Å for the 1f model, 0.70 to 1.30 Å for the 2f model, and -0.15 to 1.05 Å for the 4f model. These calculations were made with the layer doubling and combined space methods (Chapter 2); the first for N-Cu interlayer spacings greater than and equal to 0.45 Å and the second for the N-Cu spacings less than and equal to 0.60 Å.
The non-structural parameters used are detailed as follows. The atomic potential in the substrate was characterised by phase shifts (up to $l = 7$) derived from a band structure potential for copper [115], and the real part of the constant potential ($V_{or}$) between the muffin-tin spheres was initially set at -10.0 eV for both the surface layer and the bulk (Section 2.2). However values of $V_{or}$ were effectively refined later during the comparisons of experimental and calculated beam intensities. The phase shifts for N were provided by Moritz [182]; they were obtained from a nitrogen potential constructed from a superposition of free atom charge densities (PHSH3, Table 2.1). The imaginary part ($V_{oi}$) of the potential between all atomic spheres was kept constant at -5.0 eV; the Debye temperatures were taken as 343 K [162] and 731 K for copper and nitrogen respectively. The nitrogen value was chosen to ensure constant root-mean-square vibrational amplitude for all atoms [137].

Comparisons of the calculated and experimental I(E) curves for normal incidence were made both visually and with the reliability index $R_p$ (Section 2.5). Figure 5.1 shows contour plots of $R_p$ as a function of $V_{or}$ and Cu-N interlayer spacing; the level of correspondence reached for the 1f and 2f adsorption sites is sufficiently unsatisfactory that no further consideration of these sites appears warranted. The plots of $R_p$ for the 4f models show two local minima, one for N essentially coplanar with the topmost copper layer and the other for N held 0.6 Å above the surface. This second minimum corresponds to the structure proposed by Franchy et al. [77]; nevertheless the level of correspondence reached is less than satisfactory, and it is clear that further structural refinement is essential.

Another point is worth noting at this stage because of some recent discussion regarding the applicability of the layer doubling method for shorter interlayer spacings (e.g. < 0.9 Å) [183]. Figure 5.2 compares LEED intensity curves calculated for the 4f model of Cu(100)-c(2x2)-N by both the layer doubling and combined space methods for N-Cu
Figure 5.1 Contour plots for Cu(100)-c(2x2)-N of $R_p$ versus $V_{or}$ and the Cu-N interlayer spacing for normal incidence data and for the 1F, 2F and 4F structural models in which all neighbouring Cu-Cu interlayer spacings equal the bulk value (1.81 Å).
Figure 5.1 Continued.
Figure 5.2 Comparisons of experimental I(E) curves (dashed) for diffracted beams from Cu(100)-c(2x2)-N at normal incidence with those calculated with the layer-doubling (LD) and combined-space (CS) methods for the 4F model with N either 0.45 Å or 0.60 Å above the topmost copper layer. The curves designated A, B are for LD, CS respectively and 0.45 Å; those designated C, D are for LD, CS respectively and 0.60 Å.
interlayer spacings equal to 0.45 Å and 0.60 Å. It is found that the correspondence between the two methods is good at 0.60 Å, and it is still at the moderate level even at 0.45 Å. This particular case therefore appears to support the conclusion of Van Hove and Tong [53] that the layer doubling method can be used for interlayer spacings down to a lower limit of around 0.5 Å.

5.3.2 Discussion and further results

Until this subject has established its own principles, it seems reasonable to assess how structures proposed for surfaces fit the broader-based principles of structural chemistry [67,71]. One approach, for a structure appropriate to N chemisorbed on copper, is to consider whether its bonding requirements appear consistent with those in the known solid formed by these elements, namely Cu$_3$N. In this bulk structure [179], each N atom is surrounded octahedrally by six Cu atoms to give Cu-N bond distances of 1.91 Å. If this information is used in the bond length - bond valence relation (Section 1.5), then when the bond valence (s) is expressed as the valency (v) of N divided by the number (n) of close neighbours [67,71], a value of 1.65 Å is suggested for the length (r$_0$) of a Cu-N bond of unit bond valence. That value for r$_0$ may be used in Equation (1.23) to assess bond lengths in surface structures proposed for N chemisorption on the Cu(100) surface. With adsorption above 4f sites, n = 4, and for N, v = 3. The predicted value for the Cu-N bond length is then 1.76 Å, but, in the absence of lateral relaxations for the Cu(100) surface layer, that value is less than the minimum possible Cu-N bond length of 1.81 Å. Also the model seems inadequate if the topmost interlayer spacing is held at the value for bulk copper (1.81 Å). Then each N atom is sufficiently close to the Cu atom directly below in the second layer that further chemical bonding must occur with the N atom becoming effectively 5-coordinate. When Equation (1.24) is used with s = 3/5, the average Cu-N
surface bond length is predicted to be 1.84 Å. If the N atoms are assumed to be coplanar with the laterally unrelaxed topmost copper layer, then the four Cu-N bonds of length 1.81 Å would require that the fifth Cu-N distance equals 1.96 Å in order to give the suggested average value.

The above considerations were used for guiding further LEED calculations in an attempt to improve the level of correspondence with the experimental I(E) curves measured for the Cu(100)-c(2x2)-N surface. The new calculations have been made for models in which N atoms in the 4f sites of Cu(100) approach coplanarity with the topmost copper layer (specifically the N-Cu interlayer separations range from 0.60 to -0.15 Å in steps of 0.15 Å, the minus sign indicates that the N atoms sit below the first copper layer), and for which the first to second copper layer spacing is varied from 1.51 to 2.41 Å, also in steps of 0.15 Å. The small N-Cu separations required these calculations to be made with the combined space approach, although scattering between the copper layers was treated with the renormalised forward scattering formalism (Chapter 2); all non-structural parameters for these additional calculations were given the same values as those specified in Section 5.3.1.

Further contours of $R_p$ for the normal incidence data are shown in Figure 5.3. One was made with the first to second copper layer spacing fixed at 1.96 Å, while the other had N constrained to be co-planar with the topmost copper layer. The minima in these contour plots give general support for models of Cu(100)-c(2x2)-N in which the N atoms are in 4f sites, and are closely coplanar with the topmost copper layer, while the topmost Cu-Cu separation is close to 1.96 Å, as predicted by the use of Equations (1.23) and (1.24) in Chapter 1. The contours in Figure 5.3 established that $R_p$ is sensitive to variation in both these separations.

Further combined space calculations were made for the off-normal incidence data, although at this stage the N atoms were kept coplanar with the topmost Cu(100) layer.
Figure 5.3 Contour plots of $R_p$ for normal incidence data and for the 4F model of Cu(100)-c(2x2)-N. In (a) the topmost Cu-Cu interlayer spacing is fixed at 1.96 Å, while in (b) N is held coplanar with the topmost copper plane.
Values of $R_P$ formed by comparing calculations for this model with all 10 experimental I(E) curves are shown in Figure 5.4, where the contours are plotted versus the topmost interlayer spacing of copper and $V_{or}$. The minimum value of $R_P$ (0.460) corresponds to a topmost Cu-Cu interlayer spacing of 1.95 Å, and some representative I(E) curves from experiment and from calculation are compared in Figure 5.5. Both $R_P$ and visual comparison indicate that this model is superior to that in which $N$ is held at 0.60 Å above the 4f site of Cu(100).

5.3.3 Directions for refinement

LEED multiple scattering calculations reported at this stage suggest that the structure of the Cu(100)-c(2x2)-N surface studied here involves N atoms sinking so deeply into 4f adsorption sites that they essentially become coplanar with the topmost copper layer. In essentials, these structural features are similar to those reported by Imbihl et al. [182] for the Fe(100)-c(2x2)-N surface. However, the calculated curves in Figure 5.5 for the fractional beams show a good correspondence to those from experiment, while for the integral beams (particularly the (1 1) beam) the correspondence is only at the moderate level. This difference in behaviour may arise from further relaxations in the second copper layer given that half these Cu atoms are directly below a N atom whereas the other half are below empty 4f sites. Some exploration is needed for possible further relaxations in the metal induced by the adsorbed species.
Figure 5.4 Contour plot for Cu(100)-c(2x2)-N of $R_p$ versus $V_{\alpha}\beta$ and the topmost Cu-Cu interlayer spacing for all 10 beams measured and for the 4F model with N coplanar with the first copper layer.
Figure 5.5 Comparison of representative experimental I(E) curves (dashed) from Cu(100)-c(2x2)-N with those calculated for the 4F model in which N is coplanar with the first copper layer and the topmost Cu-Cu interlayer spacing is expanded to 1.96 Å.
Figure 5.5 Continued.
5.4 Structural Refinement

5.4.1 Results and discussion

Comparisons of 4F1 and 4F2 models

The study reported in Section 5.3 noted the possibility, when a half monolayer of N atoms sink deeply into hollow 4f adsorption sites of the (100) surface of copper, that those second-layer Cu atoms directly below the N atoms may be pushed down toward the third Cu layer, whereas such a relaxation tendency would not apply to the other set of Cu atoms in the second layer which are not below the N atoms. Discounting any lateral relaxations at this stage, Figure 5.6 indicates the structural parameters needed to a depth of three metal layers for defining such a system with c(2x2) translational symmetry. The first two related models designated as 4F1 and 4F2 are shown in Figure 5.7; the first is constrained with d_{N1} and d_{22} equal to zero, while the second includes these parameters in the optimisation. The optimisation strategy used in this work has been described in Chapter 4. For the 4F2 model, the optimisation over the four parameters was carried out iteratively over the ranges of parameters detailed in Table 5.1. Eleven iterations were made varying one parameter, or sometimes two parameters, while the others were fixed at values indicated by the previous cycle. The optimal sets of parameters from each iteration were found by minimising $R_{MZZ}$ (Section 2.5). Further parallel evaluations of the experimental-calculation comparison of I(E) curves were also made with $R_P$ (Section 2.5); the final results were similar in each case although $R_{MZZ}$ tended to home more consistently to the final result. Basically this R-factor was more sensitive to the structural changes; for example, from the first iteration with d_{N1} and d_{22} equal to zero to the final iteration for the 4F2 model, $R_P$ reduced by only about 10% (from 0.41 to 0.37) whereas $R_{MZZ}$ reduced by twice as much in percentage terms (from 0.34 to 0.27). The optimised parameters from each iteration in Table 5.1 are listed in Table 5.2. It is noted that the parameter d_{22} (around 0.09 Å) is well determined by
Figure 5.6 Interlayer spacings (d_{mn}) considered for the 4F2 model of the Cu(100)-c(2x2)-N surface structure. The subscripts identify the layers involved e.g. N, 1, 2... respectively for the N layer, the first Cu layer, the second Cu layer...; all other Cu-Cu interlayer spacings are fixed at the bulk value (1.81 Å).
Figure 5.7 4F1 and 4F2 models considered in the optimisation procedure for the Cu(100)-c(2x2)-N surface structure. In each case Cu atoms are represented by open circles and the N atom by a filled circle.
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Table 5.1 Ranges of the structural parameters considered for the 4F1 and 4F2 models in the optimisation procedure.
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<td>-7.2</td>
<td>0.276</td>
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<tr>
<td>7</td>
<td>4F2</td>
<td>0.08</td>
<td>1.84</td>
<td>0.09</td>
<td>1.77</td>
<td>-7.2</td>
<td>0.274</td>
</tr>
<tr>
<td>8</td>
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<td>0.08</td>
<td>1.84</td>
<td>0.09</td>
<td>1.76</td>
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<td>9</td>
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<td>1.85</td>
<td>0.09</td>
<td>1.76</td>
<td>-7.2</td>
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</tr>
<tr>
<td>10</td>
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<td>1.83</td>
<td>0.08</td>
<td>1.81</td>
<td>-7.3</td>
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<tr>
<td>11</td>
<td>4F2</td>
<td>0.06</td>
<td>1.85</td>
<td>0.09</td>
<td>1.76</td>
<td>-7.2</td>
<td>0.270</td>
</tr>
</tbody>
</table>

Table 5.2 The optimal structural parameters obtained in each iteration for the 4F1 and 4F2 models.
RMZJ in iterations 3 and 10. Also $d_{22}$ is well separated from other structural parameters, such as $d_{N1}$ and $d_{12}$, since in both iterations their values were set rather differently (e.g. in step 3: $d_{N1} = 0.00 \, \text{Å}$ and $d_{12} = 1.89 \, \text{Å}$, while in step 10: $d_{N1} = 0.06 \, \text{Å}$ and $d_{12} = 1.83 \, \text{Å}$).

Figure 5.8 reports comparisons of $I(E)$ curves for the ten measured beams with those calculated for the 4F1 and 4F2 models according to the optimal geometrical parameters for iterations 1 and 11 quoted in Table 5.2. The situation for the 4F1 model corresponds very closely to that covered in the earlier analysis in Section 5.3 (a slightly more precise value for $d_{12}$ could be given here since the increments in the spacing considered in these calculations (often 0.02 Å) were much smaller than the 0.15 Å increment used previously). Generally it can be said that the fractional-order beams from calculation give a good account of the measured $I(E)$ curves, and that the discrepancies are mainly for the integral beams. Certainly the extension from 4F1 to 4F2 improves the correspondence for the integral beams, according to both a visual analysis and the R-factor analyses, although the match is still not complete.

**Incident angle and phase shifts**

At this stage the multiple scattering calculations for the model 4F2 were repeated for a range of polar angles of incidence (specifically from 13° to 17° in a step of 2°). This angle optimisation was done by plotting the $R_{\text{MZJ}}$ versus $\theta$ curve. The minimised $R_{\text{MZJ}}$ indicates the best match between experiment and calculation remained for the previously reported value of 15°, as previously reported in Section 5.3, and therefore the discrepancies in Figure 5.8 could not be associated with this aspect of the measurement. Further calculations with a new set of $N$ phase shifts (to $l = 7$) obtained from a superposition potential (PHSH4, Table 2.1) constructed independently of the set first used (PHSH3,
Figure 5.8 Ten experimental I(E) curves measured for the Cu(100)-c(2x2)-N surface structure and compared with those calculated for the 4F1 and 4F2 models with the geometrical parameters reported in Table 5.2 (iterations 1 and 11, respectively).
Figure 5.8 'Continued.
Figure 5.8 Continued.
Table 2.1) were also performed, although this again led to no change in the overall level of correspondence shown in Figure 5.8. That suggests some refinement in the geometrical model may still be appropriate; in the following the emphasis remains in considering changes in the ordered structural arrangements, although it is recognised that in principle disorder effects could also have a role [11].

5.4.2 Other possible models

*From 4F1 to 4F3, RS1, RS2, OCT1, and OCT2*

Five further basic types of geometrical models (Figure 5.9) are explicitly considered here for the normal incidence data, although to assess them most efficiently from the computational point of view, they are first seen as an extension from the model 4F1 with \( d_{N1} \) and \( d_{22} \) both equal to zero, rather than from the more general model 4F2. Four of these models include lateral relaxations in the topmost layer to accommodate the deep penetration of N atoms into the 4f hollows of the Cu(100) surface. In the model termed 4F3, the topmost Cu atoms undergo a lateral displacement of magnitude \( \Delta \) consistently with the p4g diperiodic space group, as first recognised for the Ni(100)-(2x2)-C surface [184], and later found applicable also to the corresponding N surface [185]. These models correspond to half-monolayer coverage, and although only c(2x2) LEED patterns have been reported for N chemisorbed on Cu(100) [175], in principle the intensities for the other half-order beams, such as \((1/2 \ 0)\) and \((1 \ 1/2)\), could be undetectably low if \( \Delta \) is insufficiently large.

For the 4F3 model type most emphasis was given to the particular structural model from where, after the lateral displacement \( \Delta \), N adsorbs on the sites which maintain four equal bond lengths to neighbors in the topmost Cu layer. This seems consistent with the previous indications that the metallic structure needs to relax so as to give more room for
Figure 5.9 Five further possible models considered in this work for the N on Cu(100) chemisorption structure. In each case Cu atoms are represented by open circles and the N atom by a closed circle. Arrows indicate lateral displacements of magnitude Δ.
Figure 5.9 Continued.
N, although another possibility has the N adsorbing on those other sites, derived from the regular 4f sites, which with non-zero $\Delta$ give two shorter bonds and two longer bonds to the topmost Cu layer [184]. This was considered for the normal incidence data with $\Delta = 0.05$ and $0.10$ Å, $d_{N1}$ and $d_{22}$ both zero, and $d_{12} = 1.81(0.05)2.16$ Å, but the matching of the calculated $I(E)$ curves to those from experiment turned out to be slightly less favourable than for those calculated for $\Delta$ equal to zero.

In the models designated RS1 and RS2, the N sublayer plus the topmost Cu layer in 4F1 undergoes a rigid registry shift in the [011] and [001] directions respectively; they keep the local NCu$_4$ bonding unchanged from that in the 4F1 model, while allowing some increase in the length of the N-Cu bond to the second layer. For the two further models designated OCT1 and OCT2, an additional layer of Cu atoms is effectively superimposed on the top of the 4F1 and 4F3 models respectively, so that the N atoms are located in 6-fold sites (i.e. to be similar to the octahedral coordination applicable in bulk Cu$_3$N). The ranges of geometrical parameters considered in this analysis for the model types 4F3, RS1, RS2, OCT1 and OCT2 are detailed in Table 5.3.

Some particular comparisons of $I(E)$ curves calculated for these further models are shown in Figure 5.10. Overall it is found that the models OCT1 and OCT2 match less favourably to the experimental $I(E)$ curves, compared with the situation for 4F1, although the models 4F3, RS1 and RS2 can still give reasonable agreements provided $\Delta$ is not too large. Indeed for the models RS1 and RS2, the calculated $I(E)$ curves are essentially identical at normal incidence for given $\Delta$ in the range up to 0.30 Å. In general, values of $\Delta$ greater than 0.10 Å affect the calculated curves, especially for the integral beams, although the interlayer spacing $d_{12}$ appears as the dominant factor in determining the basic level of correspondence between calculation and experiment. The four-domain registry shift models RS1 and RS2 have some curiosity interest, although there does not appear to be
<table>
<thead>
<tr>
<th>Model</th>
<th>Structural Parameters</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>4F3</td>
<td>(d_{N1} = 0.00) (\Delta = 0.14 \ (0.13) \ 0.53), (d_{12} = 1.81 \ (0.05) \ 2.16), (d_{23} = 1.81)</td>
<td></td>
</tr>
<tr>
<td>4F3</td>
<td>(d_{N1} = 0.00) (\Delta = 0.05, \ 0.20), (d_{12} = 1.81 \ (0.05) \ 2.16), (d_{23} = 1.81)</td>
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<tr>
<td>4F3</td>
<td>(d_{N1} = 0.06, \ 0.12) (\Delta = 0.20), (d_{12} = 1.81 \ (0.05) \ 2.16), (d_{23} = 1.81)</td>
<td></td>
</tr>
<tr>
<td>RS1</td>
<td>(d_{N1} = 0.00) (\Delta = 0.00 \ (0.08) \ 0.56), (d_{12} = 1.96), (d_{23} = 1.81)</td>
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<tr>
<td>RS2</td>
<td>(d_{N1} = 0.00) (\Delta = 0.30 \ (0.03) \ 0.48), (d_{12} = 1.86 \ (0.05) \ 1.96), (d_{23} = 1.81)</td>
<td></td>
</tr>
<tr>
<td>OCT1</td>
<td>(d_{N2} = 0.00) (\Delta = 0.14 \ (0.13) \ 0.53), (d_{12} = d_{23} = 1.81 \ (0.10) \ 2.51), (d_{34} = 1.81)</td>
<td></td>
</tr>
<tr>
<td>OCT2</td>
<td>(d_{N2} = 0.00) (\Delta = 0.05, \ 0.20), (d_{12} = d_{23} = 1.81 \ (0.10) \ 2.51), (d_{34} = 1.81)</td>
<td></td>
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</tbody>
</table>

Table 5.3 Ranges of structural parameters (in Å) considered for five additional models for the Cu(100)-c(2x2)-N surface structure. \(\Delta\) is defined in Figure 5.9 and the interlayer spacings are represented by the \(d_{mn}\), where the subscripts (mn) identify the layers involved e.g. N, 1, 2... for N layer, first Cu layer, second Cu layer... All other Cu-Cu interlayer spacings are fixed at the bulk value (1.81 Å).
Figure 5.10 Comparison of three experimental I(E) curves measured for normal incidence from Cu(100)-c(2x2)-N with those calculated for some particular N coplanar models: (a) 4F1 with $d_{12} = 1.96\,\text{Å}$; (b) 4F3 with $d_{12} = 1.96\,\text{Å}$, $\Delta = 0.14\,\text{Å}$; (c) RS1 with $d_{12} = 1.96\,\text{Å}$, $\Delta = 0.30\,\text{Å}$; (d) 4F1 with $d_{12} = 1.86\,\text{Å}$; (e) 4F3 with $d_{12} = 1.86\,\text{Å}$, $\Delta = 0.14\,\text{Å}$; (f) RS1 with $d_{12} = 1.86\,\text{Å}$, $\Delta = 0.30\,\text{Å}$; (g) OCT1 with $d_{12} = d_{23} = 1.91\,\text{Å}$; (h) OCT2 with $d_{12} = d_{23} = 1.91\,\text{Å}$, $\Delta = 0.14\,\text{Å}$.
Figure 5.10 Continued.
Figure 5.10 Continued.
strong evidence for their relevance, compared with the 4F3-type model, for which the match-up of intensity curves is at least as good provided \( \Delta \) is 0.14 Å or less. The best correspondence at normal incidence for the 4F3 model with \( \Delta \) equal to 0.14 Å occurs for \( d_{12} \) close to 1.96 Å. In this specific model, the calculated intensity for the (1 1/2) beam, summed over the energy range from 46 to 218 eV, is less than one tenth that for the (1/2 1/2) beam. A curve of the ratio of the summed intensities for the beams (1 1/2) and (1/2 1/2) plotted against \( \Delta \) is shown in Figure 5.11. As can be seen in this curve, the calculated intensity of (1 1/2), and other beams which are absent for c(2x2) symmetry, goes up rapidly for the model 4F3 as \( \Delta \) increases beyond 0.14 Å.

*Further relaxation model — 4F4*

The calculated \( I(E) \) curves for the 4F2 model shown in Figure 5.8 summarise the best correspondence with the experimental data available so far for the Cu(100)-c(2x2)-N surface structure. In this model, with \( d_{\text{N1}} = 0.06 \) Å, \( d_{12} = 1.85 \) Å, \( d_{22} = 0.09 \) Å, and \( d_{23} = 1.76 \) Å, each N atom bonds to four Cu atoms in the first metal layer, and to one Cu atom in the second layer with Cu-N bond lengths of 1.81 Å and 2.00 Å respectively. The average bond length of 1.85 Å is within 0.01 Å of that predicted from a bond order - bond length relation calibrated with structural information for bulk Cu3N [179], and that therefore supports the view that this structure is basically reasonable from a chemical perspective. Nevertheless the correspondence between \( I(E) \) curves from experiment and calculation is not exact, and further displacements in the metal structure seem very likely. A possible extension from the model 4F2 is to one designated 4F4, which is indicated in Figure 5.12. This pair of models are related in the first instance as 4F1 to 4F3, although insofar as the Cu atoms in the second metal layer, which are directly below N atoms, are displaced downwards, a further p4g-type displacement can occur in the third layer.
Figure 5.11 Ratio of summed intensities versus lateral displacement ($\Delta$) for the 4F3 model with $d_{N1} = 0.0$ Å, $d_{12} = 1.96$ Å; the intensities are summed over the energy range from 46 to 218 eV in steps of 4 eV.
Figure 5.12 Lateral relaxations possible in the first and third copper layers for the model of the N on Cu(100) surface structure designated 4F4.
However, in this latter case, the overall Cu⋯Cu interactions seem best favoured by the lateral displacements in the first and third metal layers having opposite senses.

The structural details for N chemisorption on the Cu(100) surface appear to differ from those for O chemisorption which will be discussed in Chapter 6. However, the differing coordinations for O and N at the Cu(100) surface are not inconsistent with the fact that valence considerations cause different structural arrangements for the bulk Cu(I) compounds, namely Cu$_2$O and Cu$_3$N. In both cases, the structures found by LEED for the chemisorption systems are broadly consistent with bond order - bond length relations applied to the corresponding bulk compounds.

5.5 Summary

An intensity analysis with low-energy electron diffraction is reported for the c(2×2) surface structure obtained on the (100) surface of copper by the adsorption at room temperature of nitrogen activated by an ion gun. The surface was annealed at around 270°C before sets of I(E) curves were measured with the video LEED analyser. The curves measured for 10 independent diffracted beams were compared with those calculated by full multiple scattering methods. The structural conclusions differ markedly from those in two earlier reports in the literature. The surface structure revealed here involves N atoms incorporated deeply into the expected four-fold hollow sites (4f) to become closely coplanar with the topmost copper layer. Each N atom becomes essentially 5-coordinate with bonding to the atom directly below in the second copper layer, and the topmost Cu-Cu interlayer spacing is indicated to be expanded by about 8% from the bulk value.

A further multiple scattering analysis of the LEED intensities was made with consideration of relaxation effects, both vertical and lateral, in the metallic structure. The best correspondence in the comparison of experimental and calculated I(E) curves is
reached with N held 0.06 Å above the top copper layer, while the Cu atoms in the second layer directly below N are depressed by 0.09 Å compared with the other atoms in that layer. The first-to-second Cu-Cu interlayer separation is 1.85 Å. Small lateral displacements (magnitude 0.14 Å or less) consistent with the p4g diperiodic space group may occur, even though the required extra diffracted beams for a (2x2)-type LEED pattern have not been reported yet for this surface.
6.1 Introduction

The chemisorption of oxygen on the (100) surface of copper has been studied extensively over the last 20 years, especially for the chemisorption phases which are designated as $(\sqrt{2}\times\sqrt{2})_{45^\circ}$ (or c(2x2)) and $(2\sqrt{2}\times\sqrt{2})_{45^\circ}$ according to the diffraction patterns observed with LEED [79-81,85]. These phases are often reported to form sequentially, with increasing oxygen coverage, prior to the onset of bulk oxide formation [186,187]. Information on the chemisorption phases has also been provided by a range of other techniques, including X-ray photoelectron spectroscopy (XPS) [84], work function measurements [188,189], ion scattering [80,190], secondary ion mass spectrometry [78], high-resolution electron energy loss spectroscopy [191,192], photoelectron diffraction [83], and surface extended X-ray absorption fine structure (SEXAFS) [82]. Several studies have suggested that oxygen penetrates below the top copper layer, especially for the $(2\sqrt{2}\times\sqrt{2})_{45^\circ}$ surface [175,188,189,193], but other evidence has pointed to the $(\sqrt{2}\times\sqrt{2})_{45^\circ}$ and $(2\sqrt{2}\times\sqrt{2})_{45^\circ}$ surfaces as having related structures [81,83]. Attempts at quantitative structural analyses have not yet supported the model of oxygen penetration. Nevertheless the structural models reported are wide-ranging. For example, determinations by SEXAFS [82] and photoelectron diffraction [83] indicate that O atoms adsorb close to 0.7 and 0.8 Å, respectively, above hollow sites of four-fold coordination (4f), whereas an analysis with angular resolved XPS suggests O is coplanar with the topmost metal layer [84]. Some preliminary support for a nearly-
The coplanar structure was provided by LEED [81], although an earlier study, in combination with ion scattering measurements, proposed that bridge bonding may occur [80], a view that received indirect support from observations of beam splitting associated with antiphase domain boundaries [157]. However, most of these studies have assumed that the Cu atoms essentially maintain the normal relative positions for the metallic structure.

Methods such as SEXAFS, photoelectron diffraction, and angular resolved XPS apparently emphasise the immediate neighbourhood of the adsorbate, while giving only limited information about any relaxations or reconstructions of the metal surface. By contrast, the latter contributions can perhaps be assessed more directly with LEED, and this provides a motivation for undertaking the current work. Therefore new LEED crystallographic analyses have been undertaken for the oxygen on Cu(100) system with the hope of clarifying some of the conflicting information which has emerged recently for this surface, and which contrasts with the corresponding situation for Ni(100) [194]. The tendency for oxygen to form the \((2\sqrt{2} \times 2)_{45^\circ}\) structure on Cu(100) suggests that there should be some emphasis on structural models which can naturally generate this particular translational symmetry. A second point, which also distinguishes this surface from the corresponding structure formed on Ni(100), concerns the tendency for the Cu(100) surface to roughen in the presence of oxygen [195], and ultimately to form (410) facets [196]. In this regard, a structural similarity has been noted between the \((2\sqrt{2} \times 2)_{45^\circ}\) superstructure formed by oxygen on Cu(100) and the stepped nature of the (410) surface [197,198].

6.2 Experimental

The Cu(100) surface, cleaned and ordered according to the procedures described in Section 3.3, was exposed to reagent grade oxygen with continued pumping according
to two alternate procedures, which were used to form surfaces which manifest $(\sqrt{2}x\sqrt{2})45^\circ$ LEED patterns. The first procedure involved exposing the clean surface to $1\times10^{-6}$ Torr of oxygen for 5 minutes while heating the surface to $300^\circ$C, followed by annealing at the same temperature for a further 5 minutes. In the second procedure the adsorption was done at room temperature for 5 minutes, while exposing the surface to $8\times10^{-6}$ Torr of oxygen activated with the ion gun at 200 V, followed by a short anneal at $400^\circ$C. Most often this latter procedure gave the better $(\sqrt{2}x\sqrt{2})45^\circ$ LEED patterns. AES studies on the $(\sqrt{2}x\sqrt{2})45^\circ$ and $(2\sqrt{2}x\sqrt{2})45^\circ$ surface structures have been made in the references [187,188,191,199], and in this work the amount of oxygen chemisorbed was monitored by the ratio of Auger peak-to-peak height for O at 510 eV to that of Cu at 917 eV according to the following expression:

$$ R = \frac{A_{510}}{A_{917}} $$

(6.1)

The best defined $(\sqrt{2}x\sqrt{2})45^\circ$ LEED pattern correspond to an R value of about 0.09. Diffracted beam I(E) curves were measured with the VLA system (Section 3.4). For the Cu(100)-$(\sqrt{2}x\sqrt{2})45^\circ$-O surface structure, a total of 10 independent I(E) curves were measured over the energy range 50-220 eV for the beams (1 0), (1 1), (1/2 1/2) at normal incidence ($\theta = 0$), and (0 0), (1 0), (0 1), (-1 1), (1/2 1/2), (-1/2 1/2), (1/2 3/2) at an off-normal direction where the polar angle $\theta$ is $15^\circ$ and the azimuthal direction is [011] with respect to the crystal axes (i.e. the LEED pattern shows reflection symmetry about the [10] line). Some comparisons are shown in Figure 6.1 between these I(E) curves measured at normal incidence and those similarly measured from the Cu(100)-$(\sqrt{2}x\sqrt{2})45^\circ$-N surface structure (see Chapter 5).

LEED patterns corresponding to two orthogonal domains of $(2\sqrt{2}x\sqrt{2})45^\circ$-type formed on exposing the cleaned Cu(100) surface at 300 °C to oxygen at $1\times10^{-6}$ Torr for
Figure 6.1 Comparisons of I(E) curves for the (1 0), (1 1) and (1/2 1/2) beams measured at normal incidence from the two surfaces Cu(100)-(\(\sqrt{2}\times\sqrt{2})45^\circ\)-N (curves designated A), and Cu(100)-(\(\sqrt{2}\times\sqrt{2})45^\circ\)-O (curves designated B).
longer times than in the first procedure above, typically around 8 minutes, although there could be some variability in the conditions that gave the \((2\sqrt{2}\times\sqrt{2})45^\circ\) patterns in particular cases. In general, disorder contributions apparently significantly affect this system. Frequently \(1/4\) order beams could not be measured properly during the experiments, this required further experimental efforts on the surface structure preparation and data measurement. The second procedure described in the previous paragraph on structure preparation was avoided in order to eliminate any surface disorder caused by the ion gun. To reduce the exposure time of oxygen, the nozzle used initially was elongated to be directed closer to the surface sample (at about 8 cm away). Typically the sharpest LEED \((2\sqrt{2}\times\sqrt{2})45^\circ\) patterns were obtained in this way by exposing the cleaned Cu(100) surface at 300°C to the same pressure of oxygen for 5 minutes followed by a short anneal at 300°C. \((2\sqrt{2}\times\sqrt{2})45^\circ\) LEED patterns could observed for the Auger peak-to-peak ratio in the range 0.09 to about 0.20 (Equation (6.1)); the best-defined patterns corresponding to \(R\) around 0.16. \(I(E)\) curves were measured with the VLA system over the energy range 50-220 eV, and the analysis below used the beams \((1\ 0)\), \((1\ 1)\), \((1/2\ 1/2)\), \((1/2,3/2)\), \((3/2\ 3/2)\), \((3/4\ 3/4)\) at normal incidence. Incidentally our experience is that the \((2\sqrt{2}\times\sqrt{2})45^\circ\) surface structure gives sharper LEED patterns than does the \((\sqrt{2}\times\sqrt{2})45^\circ\) structure.

6.3 Calculation Methods

The methods used for the LEED intensity calculations depended on the interlayer spacing involved. Briefly, for the \((\sqrt{2}\times\sqrt{2})45^\circ\) surface, layers were combined with the renormalised forward scattering method (Section 2.4.2) when interlayer spacings are 0.9 Å or greater, the full matrix inversion procedure was used to form "composite" layers when spacings are less than 0.6 Å (Section 2.4.3), and the layer-doubling method (Section 2.4.1) was applied in intermediate situations. The atomic potential in the
substrate was characterised by phase shifts (to $l = 7$) derived from a band structure potential for copper [115], and the oxygen phase shifts used were those derived by Demuth et al. [161] (PHSH5, Table 2.1) from a superposition potential. The real part of the constant potential ($V_{\text{or}}$) between the muffin-tin spheres was initially set at -10.0 eV for both surface and bulk. The imaginary part ($V_{\text{oi}}$) of the potential between all atomic spheres was kept constant at -5.0 eV. The Debye temperatures were taken as 343 K [162] and 684 K for copper and oxygen, respectively. The value for oxygen was chosen as described for nitrogen in Section 5.3.1.

For the $(2\sqrt{2} \times \sqrt{2})45^\circ$ surface structure, the multiple scattering between layers was calculated with the renormalised forward scattering method (Section 2.4.2), although composite layers were added with the combined space formalism when small interlayer spacings were involved (Section 2.4.3). The non-structural parameters used here were the same as those in the calculations for the $(\sqrt{2} \times \sqrt{2})45^\circ$ surface. The comparisons of experimental and calculated beam intensities were done with the two LEED reliability indices $R_{\text{MZI}}$ and $R_{\text{P}}$ (Section 2.5). Appropriate domain averaging was done to the calculated $I(E)$ curves prior to comparing with those from experiment.

6.4 Investigations for the $(\sqrt{2} \times \sqrt{2})45^\circ$ Surface Structure

6.4.1 Models investigated

Figure 6.1 indicates that the $I(E)$ curves measured for the Cu(100)-$(\sqrt{2} \times \sqrt{2})45^\circ$-O surface are relatively similar to those measured for the Cu(100)-$(\sqrt{2} \times \sqrt{2})45^\circ$-N (Chapter 5). Further, since O and N have similar scattering factors [200], these two surfaces are likely to have structural features in common. The models considered for the $(\sqrt{2} \times \sqrt{2})45^\circ$-O surface therefore start from the premiss that, as for N, adsorbed O atoms occupy 4f hollow sites. From this starting point other models can be produced involving lateral and
vertical relaxations of the copper atoms. For example, because oxygen atoms in crystalline Cu$_2$O and CuO are surrounded tetrahedrally by four copper atoms [201], models are considered where O atoms occupy tetrahedral holes between the first and second layers of the Cu(100) surface, as well as relaxed models with distorted tetrahedral holes for the O atoms. Consideration is not given here to models with mixed 4f and bridge-site (2f) adsorption, as proposed by Onuferko and Woodruff [80], because they are not strongly supported by the I(E) curves calculated in that work.

The basic structures considered for the ($\sqrt{2}$x$\sqrt{2}$)45° surface are distinguished by designations of the types $X_{n,m}$ (Figure 6.2). In this notation, $X$ identifies the type of model and is represented by 4F for O adsorption in regular 4f hollow sites, by TH for adsorption in tetrahedral holes between the first and second copper layers, and by 4FT where the 4F structure with O initially coplanar with the neighbouring copper atoms is subjected to a tetrahedral-type distortion. The subscript $n$ has a value 1, 2 for the ($\sqrt{2}$x$\sqrt{2}$)45°, (2$\sqrt{2}$x2$\sqrt{2}$)45° structures respectively, while $m$ indicates the O coverage as a fraction of a monolayer (ML). Finally, a prime is added to the model designation (e.g. TH') when additional lateral relaxations are included for the copper atoms in the vicinity of the surface. For example, for the TH' models copper atoms in the top two layers are displaced in the [010] and [001] directions. These relaxations act to increase the neighbouring O-Cu bond lengths. The specific models examined in this section are detailed in Table 6.1; the headings $d_{O-Cu}$ and $d_{Cu-Cu}$ are respectively the topmost O-Cu interlayer spacing and the first Cu-Cu spacing.
Figure 6.2 Schematic indications of some $\sqrt{2}\times\sqrt{2}45^\circ$-O models discussed in the text. The dark filled circles represent oxygen atoms and the open circles correspond to copper atoms from the topmost layer of the ideal clean metal surface. A: 4F model; B: 4FT model (only one domain is shown); and C: TH models (two domains of this translational symmetry are indicated as (a) and (b) respectively).
6.4.2 Initial comparisons of experiment and calculation

Comparisons of I(E) curves measured from Cu(100)-(√2x√2)45°-O, for normal incidence, with those calculated for the range of the models considered for tetrahedral hole adsorption (i.e. the models TH and TH' in Table 6.1) showed no reasonable levels of correspondence as assessed both by visual inspection and by the use of the reliability index \( R_p \) (Section 2.5). Therefore this model does not appear relevant to this chemisorption system, an observation which is in general agreement with the previous observations \[186,187\] that bulk oxide formation occurs at much higher oxygen exposures than considered here. Figure 6.3 shows for the 4F\(_{1,0,5}\) model type a contour plot of \( R_p \) versus \( V_{cr} \) and \( d_{O-Cu} \), the topmost O-Cu interlayer spacing, for the normal incidence data ((1 0), (1 1) and (1/2 1/2) beams) when the first Cu-Cu spacing \( (d_{Cu-Cu}) \) is held at the bulk value (1.81 Å). Two local minima are apparent with almost equal values. For one the oxygen atoms are held close to coplanarity with the topmost copper layer, while for the other the adsorbed atoms are about 0.75 Å above the 4f sites. Interestingly these two minima occur for conditions similar to the conclusions, noted in the Introduction, from studies with angular resolved XPS (O close to coplanar) and with photoelectron diffraction and SEXAFS (O close to 0.75 Å above surface). Nevertheless the comparison in Figure 6.3 is not sufficient for distinguishing these two situations, one reason being that with coplanarity some vertical relaxation in the topmost Cu-Cu spacing would likely occur. Accordingly the contour plot of \( R_p \) in Figure 6.4, made for the normal incidence data with O nearly coplanar with the topmost copper layer, suggests that the optimal value of \( d_{Cu-Cu} \) is close to 1.84 Å. The contour plot of \( R_p \) shown in Figure 6.5 is calculated for both normal and off-normal incidence data with O held between 0.7 and 1.5 Å above the 4f sites. In this case \( R_p \) is minimised with \( d_{O-Cu} \) equal to 0.85 Å. Figure 6.6 compares some representative I(E) curves from experiment, for both normal
<table>
<thead>
<tr>
<th>$X_{n,m}$</th>
<th>$d_{O-Cu}$ (Å)</th>
<th>$d_{Cu-Cu}$ (Å)</th>
<th>Cu atom lateral shift (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4F_{1,0.5}$</td>
<td>-0.20 (0.20) 0.40</td>
<td>1.51 (0.15) 2.41</td>
<td>1.81</td>
</tr>
<tr>
<td></td>
<td>0.60 (0.10) 1.50</td>
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<tr>
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<td>0.00 (O₁)</td>
<td>1.81 (0.10) 2.01</td>
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<tr>
<td></td>
<td>0.55 (0.10) 0.95 (O₂)</td>
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<td></td>
</tr>
<tr>
<td>$4F_{T1,0.5}$</td>
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<td>1.51 (0.15) 2.41</td>
<td></td>
</tr>
<tr>
<td>$TH_{1,0.5}$</td>
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<td>2.00 (0.10) 2.60</td>
<td></td>
</tr>
<tr>
<td>$TH'_{1,0.5}$</td>
<td>0.90 (0.10) 1.30</td>
<td>1.80 (0.20) 2.60</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>0.90 (0.10) 1.20</td>
<td>1.80 (0.20) 2.40</td>
<td>0.37</td>
</tr>
<tr>
<td>$TH_{2,0.5}$</td>
<td>1.00 (0.05) 1.30</td>
<td>2.00 (0.10) 2.60</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1 Models ($X_{n,m}$) investigated with multiple scattering calculations for the Cu(100)-($\sqrt{2}x\sqrt{2}$)45°-O surface structure.
Figure 6.3 Contour plot of $R_p$ versus $V_{or}$ and the O-Cu interlayer spacing for normal incidence data and 4F1,0.5 models of O on Cu(100). All neighbouring Cu-Cu interlayer spacings in the calculations equal 1.81 Å.
Figure 6.4 Contour plot of $R_P$ versus the topmost Cu-Cu interlayer spacing and the O-Cu interlayer spacing for normal incidence data and 4F$_{1,0.5}$ models of O on Cu(100). $V_{or}$ is fixed equal to -8.0 eV for these comparisons.
Figure 6.5 Contour plot of $R_p$ versus $V_{or}$ and the O-Cu interlayer spacing for the ten beams measured and for $4F_{1.0,5}$ models of O on Cu(100). All neighbouring Cu-Cu interlayer spacings in the calculations equal 1.81 Å.
Figure 6.6 Comparison of representative experimental I(E) curves (dashed) from Cu(100)-(√2x√2)45°-O with those calculated for three 4F models: (i) d_O-Cu = 0.0, d_Cu-Cu = 1.88 Å (curves designated A); (ii) d_O-Cu = 0.7 Å, d_Cu-Cu = 1.81 Å (curves designated B); (iii) d_O-Cu = 0.9 Å, d_Cu-Cu = 1.81 Å (curves designated C).
Figure 6.6 Continued.
and off-normal incidence, with those calculated for 4F_{1,0.5} models, namely: (i) d_{O-Cu} = 0.0 \text{ Å}, d_{Cu-Cu} = 1.88 \text{ Å}; (ii) d_{O-Cu} = 0.7 \text{ Å}, d_{Cu-Cu} = 1.81 \text{ Å}; (iii) d_{O-Cu} = 0.9 \text{ Å}, d_{Cu-Cu} = 1.81 \text{ Å}. The minimum value of R_p calculated for the coplanar model (i) for all 10 beams is 0.69; the corresponding values for models (ii) and (iii) are 0.76 and 0.75, respectively. Insofar as the best agreement between the experimental and calculated I(E) curves corresponds to the smallest value of R_p, the coplanar model appears favoured. A similar conclusion may be reached from a visual comparison of the individual I(E) curves shown in Figure 6.6, although the correspondence remains far from ideal. The multiple scattering calculations were also made for 1-ML (\sqrt{2}x\sqrt{2})45^\circ models in which all the O atoms are held in 4f sites, but where half are coplanar with the topmost copper layer while the other half are held between 0.55 Å and 0.95 Å above the surface. These calculations showed much lower levels of correspondence with the experimental I(E) curves, than those in Figure 6.6, and so it seems safe to discount this type of inequivalent O adsorption.

6.4.3 Analysis of bond lengths

The contour plot in Figure 6.4 suggests that the correspondence between experimental and calculated I(E) curves is optimised with d_{O-Cu} = 0.17 \text{ Å} and d_{Cu-Cu} = 1.84 \text{ Å}. In this situation each O is bonded to one Cu atom (directly below) at 2.01 Å and the four Cu atoms at 1.81 Å, with the average of the five O-Cu bond lengths equalling 1.85 Å. This appears quite inconsistent with the structure of bulk CuO [201], for which each O is bonded to four Cu atoms in a distorted tetrahedral arrangement at an average distance of 1.92 Å. Even for the structure of bulk Cu_2O [201], in which the metal oxidation state is lower and therefore is more likely to be relevant to the low-coverage chemisorption situation, each O is bonded tetrahedrally to four Cu atoms at 1.85 Å. With
the bond length - bond order relation (Section 1.5), the O-Cu distance for a unit bond valence \( (r_0) \) equals 1.59 Å. Therefore, when O (valency \( v = 2 \)) is bonded to 5 neighbours \( (n = 5) \), the average bond valence is \( s = v / n = 0.4 \) and the corresponding average O-Cu bond distance is estimated to equal 1.93 Å. This suggests that further relaxations beyond those considered above may occur in the surface region for O on Cu(100) to make the average of the local O-Cu distances greater than 1.85 Å and close to 1.93 Å.

The analysis in Figure 6.4 uses just three beams and therefore the data base is insufficient to assess at this point whether the \( d_{O-Cu} \) spacing is really 0.17 Å as opposed, for example, to a smaller value. Since this section aims just to assess the broader aspects of this surface structure, the current discussion will consider models with the chemisorbed O atoms coplanar with the topmost copper layer (this increases the layer symmetry with a consequent reduction in computing cost). Given the basic coplanar 4F model as a starting point, the average O-Cu bond distance may in principle be increased by vertical and lateral relaxations either individually or in combination.

6.4.4 Variations on coplanar models

The 4FT model derives from the coplanar 4F model by having, for each O atom, two diagonally-related Cu atoms displaced vertically upwards while the other two are displaced downwards by the same amount (Figure 6.2). This allows the O-Cu bond length to increase, although the rearrangement for the topmost metal structure can be substantial for only a small increase in the adsorbate bond length. For example, with the Cu atoms vertically displaced by 0.3 Å, the O-Cu distance increases by less than 0.03 Å. As judged both by \( R_F \) and visual comparisons, the I(E) curves for the 4FT models showed no improved correspondence with the experimental I(E) curves relative to the
situations for the coplanar 4F model. Therefore the 4FT models are not considered further in this work.

6.5 Investigations for the (2\(\sqrt{2}\)x\(\sqrt{2}\))45\(^\circ\) Surface Structure

6.5.1 Evolution of the surface structures

Overall the corresponding I(E) curves measured in this work for the (\(\sqrt{2}\)x\(\sqrt{2}\))45\(^\circ\)-O and (2\(\sqrt{2}\)x\(\sqrt{2}\))45\(^\circ\)-O structures are quite similar (Figures 6.1 and 6.11), and there is a broad agreement, at least in peak positions, with curves reported previously by Onuferko and Woodruff [80] and by Yang et al. [81]. Certainly there is some variation in relative intensities, but such variations are also found in this work when making measurements from independently prepared surfaces which show a particular type of LEED pattern, especially for (\(\sqrt{2}\)x\(\sqrt{2}\))45\(^\circ\)-O surface measurements. Onuferko and Woodruff reported the existence of identical I(E) curves from surfaces with the different translational symmetries, an observation that could be taken to support the contention of Mayer et al. [85] that only one structure, of (2\(\sqrt{2}\)x\(\sqrt{2}\))45\(^\circ\) type, is produced throughout the oxygen exposure regime. Yang et al. [81] in contrast, report very similar I(E) curves for the (1/2 1/2) beam, but somewhat different (1 0) and (1 1) beams, a situation similar to that found in the present work. Some evolution of I(E) curves occurs with increasing coverage, particularly for the integral beams, although this appears more as a second-order effect.

The general similarity in peak positions for the half-order beams with changing translational symmetry (or perhaps just increasing surface order) suggests, in concert with the views of Yang et al. [81], that the environment of the chemisorbed O is essentially constant with the evolution (a conclusion that has also been reached from the photoelectron diffraction studies [83]). Whatever the initial situation, there is no doubt that ultimately chemisorbed O forms the (2\(\sqrt{2}\)x\(\sqrt{2}\))45\(^\circ\) structure on Cu(100), and therefore
that it is important that consideration be given to structural models with this translational symmetry.

### 6.5.2 TH\textsubscript{1,0.5} and TH\textsubscript{2,0.5} models

The models, TH\textsubscript{1,0.5} and TH\textsubscript{2,0.5}, investigated in the previous section, still have some interest for further discussion. TH\textsubscript{2,0.5} contains two oxygen atoms in the unit mesh (b in Figure 6.7 (A)) while TH\textsubscript{1,0.5} has only one atom per unit mesh (a in Figure 6.7 (A)), although they both have an oxygen coverage of 0.5. There are two domain orientations for each model since there are two types of tetrahedral holes in the surface. The reciprocal space representations of both models are shown schematically in Figure 6.8. The two O atoms per unit mesh of the TH\textsubscript{2,0.5} model are inequivalent and the calculation for this structure was done using a similar approach to that applied previously for the CO on Pd(100) system [202]. Figure 6.9 reports I(E) curves calculated for the TH\textsubscript{1,0.5} and TH\textsubscript{2,0.5} models, with a constant local geometry of tetrahedral site. The close similarity of the curves for each beam designation reinforces arguments of Yang et al. [81] regarding the stability of I(E) curves for corresponding beams when the local coordination is constant but the overall translational symmetry varies. The original observations of this behaviour emphasised the constancy of I(E) curves for fractional-order beams, but in this case it is clear that the curves for corresponding integral beams are also closely similar. Following the behaviour established in Figure 6.9, and in other studies [81,159,160], the I(E) curves calculated for the 4F\textsubscript{1,0.5} model are expected to be closely similar to those of the corresponding models of 4F\textsubscript{2,0.5}, and indeed also those of 4F\textsubscript{2,0.25} and 4F\textsubscript{2,0.75} types, although no actual calculations have been performed for these (2\sqrt{2}\times\sqrt{2})45\degree-O models.
Figure 6.7 (A): $TH_{1,0.5}$ and $TH_{2,0.5}$ models (only one domain is shown). (B): Schematic indication of a missing row model of the Cu(100) surface for 0.25 ML coverage of O atoms (represented by dark filled circles). With O atoms in coplanar 4f sites, some top layer Cu atoms can be displaced laterally. Further possible O chemisorbed sites are also available.
Figure 6.8  Reciprocal space representations of: (a) Cu(100)-(\sqrt{2}\times\sqrt{2})45°-O and (b) Cu(100)-(2\sqrt{2}\times\sqrt{2})45°-O surfaces for the single-domain TH models shown in Figure 6.7 (A).
Figure 6.9 Comparison of I(E) curves at normal incidence for the (1 0), (1 1) and (1/2 1/2) beams calculated for the O on Cu(100) models designated TH1,0.5 (curves identified by 1) and TH2,0.5 (curves identified by 2) with d_{O-Cu} = 1.05 Å.
6.5.3 Systematic study of missing row models

Starting point

In general with O chemisorption in coplanar 4f sites, lateral relaxations of the Cu atoms can provide an efficient route to increasing the average O-Cu bond length, although that may occur at the expense of strain in the metal structure. An exception is if the lateral relaxations are accompanied by removal of rows of Cu atoms. Missing row (MR) models have been postulated in other examples of O chemisorption, including that on the (110) surface of copper [203]. These models merit consideration since they can naturally yield the \( (2\sqrt{2} \times \sqrt{2})45^\circ \) translational symmetry for the O chemisorption structure. Figure 6.7 (B) shows a possible model for missing row formation on the Cu(100) surface for a 0.25 ML coverage of oxygen. It is clear that various adsorption sites are available for oxygen, and indeed with a missing row the \( (2\sqrt{2} \times \sqrt{2})45^\circ \) translational symmetry can in principle be maintained over the complete range of coverage from 0.25 ML to 1 ML.

The favoured coplanar model \( 4F_{1,0.5} \) with O adsorption in regular 4f sites for the \( (\sqrt{2} \times \sqrt{2})45^\circ \) surface structure, and considerations of bond length - bond order presented (Section 6.4), may give a starting point for a study of the \( (2\sqrt{2} \times \sqrt{2})45^\circ \) surface structure. The information provided by Figure 6.4 results from a \( R_p \) analysis using only three beams at normal incidence for the \( (\sqrt{2} \times \sqrt{2})45^\circ \) structure. The minimum in the contour plot suggests that the optimal value of \( d_{O-Cu} \) equals 0.17 Å and that of \( d_{Cu-Cu} \) is close to 1.84 Å. However the insufficient data base may mislead the further extensive computing work needed for most missing row models, for example the composite layer calculations may require up to five atoms per unit mesh. Therefore it should be most efficient to reassess the \( 4F_{1,0.5} \) model before the systematic MR investigations are started. When the five non-quarter-order beams measured here for the \( (2\sqrt{2} \times \sqrt{2})45^\circ - O \) surface are compared with those calculated for the \( 4F_{1,0.5} \) model, a degree of match is noted, which suggests that the
structural features involved in the simpler surface may form ingredients of the full structure for the \((2\sqrt{2}\times \sqrt{2})_{45^\circ}\)-O surface. The results of such a reliability index analysis for the \((1\ 0)\), \((1\ 1)\), \((1/2\ 1/2)\), \((1/2\ 3/2)\), and \((3/2\ 3/2)\) beams are summarised in Table 6.2. A general trend is that the optimal values of \(d_{\text{Cu-Cu}}\) increase as those of \(d_{\text{O-Cu}}\) decrease. However, overall the best correspondence is for \(d_{\text{O-Cu}}\) around 0.20 Å and \(d_{\text{Cu-Cu}}\) equal to 1.97 Å.

**Model designations**

Figure 6.10 indicates the five basic types of missing row models (designated MR1 - MR5) considered here for the Cu(100)-\((2\sqrt{2}\times \sqrt{2})_{45^\circ}\)-O surface structure. These models can differ both by the O adsorption sites and by whether the copper surface just involves missing rows parallel to the [010] direction (MR1 - MR4), or whether the copper atoms released during the formation of the missing rows additionally line up as overlayer chains parallel to [010] and equi-spaced to the missing rows (MR5). The model MR1 retains adsorption in the regular uppermost 4f sites and corresponds to 0.25 ML coverage. The coverage is increased to 0.5 ML in model MR2, where O atoms additionally adsorb in the open 4f sites available in the second copper layer with a vertical O-Cu separation of 0.7 Å. It was noted, from bond order - bond length considerations (Section 1.5), that this structure, if relevant, could perhaps naturally resolve the apparent discrepancy between structural observations from angular resolved X-ray photoemission and LEED on the one hand, and SEXAFS and photoelectron diffraction on the other. Superficially this model appears consistent with the reports that oxygen ultimately incorporates below the first copper layer [188,189,199]. In each of the remaining models MR3 - MR5, the total coverage is 0.5 ML and all the O atoms are equivalent. In MR3 each O adsorbs with two pairs of O-Cu bonds, analogously to the long-bridge adsorption reported on the (110)
<table>
<thead>
<tr>
<th>d_{O-Cu} (Å)</th>
<th>d_{Cu-Cu} (Å)</th>
<th>Optimal d_{Cu-Cu} (Å)</th>
<th>R_{MZJ} (R_p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.76 (0.05) 2.11</td>
<td>2.10 (2.06)</td>
<td>0.319 (0.627)</td>
</tr>
<tr>
<td>0.10</td>
<td>1.81 (0.05) 2.16</td>
<td>2.04 (2.06)</td>
<td>0.237 (0.518)</td>
</tr>
<tr>
<td>0.20</td>
<td>1.81 (0.05) 2.16</td>
<td>1.97 (1.98)</td>
<td>0.216 (0.467)</td>
</tr>
<tr>
<td>0.30</td>
<td>1.81 (0.05) 2.16</td>
<td>1.94 (1.94)</td>
<td>0.276 (0.621)</td>
</tr>
</tbody>
</table>

Table 6.2 Optimisation of d_{Cu-Cu} for different values of d_{O-Cu} for oxygen chemisorption on the Cu(100) surface. The I(E) curves were measured at normal incidence for two integral and three half-order beams from a (2\sqrt{2}\times\sqrt{2})R45° surface and compared with curves calculated for the 4F_{1,0.5} model.
Figure 6.10 Missing row models and adsorption sites considered for the Cu(100)-(2√2x√2)45°-O surface structure. In (a) the circles formed by continuous and dashed lines represent Cu atoms in the first and second layers respectively. This notation extends to (b) where the circles formed by thick lines indicate Cu atoms which are released from the missing rows and which line up as overlayer chains parallel to [010] direction. The letters A-E identify adsorption sites which in turn identify the missing row models considered: MR1 all A sites (0.25 ML); MR2 all A and all B sites (0.5 ML); MR3 all C sites (0.5 ML - the parameter δ is chosen so there are two pairs of equal O-Cu bond distances which correspond as closely as possible to the surface structure reported for Cu(110)-(2x1)-O); MR4 all D sites (0.5 ML); MR5 all E sites (0.5 ML).
surface of copper [204], whereas in MR4 and MR5 models O adsorbs directly above a second layer Cu atom as defined in Figure 6.10. These models give three equal O-Cu bonds and one different O-Cu bond in the event the metal structure shows no lateral relaxations.

*Phase shift considerations*

The oxygen phase shifts used in this work are those derived by Demuth et al. [161] (PHSH5, Table 2.1) from a superposition potential appropriate to a hypothetical three-dimensional bcc crystal of oxygen atoms. Other similar potentials could be derived for models which are closer to the actual arrangements of O atoms in the particular surface structure. Some "more realistic" crystal lattices either for "copper oxide" models (PHSH6 and PHSH7, Table 2.1) or a different "hypothetical" simple cubic (SC) crystal lattice (PHSH8, Table 2.1) of oxygen have been discussed in Section 2.2.2. The calculations with these different oxygen phase shifts were performed individually for the $4F_{1,0.5}$ model with $d_{O-Cu} = 0.20 \text{ Å}$ and $d_{Cu-Cu} = 1.81(0.05)2.01 \text{ Å}$. The calculated $I(E)$ curves with these different phase shifts are not significantly different from each other visually, and similar observations were also made by Demuth et al. for the Ni(100)-c(2x2)-O system [194]. A summary of these studies is listed in Table 6.3 and the structural conclusions from the different calculations are similar, although the overall best correspondence appears with the phase shifts introduced by Demuth et al. [161]. Accordingly the oxygen phase shifts from Demuth et al. will continue to be used in these studies.
Table 6.3 Studies of different oxygen phase shifts by comparing experimental data from \((2\sqrt{2}x\sqrt{2})45^\circ\)-O surface with calculations performed for the 4F\(_{1,0.5}\) models (see the text). The different sets of oxygen phase shifts are represented by PHSH5, PHSH6, PHSH7 and PHSH8, as detailed in Table 2.1.

<table>
<thead>
<tr>
<th>d(_{\text{O-Cu}}) Å</th>
<th>d(_{\text{Cu-Cu}}) Å</th>
<th>Phase Shifts</th>
<th>Optimal d(_{\text{Cu-Cu}}) Å</th>
<th>R(<em>{\text{MZJ}}) (R(</em>{\text{P}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>1.81 (0.05) 2.16</td>
<td>PHSH5</td>
<td>1.97 (1.98)</td>
<td>0.216 (0.467)</td>
</tr>
<tr>
<td>0.20</td>
<td>1.81 (0.05) 2.16</td>
<td>PHSH6</td>
<td>1.96 (2.01)</td>
<td>0.258 (0.556)</td>
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<tr>
<td>0.20</td>
<td>1.81 (0.05) 2.16</td>
<td>PHSH7</td>
<td>1.95 (1.97)</td>
<td>0.286 (0.599)</td>
</tr>
<tr>
<td>0.20</td>
<td>1.81 (0.05) 2.16</td>
<td>PHSH8</td>
<td>1.97 (2.00)</td>
<td>0.216 (0.505)</td>
</tr>
</tbody>
</table>
6.5.4 Results and discussion

Comparisons of missing row models

The ranges of structural parameters included in the multiple scattering calculations for five basic types of missing row models are detailed in Table 6.4, and the results of the reliability index studies, including the optimisation of appropriate structural parameters for the models listed in Table 6.4, are summarised in Table 6.5; such analyses were supplemented by close visual scrutiny of all I(E) curve comparisons.

There are clear indications that the models MR1, MR2, and MR5 do not provide the basis for the correct surface structure. The model MR3 was not investigated in depth at this stage since once further lateral relaxations are included this model can readily merge with MR4. The latter unambiguously appears as the favoured initial model according to the visual analysis as well as to the use of the reliability indices $R_{MZJ}$ and $R_p$ (Section 2.5). Most calculated I(E) curves do not change strongly with $\Delta$, the parameter that represents the lateral displacement toward the missing row experienced by top layer Cu atoms adjacent to the missing row, nevertheless the correspondence of experimental and calculated intensity curves is improved with a value around 0.20 Å, although this has not yet been fully optimised. The I(E) curves calculated for normal incidence for two versions of the MR4 model with $\Delta$ fixed at 0.20 Å (one with $d_{O1} = 0.10$ Å, $d_{12} = 2.06$ Å, the other with $d_{O1} = 0.20$ Å, $d_{12} = 2.01$ Å), are compared in Figure 6.11 with those from experiment. $R_{MZJ}$ indicates the values $d_{O1} = 0.14$ Å and $d_{12} = 2.02$ Å for the optimised structure; overall the correspondence is at a reasonable level, including for the (3/4 3/4) beam. The remaining discrepancies, especially for the (1/2 3/2) and (3/2 3/2) beams, may arise from higher-order relaxations in the copper structure, and perhaps in the O position, than what has been included in the analysis here.
<table>
<thead>
<tr>
<th>Model</th>
<th>Structural</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR1</td>
<td>( \Delta = 0.00 )</td>
<td>( d_{12} = 1.660 (0.075) \ 2.185 )</td>
</tr>
<tr>
<td>MR1</td>
<td>( \Delta = 0.00, 0.20 )</td>
<td>( d_{12} = 1.660 (0.075) \ 2.185 )</td>
</tr>
<tr>
<td>MR2</td>
<td>( \Delta = 0.20 )</td>
<td>( d_{O2} = 0.70 )</td>
</tr>
<tr>
<td>MR3</td>
<td>( \Delta = 0.00 )</td>
<td>( \delta = 0.24 )</td>
</tr>
<tr>
<td>MR4</td>
<td>( \Delta = 0.00, 0.20, 0.40 )</td>
<td>( d_{12} = 1.81 (0.05) \ 2.16 )</td>
</tr>
<tr>
<td>MR4</td>
<td>( \Delta = 0.20 )</td>
<td>( d_{12} = 1.81 (0.05) \ 2.16 )</td>
</tr>
<tr>
<td>MR5</td>
<td>( \Delta = 0.20 )</td>
<td>( d_{O2} = 0.15 )</td>
</tr>
</tbody>
</table>

Table 6.4 Ranges of structural parameters (in Å) considered for the five missing row models of Cu(100)-(2\sqrt{2}x\sqrt{2})45°-O designated MR1 to MR5.
Table 6.5 Best combination of structural parameters and associated lowest LEED reliability index for each of the five model types considered for missing row models of the Cu(100)-(2√2x√2)45°-O surface. Refer to Table 6.4 to see which parameters are not varied.

<table>
<thead>
<tr>
<th>Model</th>
<th>Structural Parameters</th>
<th>Parameters</th>
<th>RMZJ (R_P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR1</td>
<td>d_{O1} = 0.15 Å, Δ = 0.20 Å,</td>
<td>d_{12} = 2.05 (2.04) Å,</td>
<td>R = 0.306 (0.624)</td>
</tr>
<tr>
<td>MR2</td>
<td>d_{O1} = 0.00 Å, Δ = 0.20 Å, d_{O2} = 0.70 Å,</td>
<td>d_{12} = 1.90 (2.00) Å,</td>
<td>R = 0.344 (0.584)</td>
</tr>
<tr>
<td>MR3</td>
<td>d_{O1} = 0.24 Å, Δ = 0.00 Å, δ = 0.24 Å,</td>
<td>d_{12} = 1.88 (1.98) Å,</td>
<td>R = 0.262 (0.592)</td>
</tr>
<tr>
<td>MR4</td>
<td>d_{O1} = 0.14 (0.13) Å, Δ = 0.20 Å,</td>
<td>d_{12} = 2.02 (2.03) Å,</td>
<td>R = 0.172 (0.349)</td>
</tr>
<tr>
<td>MR5</td>
<td>d_{O1} = 0.166 (1.66) Å, Δ = 0.20 Å, d_{O2} = 0.15 Å,</td>
<td>d_{23} = 1.96 Å,</td>
<td>R = 0.342 (0.667)</td>
</tr>
</tbody>
</table>
Figure 6.11 I(E) curves measured at normal incidence for the (1 0), (1 1), (1/2 1/2), (1/2 3/2), (3/2 3/2), (3/4 3/4) beams (shown as dashed lines) from Cu(100)-
(2√2x√2)45°-O and compared with calculated curves for two versions of the model
MR4 with \( \Delta = 0.20 \, \text{Å} \), namely: \( d_{O1} = 0.10 \, \text{Å}, d_{12} = 2.06 \, \text{Å} \) (curves marked A)
and \( d_{O1} = 0.20 \, \text{Å}, d_{12} = 2.01 \, \text{Å} \) (curves marked B).
Formation of the Cu(100)-(2√2×√2)45°-O structure

Figure 6.12 outlines a tentative mechanism to form the (2√2×√2)45° surface. First, a few O atoms adsorb randomly on regular 4f sites of the regular Cu(100) surface. Second, a migrating O atom may work together with another neighbouring adsorbed O atom to remove a common Cu atom between them. Any energetic penalty in removing Cu may presumably be counterbalanced by the formation of stable O-Cu bonds. Once a Cu atom has been removed, the neighbouring 4f site becomes a potentially "active" adsorption site and is especially able to accommodate another incoming O atom and so start to form a missing row. Incidentally once a missing row starts to form, that may also help the initial O₂ dissociation. The latter requires some transfer of electrons from the metal surface to the antibonding 2π* orbital of the molecules. This transfer is likely to become easier as the surface roughness increases, which generally parallels a decrease in work function [188,189].

Antiphase domain analysis

With two copper layers involved in the ideal structure, antiphase domain boundaries can occur across atomic steps, as indicated by the examples in Figure 6.13. Beam splittings, as a result of antiphase scattering, are determined by the parallel component of the vector which links related positions across the domain boundaries (i.e. of the type \( \mathbf{d} = d_x a_x + d_y a_y \) shown in Figure 6.13). The (h k) beam is split according to the antiphase scattering mechanism, in directions perpendicular to the domain boundaries, whenever Equation (4.1) is satisfied. Several domain boundaries are possible, but Figure 6.13 shows the two different types of vector \( \mathbf{d} \) that can occur. With these, the missing row model predicts splittings for the beams (1/2 1/2) and (1 0), but not (1 1), as reported by Onuferko and Woodruff [80], and by Richter and Gerhardt [157]. However, the
Figure 6.12 A possible route to the formation of a missing row model for the Cu(100)-(2\sqrt{2}x\sqrt{2})45^\circ-O surface structure.
Figure 6.13 Illustration of two types of antiphase boundaries with the missing row model. The parallel vectors shown satisfy $d_1 = 3/2a_x + 3/2a_y$ and $d_2 = 1/2a_x + 3/2a_y$. The dots represent oxygen atoms, and the first, second and third copper layers are represented by hatched circles, open continuous circles and dashed circles respectively.
present analysis does not follow these other authors in concluding that the splittings reported indicate that the O chemisorption occurs on bridge sites.

Further improvement

The LEED crystallographic studies presented above for the O on Cu(100) surface structure have added our knowledge for this complicated system. However, it is expected that a fuller resolution of the structural details for the \((2\sqrt{2}x\sqrt{2})45^\circ\) surface will require a combined investigations with other techniques including high-energy ion scattering, high-resolution electron energy loss spectroscopy and scanning tunneling microscopy. Incidentally, Wuttig et al. determined a oxygen coverage for the Cu(100)-(2\(\sqrt{2}\times\sqrt{2}\))45\(^\circ\)-O surface structure by an in-situ Auger electron spectroscopy comparison for two crystals (Cu(100) and Ni(100)) in a very recent HREELS study [205]. Their findings also suggest that the \((2\sqrt{2}x\sqrt{2})45^\circ\) structure is the only well-ordered overlayer at room temperature, and that this structure corresponds to an oxygen coverage of 0.48±0.05. Therefore the MR4 model is consistent with the surface coverage determined. Finally it is noted that while the structure here is based on the model MR4 with a 0.5 ML coverage, there have been reports that the \((2\sqrt{2}x\sqrt{2})45^\circ\)-O structure may correspond to 0.75 ML [83,198]. A model of this type would correspond to the 0.75 ML oxygen coverage reported by Boulliard and Sotto [198]. Although they did not consider the missing row model, Boulliard and Sotto proposed a model with 0.75 ML oxygen sitting at regular four-fold sites on Cu(100) surface. This is somewhat analogous to the model in Figure 6.10 with O adsorption on both sites A and D types. Certainly further clarification is needed here, not least on whether calculated I(E) curves for this model could be give comparable, or even better, correspondence with the experimental I(E) curves than does
the model MR4. Whether there could be some change over of O adsorption sites between 0.5 and 0.75 ML coverage is a topic for further surface structural investigation.

6.6 Summary

This chapter describes two stages in a study of the Cu(100)-(2√2x√2)45°-O surface structure. In the first stage, LEED crystallographic investigations are reported for surface structures obtained by adsorbing submonolayer amounts of oxygen on the (100) surface of copper. It is found for chemisorption on the four-coordinate hollow sites that the correspondence between experimental and calculated I(E) curves, for 10 diffracted beams, is slightly better for coplanar adsorption than for adsorption about 0.75 Å above the surface. Nevertheless, in neither of these contrasting situations is the agreement sufficient to conclude that the structural analysis is complete. Evidence is presented that nearly coplanar chemisorption, in combination with a missing row model, can accommodate a number of structural features for this system, including the existence of the (2√2x√2)45°-O phase, beam splittings resulting from antiphase domain boundaries, and the structural analogy noted in other studies between the (2√2x√2)45°-O phase and the stepped nature of the (410) copper surface which can form by faceting in oxygen. Considerations of O-Cu surface bond lengths, guided by those in bulk Cu2O, suggest that additional lateral relaxations are likely in the topmost copper layer. The study provides no support for the O chemisorption occurring in tetrahedral-type sites. In the second stage of study, a systematic multiple scattering analysis of LEED intensities has been made for the Cu(100)-(2√2x√2)45°-O surface structure following the indications from stage one. An improved, but still less than ideal, level of correspondence between experimental and calculated I(E) curves has been reached for six beams at normal incidence, and that suggests some basic ingredients for the Cu(100)-(2√2x√2)45°-O surface structure appear
to have been identified. Briefly, the best model so far for this surface has missing rows of atoms in the topmost copper layer; they are oriented parallel to the [010] direction and spaced to give the \( (2\sqrt{2}\times\sqrt{2})45^\circ \) unit mesh while the \( O \) atoms adsorb close to 0.15 Å above the hollow sites adjacent to the missing rows. In this model, each \( O \) atom bonds to four neighbouring \( Cu \) atoms at the distances 1.82 Å (three times) and 2.16 Å; this gives an averaged \( O-Cu \) bond length of 1.91 Å which is intermediate between the mean distance in \( CuO \) (1.95 Å) and that in \( Cu_2O \) (1.84 Å) [201]. The small \( O-Cu \) interlayer spacing results in an appreciable expansion in the topmost \( Cu-Cu \) interlayer spacing; this structure is likely to be supplemented by additional lateral displacements in the top copper layer.
CHAPTER 7
CONCLUDING REMARKS AND FUTURE WORK

The LEED crystallographic studies reported for the chemisorption of S, N and O on the (100) surface of copper have clarified some problems in this area of surface structural determination, although the final solutions still appear challenging in some cases. Further work required for these surface structures is discussed in this concluding chapter.

7.1 The Cu(100)-(2x2)-S Surface Structure

The structural parameters listed in Table 4.2 represent the best surface structural information available from LEED crystallography. These parameters have now been input to a preliminary multiple-scattering calculation for the off-normal incidence experiment \( \theta = 7.5^\circ \) for the beams \((0 \ 0), (0 \ 1), (-1 \ 1), (0 \ 1/2), (1/2 \ 0), (1/2 \ 1/2) \) and \((1/2 \ 1)\). The correspondence between the experimental and calculated I(E) curves still appears better than for the non-relaxation model (Section 4.3), but further systematic analyses using the experimental data at off-normal incidence are needed to refine this structural model using the larger data base.

7.2 The Cu(100)-c(2x2)-N Surface

The calculations for this surface structure have mainly concentrated on the structural parameters (Chapter 5). However, several non-structural parameters, such as the Debye temperatures and the imaginary part of the inner potential, can still be tested, although it is believed that these parameters are not as important as the structural ones [110].

Further experimental efforts should be focused on preparation methods. For example, it would be interesting to compare I(E) curves measured from a surface
prepared by adsorbing NH$_3$ at low temperature [77], followed by subsequent heating, with those measured from a surface prepared by the bombardment method [175] used in this work. Additionally, it may be worth exploring whether having a trace of an electron-rich alkali metal on the surface may help N$_2$ dissociation. A comparison of these experimental I(E) curves might be very useful before attacking the more complex model 4F4 proposed in Chapter 5.

7.3 The Chemisorption of Oxygen on the Cu(100) Surface

In their very recent HREELS studies, Wuttig et al. proposed two models for the (2$\sqrt{2}$x2$\sqrt{2}$)45° surface [205] which are shown in Figure 7.1. These combine both vertical and lateral relaxations. The investigation of 4FT models in Section 6.4 provided no evidence for differential vertical relaxations for metal atoms in the topmost Cu layer. Also, it is difficult for us to understand why there could be lateral displacements which reduce the O-Cu bond distance. Nevertheless it would be reasonable to test these models with multiple-scattering LEED calculations. Another possibility, which was not considered in this thesis, concerns whether O chemisorbed in the four-fold sites of Cu(100) could be displaced off-centre, as has been reported on Ni(100) [194, 206].

One factor that definitely seems relevant to this surface structure concerns considerations of order-disorder phenomena, and it would be helpful to study these surfaces by both the high-resolution SPALEED [11] technique and STM. Indeed a very recent and preliminary attempt by Woll [207] to find the missing rows in this system using STM reported both (4$\sqrt{2}$x4$\sqrt{2}$)45° and (2$\sqrt{2}$x2$\sqrt{2}$)45° structures on the surface. An apparent pairing of O atoms is indicated for the latter structure with a low degree of corrugation. That opens the question of how to fit that result with our proposal for the missing row model. With the latter, lateral displacements are likely as indicated in Figure 7.2. In the limit of equal Cu-Cu neighbouring distances being formed in the topmost
Figure 7.1 Two surface models proposed by Wuttig et al. for the $(2\sqrt{2} \times 2\sqrt{2})45^\circ$ structure. Plus and minus signs denote displacements perpendicular to the surface whereas the arrows denote displacements parallel to the surface. Only one domain is shown in each case (reproduced from ref.205).
Figure 7.2 Schematic indications of further possible lateral and vertical relaxations occurring in the first copper layer with a missing row. Plus signs denote vertical relaxations whereas the arrows indicate the lateral displacements.
Figure 7.3 A model showing the coexistence of the $\sqrt{2}\times\sqrt{2}45^\circ$ and $2\sqrt{2}\times\sqrt{2}45^\circ$ structures for the O on Cu(100) system. In the latter structure, the toplayer Cu atoms (dotted large circles) have equal Cu-Cu neighbouring distances and the O atoms (small dark circles) show a pairing tendency as observed by STM.
layer, the model shown on the right hand side of Figure 7.3 is possible. Indeed this model of the \((\sqrt{2}\times\sqrt{2})45^\circ\) and \((2\sqrt{2}\times\sqrt{2})45^\circ\) structures corresponds very closely to the preliminary information so far available from STM. With substantial structural rearrangements in the topmost copper layer relative distortions would seem inevitable in the second and the lower layers, and this would affect the calculated I(E) curves. Such details may account for the discrepancies between experiment and calculation that are still present in our best comparisons of I(E) curves (e.g. Figure 6.11).

7.4 Publications on This Work

The new research described in this thesis has been published, or accepted for publication, in references [208-214].
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