LEED CRYSTALLOGRAPHIC STUDIES FOR CHEMISORPTION-
INDUCED RELAXATIONS AND RECONSTRUCTIONS OF
COPPER AND RHODIUM SURFACES

by

WEI LIU

B.Sc., Xiamen University, 1990

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE STUDIES
(Department of Chemistry)

We accept this thesis as conforming

to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

APRIL 1996

© Wei Liu, 1996
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the head of my department or by his or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Chemistry

The University of British Columbia
Vancouver, Canada

Date Feb April 25, 1996
Abstract

Low-energy electron diffraction (LEED) has been used to investigate some structures formed by electronegative atoms (O and P) on copper and rhodium single crystal surfaces. The motivation is to provide new atomic-scale details, to develop fundamental understanding of surface structural chemical principles, and to help establish approaches for determining relatively complex surface structures using tensor LEED.

A detailed analysis for the Cu(110)-c(6x2)-O surface indicates that this structure is composed of double-stranded chains built from 12-membered rings formed by alternating O and Cu atoms. This analysis provides direct information on the structural details, which support the view that the driving force for this structure relates to sufficient O being incorporated in order to stabilize the surface as a modified (211) plane of bulk Cu$_2$O. Together with the structural details from LEED analyses for two other oxygen on copper surfaces, designated as Cu(110)-(2x1)-O and Cu(100)-(2√2x√2)R45°-O, certain common features are identified. It is found that all these structures receive some stability from being able to fit O-Cu-O three-atom building blocks, of the sort needed to construct bulk Cu$_2$O, on to the clean surfaces, while ensuring that each O atom maintains its favorable four-coordinate status with reasonable O-Cu bond lengths (average close to 1.90 Å).

A study of the Cu(110)-(\begin{pmatrix} 2 & 2 \\ -1 & 1 \end{pmatrix})-P surface establishes a new type of reconstruction in which all P atoms occupy identical six-coordinate sites; the reconstruction involves 0.25 ML of "added Cu" atoms at hollow sites, each bonded to two neighboring P atoms, which line up along the [\Bar{1}12] direction. Appreciable relaxations, both vertical and lateral, are carefully rationalized; the average P-Cu bond length is determined to be 2.33 Å.
An analysis for the Rh(111)-($\sqrt{7}x\sqrt{7}$)R19.1°-P surface has identified a novel reconstruction for the topmost metallic layer, which involves a packed arrangement of Rh pentagons and triangles. Each P atom has an identical environment and bonds to eight neighboring Rh atoms with P-Rh bond lengths ranging from 2.17 to 2.97 Å. The nearly flat, densely-packed Rh-P layer (with five Rh and three P per seven substrate atoms in the unit mesh) appears to give this surface a high general stability. This represents the first successful determination for a complex $\sqrt{7}x\sqrt{7}$ surface structure. The model type identified may have wider applicability, for example the analogous system formed by S on Pd(111); suggestions are also made in the latter case on how the structural form may influence chemical reactivity, such as for the cyclization of acetylene to thiophene.
# Table of contents

Abstract ii  
Table of contents iv  
List of tables vii  
List of figures viii  
Acknowledgments xi  

Chapter 1 Introduction 1
  1.1 Interfacial science and structure 1
  1.2 Low-energy electron diffraction 2  
    1.2.1 Historical overview 2  
    1.2.2 Basic principles 5  
    1.2.3 Diffraction condition 7  
    1.2.4 Notation 11  
    1.2.5 Structural characterizations of surfaces by LEED 16  
  1.3 Auger electron spectroscopy (AES) 18  
  1.4 Surface structural chemical principles 20  
  1.5 Aims of thesis 21  

Chapter 2 Calculations 23  
  2.1 Introduction 23  
  2.2 Atomic scattering 26  
    2.2.1 Stationary atom 26  
    2.2.2 Temperature effect 27  
  2.3 Multiple scattering 28  
    2.3.1 Scattering by two atoms 28  
    2.3.2 Scattering by an atomic layer 29  
    2.3.3 Scattering by a stack of atomic layers 32  
  2.4 Comparison of experimental and calculated I(E) curves 37  
  2.5 Tensor LEED 39  
    2.5.1 Basic theory 39  
    2.5.2 Implementation 40
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>3.1</td>
<td>UHV system</td>
<td>44</td>
</tr>
<tr>
<td>3</td>
<td>3.2</td>
<td>Instrumentation</td>
<td>46</td>
</tr>
<tr>
<td>3</td>
<td>3.2.1</td>
<td>LEED</td>
<td>46</td>
</tr>
<tr>
<td>3</td>
<td>3.2.2</td>
<td>Auger electron spectroscopy</td>
<td>49</td>
</tr>
<tr>
<td>3</td>
<td>3.3</td>
<td>Sample preparation</td>
<td>51</td>
</tr>
<tr>
<td>3</td>
<td>3.4</td>
<td>I(E) curve measurement and data processing</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>4.1</td>
<td>Introduction</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>4.2</td>
<td>Experiment</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>4.3</td>
<td>Calculation</td>
<td>61</td>
</tr>
<tr>
<td>4</td>
<td>4.4</td>
<td>Structural analysis</td>
<td>62</td>
</tr>
<tr>
<td>4</td>
<td>4.4.1</td>
<td>Primary structure</td>
<td>62</td>
</tr>
<tr>
<td>4</td>
<td>4.4.2</td>
<td>Other models considered</td>
<td>62</td>
</tr>
<tr>
<td>4</td>
<td>4.4.3</td>
<td>Structural features</td>
<td>67</td>
</tr>
<tr>
<td>4</td>
<td>4.5</td>
<td>Discussion</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>5.1</td>
<td>Introduction</td>
<td>73</td>
</tr>
<tr>
<td>5</td>
<td>5.2</td>
<td>Re-analysis of the Cu(110)-(2x1)-O surface</td>
<td>74</td>
</tr>
<tr>
<td>5</td>
<td>5.3</td>
<td>Re-analysis of the Cu(100)-(2\sqrt{2}\times\sqrt{2})R45^\circ-O surface</td>
<td>75</td>
</tr>
<tr>
<td>5</td>
<td>5.4</td>
<td>Common features and the analogies to bulk Cu$_2$O</td>
<td>79</td>
</tr>
<tr>
<td>5</td>
<td>5.5</td>
<td>Comparisons with other surfaces</td>
<td>88</td>
</tr>
<tr>
<td>5</td>
<td>5.6</td>
<td>Concluding remarks</td>
<td>90</td>
</tr>
<tr>
<td>6</td>
<td>6.1</td>
<td>Introduction</td>
<td>91</td>
</tr>
<tr>
<td>6</td>
<td>6.2</td>
<td>Experiment</td>
<td>91</td>
</tr>
<tr>
<td>6</td>
<td>6.3</td>
<td>Calculation</td>
<td>92</td>
</tr>
<tr>
<td>6</td>
<td>6.4</td>
<td>Initial structural analysis</td>
<td>93</td>
</tr>
<tr>
<td>6</td>
<td>6.4.1</td>
<td>Model types</td>
<td>93</td>
</tr>
<tr>
<td>6</td>
<td>6.4.2</td>
<td>Rationalization of favored structural type</td>
<td>95</td>
</tr>
</tbody>
</table>
List of tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1.1</td>
<td>Summary of some techniques for surface structure and analysis.</td>
<td>3</td>
</tr>
<tr>
<td>Table 1.2</td>
<td>Comparison of some characteristics of X-ray diffraction and low-energy electron diffraction for structure determination.</td>
<td>4</td>
</tr>
<tr>
<td>Table 4.1</td>
<td>Atomic coordinates for the TLEED-determined structure of the Cu(110)-c(6x2)-O surface.</td>
<td>65</td>
</tr>
<tr>
<td>Table 4.2</td>
<td>Summary of structural parameters which specify relaxation effects in the Cu(110)-c(6x2)-O surface.</td>
<td>69</td>
</tr>
<tr>
<td>Table 5.1</td>
<td>(a) Atomic coordinates for the TLEED-determined structure of the Cu(110)-(2x1)-O surface. (b) Structural parameters from different studies for the Cu(110)-(2x1)-O surface.</td>
<td>78</td>
</tr>
<tr>
<td>Table 5.2</td>
<td>(a) Atomic coordinates for the TLEED-determined structure of the Cu(100)-(2√2x√2)R45°-O surface. (b) Structural parameters for the Cu(100)-(2√2x√2)R45°-O surface.</td>
<td>81</td>
</tr>
<tr>
<td>Table 5.3</td>
<td>Comparison of structural features for bulk Cu₂O and O/Cu surface systems.</td>
<td>84</td>
</tr>
<tr>
<td>Table 6.1</td>
<td>Optimized R_p values from TLEED analysis for the eight model types for the P on Cu(110) surface structure.</td>
<td>96</td>
</tr>
<tr>
<td>Table 6.2</td>
<td>Atomic coordinates for the TLEED-determined structure of the Cu(110)-(2 2 2 2)-P surface.</td>
<td>97</td>
</tr>
<tr>
<td>Table 6.3</td>
<td>Some individual P-Cu and averaged Cu-Cu bond lengths in the P on Cu(110) surface structure determined by TLEED analysis.</td>
<td>99</td>
</tr>
<tr>
<td>Table 6.4</td>
<td>Comparison of z-coordinates for atoms in the second and fourth Cu layers in the Cu(110)-(2 2 2 2)-P surface structure.</td>
<td>108</td>
</tr>
<tr>
<td>Table 7.1</td>
<td>Atomic coordinates for the TLEED-determined structure of the Rh(111)-(√7x√7)R19.1°-P surface.</td>
<td>125</td>
</tr>
<tr>
<td>Table 7.2</td>
<td>Some important bond lengths in the Rh(111)-(√7x√7)R19.1°-P surface structure.</td>
<td>128</td>
</tr>
</tbody>
</table>
List of figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Schematic diagram of an incident electron beam and the specularly diffracted beam in LEED.</td>
<td>6</td>
</tr>
<tr>
<td>1.2</td>
<td>Typical dependence of electron mean free path on energy in metals.</td>
<td>8</td>
</tr>
<tr>
<td>1.3</td>
<td>Schematic diagram indicating some possible multiple-scattering paths in low-energy electron diffraction.</td>
<td>9</td>
</tr>
<tr>
<td>1.4</td>
<td>Schematic diagrams of the real surface and diffraction pattern for the five surface structures investigated in this thesis.</td>
<td>12</td>
</tr>
<tr>
<td>1.5</td>
<td>Different applications of LEED for studies in surface structure.</td>
<td>17</td>
</tr>
<tr>
<td>1.6</td>
<td>Processes for de-excitation of atomic core holes: (a) Auger electron emission; (b) X-ray emission.</td>
<td>19</td>
</tr>
<tr>
<td>2.1</td>
<td>Variation of potential with position in the “muffin-tin” approximation.</td>
<td>25</td>
</tr>
<tr>
<td>2.2</td>
<td>Schematic indication of multiple scattering between two atoms.</td>
<td>25</td>
</tr>
<tr>
<td>2.3</td>
<td>Schematic indication of “layers” and “planes” for LEED calculations.</td>
<td>30</td>
</tr>
<tr>
<td>2.4</td>
<td>Illustration of paths in the renormalized forward scattering method.</td>
<td>33</td>
</tr>
<tr>
<td>2.5</td>
<td>Schematic diagram of the layer-doubling scheme.</td>
<td>35</td>
</tr>
<tr>
<td>2.6</td>
<td>Directed search optimization scheme for structural analysis by tensor LEED.</td>
<td>42</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic diagram of the Varian UHV chamber and associated arrangement of various instruments.</td>
<td>45</td>
</tr>
<tr>
<td>3.2</td>
<td>Schematic diagram of pumping systems and gas line for UHV chamber.</td>
<td>47</td>
</tr>
<tr>
<td>3.3</td>
<td>Electron gun and detection system used for LEED.</td>
<td>48</td>
</tr>
<tr>
<td>3.4</td>
<td>Single-pass CMA with glancing electron gun for AES.</td>
<td>50</td>
</tr>
<tr>
<td>3.5</td>
<td>Auger spectra for Cu(110) surface during and after the cleaning process.</td>
<td>53</td>
</tr>
<tr>
<td>3.6</td>
<td>Auger spectra for Rh(111) surface during and after the cleaning process.</td>
<td>54</td>
</tr>
<tr>
<td>3.7</td>
<td>Block diagram of the video LEED analyzer (VLA) used for measurement</td>
<td></td>
</tr>
</tbody>
</table>
of LEED intensities.

Figure 3.8 I(E) curves for four symmetrically equivalent beams, and those after averaging and smoothing.

Figure 3.9 Comparison of two sets of I(E) curves measured from independently prepared Rh(111)-(7√7x7√7)R19.1°-P surfaces.

Figure 4.1 Basic form of the Cu(110)-c(6x2)-O surface corresponding to 2/3 ML O.

Figure 4.2 Comparison of experimental I(E) curves measured for normal incidence from the Cu(110)-c(6x2)-O surface structure with those calculated for the favored geometry according to the tensor LEED analysis.

Figure 4.3 Two additional c(6x2) models considered in the TLEED analysis.

Figure 4.4 Specification of notation used for discussing the details of the Cu(110)-c(6x2)-O surface structure.

Figure 5.1 Schematic drawings for three surface structures: (I) Cu(110)-(2x1)-O, (II) Cu(110)-c(6x2)-O and (III) Cu(100)-(2√2x√2)R45°-O.

Figure 5.2 Comparison of experimental I(E) curves measured for normal incidence from the Cu(110)-(2x1)-O surface structure with those calculated for the favored geometry according to the tensor LEED analysis.

Figure 5.3 Comparison of experimental I(E) curves measured for normal incidence from the Cu(110)-(2√2x√2)R45°-O surface structure with those calculated for the favored geometry according to the tensor LEED analysis.

Figure 5.4 Schematic diagram of bulk Cu₂O crystal structure.

Figure 5.5 Comparison of superstructures formed on the Cu(110) substrate with planes of bulk Cu₂O.

Figure 6.1 Eight model types considered in the TLEED analyses for the P on the Cu(110) surface structure.

Figure 6.2 The Cu(110)-$$\begin{pmatrix} 2 & 2 \\ -1 & 1 \end{pmatrix}$$-P surface structure.

Figure 6.3 Comparison of experimental I(E) curves measured for normal incidence from the Cu(110)-$$\begin{pmatrix} 2 & 2 \\ -1 & 1 \end{pmatrix}$$-P surface structure with those calculated for the favored geometry according to the tensor LEED analysis.
Figure 7.1  Auger spectrum taken on the P-chemisorbed Rh(111) surface.

Figure 7.2  LEED pattern observed at 114 eV from the Rh(111)-(\(\sqrt{7}x\sqrt{7}\))R19.1°-P surface.

Figure 7.3  Plot of the Auger ratio \(R = \frac{A_{130}}{A_{302}}\) as a function of PH₃ dosage before and after annealing (to 1000°C).

Figure 7.4  Some models considered in TLEED analyses for the Rh(111)-(\(\sqrt{7}x\sqrt{7}\))R19.1°-P surface.

Figure 7.5  The Rh(111)-(\(\sqrt{7}x\sqrt{7}\))R19.1°-P surface structure.

Figure 7.6  Comparison of experimental I(E) curves with those calculated for the favored geometry for the Rh(111)-(\(\sqrt{7}x\sqrt{7}\))R19.1°-P surface.

Figure 7.7  Another view of the topmost layer in the Rh(111)-(\(\sqrt{7}x\sqrt{7}\))R19.1°-P surface structure with associated bond lengths.

Figure 7.8  Schematic indication of a possible route for the formation of thiophene from the cyclization of acetylene on Pd(111)-(\(\sqrt{7}x\sqrt{7}\))R19.1°-S structures.

Figure 8.1  Structure of the Cu(410) surface.

Figure 8.2  A possible low-coverage structural model for O adsorbed at the Cu(410) surface.

Figure 8.3  A possible high-coverage structural model for O adsorbed at the Cu(410) surface.

Figure 8.4  A possible structural model for P adsorbed at the Cu(410) surface.
Acknowledgments

I would like to thank my supervisor, Professor K.A.R. Mitchell, for introducing and directing me into these challenging surface structure problems, and for his patience, encouragement and continuous support during the past five years.

I thank Mr. K.C. Wong for the wonderful cooperation in the O/Cu and P/Rh projects, and Dr. D.T. Vu for her friendship and patience in guiding me as a new graduate student. I thank Dr. Y.S. Li for introducing me into the UHV wonderland. I have also greatly appreciated my interactions with other colleagues in our Surface Science Laboratory including Prof. M.Y. Zhou, Dr. P.C. Wong, Dr. U. Hess, Dr. J.R. Lou, Dr. B. Flinn, Dr. H. Wang, Ms. Y.L. Leung, Ms. Y.M. Wang, Ms. W.F. Heung, Mr. M. Saidy, Ms. J. Fang and Ms. M. Kono.

Special thanks are due to Dr. M.A. Van Hove (University of California, Berkeley) for providing the LEED program codes, and for his continuous support. I am also indebted to the staff of the Chemistry Department mechanical and electronic shops for their assistance in maintaining our UHV equipment.

It has been an emotional five years for me. I wish to thank my parents, my sister, for their endless love and continuous support throughout this period. To them, I dedicate this thesis.
“Science is created by individuals who put their personal stamp on it through their hard and careful work, their perspective, their emotions, and their dreams.”

—G.A. Somorjai
Chapter 1  Introduction

1.1  Interfacial science and structure

A surface, or more generally an interface, corresponds to the boundary region between two different phases in contact. There is great interest in learning about and understanding solid/solid, solid/liquid, solid/gas, liquid/liquid and liquid/gas interfaces, which are important in many technological fields including, for example, heterogeneous catalysis, semiconductor devices, corrosion, colloids, electrochemistry, adhesion and friction. Understanding phenomena in these areas requires specific knowledge for the chemical and physical properties of the interfaces involved, which can be different from those of the bulk phases [1].

Much fundamental progress has occurred recently by studying the solid/gas (in practice includes solid/vacuum) interface, for which the term “surface” is commonly used. Besides the associated technological importance, this emphasis has arisen because such systems can have well-defined boundaries, and be relatively easy to prepare, characterize and maintain, particularly in an ultrahigh vacuum (UHV) environment. Also, many surface sensitive techniques are well-developed and available for this kind of study [2-5], and the complementary information gathered from the different methods can now lead to quite detailed knowledge for the systems under investigation. Often such studies are conducted on well-ordered single-crystal surfaces.

Many properties of a solid surface are determined by its geometrical structure, and therefore the identification of its atomic structure represents one vital step for understanding its broader physical and chemical properties. In general, due to their unsatisfied bonding capacity, surface atoms have a strong tendency to lower their free energy through the formation of additional bonds through adsorption, or by undergoing a surface relaxation or reconstruction.
This explains why clean single-crystal surfaces may manifest a rearrangement of the surface atoms, or have a contracted first interlayer spacing compared with the bulk value; similarly the cleaned surfaces may easily become contaminated. Examples of elemental surface reconstructions include the (7x7) surface of Si(111) [6] and the (1x5) surface of Au(100) [7]. A range of structural complications may arise when electronegative species are introduced to an ordered metal surface, and examples of such types of chemisorbed systems provide the focus for the work described in this thesis.

Table 1.1 lists some techniques which use electron, ion and photon probes to determine the nature and structural arrangements of atoms at surfaces. Among them, low-energy electron diffraction (LEED) is the most developed for determining ordered surface structure, although with new synchrotron sources it is likely that surface X-ray diffraction (SXRD) [15] will ultimately become very prominent, and the ion scattering methods are powerful for more heterogeneous surfaces [10d]. Table 1.2 compares some characteristics of LEED with those of X-ray diffraction [18] for determining bulk structure. The work in this thesis specifically uses LEED and Auger electron spectroscopy (AES); therefore these two techniques are described in more detail in the following sections.

1.2 Low-energy electron diffraction (LEED)

1.2.1 Historical overview

The potential of LEED to probe atomic arrangements at single crystal surfaces was first realized by Davisson and Germer in 1927 [19], when they discovered the phenomenon of electron diffraction, but little progress occurred for many years. Two obstacles delayed progress. One concerned being able to make experimental measurements within the time frame over which the surface being investigated remained in a reasonably constant state. The second obstacle was
Table 1.1  Summary of some techniques for surface structure and analysis.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Acronym</th>
<th>Probe with</th>
<th>Physical basis</th>
<th>Information gained</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Auger electron spectroscopy</td>
<td>AES</td>
<td>electrons or photons</td>
<td>kinetic energies measured for electrons emitted by de-excitation of core holes</td>
<td>surface elemental composition</td>
<td>[8]</td>
</tr>
<tr>
<td>High-resolution electron energy loss spectroscopy</td>
<td>HREELS</td>
<td>electrons</td>
<td>measure small energy losses in monochromatized beam</td>
<td>vibrational modes (⊥ and ∥)</td>
<td>[9]</td>
</tr>
<tr>
<td>Ion scattering</td>
<td>LEIS, MEIS, ISS</td>
<td>ions</td>
<td>measure directions and energies of scattered ions</td>
<td>geometrical structure, composition</td>
<td>[10]</td>
</tr>
<tr>
<td>Low energy electron diffraction</td>
<td>LEED</td>
<td>electrons</td>
<td>elastic electron back diffraction</td>
<td>atomic surface structure and bonding</td>
<td>[11]</td>
</tr>
<tr>
<td>Surface-extended X-ray absorption fine structure</td>
<td>SEXAFS</td>
<td>X-rays</td>
<td>absorption structure related to electron interference</td>
<td>bond lengths</td>
<td>[12]</td>
</tr>
<tr>
<td>Secondary ion mass spectrometry</td>
<td>SIMS</td>
<td>ions</td>
<td>sputtering of ions from surface</td>
<td>surface composition</td>
<td>[13]</td>
</tr>
<tr>
<td>Scanning tunneling microscopy</td>
<td>STM</td>
<td>electrons</td>
<td>electron tunneling between sharp tip and sample surface</td>
<td>geometrical and electronic structure</td>
<td>[14]</td>
</tr>
<tr>
<td>Surface X-ray diffraction</td>
<td>SXRD</td>
<td>X-rays</td>
<td>diffraction at glancing incidence</td>
<td>geometrical structure</td>
<td>[15]</td>
</tr>
<tr>
<td>Thermal desorption spectroscopy</td>
<td>TDS</td>
<td>heat</td>
<td>measure desorption and decomposition products</td>
<td>desorption energy, multiple bonding states</td>
<td>[16]</td>
</tr>
<tr>
<td>UV photoelectron spectroscopy</td>
<td>UPS</td>
<td>UV light</td>
<td>photoemission from valence shells</td>
<td>valence structure</td>
<td>[17]</td>
</tr>
<tr>
<td>X-ray photoelectron spectroscopy</td>
<td>XPS</td>
<td>X-rays</td>
<td>photoemission of core electrons</td>
<td>surface composition, chemical states</td>
<td>[8]</td>
</tr>
</tbody>
</table>
Table 1.2  Comparison of some characteristics of X-ray diffraction and low-energy electron diffraction for structure determination.

<table>
<thead>
<tr>
<th>Information gained:</th>
<th>X-ray diffraction</th>
<th>LEED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Probe with:</td>
<td>bulk structure</td>
<td>surface structure</td>
</tr>
<tr>
<td>Energies of probe:</td>
<td>5 - 18 keV</td>
<td>30 - 300 eV</td>
</tr>
<tr>
<td>Wavelengths:</td>
<td>0.7 - 2.3 Å</td>
<td>0.7 - 2.2 Å</td>
</tr>
<tr>
<td>Strength of interaction with matter:</td>
<td>weak</td>
<td>strong</td>
</tr>
<tr>
<td>Scattering character:</td>
<td>single</td>
<td>multiple</td>
</tr>
<tr>
<td>Probing depth:</td>
<td>~ 10^6 Å</td>
<td>~ 10 Å</td>
</tr>
<tr>
<td>Periodicity of ordered structure probed:</td>
<td>triperiodic</td>
<td>diperiodic</td>
</tr>
<tr>
<td>Structural repeat unit:</td>
<td>unit cell (in 3-D lattice)</td>
<td>unit mesh (in 2-D net)</td>
</tr>
</tbody>
</table>
the lack of an appropriate electron scattering theory. The renaissance of LEED started with experimental advances in the 1960s, represented by the development of display systems for diffraction patterns [20, 21], the commercialization of ion-pump based UHV systems, and the introduction of detection schemes for Auger electron spectra. At about the same time, a series of theoretical studies applied procedures developed for electron band calculations of solids to the problem of electron multiple scattering by ordered surfaces. Relevant studies included those by McRae [22], Boudreaux and Heine [23], Beeby [24], and Jepsen and Marcus [25], although Duke [26] emphasized the need to include strong inelastic scattering in the calculations. By 1972, computational procedures were available which confirmed that the basic physics of the scattering process was included in the calculations [27]. The development of practical procedures, for use in experimental laboratories, followed with the general advances in computer technology and the introduction of perturbative schemes for LEED calculations, especially by Pendry [28], and Van Hove and Tong [29]. In the past two decades, LEED crystallography has gradually developed into a powerful tool for surface structural determination [30], and the introduction of tensor LEED [31] has further opened application to the more challenging surfaces. At this time LEED crystallography appears as the primary technique for surface structural determination of ordered surfaces.

1.2.2 Basic principles

The experiment of low-energy electron diffraction involves directing a beam of electrons (typical energy range 30 - 300 eV) on to a well-ordered surface, and observing the elastically backscattered diffracted beams (Fig. 1.1). Diffraction occurs because the electron wavelength (0.7 - 2.2 Å), according to the de Broglie relation
Figure 1.1 Schematic diagram of an incident electron beam (with energy $E$ and direction $(\theta, \phi)$) and the specularly diffracted $(0 \ 0)$ beam in LEED. The insert indicates the variation of beam intensity with energy.
\[ \lambda (\text{Å}) = \frac{\hbar}{p} = \sqrt{\frac{150.4}{E(\text{eV})}} \]  

(1.1)

(h is Planck's constant, p electron momentum), is comparable to the interatomic and interlayer spacings in the crystalline surfaces.

The LEED electron is scattered by the nuclei and electrons in its path. Strong inelastic interactions result from plasmon excitations [28], and this ensures that a LEED electron has a short mean free path in the solid. The electron mean free path is the average distance travelled by an electron in a solid before it loses energy, and a plot as a function of energy is shown in Fig. 1.2. For the LEED energy range, a typical mean free path for a metal is around 5 - 10 Å [32], and this ensures LEED especially probes the topmost four or five atomic layers. The suitable electron wavelength and the limited penetration depth are the two basic factors that make LEED a surface sensitive technique for structure determination.

Another important characteristic feature of the LEED process is its multiple-scattering nature (Fig. 1.3). The large scattering cross sections for the LEED electrons (about six orders of magnitude larger than for x-ray photons) ensure that most of them are scattered more than once in the solid before they can return to vacuum. Forward scattering is more probable than back scattering and, with the strong inelastic scattering, this ensures that only a small fraction (e.g., 1 - 5\%) of the incident electrons escape elastically from the surface to be detected.

1.2.3 Diffraction condition

An electron beam in vacuum can be described by a plane wave

\[ \Psi(r) = \exp(i\mathbf{k} \cdot \mathbf{r}) \]  

(1.2)

where \( \mathbf{k} \) is the wave vector (magnitude \( 2\pi/\lambda \) with direction of beam), and \( \mathbf{r} \) defines position with respect to an origin. Elastic scattering requires
Figure 1.2 Typical dependence of electron mean free path on energy in metals.
Figure 1.3 Schematic diagram indicating some possible multiple-scattering paths in low-energy electron diffraction.
\[ |k_i| = |k_d| \]  \hspace{1cm} (1.3)

where \( k_i \) and \( k_d \) are the wave vectors of the incident and diffracted beams respectively. More generally, for a particle scattering into solid angle \( d\Omega \), the differential cross-section

\[
\frac{d\sigma}{d\Omega} = \left( \frac{m}{2\pi\hbar^2} \right)^2 |\langle \Psi_d | T | \Psi_i \rangle|^2
\]  \hspace{1cm} (1.4)

is determined by a matrix element \( \langle \Psi_d | T | \Psi_i \rangle \) of the transition operator \( T \). If the Hamiltonian of the LEED electron in the presence of the scattering crystal is invariant under a symmetry operation \( S \) of the crystal, then following Messiah [33]

\[
\langle \Psi_d | T | \Psi_i \rangle = \langle \Psi_d | S^{-1}TS | \Psi_i \rangle = \langle S\Psi_d | T | S\Psi_i \rangle
\]  \hspace{1cm} (1.5)

If, in particular, \( S \) represents a diperiodic translation vector \( t \) of the surface net, then

\[
S\Psi_i(r) = \Psi_i(r + t) = \exp[i\mathbf{k}(r + t)]
\]  \hspace{1cm} (1.6)

Here \( S \) has the effect of translation from \( r \) to \( r + t \). A corresponding relation holds for \( S\Psi_d(r) \), and hence the two ends of Eq. (1.5) give

\[
\langle \Psi_d | T | \Psi_i \rangle = \exp[i(k_i - k_d) \cdot t] \langle \Psi_d | T | \Psi_i \rangle
\]  \hspace{1cm} (1.7)

which with Eq. (1.4) immediately requires either \( \langle \Psi_d | T | \Psi_i \rangle = 0 \) (i.e., no scattering intensity) or

\[
\exp[i(k_i - k_d) \cdot t] = 1
\]  \hspace{1cm} (1.8)

Equation (1.8) is satisfied by

\[
(k_i - k_d) \cdot t = 2\pi p \hspace{1cm} (p \text{ is an integer})
\]  \hspace{1cm} (1.9)

or alternatively

\[
k_d \parallel = k_i \parallel + g \hspace{1cm} \text{(diffraction condition)}
\]  \hspace{1cm} (1.10)

where the subscript \( \parallel \) indicates a component parallel to the surface, and \( g \) is a reciprocal net vector of the diperiodic surface which can be expressed as

\[
g = hs_i + ks_j \hspace{1cm} (h, k \text{ integers})
\]  \hspace{1cm} (1.11)
with
\[ s_1 \cdot s_1^* = 2\pi \quad s_1 \cdot s_2^* = 0 \]
\[ s_2 \cdot s_2^* = 2\pi \quad s_2 \cdot s_1^* = 0 \]
(1.12)

where \((s_1, s_2)\) are unit mesh (i.e., the diperiodic repeat unit) vectors in real space, so that the general translation is given by

\[ t = m s_1 + n s_2 \quad (m, n \text{ are integers}) \]
(1.13)

and \((s_1^*, s_2^*)\) are the corresponding unit mesh vectors in reciprocal space.

Together, Eqs. (1.3) and (1.10) represent the two basic conservation conditions for LEED; the latter determines the directions of diffracted beams according to the constant momentum transfer parallel to the surface.

1.2.4 Notation

Figure 1.4 shows translational symmetries associated with the five surfaces studied in this thesis (in real space) and the observed LEED patterns (in reciprocal space). Here \((a_1, a_2)\) are the basic net vectors for the substrate (i.e., the ideal surface truncated from the single-crystal bulk) and the corresponding basic reciprocal net vectors \((a_1^*, a_2^*)\) are determined analogously to the relations for \((s_1^*, s_2^*)\) and \((s_1, s_2)\) shown in Eq. (1.12). A common notation introduced by Wood [34] for describing an ordered surface is

\[ S(hkl) - i (s_1/a_1 \times s_2/a_2) \text{ R} \alpha - A \]

where \((hkl)\) specifies the Miller indices of the substrate surface identified by the chemical symbol \(S\), \(A\) denotes the adsorbed species, and \(i\) is either “p” (for primitive) or “c” (for center) according to the way in which the unit mesh of the surface is defined (although the “p” can be dropped). The quantity \((s_1/a_1 \times s_2/a_2)\) indicates ratios of magnitudes of the unit mesh vectors of the surface.
Figure 1.4 Schematic diagrams of the real surface and diffraction pattern for the five surface structures investigated in this thesis. For the real surface, large open circles represent the substrate atoms, while the small filled circles represent adsorbed atoms; for the diffraction patterns, open circles correspond to integral beams from the clean surface, with additional fractional beams (filled circles) for the chemisorbed surface. Unit mesh vectors are indicated in each diagram.
Figure 1.4, continued
Figure 1.4, continued
layer to those of the substrate, and $R\alpha$ specifies the angle of rotation between these two sets of vectors. Examples include the Cu(110)-(2x1)-O, Cu(110)-c(6x2)-O, Cu(100)-(2$\sqrt{2}$ x$\sqrt{2}$ )R45°-O and Rh(111)-(sqrt(7)xsqrt(7))19.1°-P surfaces as illustrated in Fig. 1.4 (a), (b), (d) & (e).

Wood's notation is not applicable for surfaces where the angles between $S_1$ and $S_2$ and between $a_1$ and $a_2$ are different. In such cases, a more general matrix notation, introduced by Park and Madden [35], is used:

$$S(hkl) = \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix} - A$$

where

$$s_1 = m_{11} a_1 + m_{12} a_2$$

$$s_2 = m_{21} a_1 + m_{22} a_2$$

(1.14)

and the example for the Cu(110)-\begin{pmatrix} 2 & 2 \\ -1 & 1 \end{pmatrix}-P surface is shown in Fig. 1.4 (c).

In general surfaces are less than ideally ordered, and when an adsorption structure has a lower symmetry than the substrate on which it is formed, differently oriented domains may occur. Examples are shown in Fig 1.4 for the Cu(110)-\begin{pmatrix} 2 & 2 \\ -1 & 1 \end{pmatrix}-P, Cu(100)-(2$\sqrt{2}$ x$\sqrt{2}$ )R45°-O and Rh(111)-(sqrt(7)xsqrt(7))19.1°-P surfaces. In each case two possible domains coexist, one being the mirror image of the other (Fig. 1.4 (c)-(e)). In such examples, the observed diffraction pattern represents a summation of patterns from the individual types of domain provided the dimension of each is sufficiently large compared with the instrumental transfer width [36].
1.2.5 Structural characterizations of surfaces by LEED

Figure 1.5 indicates the three types of structural information that can be determined for a surface by using LEED. First, the positions of diffracted spots on the fluorescent screen indicate the size and shape of the unit mesh for the real surface, while the sharpness of the spots and the level of background qualitatively reflect the degree of surface order. This indicates the most common use of LEED. Secondly, the measurement of spot profiles across a diffracted beam can yield quantitative information on the surface ordering, including the extraction of step densities, domain sizes and island dimensions [37]. This spot profile analysis in LEED (SPAEEED) can provide an important characterization of a surface with only small computing demands. The third use of LEED is to analyze diffracted beam intensities to determine surface geometrical structure. This involves comparing experimental intensity-versus-energy (or I(E)) curves for the different diffracted beams with theoretical curves calculated for various trial atomic models of the surface. This approach can have large computing demands, but it provides very fundamental information for the local atomic structural details.

The approach to a LEED crystallographic analysis starts with sample preparation and experimental measurement of I(E) curves for a set of diffracted beams. Next, theoretical calculations of I(E) curves are made for a set of different structural models, and a continuous assessment of the experimental and calculated I(E) curves is made, with a search for the geometrical parameters in the calculations which optimize the correspondence. The basic approach is therefore a trial-and-error one, although the development of tensor LEED [31] (see Chapter 2) does help to speed up the optimization of various geometrical parameters. Still the time needed for solving a structure can be significant. For example, for solving the Rh(111)-(\(\sqrt{7}\times\sqrt{7}\))19.1°-P surface structure, a total time span of over one year was required; without
Figure 1.5 Different applications of LEED for studies in surface structure.
tensor LEED this analysis would have been impossible, but more than 1000 CPU hours on the IBM RISC 6000 system (with 128 MB memory) was still needed.

1.3 Auger electron spectroscopy (AES)

The phenomenon of electron emission by a two electron process associated with the relaxation of a core hole was first observed by Auger in 1925 in a study of the photoelectric effect using hard x-ray radiation [38]. The emission process is indicated in Fig. 1.6 (a). For ionized core states with binding energies of less than 2 keV, Auger emission is always a more probable process than the alternative of X-ray emission (Fig. 1.6 (b)) [8]. As early as 1953, Lander [39] succeeded in identifying Auger electron emission in the energy distribution of secondary electrons emitted from solid samples on electron impact, and he also pointed out that the Auger electrons might be used for surface analysis. However that idea was only followed up after 1967 [40]. Since then, Auger electron spectroscopy (AES) has developed into a very powerful tool for surface analysis [8, 41], and moreover it is one that provides complementary information to LEED. In this work AES is used to monitor surface impurities, and to follow the amounts of adsorbate in chemisorption studies.

To a first approximation, an Auger electron is emitted with kinetic energy $E_{\text{kin}} = E_1 - E_2 - E_3$, where $E_1$, $E_2$ and $E_3$ are the binding energies for the levels involved (Figure 1.6 (a)), although account is strictly needed for relaxation and correlation effects [41]. The point for our purpose though is that different atoms have Auger transitions with characteristic energies, and this allows the identification of elements involved by comparing the observed Auger kinetic energies (like fingerprints) with information in standard databases [42]. Additionally, quantitative information for a particular element can be provided by comparing the magnitudes of Auger signals in different situations (strictly the determination of absolute coverages requires comparison with
Figure 1.6 Processes for de-excitation of atomic core holes: (a) Auger electron emission; (b) X-ray emission.
reference standards [8]). In this work, amounts of adsorbate are compared through peak-to-peak amplitudes in differentiated spectra; these are proportional to the actual Auger currents (and therefore amounts on the surface) provided the shape and peak width are constant for the Auger signal in the undifferentiated mode. Auger electrons with kinetic energies of 2 keV or less are surface sensitive because of the strong inelastic scattering experienced by electrons in this energy range (for metals mean free paths are still only of the order of 10 Å [32]).

1.4 Surface structural chemical principles

When electronegative atoms react with a metal surface to give a coverage of the order of 1 monolayer (ML) or less, the structural arrangement formed may correspond to (i) simple chemisorption, where the electronegative atoms bond to a relaxed, but not dramatically changed, metal surface; (ii) underlayer absorption; (iii) surface compound formation, where a thin layer of a compound, likely in a non-polar orientation, bonds to the metallic substrate; (iv) an independent adsorbate-induced reconstruction. The challenge is to identify which type of structure forms in each case, and why. Comparisons with the bulk are useful insofar as in both surface and bulk structures there are basic units which contain chemical bonds with well-defined lengths and angles. However the situation at the surface is fundamentally different from the bulk, which has more structural “degree of freedom” in the sense that the latter can grow in all directions, while an ordered surface structure is constrained to match to the substrate. Additionally, surface structures can still evolve with coverage of the adsorbing species.

One important bridge between surface and bulk structures is provided by the measured bond lengths. X-ray crystallographers have for long correlated a lot of experimental bond length data with a Pauling-type bond length - bond order relation [43]

\[ r(p) = r(1) - 0.85 \log p \]  

(1.15)
where \( r(p) \) is the interatomic distance between a metallic atom M and an electronegative atom X for bond order \( p \), and \( r(1) \) is the corresponding single bond distance. Work from this laboratory [44] has shown that this relation can often be useful for correlating surface X–M bond lengths. Then \( p \) is taken as the valency of X divided by its number of neighboring M atoms, and \( r(1) \) may be usefully parametrized by an appropriate bulk compound. For example, for O/Cu surface systems, the bulk compound \( \text{Cu}_2\text{O} \) seems an appropriate reference compound, whereas for O/Ni and N/Cu surfaces the bulk compounds NiO and \( \text{Cu}_3\text{N} \) can similarly offer guidance. Where there is a choice of bulk compounds formed by M and X, the one with the lowest oxidation state for M appears preferred for assessing surface bond lengths [44]. Use is made of Eq. (1.15) in the following chapters to check the reasonableness or otherwise of X–M bond lengths obtained from LEED crystallographic analyses, but additionally it can help give guidance in the choice of initial reference structures for tensor LEED studies.

1.5 Aims of thesis

The work described in this thesis covers structural investigations of several surfaces formed by the chemisorption of electronegative atoms (O, P and S) on copper and rhodium single crystal surfaces. The next two chapters outline the theoretical (Chapter 2) and experimental (Chapter 3) methods involved. This introduction is followed by detailed descriptions of new structural determinations with LEED crystallography applied to the surfaces designated as Cu(110)-c(6x2)-O (Chapter 4), Cu(110)-(2x1)-O and Cu(100)-(2\sqrt{2} \times \sqrt{2})R45°-O (Chapter 5), Cu(110)-\begin{pmatrix} 2 & 2 \\ -1 & 1 \end{pmatrix}\text{-P (Chapter 6), and Rh(111)-(\sqrt{7}\times\sqrt{7})19.1°-P (Chapter 7). The overall motivation is to provide new details of structures at the atomic scale, to help establish approaches
for determining relatively complex surface structures using LEED, and thereby gain improved understanding of surface structural chemical principles.
Chapter 2  Calculations

2.1  Introduction

In low energy electron diffraction (LEED), the total wave function outside the crystal can be written as

\[ \Psi_{\text{out}}(\mathbf{r}) = \exp(i\mathbf{k}_i \cdot \mathbf{r}) + \sum_g c_g \exp(i\mathbf{k}_g \cdot \mathbf{r}) \]  \hspace{1cm} (2.1)

where \( \exp(i\mathbf{k}_i \cdot \mathbf{r}) \) and \( \exp(i\mathbf{k}_g \cdot \mathbf{r}) \) represent the incident and diffracted plane waves respectively. If the scattered amplitude \( c_g \) is known, the beam intensity (or reflectivity) of the \( g \)th diffracted beam can then be attained through

\[ R_g = \frac{k_{g\perp}}{k_{i\perp}} |c_g|^2 \]  \hspace{1cm} (2.2)

where \( k_{g\perp} \) and \( k_{i\perp} \) are the perpendicular components of wave vectors of the diffracted and incident beams respectively [45]. The objective of the LEED calculations is to attain theoretical intensities of the elastically diffracted beams, which can be compared with experimental values measured outside the crystal; then the structural models and/or geometrical parameters can be changed in the search for the geometrical structure of the surface region which gives the best correspondence between calculation and experiment.

The diffraction of low energy electrons from a crystal surface is strictly an \( N + 1 \) electron problem (\( N \) electrons from the crystal plus one LEED electron), but Pendry [28] has demonstrated that this many-body problem can effectively be reduced to solving an one-electron Schrödinger equation

\[ \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \Psi_{\text{in}}(\mathbf{r}) = E \Psi_{\text{in}}(\mathbf{r}) \]  \hspace{1cm} (2.3)
where \( \Psi_m(r) \) is the wave function for the LEED electron inside the crystal, and \( V(r) \) is an effective potential for the solid, which includes the regular Coulomb and exchange terms, plus the effect of inelastic excitations in the valence electrons of the solid. Just one LEED electron need be considered here because: (i) the incident electrons are too well separated for them to interact with each other, and (ii) any changes in the crystal caused by the impact of one LEED electron do not last long enough to affect the next approaching LEED electron. Further, with the solid treated as composed of ion cores and electrons, any polarization of the ion cores by the electrostatic field of the incident LEED electron can be neglected [28]. The wave function of a LEED electron \( \Psi_m(r) \) inside the crystal, and its first derivative, must match smoothly to \( \Psi_{\text{out}}(r) \) at the crystal boundary [46].

The basic potential of the scattering crystal is represented by a “muffin-tin” model (Fig. 2.1) as used in electron band structure theory [28]: the largest possible non-overlapping spheres are drawn around each atomic nucleus; the potential inside is assumed spherically symmetric, while that outside is taken as constant (“muffin-tin constant” \( V_0 \)). With this potential, the Schrödinger equation is solvable in terms of “partial waves” for inside the ion core [28], whereas the waves propagating in the region of constant potential have the plane wave form. In practical calculations for LEED, the muffin-tin constant has real and imaginary components

\[
V_0 = V_0 + iV_0i \quad (2.4)
\]

The real component, \( V_0 \), indicates the amount that the muffin-tin constant is below the vacuum level, and it is treated as an adjustable parameter to optimize the fit between calculated and experimental \( I(E) \) curves. The imaginary component, \( V_0i \) (when negative), acts to simulate the attenuation of beam intensity inside the solid [28].
Figure 2.1 Variation of potential with position along xx' in the "muffin-tin" approximation.

Figure 2.2 Schematic indication of multiple scattering between two atoms.
The approach to the multiple-scattering (or so-called dynamical) calculations in LEED is to calculate scattering amplitudes from individual atoms, then generate scattering amplitudes from individual atomic layers, and finally sum up diffracting amplitudes from an appropriate stack of layers which represents the scattering system of interest. Mathematically, two different types of basis functions are suggested: (i) spherical waves (whose use defines the L-space representation), which occur naturally for scattering by spherically symmetric potentials; and (ii) plane waves (whose use defines the K-space representation), which occur naturally for regions of constant potential. In principle, the wave function for the LEED electron inside a crystal surface can be expanded in terms of either spherical waves or plane waves, and Marcus [47] has discussed the interconversion between the L- and K-space representations. Throughout the formulation of a LEED calculation, these two approaches are available; which is used at each point is decided by efficiency for the whole calculation.

More complete discussions of LEED theory have been given by Pendry [28], Tong [48] and Van Hove et al. [11]. A brief outline of the ideas involved, and their implementation, are given through the rest of this chapter.

2.2 Atomic scattering

2.2.1 Stationary atom

The scattering of a plane wave (wave vector \( \mathbf{k} \)) by a spherically symmetric potential has the following asymptotic form:

\[
\exp(i\mathbf{k} \cdot \mathbf{r}) + t(\theta) \frac{\exp(ikr)}{r}
\]

(2.5)

where \( \theta \) is the scattering angle and \( \mathbf{r} \) is the position vector from the chosen origin (e.g., atomic nucleus). The scattering amplitude \( t(\theta) \) can be expanded over spherical waves as
\[ t(\theta) = 4\pi \sum_l (2l + 1)t_l P_l(\cos \theta) \]  
(2.6)

where \( P_l \) is a Legendre polynomial and the t-matrix element is given by

\[ t_l = \frac{\hbar^2 [\exp(2i\delta_l) - 1]}{4imk} \]  
(2.7)

This is applicable to the LEED theory problem given that atoms are represented by spherical potentials in the muffin-tin approximation, but the value of this approach depends on the convergence of the expansion in Eq. (2.6), and in particular on how many phase shifts \( \delta_l \) are needed to describe the atomic scattering.

The phase shifts \( \delta_l \) are attained by integration of the radial Schrödinger equation in the presence of the ion core potential; they are functions of electron energy, atomic potential and muffin-tin radius [29]. Although Eq. (2.6) appears as an infinite sum, in practice only a restricted number of phase shifts are needed for a LEED calculation. In general the number of phase shifts required is smaller for weakly scattering atoms than for those that are strongly scattering; also the number required increases with energy. In practical LEED analyses with energy to 250 eV or less, the inclusion of eight phase shifts (i.e., to \( l_{\max} = 7 \)) is generally satisfactory.

2.2.2 Temperature effect

The effect of thermal vibrations for the scattering atoms is represented by multiplying the atomic scattering amplitude \( t(\theta) \) with a Debye-Waller factor:

\[ t^T(\theta) = \exp (-M) t(\theta) \]  
(2.8)

where \( t^T(\theta) \) is the effective atomic scattering amplitude and

\[ M = \frac{1}{6} |\Delta k|^2 < (\Delta r)^2 > \]  
(2.9)
Here $\Delta k = k_d - k_i$ is the momentum transfer for the beam under consideration, and $< (\Delta r)^2 >$ is the mean square vibration amplitude for the surface atoms. For isotropic vibrations in the harmonic approximation [49], Eq. (2.9) takes the form

$$M = \frac{3\hbar^2 |\Delta k|^2}{2m_a k_B \theta_D^2}$$

in the high-temperature limit. In Eq. (2.10), $m_a$ is the atomic mass, $k_B$ the Boltzmann constant and $\theta_D$ the Debye temperature. $\theta_D$ indicates the rigidity of the lattice with respect to vibrations; the higher its value the stronger the bonding in the solid [49]. For these assumptions, Jepsen et al. [27] showed that the effect of a vibrating lattice can be included by a renormalization of the atomic phase shifts for the corresponding stationary lattice. Given this, the temperature-dependent phase shifts ($\delta_D^T$) for a LEED calculation are generated automatically by the computer program given the basic input parameters including phase shifts for stationary atoms ($\delta_i$), Debye temperatures ($\theta_D$) and the experimental temperature ($T$).

The scattering properties of an atom therefore enter the LEED calculation via the atomic phase shifts, which are determined by the potential from the nucleus to the muffin-tin radius. However the atomic properties that are input to the LEED calculation effectively treat each atom as a point scatterer in a constant potential. The scattering from one atom to another may be covered by damped plane waves in the K-space representation, or, in the L-space representation, by propagators (Green’s functions) which propagate spherical waves between the atoms.

2.3 Multiple scattering

2.3.1 Scattering by two atoms
The multiple-scattering by two atoms can be set up in the L-space representation in terms of Green's functions (G^{21} and G^{12} in Fig. 2.2) which describe the free-space propagation of a scattered spherical wave from one atom to the other and are implicit functions of atomic positions [11]. The t^1 and t^2 are the respective t-matrices (assumed for vibrating atoms), and the product G^{21}t^1 simply represents the amplitude of a wave which arrives at the second atom after being scattered by the first. The process shown in Fig 2.2 is represented by the product t^1G^{12}t^2G^{21}t^1; this describes a triple scattering event (read from right to left) in which an incident wave scattered by atom 1 (t^1), propagates to atom 2 (G^{21}), is then scattered by atom 2 (t^2), propagates to atom 1 (G^{12}), and finally is scattered by atom 1 (t^1) again. The amplitudes summed over all possible scattering paths that terminate at atom 1 (denoted as T^1) or atom 2 (T^2) are

\[ T^1 = t^1 + t^1G^{12}t^2 + t^1G^{12}G^{21}t^1 + t^1G^{12}t^2G^{31}t'G^{12}t^2 + \ldots = t^1 + t^1G^{12}T^2 \]
\[ T^2 = t^2 + t^2G^{21}t^1 + t^2G^{21}t^1G^{12}t^2 + t^2G^{21}t^1G^{12}G^{31}t'G^{12}t^2 + \ldots = t^2 + t^2G^{21}T^1 \] (2.11)

or equivalently

\[
\begin{pmatrix}
T^1 \\
T^2
\end{pmatrix} = \begin{pmatrix}
I & -t^1G^{12} \\
-t^2G^{21} & I
\end{pmatrix}^{-1} \begin{pmatrix}
t^1 \\
t^2
\end{pmatrix}\] (2.12)

where I is a unit matrix. Solution of this matrix equation amounts to obtaining self-consistent solutions for T^1 and T^2 given the t^1 and t^2.

2.3.2 Scattering by an atomic layer

Analogous matrix equations have been set up for the extension of Eq. (2.12) to a single, and infinite, diperiodic plane with just one atom per unit mesh, in which case all the T^j are identical (taken equal to t). It can be convenient to define a layer, for the purposes of LEED calculations, as a composite of these individual planes (Fig. 2.3), although atoms in one plane...
Figure 2.3 Schematic indication of "layers" and "planes" for LEED calculations.
may be chemically different from those in another. Van Hove [11] has summarized that the
scattering from a layer of N planes (with scattering power represented by matrices $\tau^i, \tau^2, \ldots, \tau^N$) is
described by

$$
\begin{pmatrix}
T^1 \\
T^2 \\
T^3 \\
\vdots \\
T^N
\end{pmatrix} =
\begin{pmatrix}
I & -\tau^1 G^{12} & -\tau^1 G^{13} & \cdots & -\tau^1 G^{1N} \\
-\tau^2 G^{21} & I & -\tau^2 G^{23} & \cdots & -\tau^2 G^{2N} \\
-\tau^3 G^{31} & -\tau^3 G^{32} & I & \cdots & -\tau^3 G^{3N} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
-\tau^N G^{N1} & -\tau^N G^{N2} & -\tau^N G^{N3} & \cdots & I
\end{pmatrix}^{-1}
\begin{pmatrix}
\tau^1 \\
\tau^2 \\
\tau^3 \\
\vdots \\
\tau^N
\end{pmatrix}
$$

(2.13)

Each $T^i$ (with matrix elements $T^i_{ll'}$) includes all scattering paths that terminate at an atom in
plane $i$, while $G^{ij}$ is the structural propagator which describes all propagations of spherical
waves from atoms in plane $j$ to atoms in plane $i$, and is therefore a function of atomic positions in
the two planes. The total scattering amplitude (in the spherical-wave representation) from such a
single layer (Fig. 2.3) is

$$
T_{ll'} = \sum_{i=1}^{N} \exp[i(k_i - k_d) \cdot r_i] T^i_{ll'}
$$

(2.14)

after taking effect of the phase differences associated with the origins ($r_i$) for the different planes
(i).

In principle, this approach can be used to determine the scattering amplitude from a
surface under investigation if it can be sufficiently described by the N planes. Frequently, in
practice, more efficient schemes are available, although variations in this approach are needed
when the spacings between layers are very small (e.g., < 0.5 Å). With wider separations between
the atomic planes, other methods, based on the plane wave representation, are used to stack the
atomic layers (each may contain several Bravais-net planes which are treated by the approaches
indicated in the following section), and they give much faster computations.
2.3.3 Scattering by a stack of atomic layers

For generating scattering amplitudes from a stack of layers using the plane wave (K-space) representation, Tong [48] showed that the amplitude of a plane wave $k_g^\pm$ diffracted from a layer of $N$ planes is

$$M_{g,k}^{\pm} = \frac{16\pi^2\text{im}}{Ak_g^2\hbar^2} \sum_{LL'} Y_L(k_g^\pm)T_{LL'}Y_{L'}^*(k_g^\pm)$$

for an incident wave $k_g^\pm$ of unit amplitude. In Eq. (2.15), $T_{LL'}$ is from Eq. (2.14) and $A$ is the area of the layer unit mesh. This expression covers both forward (denoted as "++" and "−−") and backward (denoted as "+-" and "−+"") scatterings; the respective transmission and reflection matrices

$$r^{++} = M^{++}, r^{−−} = M^{−−}, t^{++} = M^{++} + I, t^{−−} = M^{−−} + I$$

are used to treat the scattering from a stack of layers. Specific methods available are the renormalized-forward-scattering (RFS) method and the layer-doubling (LD) method, both introduced by Pendry [28], and the combined-space (CS) method introduced by Tong and Van Hove [50].

(I) Renormalized-forward-scattering method

Typically in the LEED energy range, forward scattering is much stronger than back scattering. Nevertheless back scattering must occur in order for a diffraction pattern to be displayed on a screen. The RFS method groups all possible scattering paths (Fig. 2.4) for an electron in a crystal into groups of decreasing probability. Those of first order contain all paths that have been reflected just once, but transmitted any number of times within the damping length; those of second order include all paths that have three reflections and contribute...
Figure 2.4 (a) Illustration of paths in the renormalized forward scattering method with different numbers (orders) of back scatterings. Propagating waves shown for penetrating directions in (b) and for emerging directions in (c).
significant amplitude to the diffracted beams in vacuum; …; those of nth order include significantly contributing paths that have been reflected \((2n-1)\) times in the crystal. Mathematically, the plane wave amplitudes \(a_{i|g}\) in the ith interlayer spacing are computed iteratively with
\[
a_{i|g}^{\text{new}} = \sum_{g'} \left( t_{gg'}^{+} P^{+} a_{i-1|g}^{(-1)g'} + r_{gg'}^{+} P^{-} a_{i|g}^{(+1)g'} \right)
\] (2.17)
for penetration and
\[
a_{i|g}^{\text{new}} = \sum_{g'} \left( t_{gg'}^{-} P^{-} a_{i+1|g}^{(-1)g'} + r_{gg'}^{-} P^{+} a_{i|g}^{(+1)g'} \right)
\] (2.18)
for emergence, where \(P_{g}^{\pm} \) 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
\[
a_{1|g} = 0 \quad \text{for all } i \text{ and } g, \text{ except } a_{1|0} = 1 \tag{2.19}
\]
In practice the RFS scheme typically uses 12 to 15 layers for the crystal, and the calculated diffracted beam intensities require three to four orders of iteration for convergence. The computing demands are relatively modest; however, with strong atomic scatterers, and/or weak inelastic scattering, the method may fail to converge well. Also it may not be reliable for interlayer spacings less than about 1.0 Å. In such cases the LD method or CS method should be used instead.

(II) Layer-doubling method

The LD method calculates diffraction amplitudes for a stack of layers in a quite different fashion. It starts with a calculation for a pair of layers whose diffraction amplitudes are known, and generates scattering amplitudes from the combined layer. For example, if A and B label two neighboring layers, and \(P_{A}^{\pm} \) is the plane wave propagator between A and B (Fig. 2.5), the reflectivity of the layer pair \(A + B\) can be written as
Figure 2.5 Schematic diagram of the layer-doubling scheme to generate an eight-layer slab starting with two individual layers A and B.
\[ R^{+} = r_{A}^{+} + t_{A}^{-}P_{b}^{-}P_{a}^{-}t_{A}^{++} + t_{A}^{-}P_{b}^{-}P_{a}^{-}r_{a}^{+}P_{b}^{-}r_{b}^{+}P_{a}^{+}t_{A}^{++} + \cdots \]

\[ = r_{A}^{+} + t_{A}^{-}P_{b}^{-}P_{a}^{-} (I - r_{a}^{+}P_{b}^{-}r_{b}^{+}P_{a}^{+})^{-1} t_{A}^{++} \]  

(2.20a)

Similarly, the other reflection and transmission matrices are expressed as

\[ R^{-} = r_{b}^{+} + t_{b}^{-}P_{a}^{-}P_{b}^{-} (I - r_{a}^{+}P_{b}^{-}r_{b}^{+}P_{a}^{+})^{-1} t_{b}^{--} \]  

(2.20b)

\[ T^{+} = t_{b}^{-}P_{a}^{-} (I - r_{a}^{+}P_{b}^{-}r_{b}^{+}P_{a}^{+})^{-1} t_{A}^{++} \]  

(2.20c)

\[ T^{-} = t_{A}^{-}P_{b}^{-} (I - r_{b}^{-}P_{a}^{-}r_{a}^{+}P_{b}^{+})^{-1} t_{b}^{--} \]  

(2.20d)

with

\[ P_{g}^{\pm} = \exp (\pm i k_{g} r_{BA}) \]  

(2.21)

The vector \( r_{BA} \) links the reference origins in layers A and B.

The process implied by Eqs. (2.20a) to (2.20d) can be continued through a second doubling process, which includes two double-layer slabs whose diffraction amplitudes are determined from the first doubling process. A third doubling process then applies to a stack of two four-layer slabs, and such an iterative process of stacking layers onto a growing slab is continued until convergence is reached in the reflected diffracted beam intensities.

After adding layers to simulate a substrate by the LD method, different layers can be added, also using Eqs. (2.20), to simulate adsorbed or reconstructed layers. This method is also most effective with appreciable electron damping, and typically about four iterations (to produce a 16-layer stack) are required for satisfactory convergence. Again this method fails with very short spacings (e.g., less than 0.5 Å), but generally it is favored when the system of interest has interlayer spacings in the range of 0.5 - 1.0 Å.

(III) Combined-space method
Both the RFS and LD methods use the plane wave representation to calculate the scattering amplitude from a stack of layers, but with close spacings (≤ 0.5 Å) a greatly increased number of plane waves is needed with a consequence that the dimension of the matrices involved becomes too large for numerical reliability. In such circumstance it is necessary to use the L-space representation, as in Eqs. (2.13) and (2.14), but this is time-consuming especially because of the need to invert large matrices for each change in geometry and for different beams. However a compromise is possible for the many surfaces which have some close interlayer spacings, while others are more widely spaced. For this situation, Tong and Van Hove [50] formulated a combined space (CS) approach which effectively combines both the plane-wave and spherical-wave representations. The method is set up so that the former representation is used for calculating multiple scattering between atomic layers with relative large interlayer spacings, while the latter representation is used to deal with scattering between the close layers. Two approaches are available to ease the L-space calculations. Beeby [24] formulated a more efficient matrix inversion scheme to reduce the times required for the different diffracted beams \( g \), and Zimmer and Holland [51] introduced the reverse scattering perturbation (RSP) method, which is an L-space analog of the RFS method. Detailed descriptions of these methods and their computational implementation can be found in Ref. [29].

2.4 Comparison of experimental and calculated I(E) curves

To compare sets of experimental and calculated I(E) curves, the focus is to examine peak positions, relative peak intensities, and curve shapes including the existence or absence of shoulders. Initially visual analysis was done but that proves too subjective and unwieldy for modern work [52]. A number of different reliability indices (or R-factors) have been introduced for LEED crystallographic analysis [53], and each has been set up mathematically so that the
value of the index $R$ gets less as the correspondence between the two sets of curves improves. Each has a lower limit of zero for comparing identical curves, but the upper limit varies [53]. All analyses presented in this thesis used the index introduced by Pendry ($R_P$) [54], and therefore just that one is described here.

Pendry's R-factor uses the function

$$Y = \frac{L}{1 + L^2 V_{0i}}$$  \hspace{1cm} (2.22)

where $L(E)$ is the logarithmic derivative of an $I(E)$ curve

$$L = \frac{I'}{I}$$ \hspace{1cm} (2.23)

and $V_{0i}$ is the imaginary part of the muffin-tin potential used in the calculations. Pendry's R-factor for a single beam is then defined in terms of the $Y$ functions:

$$r_p = \frac{\int (Y_e - Y_t)^2 dE}{\int (Y_e^2 + Y_t^2) dE}$$ \hspace{1cm} (2.24)

where subscripts “e” and “t” refer to “experimental” and “theoretical” respectively. This R-factor is particularly sensitive to the peak and valley positions in the $I(E)$ curves; it gives essentially equal weights to large peaks/valleys as to small ones.

In an actual LEED crystallographic study, $I(E)$ curves are compared for a set of diffracted beams, and therefore an average R-factor is defined:

$$R_p = \frac{\sum_i \Delta E_i r_p^i}{\sum_i \Delta E_i}$$ \hspace{1cm} (2.25)

where the summation is over all beams $i$, each having a weight proportional to the energy range $\Delta E_i$ available for that beam. $R_p$ is the actual reliability index used in all the analyses discussed in this thesis.
2.5 Tensor LEED

2.5.1 Basic theory

A difficulty for LEED crystallography compared with X-ray crystallography has been the inability to invert experimental intensity data to get structural information directly. The multiple scattering in LEED has so far prevented the establishment of so-called “direct methods», although research on this continues. A development that is proving very useful, however, is that of tensor LEED (TLEED) [55-58]. In principle, tensor LEED theory represents an approximate scheme for calculating diffracted beam intensities, which attempts to retrieve the simplicity of X-ray diffraction in the presence of strong atomic scattering. The approach starts with a particular geometrical structure, or reference structure, for which the scattered electron wavefield is calculated exactly. Structural distortions from the reference structure are treated as a perturbation, and Pendry and his collaborators showed that if the atomic displacements are sufficiently small, their effect on the LEED intensities can be calculated directly in terms of scattering matrices stored from the calculation for the reference structure [55-58].

For a set of displacements \( \delta r_j \) (relative to the positions \( r_j \) in the reference structure), the atomic t-matrix (see also Eq. (2.7)) after the displacements can be written as

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

(2.26)

where \( t_j \) is the element of the t-matrix for the undisplaced atom \( j \), and \( \delta t_j \) is the change caused by the displacement \( \delta r_j \). The term \( \delta t_j \) can be evaluated [31] as

\[
\delta t_{lm,lm'} = \sum_{j,l_m'} G_{lm,l_m'}(\delta r_j) t_{lj,m,m'}(-\delta r_j) - t_{lj} \delta_{ll'}
\]

(2.27)

where the propagator \( G \) converts a spherical wave centered on the original position of atom \( j \) \( (r_j) \) into a set of spherical waves centered on \( r_j + \delta r_j \); \( \delta_{ll'} \) is the Kronecker delta function. Then the change in the diffraction amplitude
\[
\delta A = \sum_j <\Psi(k'_j)|\delta t_j|\Psi(k_j)>
\]  
(2.28)

for a LEED beam with momentum transfer parallel to the surface of \(k'_j - k_j\), can be rewritten in an angular momentum basis as

\[
\delta A = \frac{1}{N} \sum_j \sum_{l'l''} \Gamma^j_{l'l''} S_{l'l''}(\delta r_j)
\]  
(2.29)

Here \(N\) is the number of displaced atoms and the matrix \(S\) is a function of atomic displacements alone, while the tensor quantity \(\Gamma\) depends only on the reference structure. Once \(\Gamma\) has been calculated in the full dynamical calculation for the reference structure, the diffracted intensities for any trial structure (i.e., resulting from distortions from the reference structure) can be determined from the evaluation of \(S\) for each displaced atom and the resumming of Eq. (2.29). This provides a major saving in computing time, although it is necessary that the trial structure has not displaced too far from the reference structure. Rous [31] has suggested, for simple chemisorption systems, that TLEED remains effective for atomic displacements up to 0.4 Å; however the ranges of reliability still need assessing for the more complex structures. In part this is due to the fact that TLEED neglects multiple scattering correlations between displaced atoms. A more sophisticated approach in principle is the cluster-corrected tensor LEED method [31], which includes multiple scattering correlations between displaced atoms, although this variation is more complex and it has not yet been implemented in practice.

2.5.2 Implementation

The tensor LEED calculations in this work used computer programs provided by Dr. Van Hove (UC Berkeley), which consist of two parts: program I is used to perform full dynamical calculations for reference structures, following the basic schemes described in Sections 2.1-2.3;
program II undertakes search procedures for finding the optimal structural and non-structural (such as muffin-tin constant) parameters. When program I calculates the amplitude of each diffracted beam for the reference structure, it also produces the tensor $\Gamma$ for each beam at each energy and for each atom displaced from its position in the reference structure. These $\Gamma$s are stored and are available for use with program II to generate the LEED I(E) data for the new trial structures, which are then evaluated immediately by comparing with the experimental data through R-factor calculations. If a minimum in R is not reached, another trial structure is calculated and evaluated using the same set of $\Gamma$'s. These procedures are repeated until a minimum is found in the R-factor. Figure 2.6 illustrates the automated search strategy as realized in the TLEED programs.

One remaining problem concerns how to identify whether the lowest R-factor attained in a particular study is truly a “global” rather than a “local” minimum. This is an important issue and actually includes two interlinked problems since use of TLEED still involves testing, on a trial-and-error basis, a range of geometrical parameters within particular types of structural model: (i) Does the minimum R-factor attained identify the correct basic structural model type? (ii) If the answer to (i) is “yes”, is the minimum R-factor the lowest available for that particular structural model type? In order to be able to answer the first question, all conceivable structural model types have to be tested. In general, guidance may also be needed from any additional experimental observations (e.g., from STM, LEIS and SXRD), and from structural chemical principles insofar as the indicated bond lengths broadly fit requirements of coordination numbers, especially for the adsorbing species. This model searching can still be a very time-consuming process, especially for surfaces with relatively large unit meshes (e.g., $\sqrt{7}\times\sqrt{7}$). No direct method can be applied to solve the second problem at this point. One can only approach with
Figure 2.6 Directed search optimization scheme for structural analysis by tensor LEED.
extensive explorations of different starting points for the particular structural model type. These
ideas are developed further in our approach to the structural determinations discussed in this
thesis, especially those for the Rh(111)-(√7×√7)R19.1°-P and Cu(110)-\[
\begin{pmatrix}
2 & 2 \\
-1 & 1
\end{pmatrix}
\]-P surfaces.
Chapter 3 Experimental methods

3.1 UHV system

Ultrahigh vacuum (UHV) conditions (pressures $10^9$ Torr or less) are generally required for modern surface science research. There are two main reasons: (i) Many surface science techniques utilize free particles such as electrons and ions, and these particles need sufficiently long mean free paths (e.g., several cm or more) in order to reach the sample and detector without being affected significantly by collisions with gas phase molecules. This normally requires a background gas pressure below $10^4$ Torr. (ii) Fundamental studies often need to start with a clean and well characterized sample surface, and to keep such a surface free of significant residual gas contamination during the experimental time span. Kinetic gas theory [3] indicates that for a pressure of $2 \times 10^{-10}$ Torr, a “clean” surface could be covered by a monolayer (ML) of residual gas molecules within one hour for a sticking coefficient of unity. In practice, sticking coefficients (i.e., the probability that an impinging particle becomes adsorbed) are often less than unity, but it is clear that background pressures around $10^{-10}$ Torr or less are necessary for well-controlled research. An additional advantage of conducting experiments in a UHV environment lies in the fact that it helps to achieve longer instrument lifetimes, especially for fragile components such as filaments, channeltrons and channel plates.

Surface science experiments are commonly conducted in non-magnetic stainless-steel chambers connected with a series of vacuum pumps, and the chamber has a number of ports for hosting various surface science instruments and ancillary components. Vacuum seals between flanges are made using copper gaskets pinched between steel knife-edges. Figure 3.1 shows a schematic drawing of the UHV chamber (Varian 981-2001) used for the various projects in this
Figure 3.1 Schematic diagram (topview) of the Varian UHV chamber and associated arrangement of various instruments.
thesis. The chamber is equipped with four-grid LEED optics (Varian 981-0127), a single-pass cylindrical mirror analyzer (CMA, Varian 981-2607) for AES measurement, an Ar⁺ sputtering gun for sample cleaning, a quadrupole mass spectrometer for ambient gas assessment and a fine-controlled leak valve for gas dosing (for chemisorption or sample cleaning processes). Figure 3.2 shows the arrangement of pumping systems and gas lines associated with this UHV chamber. The procedures for attaining pressures in the 10⁻¹⁰ Torr range are standard and involve roughing with the sorption pump (to ~ 10⁻³ Torr), followed by the use of diffusion pump (to ~ 10⁻⁶ Torr), ion pump (to low 10⁻⁸ Torr range), baking (e.g., 12 hrs at 120 - 150°C) and outgasing of all filaments. Extra pumping was available with the titanium sublimation pump. Pressures were measured with the thermocouple gauge (for pressure range 10 - 10⁻³ Torr) and ion gauge (10⁻⁴ - 10⁻¹¹ Torr). The whole sample stage is mounted on a precision manipulator with capability of three translational motions (x, y, z) and two rotational motions (polar and flipping), so that the sample can be appropriately positioned for Ar⁺ sputtering or for LEED and AES measurements.

3.2 Instrumentation

3.2.1 LEED

The Varian LEED system used for this work has two main parts: an electron gun and a detector system as schematically illustrated in Fig. 3.3. The electron gun contains a tungsten cathode for providing the electron emission, a set of lenses for focusing and deflection, and a drift tube. For the energy range of around 30 to 300 eV, this gun typically gives a beam of diameter 1 mm or less over the sample (about 10 cm away), a current of around 1 µA and an energy spread less than 1 eV. The filament assembly is mounted at a small angle off the main gun axis to provide optical baffling of the filament from the exit aperture, and this also prevents
Figure 3.2 Schematic diagram of pumping systems and gas line for UHV chamber.
Figure 3.3 Electron gun and detection system used for LEED.
any contamination of the sample by evaporation of cathode material. In the usual mode of operation, the drift tube is grounded, as is the sample, so that the electrons travel in field-free space.

The detector system includes a fluorescent screen and a set of hemispherical grids as shown in Fig. 3.3. The first grid is grounded, but the second and third grids are connected and biased at a potential slightly less than the primary electron energy to ensure that essentially only the elastically scattered electrons can pass through and reach the fluorescent screen. The fourth grid is grounded to shield the field due to the positive bias at the fluorescent screen (~ 5 keV). A set of Helmholtz coils are placed around the chamber to cancel any magnetic disturbance, especially from the earth's field.

### 3.2.2 Auger electron spectroscopy

A single-pass cylindrical mirror analyzer (CMA) with glancing incidence electron gun (Fig. 3.4) is used for measuring the intensity of Auger electrons. The gun design is similar to that in the LEED system, but it is set to provide higher beam energy (3 - 5 keV) and current (100 µA at 3 keV), and the beam size is smaller (around 0.5 mm). The CMA was first introduced for surface analysis by Palmberg et al. [59]. It consists of two co-axial cylinders; the inner one is grounded while the outer cylinder has a deflecting potential -V. Auger electrons emitted from a sample on axis, at an angle α, pass through the entrance aperture and those of a particular energy E are deflected by the outer cylinder back through the exit aperture to a focus (also on axis), where an electron multiplier is placed. The angle α is set at around 42.3°, which ensures second-order focusing and a high transmission for a given energy resolution [60]. The larger incident
Figure 3.4 Single-pass CMA with glancing electron gun for AES.
energy is chosen because ionization cross-sections for an initial core level are typically optimized with primary energies around 3 – 5 times the core level binding energy [41].

The Auger electron signal is small on a large background of secondary electrons, and therefore in practice AES measurements are often made in the derivative mode. This is accomplished by superimposing a small modulating voltage ($v_0 \sin \omega t$) on the deflecting voltage (which is swept over a finite range of interest, typically 40 - 1000 eV), and the current at the electron multiplier with modulation frequency $\omega$ is synchronously detected with a lock-in amplifier. This directly generates the Auger spectrum (in $dN(E)/dE$ vs. E form) [41], which can be recorded on an x-y plotter or displayed on an oscilloscope. A CMA improves the signal-to-noise ratio (by $\sim 10^2$) over a retarding field analyzer based on a four-grid LEED optics. In principle, it can detect less than 1% of a monolayer of impurity.

3.3 Sample preparation

Samples used in the work described in this thesis were originally cut by spark erosion from single crystal rods (Cu 99.999% from Dr. A. Akhtar; Rh 99.99% from LEICO) after orientation with Laue X-ray diffraction [61,62]. In each case, polishing of the sample surface started with a planetary lapping system using progressively finer grades of diamond paste (from 9 to 1 $\mu$m), and hand polishing was used to finish with 0.3 and 0.05 $\mu$m alumina powder. From time to time during the polishing process, the sample orientation was rechecked by Laue X-ray diffraction, while the optical alignment was done with a He/Ne laser [63]. A typical sample for LEED study has an optically shining face, and is about 1 mm thick and 8 mm in diameter.

After the initial preparation, the polished single crystal samples were cleaned and ordered in the UHV chamber. The Cu(110) sample was mounted on a molybdenum cup, and heated
resistively with a thermal heater at the back; the Rh(111) sample was mounted on a tantalum plate, and heating provided by electron bombardment. Sample temperatures were measured by an alumel-chromel thermocouple (to 1000°C) spot-welded to the molybdenum cup/tantalum plate or by a pyrometer (above 1000°C). The main impurities on the Cu(110) were carbon, chlorine and sulfur [61]. The initial cleaning involved cycles of gentle ion bombardment ($5 \times 10^5$ Torr Ar, accelerating voltage 400 - 600 V, 2 - 4 hrs at current density ~ 2 $\mu$Acm$^2$) followed by a 10 - 15 min anneal at 550 - 700°C. These steps efficiently removed the carbon and chlorine, but many more bombardment / anneal cycles were needed to remove sulfur which segregated to the surface from the bulk at above 500°C. Hence lower anneal temperatures (e.g., 450°C) were used in the final stages of cleaning after the sulfur content had been depleted. Similarly carbon and sulfur were the main impurities found on the initial Rh(111) sample surface [62]. Cycles of Ar$^+$ bombardment (800 V, 1 hr at current density ~ 5 $\mu$Acm$^2$) followed by a 15 min anneal at 1000°C proved effective for reducing levels of carbon and sulfur contamination.

After the initial cleaning and ordering phase, the cleaning procedures on a day-to-day basis for the Cu(110) sample involved Ar$^+$ bombardment (800 V, 40 min at current density ~ 6 $\mu$Acm$^2$), followed by an anneal (450°C, 20 min). A similar Ar$^+$ bombardment treatment was done for the Rh(111) sample, but the annealing required a brief flash to 1100°C. Throughout, AES and LEED were used regularly during the sample treatments to check the surface cleaning and ordering. A sample surface is considered sufficiently clean and well-ordered for further study if no impurities are seen within the AES detection limit and a sharp (1x1) pattern is observed with low background. Figures 3.5 and 3.6 show Auger electron spectra for Cu(110) and Rh(111) samples taken during and after the cleaning processes.
Figure 3.5 Auger spectra for Cu(110) surface during (a) and after the cleaning process (b).
Figure 3.6 Auger spectra for Rh(111) surface during (a) and after the cleaning process (b).
3.4 I(E) curve measurement and data processing

All experimental data used in these studies were measured for normal incidence with a video LEED analyzer (VLA, Data-Quire Co., Stony Brook, N.Y.) connected to an IBM PC (Intel 486, 66 MHz) as indicated in Fig. 3.7. This approach for measuring intensities of diffracted beams involves two electron/photon signal conversions: (i) from diffracted beam electron flux to photon flux from the LEED screen; and (ii) from photons from the screen to electrons by the silicon-intensified TV camera positioned in front of the viewing port. The final signals are transferred to the PC where data are stored and processed, and to a TV monitor on which the diffraction pattern can be displayed. Through a digital/analog (D/A) interface, the energy of the incident beam can be changed as preprogrammed on the PC. The software (Data-Quire Co.) was used to extract the beam intensities. Adjustable “scanning windows” (e.g., 10 x 10 pixel) covered the diffracted spots and automatically tracked them as the incident electron energy was varied. The intensity of each spot is attained by summing the digitized signal within each window. To increase the signal-to-noise ratio, multiple scanning was used (typically 10 scans for intense beams and 20 or more for weaker beams).

Normal incidence was attained by comparing I(E) curves measured for those beams which are expected to be symmetrically equivalent, and adjusting the polar and tilting angles of the sample until the intensity curves matched closely. Although the method for measuring the diffracted beam intensities on the screen is somewhat indirect, tests have shown that the measured I(E) spectra can be essentially identical to those measured more directly with a movable Faraday cup [64]. The electron-to-photon-to-electron conversions are basically linear provided the diffracted beam intensities vary only around two orders of magnitude (i.e., from the strongest to the weakest beam intensities, which seems sufficient for current LEED crystallographic study). The special advantage of the VLA method lies in its ability to greatly...
Figure 3.7 Block diagram of the video LEED analyzer (VLA) used for measurement of LEED intensities.
shorten the time required for the measurements (by approximately an order of magnitude compared with the Faraday cup method). Even so measurements with the VLA for twelve symmetrically inequivalent beams (e.g., over range 30 - 250 eV, interval 1 eV, including multiple scanning over all available equivalent beams) can take at least two hours. Independent sets therefore have to be measured, ideally with the beams being measured in different sequences each time. For a less stable surface (not a problem in this work though), measurements need speeding up (e.g., by measuring a smaller number of equivalent beams at one time, less multiple scanning).

The raw data were then stored and processed in the computer. The first step of processing is to normalize the measured diffracted beam intensities to a constant incident beam current according to

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

(3.1)

where \( i \) and \( i_0 \) are measured diffracted and incident currents respectively. This step is necessary because the current from the LEED gun varies significantly with energy, especially below 120 eV. The second step involves averaging the summed intensities for the symmetrically equivalent beams; this helps minimize any error associated with small surface misalignment [65]. The final processing step involves smoothing the \( I(E) \) curves to reduce any noise which could affect the later R-factor comparisons with the calculated curves (Chapter 2). Software developed by K.C. Wong [66] which used a Fourier-transform smoothing scheme was used for this task. Figure 3.8 gives examples to illustrate the averaging and smoothing procedures applied to the measurement of experimental intensities for the P/Rh(111) system (Chapter 7), while Fig. 3.9 compares two sets of \( I(E) \) curves measured from independently prepared surfaces. The correspondence between the latter surfaces appears at a good level.
Figure 3.8 I(E) curves for four symmetrically equivalent beams (a)-(d), and those after averaging and smoothing.
Figure 3.9 Comparison of two sets of I(E) curves measured from independently prepared Rh(111)-(√7x√7)R19.1°-P surfaces.
Chapter 4 Structural analysis for the Cu(110)-c(6x2)-O surface

4.1 Introduction

The reconstructions induced by oxygen on the (110) surface of copper have provided an interesting and important problem for surface structural chemistry [67]. In summary, surfaces with (2x1) and c(6x2) translational symmetries are formed respectively at 1/2 and 2/3 monolayer (ML) coverages of O. The structural details for the lower-coverage form have been intensively studied by many surface techniques (e.g., LEED, STM, SXRD, LEIS, SEXAFS) [67], from which the so-called “added row” model is now quite well established [68] (see also Chapter 5). By comparison, although guidance to the broad features of the higher coverage c(6x2) form has been provided by a range of structural investigations [67], including STM [69-71], SXRD [69,72] and LEIS [10c,73], no detailed LEED analysis has been conducted on this surface, and the lack of full geometric information could inhibit the development of further understanding for such a complex structure. By building on the previously obtained results, the present study used LEED in an attempt to gain more precise information for the Cu(110)-c(6x2)-O surface structure. In turn, it is hoped that this work can lead to an identification of the principles involved in the structural evolution for the O on Cu(110) surface system.

4.2 Experiment

The experiment was conducted in a UHV chamber (base pressure 2x10^{-10} Torr) as described in Chapter 3. The sample was cut and polished to within 0.2° of the (110) plane following standard procedures [61]. Typical cleaning and ordering cycles as detailed in Chapter 3 were applied until no impurities could be detected by AES, and LEED showed a sharp (1x1) diffraction pattern with
low background. The optimal c(6x2) patterns were obtained using the following recipe: the cleaned Cu(110) surface at 300°C was exposed to $6 \times 10^5$ Torr of oxygen for 3 min ($\sim 1 \times 10^4$ Langmuir, $1 \text{ L} = 10^{-6}$ Torr s), followed by a 10 min anneal at the same temperature. Intensity-versus-energy ($I(E)$) curves were measured from such a surface, using a video LEED analyzer, for the 13 inequivalent beams designated $(1\ 1)$, $(0\ 1)$, $(1\ 0)$, $(0\ 2)$, $(2\ 0)$, $(2\ 1)$, $(1/2\ 1/2)$, $(0\ 2/3)$, $(1/2\ 5/6)$, $(3/2\ 1/2)$, $(1\ 2/3)$, $(0\ 4/3)$, and $(1\ 4/3)$, and the beam notation is indicated in Fig. 1.4. The total energy range of the measured intensities is 1575 eV, with 947 and 628 eV for the integral and fractional beams, respectively.

4.3 Calculation

The multiple-scattering calculations for the LEED $I(E)$ curves are done in the context of the tensor LEED method (Chapter 2) [31]. The combined-space (CS) formalism was used to calculate diffraction matrixes for up to three atomic layers, with O atoms being included in the topmost Cu layer. Layer stacking was accomplished with the renormalized forward scattering (RFS) method. This work used the TLEED programs provided by Van Hove [74], and comparisons of intensity curves were done using the R-factor ($R_P$) introduced by Pendry [54]. Non-structural parameters used in the calculations are specified as follows. Atomic phase shifts were used up to $l = 7$: those for copper were derived from a band structure calculation [75], and those for oxygen were first used by Demuth et al. [76]. The real part of the constant potential between all muffin-tin spheres ($V_{0r}$) was initially set at -10 eV, although it was continually refined during the analysis; the imaginary part ($V_{0i}$) was fixed at -5.0 eV throughout. The Debye temperature was kept at the bulk value (343 K) for all Cu atoms, while that for O (684 K) was chosen so all vibrating atoms probed by LEED have a constant root-mean-square amplitude [29].
4.4 Structural analysis

4.4.1 Primary structure

The primary structural type emphasized in this work is that proposed by Feidenhansl et al. [69] (Fig. 4.1). A range of starting reference structures were considered for the TLEED analysis, based on previous investigations and plausible bond length arguments (i.e., Eq. (1.15)) [44], and $R_p$ guided the optimization of correspondence between the experimental and calculated $I(E)$ curves by varying coordinate values for 15 atoms per unit mesh (one, four and six Cu atoms in the first, second and third metal layers respectively, plus four O atoms). Local minima appear through the analysis, but the best match reached between the intensity curves is shown in Fig. 4.2. As discussed below, this is believed to be a fully stable result, and the atomic coordinates for the optimized geometry are listed in Table 4.1. The parameters in the final structure converged well in the analysis (atomic displacements in the final structure are never more than 0.02 Å from those assumed in the closest reference structure). The minimum $R_p$ value is 0.271, and this indicates a good level of agreement for such a relatively complex structure. In turn, this analysis provides strong independent support for the basic structural model shown in Fig. 4.1. In the first instance, this model can be considered as formed from two O-Cu-O-Cu chains for every three Cu-Cu substrate spacings in the [1 1 0] direction, with additional Cu atoms on the "empty substrate row" to join the most separated Cu-O-Cu-O chains. The Cu and O atoms in the chain inevitably displace respectively off the original center and long-bridge sites of the Cu(110) substrate.

4.4.2 Other models considered

In the early part of the analysis, the two other model types indicated in Fig. 4.3 were also considered. Both models I and II maintain the characteristic diamond-shaped arrangement of
Figure 4.1 Basic form of the Cu(110)-c(6x2)-O surface corresponding to 2/3 ML O as reviewed in Ref. [67]. The small dark circles represent O atoms, and the larger circles are Cu atoms. The darkness of shading for Cu atoms indicates their relative heights (see also Fig. 4.4).
Figure 4.2 Comparison of experimental I(E) curves (dot-dashed lines) measured for normal incidence from the Cu(110)-c(6x2)-O surface structure with those calculated (solid lines) for the favored geometry according to the tensor LEED analysis.
Table 4.1 Atomic coordinates in Å for the TLEED-determined structure of the Cu(110)-c(6x2)-O surface. The atomic labels are defined in Fig. 4.4. The z-direction is perpendicular to the surface, and the x- and y-directions are parallel to [001] and [1 1 0] respectively.

<table>
<thead>
<tr>
<th>Atomic label</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x</td>
</tr>
<tr>
<td>O1</td>
<td>0</td>
</tr>
<tr>
<td>O2</td>
<td>0</td>
</tr>
<tr>
<td>Cu1</td>
<td>0</td>
</tr>
<tr>
<td>Cu2</td>
<td>1.65</td>
</tr>
<tr>
<td>Cu3</td>
<td>-1.65</td>
</tr>
<tr>
<td>Cu4</td>
<td>1.65</td>
</tr>
<tr>
<td>Cu5</td>
<td>-1.65</td>
</tr>
<tr>
<td>O3</td>
<td>0</td>
</tr>
<tr>
<td>O4</td>
<td>0</td>
</tr>
<tr>
<td>Cu6</td>
<td>0</td>
</tr>
<tr>
<td>Cu7</td>
<td>0</td>
</tr>
<tr>
<td>Cu8</td>
<td>0</td>
</tr>
<tr>
<td>Cu9</td>
<td>0</td>
</tr>
<tr>
<td>Cu10</td>
<td>0</td>
</tr>
<tr>
<td>Cu11</td>
<td>0</td>
</tr>
<tr>
<td>bulk repeat vector</td>
<td>1.807</td>
</tr>
<tr>
<td>2D repeat vectors</td>
<td>3.615</td>
</tr>
<tr>
<td></td>
<td>3.615</td>
</tr>
</tbody>
</table>
Figure 4.3 Two additional c(6x2) models considered in the TLEED analysis.
“added” Cu atoms as indicated in STM studies [69-71] on this c(6x2) surface. In fact, structure I also possesses reconstruction formed by two O-Cu-O-Cu chains for every three Cu-Cu substrate spacings in the [1 \bar{1} 0] direction, the same as the primary structure. The only difference here is that the additional Cu atoms are on the "neighboring substrate row" to join two neighboring Cu-O-Cu-O chains. The TLEED analysis quickly ruled out these two models since the $R_p$ values obtained were always in the 0.60 - 0.80 ranges and the visual comparisons of the experimental and calculated I(E) curves show unambiguously a much poorer agreement.

4.4.3 Structural features

The new structural features for the Cu(110)-c(6x2)-O surface structure can be summarized as in the following (where reference is made to displacements indicated in Fig. 4.4 and Table 4.2):

(i) The Cu-O-Cu-O chains parallel to the [001] direction have a zigzag shape which directly results from the bonding between O atoms and the topmost Cu "adatoms". The width of the zigzag chain projected on to the (110) plane is about 0.58 Å; vertically, the O atoms at long-bridge sites (i.e., O3 and O4) reside around 0.20 Å below the second Cu layer, while the other O atoms which bond to a topmost Cu atom (i.e., O1 and O2) are about 0.31 Å above the second Cu layer, and are essentially coplanar with the topmost Cu adatoms. (ii) Each group of four Cu atoms in the second layer, which surround a topmost Cu adatom, are indicated to displace laterally by 0.33 Å from the "ideal" center site, approximately toward the group's center; a consequence is that the neighboring Cu-O-Cu-O chains shift away from each other by 0.59 Å along the [1 \bar{1} 0] direction. (iii) Substantial relaxations are also present in the third Cu layer (i.e., the first regular Cu(110)-type layer); these can be summarized as a vertical buckling and lateral displacements of magnitudes up to about 0.16 and 0.10 Å respectively. This vertical relaxation results directly from the lateral displacements in the
Figure 4.4 Specification of notation used for discussing the details of the Cu(110)-c(6x2)-O surface structure.
Table 4.2  Summary of structural parameters in Å which are defined in Fig. 4.4 and which specify relaxation effects in the Cu(110)-c(6x2)-O surface structure according to the TLEED analysis.

<table>
<thead>
<tr>
<th></th>
<th>$d_{12}$</th>
<th>$d_{23}$</th>
<th>$d_{34}$</th>
<th>$D_1$</th>
<th>$D_2$</th>
<th>$D_3$</th>
<th>$D_4$</th>
<th>$D_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.29</td>
<td>1.69</td>
<td>1.30</td>
<td>0.02</td>
<td>0.48</td>
<td>0.10</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>$l_1$</td>
<td>1.82</td>
<td>2.41</td>
<td>0.30</td>
<td>0.16</td>
<td>0.03</td>
<td>0.10</td>
<td>0.05</td>
<td></td>
</tr>
</tbody>
</table>
second Cu layer; these in effect amount to the combinations of atoms Cu6 - Cu7 and Cu8 - Cu11 being respectively lifted up and pushed down. Further, these third layer Cu atoms shift laterally so as to move closer to the O atoms to which they bond. (iv) As a consequence of the relaxations in (i) to (iii), the second- to third-Cu interlayer spacing \(d_{23}\) (defined by "center of mass" planes) increases to about 1.69 Å, an expansion of 31.9% from the bulk value (1.278 Å). This expansion is inevitably greater than the corresponding 16.3% expansion found in the (2x1)-O structure (Chapter 5), where the O atoms are almost coplanar with the topmost Cu atoms. For c(6x2), the third- to fourth-Cu interlayer spacing \(d_{34}\) expands by 1.4% from the bulk value; this observation appears generally appropriate given that the third Cu layer is involved in bonding to O atoms [77]. (v) The displacements noted above ensure that each O atom essentially maintains the four-fold coordination which is a distinctive characteristic of the 0.5 ML structures formed by O on the (100) and (110) surfaces of copper (see also Chapter 5). In Cu(110)-c(6x2)-O, each Cu atom in the topmost two metal layers bonds to two O atoms; additionally the first- and second-layer Cu atoms are also in the vicinity respectively of six and seven other Cu atoms.

4.5 Discussion

Table 4.2 summarizes structural parameters (see Fig. 4.4) which define relaxation effects in Cu(110)-c(6x2)-O according to the TLEED analysis. Some degree of comparison can be made with information from other surface structural techniques, especially SXRD [72] and LEIS [73], although the limits of reliability from all these techniques are often still uncertain, and moreover they can vary with the particular parameter type. For example, SXRD is likely to be most reliable for lateral displacements, particularly when only Cu atoms are involved. In that context, the value of the \(L_1\) parameter from TLEED (0.30 Å) appears in close correspondence with the values from SXRD (0.28 Å) and from LEIS (0.28 Å). Values from TLEED for \(l_1\) (1.82 Å) and \(l_2\) (2.41 Å), other
lateral parameters which involve the weaker-scattering O atoms, compare respectively with 1.76 Å and 2.53 Å from SXRD, and 1.78 Å and 2.47 Å from LEIS. Among the vertical displacement parameters, the TLEED values for $d_{12}$, $D_1$ and $D_2$ of 0.29, 0.02 and 0.48 Å respectively, compare with the corresponding values of 0.45, -0.05 and 0.57 Å from LEIS.

The largest discrepancies between TLEED and LEIS are for the lateral displacement $L_2$ (values 0.16 and 0.03 Å respectively) and for $d_{12}$, although other parameters are not independently identified by LEIS, for example $d_{23}$. If that value is assumed to equal 1.52 Å, guided by the (2x1) structure (Chapter 5), then the $R_p$ value for $I(E)$ curves calculated as well as possible for the (extended) LEIS result is 0.490. This is obviously much greater, and visual analysis confirms a far inferior calculation-experiment comparison, than for the value (0.271) for the final structure reported here. Nevertheless the FD/TLEED analysis from the LEIS starting point does converge to the structure defined in Table 4.2, and in that sense our structural details for Cu(110)-c(6x2)-O can be seen as arising from a refinement of the LEIS structure.

Another possible point of comparison for the TLEED result is provided by a conclusion from STM studies on Cu(110) surfaces, with co-existing (2x1)- and c(6x2)-O regions, that the topmost Cu adatoms in c(6x2) are above the (2x1) structure by 0.6 Å [69,71]. Using the TLEED results for c(6x2)-O and (2x1)-O (Chapter 5), and the assumption that the fourth Cu layer in (2x1) is coplanar with the fifth Cu layer in c(6x2), the height difference between these two surface regions is indicated to be 0.52 Å. An independent and preliminary LEED study [78] would predict 0.85 Å for this separation, although another STM study by Coulman et al. [70] indicated that this value may appear to vary from 0.3 to 0.8 Å depending on the specific experimental conditions.

The Cu-Cu bond distances for Cu atoms 1 and 2 differ somewhat from the value in the bulk metal (2.556 Å), and this reflects the different bonding situation for the Cu adatoms, particularly their bonding to short-bridge sites of the regular fcc(110) structure, and the subsequent relaxations.
The adatom Cu1 has six metal atom neighbors, and these Cu-Cu distances are indicated by the TLEED analysis to have magnitudes equal to 2.41 Å (two) and 2.81 Å (four), to give an overall average of 2.68 Å. For Cu2, the distances to neighboring Cu atoms range from 2.57 Å (to Cu8) to 3.16 (to Cu5) to give an average of 2.87 Å over the seven neighboring metal atoms.

Further in c(6x2), the average O-Cu bond length of 1.85 Å for a topmost O atom, which bonds to just one third-layer Cu atom (which itself also bonds to 10 other Cu atoms), is clearly indicated, as expected, to be shorter than that (1.94 Å) for the lower O atoms, which each bond to two third-layer Cu atoms. Overall, the average O-Cu bond length in c(6x2) structure was determined to be 1.90 Å. This corresponds closely with the values in the Cu(110)-(2x1)-O (1.91 Å) and Cu(100)-(2√2x√2 )R45°-O (1.89 Å) surfaces, although it is slightly longer than that in the bulk Cu2O structure (1.85 Å). The similarities between these four structures are indicated further in the next chapter.
Chapter 5  What determines the structures formed by O chemisorbed on low index surfaces of Cu?

5.1  Introduction

The interaction of O with low-index single-crystal surfaces of copper has been widely studied for many years with many different surface techniques (e.g., LEED, STM, SXRD, LEIS, SEXAFS), and a comprehensive review was published recently [67]. There are several reasons why there is high interest in these studies: (i) The kind of surface reactions observed relate to a number of important technological processes such as bulk oxidation, corrosion, and heterogeneous catalysis [1]. (ii) The strong O-Cu bonding resulting from the chemisorption often also involves the breaking of metal-metal bonds and the creation of a series of unique types of reconstructed surfaces, which have provided great challenges to the various surface techniques. (iii) Through extensive study of the structural details associated with the formation of these O/Cu surfaces, there is an expectation that the sort of information obtained can help understand the reasons why a particular structural type is chosen in each case, and hence lead to a broader understanding of the principles of surface structural chemistry.

The emphasis in this chapter is on the results from tensor LEED analyses for three reconstructed O/Cu surfaces: specifically the \((2\sqrt{2} \times \sqrt{2})R45^\circ\) structure formed on Cu(100), as well as the \((2x1)\) and \(c(6x2)\) structures formed on Cu(110). The O coverages are generally believed to correspond to 1/2, 1/2 and 2/3 monolayer (ML) respectively. Both the \((2x1)\) and \((2\sqrt{2} \times \sqrt{2})R45^\circ\) surfaces have been previously investigated by H.C. Zeng et al. [68b,79] and several other groups [80,81] using the conventional LEED method, and the basic structure types have been confirmed by other techniques [67]. But it is hoped that the refined analyses of these
two structures by tensor LEED can add geometrical detail, to the level now obtained for c(6x2) surface (Chapter 4), so that further understanding can be developed on why these structures are built. In fact, the case is made here that in detail these different structures have a number of basic features in common, and that these features appear relevant in establishing the reasons that the particular structures occur as favorable forms. Comparisons are additionally made with other related systems, specifically those formed by O interacting with Ag surfaces, O with Ni surfaces, and N with Cu surfaces.

5.2 Re-analysis of the Cu(110)-(2x1)-O surface

New experimental measurements were made for the (2x1) surface following standard procedures (see Chapter 4) in which surface cleanliness was assessed with Auger electron spectroscopy and surface ordering by LEED. The (2x1) surface was prepared by exposing the cleaned, well-ordered Cu(110) surface at 400°C to $6 \times 10^{-7}$ Torr of $O_2$ for 15 min, followed by an anneal for 6 min at the same temperature. Intensity-versus-energy (I(E)) curves for normal incidence were measured at room temperature with a video LEED analyzer. After averaging the symmetrically-equivalent beams, data were available for 12 independent beams over a total energy of 1906 eV (968 eV for six integral beams and 938 eV for six fractional beams), which are designated as (0 1), (1 0), (1 1), (0 2), (2 0), (2 1), (0 1/2), (1 3/2), (1 1/2), (2 1/2), (0 3/2) and (2 3/2), using the beam notation indicated in Fig. 1.4.

The LEED calculations were done in the context of tensor LEED [31], and comparisons of experimental and calculated I(E) curves were done using the R-factor ($R_p$) introduced by Pendry [54]. The non-structural parameters used were those for the c(6x2) surface as detailed in the previous chapter.
The structural analysis was mainly focused on the well-established “added row” model (Fig. 5.1). The best correspondence reached between the experimental and calculated I(E) curves for the (2x1) surface is shown in Fig. 5.2; it corresponds to a minimized R_p value equal to 0.299. In this analysis, the coordinates of one O and five Cu atoms (involving the top three metal layers) were varied within the unit mesh. The optimal coordinates of each atom and the associated structural parameters are listed in Table 5.1. This “added row” structure is characterized by Cu-O-Cu-O chains parallel to the [001] direction. The O atoms are indicated to be about 0.03 Å (d_o) above the long bridge sites of the “added Cu rows”, and to bond with four Cu neighbors; there are two pairs of Cu-O bond lengths, one pair to top layer Cu atoms at 1.81 Å, and the other to second layer Cu atoms at 2.01 Å. The comparisons in Table 5.1 also give an interesting indication of how the same structure is viewed by the techniques of low-energy ion scattering (LEIS) [82] and surface X-ray diffraction (SXRD) [68a], in addition to LEED [this work,68b,80]. It is clear that the various LEED and LEIS studies agree well in relation to the neighboring O-Cu distances for O bonding in long bridge sites.

5.3 Re-analysis of the Cu(100)-\( (2\sqrt{2}x\sqrt{2})R45^\circ \)-O surface

No new measurements were made for the \( (2\sqrt{2}x\sqrt{2})R45^\circ \) surface, and an earlier set of I(E) curves [79] was reused in this analysis; the six beams designated (1 0), (1 1), (1/2 1/2), (1/2 3/2), (3/2 3/2) and (3/4 3/4) (using notation identified in Fig. 1.4), were available for normal incidence over a total energy range of 691 eV. Again, the calculations were done in the context of tensor LEED using the same program package, non-structural parameters, and R_p as indicated above.
Figure 5.1 Schematic drawings for three surface structures: (I) Cu(110)-(2x1)-O, (II) Cu(110)-c(6x2)-O and (III) Cu(100)-(2√2x√2)R45°-O. The small dark circles represent O atoms, and the larger circles are Cu atoms. Interlayer spacings correspond to center-of-mass separations (e.g., \( d_{12} \)); spacings within a layer (e.g., \( d_{22} \)) correspond to the maximum vertical separations.
Figure 5.2 Comparison of experimental I(E) curves (dot-dashed lines) measured for normal incidence from the Cu(110)-(2x1)-O surface structure with those calculated (solid lines) for the favored geometry according to the tensor LEED analysis.
Table 5.1 (a) Atomic coordinates in Å for the TLEED-determined structure of the Cu(110)-(2x1)-O surface. The z-direction is perpendicular to the surface, and the x- and y-directions are parallel to [001] and [1 1 0] respectively.

<table>
<thead>
<tr>
<th>Atomic label</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x</td>
</tr>
<tr>
<td>O</td>
<td>1.807</td>
</tr>
<tr>
<td>Cu1</td>
<td>0</td>
</tr>
<tr>
<td>Cu2</td>
<td>1.807</td>
</tr>
<tr>
<td>Cu3</td>
<td>-1.807</td>
</tr>
<tr>
<td>Cu4</td>
<td>0</td>
</tr>
<tr>
<td>Cu5</td>
<td>0</td>
</tr>
<tr>
<td>bulk repeat vector</td>
<td>1.807</td>
</tr>
<tr>
<td>2D repeat vectors</td>
<td>3.615</td>
</tr>
<tr>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

Table 5.1 (b) Structural parameters (in Å) from different studies for the Cu(110)-(2x1)-O surface.

<table>
<thead>
<tr>
<th>Method</th>
<th>d_0</th>
<th>d_{12}</th>
<th>d_{23}</th>
<th>d_{33}</th>
<th>d_{34}</th>
<th>Δ_{Cu}</th>
<th>Cu-O bond lengths</th>
</tr>
</thead>
<tbody>
<tr>
<td>TLEED (this work)</td>
<td>0.03</td>
<td>1.49</td>
<td>1.29</td>
<td>0.03</td>
<td>1.25</td>
<td>0.03</td>
<td>1.81 (2), 2.01 (2)</td>
</tr>
<tr>
<td>LEED [68b]</td>
<td>0.04</td>
<td>1.49</td>
<td>1.21</td>
<td>0.03</td>
<td>1.25</td>
<td>0.03</td>
<td>1.81 (2), 2.01 (2)</td>
</tr>
<tr>
<td>LEED [80]</td>
<td>0.02</td>
<td>1.50</td>
<td>1.25</td>
<td>0.10</td>
<td>1.25</td>
<td>0.10</td>
<td>1.81 (2), 2.05 (2)</td>
</tr>
<tr>
<td>LEIS [82]</td>
<td>-0.08</td>
<td>1.51</td>
<td>1.28</td>
<td>0.12</td>
<td>1.28</td>
<td>0.12</td>
<td>1.81 (2), 2.00 (2)</td>
</tr>
<tr>
<td>SXRD [68a]</td>
<td>-0.34</td>
<td>1.65</td>
<td>1.28</td>
<td>0.031</td>
<td>1.85</td>
<td>0.031</td>
<td>1.84 (2), 1.85 (2)</td>
</tr>
</tbody>
</table>
The $(2\sqrt{2}x\sqrt{2})R45^\circ$ surface was earlier determined to have a "missing row" type structure [79] (Fig. 5.1). Compared with the previous LEED study, the TLEED analysis reduced the $R_p$ value from 0.326 to 0.240 (coordinates of 13 atoms per unit mesh were varied). The best correspondence reached between the experimental and calculated $I(E)$ curves is shown in Fig. 5.3, and the optimal coordinates of each atom and the associated structural parameters are listed in Table 5.2. The O atoms are indicated to be slightly above the topmost Cu layer ($d_o = 0.11\AA$), each bonded with four Cu atoms, and the resulting Cu-O bond lengths are 1.80 (1), 1.83 (2) and 2.12 Å (1), close to the previously indicated values (1.81, 1.84 and 2.04 Å, respectively) [79]. Referring to the lateral displacements of the topmost layer Cu and O atoms, this analysis shows that the Cu atoms next to the missing row are laterally displaced towards the missing row (by about 0.27 Å), while each O atom essentially stays directly above a second layer Cu atom. This result confirms the previous LEED analysis, and corresponds closely to observations with SXRD [83] and STM [84,85] that suggested Cu displacements of around 0.30 - 0.35 Å. Another unique feature found is that the topmost layer Cu atoms are not coplanar, instead Cu atoms in the Cu-O-Cu-O rows are relaxed vertically outwards with respect to the neighboring "clean" Cu rows (separation about 0.11 Å), in close correspondence with earlier results from LEED [79].

5.4 Common features and the analogies to bulk Cu$_2$O

Figure 5.1 indicates schematically the three related O/Cu structures considered here, namely the Cu(110)-(2x1)-O (I), Cu(110)-c(6x2)-O (II) and Cu(100)-$(2\sqrt{2}x\sqrt{2})R45^\circ$-O (III) surfaces. Despite the differences in O coverages, reconstruction types and relaxations of individual Cu and O atoms, detailed analysis does show that these structures have certain key features in common: in particular each O atom bonds unambiguously to just four Cu atoms, the
Figure 5.3 Comparison of experimental I(E) curves (dot-dashed lines) measured for normal incidence from the Cu(110)-(2√2x√2 )R45°-O surface structure with those calculated (solid lines) for the favored geometry according to the tensor LEED analysis.
Table 5.2 (a) Atomic coordinates in Å for the TLEED-determined structure of the Cu(100)-(2√2x√2 )R45°-O surface. The z-direction is perpendicular to the surface, and the x- and y-directions are parallel to [011] and [01\bar{1}] respectively.

<table>
<thead>
<tr>
<th>Atomic label</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x</td>
</tr>
<tr>
<td>O1</td>
<td>1.26</td>
</tr>
<tr>
<td>O2</td>
<td>-1.26</td>
</tr>
<tr>
<td>Cu1</td>
<td>2.75</td>
</tr>
<tr>
<td>Cu2</td>
<td>-2.75</td>
</tr>
<tr>
<td>Cu3</td>
<td>0</td>
</tr>
<tr>
<td>Cu4</td>
<td>1.29</td>
</tr>
<tr>
<td>Cu5</td>
<td>-1.29</td>
</tr>
<tr>
<td>Cu6</td>
<td>1.278</td>
</tr>
<tr>
<td>Cu7</td>
<td>3.83</td>
</tr>
<tr>
<td>Cu8</td>
<td>0</td>
</tr>
<tr>
<td>Cu9</td>
<td>2.56</td>
</tr>
<tr>
<td>Cu10</td>
<td>-2.56</td>
</tr>
<tr>
<td>Cu11</td>
<td>2.556</td>
</tr>
<tr>
<td></td>
<td>1.278</td>
</tr>
<tr>
<td></td>
<td>2.556</td>
</tr>
<tr>
<td></td>
<td>5.112</td>
</tr>
</tbody>
</table>

Table 5.2 (b) Structural parameters (in Å) for the Cu(100)-(2√2x√2 )R45°-O surface.

<table>
<thead>
<tr>
<th>d_o</th>
<th>d_{12}</th>
<th>d_{23}</th>
<th>d_{34}</th>
<th>d_{11}</th>
<th>d_{22}</th>
<th>D_1</th>
<th>d_{33}</th>
<th>D_2</th>
<th>Δ_{Cu}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.11</td>
<td>2.06</td>
<td>1.78</td>
<td>1.83</td>
<td>0.15</td>
<td>0.17</td>
<td>0.13</td>
<td>0.14</td>
<td>0.10</td>
<td>0.27</td>
</tr>
</tbody>
</table>
TLEED determined average O-Cu bond lengths in the (2x1) (1.91 Å), c(6x2) (1.90 Å) and \((2\sqrt{2}\times\sqrt{2})R45^\circ\) (1.89 Å) structures match very closely, and each structure is composed of basic O-Cu-O building blocks of the sort used in the construction of bulk Cu_2O (Fig. 5.4) [86]. These features are summarized in Table 5.3 where comparison is also made with the corresponding parameters in the bulk Cu_2O structure.

In bulk Cu_2O, the O-Cu-O bond angle is 180° and the O-Cu-O building block length is 3.69 Å; it is clear that comparable values are found in each of the surface structures considered here. If the (2x1)-O structure is based on linear O-Cu-O-Cu chains, that for c(6x2)-O is strictly based on O-Cu-O fragments, which form the zigzag chains, and that for \((2\sqrt{2}\times\sqrt{2})R45^\circ\) has both features. Dimensions for the O-Cu-O block length for c(6x2) appear slightly more "Cu_2O bulk-like" compared with (2x1)-O and \((2\sqrt{2}\times\sqrt{2})R45^\circ\) (Table 5.3), but the strong tendency for O to have a four-coordinated bonding environment appears as a decisive factor for these O/Cu surface reconstructions and relaxations.

Nevertheless differences are not unexpected because in each surface situation a top layer has to match to the substrate, which inevitably has a different structure from the bulk oxide. Differences are apparent in the Cu-O-Cu angle, which has the tetrahedral value in bulk Cu_2O, but in the joining of the O-Cu-O units this angle usually opens. The ways that the O-Cu-O units join up are different in each case. Thus in the (2x1) structure each O is shared between two of these units, whereas in the c(6x2) structure half the O atoms are shared between two units, and the other half are shared between three units; in the \((2\sqrt{2}\times\sqrt{2})R45^\circ\) structure each O is shared between three O-Cu-O units.

Differences are also apparent with regard to the copper coordination number. For example, whereas in bulk Cu_2O each Cu atom bonds to two O atoms only, the surface situation is
Figure 5.4 Schematic diagram of bulk Cu$_2$O crystal structure. The small dark circles represent O atoms, and the larger circles are Cu atoms.
Table 5.3 Comparison of structural features for bulk Cu$_2$O and O/Cu surface systems.

<table>
<thead>
<tr>
<th></th>
<th>(2x1)</th>
<th>c(6x2)</th>
<th>(2√2x√2 R45°)</th>
<th>Cu$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>O coordination no.</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>lengths (in Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-O</td>
<td>1.91</td>
<td>1.90</td>
<td>1.89</td>
<td>1.85</td>
</tr>
<tr>
<td>O-Cu-O</td>
<td>3.62</td>
<td>3.65, 3.71</td>
<td>3.60, 3.66</td>
<td>3.69</td>
</tr>
<tr>
<td>angles</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>∠O-Cu-O</td>
<td>178°</td>
<td>179°, 169°</td>
<td>161°, 167°</td>
<td>180°</td>
</tr>
<tr>
<td>∠Cu-O-Cu</td>
<td>178°</td>
<td>104°, 166°</td>
<td>161°</td>
<td>109.5°</td>
</tr>
</tbody>
</table>
more complex, particularly for O bonding to the second layer metal atoms. Thus in the 
\((2\sqrt{2}\times\sqrt{2})R45^\circ\) structure, the second layer Cu atom which bonds to O also bonds to 11 other Cu 
atoms, which inevitably dilates the O-Cu distance. In any event, for matching to the substrate, the 
O-Cu distances parallel to the surface are most significant. All the surface structures give a 
relationship to the bulk Cu$_2$O form because in each the distance across the three atom O-Cu-O 
unit can match closely to the metallic substrate with only small distortions (less than 3%).

Since other studies have confirmed the formation of bulk Cu$_2$O at oxygen exposures on 
Cu(110) higher than those which yield the c(6x2) surface [87], any relationships between these 
structures could be helpful for understanding the structural evolution. In this connection, Fig. 5.5 
indicates the similarities between the (211) plane of Cu$_2$O and the topmost layers of the Cu(110)-
c(6x2)-O surface structure. It is clear that both have a double-stranded chain structure built from 
12-membered rings of alternating Cu and O atoms, and that the O to O distance in the O-Cu-O 
built blocks are equal to within about 1% (e.g., parameter p in Fig. 5.5). Given this analogy, 
two further differences are apparent: (i) The (211) plane of Cu$_2$O must be flattened in order to 
match to the surface structure. This is done by modifying the Cu-O-Cu angles in the 12-membered 
rings. These angles have the tetrahedral value \(109.5^\circ\) in Cu$_2$O, but of the six such angles in each 
ring in the c(6x2) surface structure, four reduce to 104°, but most significantly two increase to 166° 
(i.e., they approach the 180° already established in Cu(110)-(2x1)-O). (ii) The flattening required 
for the surface structure is also accompanied by a lateral shift in the direction of the chain 
(magnitude half the repeat distance) between the neighboring chains (otherwise a (3x2) surface may 
be expected). This appears to help stabilize the surface structure by reducing non-bonding 
interactions between the chains, e.g., the repulsive interactions between O atoms in neighboring 
double-stranded chains.
Figure 5.5 Comparison of superstructures formed on the Cu(110) substrate with planes of bulk Cu$_2$O: (a) (2x1), (b) (011) plane, (c) c(6x2) and (d) (211) plane. The small atoms are O and the larger atoms are Cu. The lightness or darkness of shading indicates position of the atoms below or above the plane of projection. In (b), the Cu atoms shown define the (011) plane, while in (d), the parallel three-atom O-Cu-O units define the (211) plane.
As a result of the chain flattening, it is noted that the parameter q in Fig. 5.5 increases from 6.04 Å in the (211) plane of Cu$_2$O to 7.23 Å in the c(6x2) surface structure, but this is a direct consequence of the Cu-O-Cu angle change already noted. The other parameter r, which has the value 7.395 Å in the (211) plane of Cu$_2$O, increases by about 3.7% to the 7.668 Å required for the match to the Cu(110) substrate. This close match appears to give further insight to the appropriateness of the (211) plane of Cu$_2$O for providing a basis for the Cu(110)-c(6x2)-O surface structure.

Incidentally, the Cu(110)-(2x1)-O structure can equally be seen as resulting from a flattened and elongated form of the (011) plane of Cu$_2$O (Fig. 5.5). For the (2x1) structure, the interchain separation increases from 4.27 Å in the bulk to 5.11 Å on the surface, but this value is set by twice the Cu-Cu nearest neighbor distance. Interchain repulsions between neighboring O-Cu-O-Cu chains appear too large to allow the formation of any (1x1) patches on the surface [88], but weak attractive interactions between the Cu-O-Cu-O chains (10 meV per Cu-O bond) in the (2x1) arrangement may help stabilize that structure [67,71].

According to these arguments, both the (2x1) and c(6x2) surface structures can be seen as being related to distorted forms of the Cu$_2$O crystal planes. On that basis, the driving force for the structure evolution from (2x1) to c(6x2) on Cu(110) is governed by the modified (211) plane of Cu$_2$O being able to accommodate an increase in O coverage compared with the modified (011) plane. Additionally, as the O coverage increases, so does the "added" Cu coverage; the latter changes from 0.5 to 0.83 ML with respect to the Cu(110) substrate. Thus the evolution in surface stoichiometry from the (2x1) to the c(6x2) forms can be summarized as

$$(2x1) \ (1/2 \ ML \ O + 1/2 \ ML \ Cu) + 1/6 \ ML \ Cu_2O \to c(6x2) \ (2/3 \ ML \ O + 5/6 \ ML \ Cu)$$
5.5 Comparisons with other surfaces

The interaction of O with the Cu(111) surface yields two ordered surface structures with unit mesh areas 29 and 44 times larger than that of the (1x1) substrate. Although details of such complex structures are still unknown, interpretations based on STM, high energy ion scattering (HEIS), nuclear reaction analysis (NRA) and AES studies have assumed that they involve coincidence site superpositions associated with the (111) plane of bulk Cu$_2$O [89]. A start has also been made to study O interactions with the Cu(410) stepped surface, which is based on (100) terraces and (110) steps, using STM [90] and SXRD [83].

In other contexts, it may be noted that the 2/3 ML structure formed by O on Ni(110) is believed to have a related structure [67] to that for O on Cu(110), but there are also differences, since the former has a (3x1) translational structure, which may derive from the bulk oxide for nickel (NiO) having a different structural type from Cu$_2$O [91]. By contrast, a (2x1) to c(6x2) structural evolution is also seen for O on Ag(110), and the similarities in the bulk structures of Ag$_2$O and Cu$_2$O (both have the same structural type) [91] appear to provide background to a determination by LEIS that indicated the same type of c(6x2) reconstruction on Ag(110) [92].

Improved understanding is required for the comparison between the observations noted here for O interacting with Cu surfaces, and those in related systems such as the O/Ni and N/Cu surfaces. Some guidance can be suggested by using the Pauling-type bond length - bond order relation as shown in Eq. (1.15), namely

\[ r(p) = r(1) - 0.85 \log p \]

where \( r(p) \) is the interatomic separation between M and X for bond order p. The single bond distance for the O/Cu surface systems can be parametrized by the appropriate bulk compound Cu$_2$O, whereas for O/Ni and N/Cu surfaces the bulk compounds NiO and Cu$_3$N offer similar guidance.
In $\text{Cu}_2\text{O}$, as noted above, each O atom bonds to four Cu atoms at 1.85 Å [86]. If it is assumed that O atoms may want to chemisorb on the center site of the Cu(100) surface, in analogy with the situation on Ni(100), then a plausible assumption would be that the O atoms position themselves in those sites so that each bonds to the four neighboring Cu atoms at 1.85 Å. A problem is that assumption brings O too close (2.20 Å) to the fifth Cu atom in the second metal layer to negate the initial assumption of four-fold coordination. An alternative is to start by assuming five-coordination; now Eq. (1.15), parametrized to bulk $\text{Cu}_2\text{O}$, suggests four O-Cu distances at 1.88 Å and one at 2.31 Å, although strictly this is likely to be taking the equation beyond its range of reliable operation, and it ignores differences in coordination numbers for the Cu atoms [93]. But in any event for initial guidance, the difference in the bond lengths seems too great for stable bonding; alternatively the angle (149°) in the O-Cu-O unit may appear rather far below 180°. One way of overcoming these (possible) deficiencies is to reconstruct the surface so that each O atom bonds to just four Cu atoms, with stronger overall bonding, and that is fully consistent with the three surface structures discussed here.

When the approach in the previous paragraph is applied to the O on Ni(100) surface, a difference is immediately seen. Now the parametrization based on bulk NiO [86] would predict that O can bond to the center site of Ni(100) with four bonds at 1.93 Å, in satisfactory correspondence with values 1.92 & 1.93 Å reported recently by LEED for these p(2x2) and c(2x2) structures [94]. Likewise simple chemisorption occurs for O on Ni(111) in both the (2x2) (0.25 ML) and the ($\sqrt{3}\times\sqrt{3}$)R30° (0.33 ML) structures, and the predicted O-Ni bond distance (1.82 Å) for O in a three-fold hollow site, agrees well with the recently-determined values (from 1.80 Å to 1.83 Å) [77,95].
Earlier studies for N on Cu(100) indicated that the parametrization with Cu$_3$N [86] can account for the fact that in this c(2x2) structure N bonds deeply down into the hollow site to become five-coordinate [96]. Indeed in this case the surface structure can be seen as involving incipient compound formation with a layer of Cu$_3$N(100) superimposed on the Cu(100) substrate; likewise the (2x3) N structure formed on Cu(110) can also be described as a (corrugated) layer of Cu$_3$N(100) superimposed on the Cu(110) substrate [97].

5.6 Concluding remarks

It is concluded from the studies reported in this chapter and Chapter 4 that the particular structures formed by oxygen at the (110) and (100) surfaces of copper have significant features in common. Each is believed to receive some stability from being able to fit O-Cu-O building blocks, of the sort needed to construct bulk Cu$_2$O, on to the surfaces, while ensuring that each O atom maintains its favorable four-coordinate status with reasonable O-Cu bond lengths.
Chapter 6 Structural analysis for the Cu(110)-[2 2
-1 1]-P surface

6.1 Introduction

In the previous two chapters, we have discussed some structures formed by O on the (110) and (100) surfaces of copper, and they demonstrate different ways for fitting O-Cu-O building blocks onto the substrates for the different experimental conditions. Somewhat similarly, both the Cu(100)-c(2x2)-N [96] and Cu(110)-(2x3)-N [97] surfaces may be seen as involving a layer of Cu₃N(100) superimposed on the Cu substrates. The interest here is to assess another related system, specifically for P bonded on the Cu(110) surface, and to compare the reconstruction and relaxations formed with those resulting from the smaller and lighter elements like N and O. Although many P to transition-metal bonding situations have been studied by X-ray crystallography [91,98], this element remains relatively unstudied as a chemisorbed species in quantitative surface structural chemistry [99]. Accordingly, this chapter reports a structural study with low-energy electron diffraction (LEED) for an ordered surface formed by P on Cu(110), designated as Cu(110)-

\[
\begin{pmatrix}
2 & 2 \\
-1 & 1
\end{pmatrix}
\] -P.

6.2 Experiment

The experiment was conducted in a UHV chamber with base pressure around 2x10⁻¹⁰ Torr, and the sample preparation and cleaning procedures were as described in the previous chapters. The adsorption behavior of PH₃ on the Cu(110) surface was monitored by following changes both in the diffraction pattern and in the ratio \( R = A_{120}/A_{60} \), where \( A_{120} \) and \( A_{60} \) are Auger peak-to-peak heights respectively for phosphorus at 120 eV and copper at 60 eV. Extensive study for this system
over exposures up to 5.0 L (1 Langmuir = $10^6$ Torr s) and annealing temperatures to 450°C identified just one ordered LEED pattern, which is designated $\begin{pmatrix} 2 \\ -1 \\ 2 \\ 1 \end{pmatrix}$ and illustrated schematically in Fig. 1.4. Optimal sharpness for this pattern was obtained by dosing PH$_3$ at $2 \times 10^{-8}$ Torr for 2 min on to the clean and well-ordered Cu(110) surface, followed by a 5 min anneal at 450°C and cooling to room temperature. It is believed that this annealing is sufficient to desorb any H atoms and physisorbed PH$_3$ [100]. This surface structure corresponded to $R = 0.49$, and it turned out to be very stable and non-reactive. For example, on keeping under UHV for seven days R did not change significantly, and the (1/2,1/2) beams remained almost as intense as the integral beams. Further dosing of PH$_3$ increased R, which indicates a higher P coverage, but the LEED pattern showed that this also led to increased background.

Intensity-versus-energy (I(E)) curves from a freshly-prepared, ordered surface were measured with a video LEED analyzer for sets of diffracted beams for normal incidence. After averaging symmetrically equivalent beams, data were available for 13 inequivalent beams, namely (1,0), (0,1), (1,1), (2,0), (0,2), (2,1), (1,2), (1/4,1/4), (3/4,1/4), (3/4,3/4), (5/4,3/4), (1/2,1/2) and (3/2,1/2) using the notation in Fig. 1.4. The total energy range covered is 1475 eV (1051 eV for the seven integral beams and 424 eV for the six fractional beams).

6.3 Calculation

In this work, the correspondence between the experimental and calculated I(E) curves was assessed with the many-beam reliability index ($R_P$) introduced by Pendry [54], and the tensor LEED approach [31] was used in order to make the calculations as efficient as possible. For the calculations, the surface region is modelled by a standard potential with the muffin-tin form. The atomic potential of copper was characterized by phase shifts up to $l = 7$ from a band structure.
calculation [75], whereas those for phosphorus were derived from a superposition potential derived by Lou and Mitchell [99]. The real part of the constant potential \( (V_{\text{re}}) \) between all muffin tin spheres was initially set at -10.0 eV, although this was refined during the calculations; the imaginary part of the constant potential \( (V_{\text{im}}) \) was fixed at -5.0 eV. The Debye temperature was kept at 343 K for all Cu atoms, which matches very closely the value optimized for the clean surface [101], while that for P (491 K) was chosen so all vibrating atoms probed by LEED have a constant root-mean-square amplitude [29].

6.4 Initial structural analysis

6.4.1 Model types

Calculations were made for eight different model types which are indicated schematically in Fig. 6.1. The models can be distinguished by the P coverage (0.25 ML for models 1 to 4, 0.5 ML for models 5 and 8, 0.75 ML for models 6 and 7), and by the form of the metallic structure near the surface. The Cu structure in the vicinity of P may be characterized as: (i) being unreconstructed (models 1 and 6); (ii) having Cu missing rows (models 3 and 4); (iii) having P rows substituted for Cu rows (models 2, 4 and 5); and (iv) having added Cu rows (models 7 and 8). All these models effectively have Cu-P-Cu-P chains parallel to the \([\bar{1}12]\) direction; this ensures consistency with the observed LEED pattern, which appears analogous to that formed by a 0.5 ML coverage of O on Cu(100) according to the \((2\sqrt{2}\times\sqrt{2})\)R45° structure designation (Fig. 1.4). In fact the only difference between these two diffraction patterns arises because the Cu(100) substrate is based on a square unit mesh, whereas that for Cu(110) is rectangular.

The tensor LEED calculations allowed variations in atomic coordinates, for P and for the first three metal layers, in order to optimize the fit to the experimental I(E) curves (i.e., minimize
Figure 6.1 Eight model types considered in the TLEED analyses for the P on Cu(110) surface structure where P atoms are represented by filled black circles. The open and dashed circles identify regular surface Cu atoms and missing Cu atoms respectively. The hatched circles represent Cu atoms added to the original metal surface.
RP); throughout deeper metal atoms were kept fixed at the bulk positions. For each model type, the initial reference structure also had all required Cu atoms at the bulk positions, while P atoms of radius 1.10 Å were placed in symmetrical sites. The iterative TLEED cycles were continued until all vertical and lateral displacements of the optimized atomic positions were no more than 0.02 and 0.06 Å respectively from the current reference structure. Optimized RP values are listed in Table 6.1 for each model type.

The R-factor analysis indicates that the best level of correspondence between the experimental and calculated I(E) curves is reached with the model type 8 (the corresponding set of optimized atomic coordinates are given in Table 6.2; see also Fig. 6.2 for atomic labels), and detailed visual comparison for the individual intensity curves also supports the ruling out of the other seven model types. This perhaps appears not unreasonable on other grounds. Aside from consistency with the LEED pattern, we have not found any strong chemical reason for the adoption of models 1 to 4, particularly as structures of high stability. Also, model 5 represents a combination of models 1 and 2, and, although not intrinsically impossible, variations in the stability of the two different P environments may be expected if this were the correct structure. Similar statements could be made for model 6 and 7 which both are based on chemisorbed P3 chains. However, it is noted that for model 7, the best RP value and the calculated I(E) curves appear somewhat close to those for model 8; this results from the fact that in the absence of relaxations the metal structure for model 7 is identical with model 8 and the structure just has one more P atom per unit mesh.

6.4.2 Rationalization of favored structural type

Bond length information is reported in Table 6.3. The details are assessed later, but the broader features of the structure are considered first. A key feature of model 8 is that the metallic structure reconstructs to allow each P atom to bond to six neighboring Cu atoms. The average P-
Table 6.1  Optimized $R_p$ values from TLEED analysis for the eight model types shown in Fig. 6.1 for the P on Cu(110) surface structure.

<table>
<thead>
<tr>
<th>Model</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_p$</td>
<td>0.359</td>
<td>0.359</td>
<td>0.391</td>
<td>0.344</td>
<td>0.352</td>
<td>0.578</td>
<td>0.290</td>
<td>0.255</td>
</tr>
</tbody>
</table>
Table 6.2 Atomic coordinates (in Å) for the TLEED-determined structure of the Cu-$\begin{pmatrix} 2 & 2 \\ -1 & 1 \end{pmatrix}$-P surface. The $\Delta x$ and $\Delta y$ are lateral displacements from appropriate high-symmetry sites, while the $\Delta z$ give vertical displacements from the center-of-mass plane for the appropriate atomic layer. The atom designations are identified in Fig. 6.2.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>$x (\Delta x)$</th>
<th>$y (\Delta y)$</th>
<th>$z (\Delta z)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1</td>
<td>3.615 (0)</td>
<td>2.556 (0)</td>
<td>0 (0)</td>
</tr>
<tr>
<td>P1</td>
<td>-0.20 (-0.20)</td>
<td>2.81 (0.25)</td>
<td>0.40</td>
</tr>
<tr>
<td>P2</td>
<td>0.20 (0.20)</td>
<td>-2.81 (-0.25)</td>
<td>0.40</td>
</tr>
<tr>
<td>Cu2</td>
<td>1.55 (-0.26)</td>
<td>1.25 (-0.03)</td>
<td>1.06 (-0.09)</td>
</tr>
<tr>
<td>Cu3</td>
<td>-1.55 (0.26)</td>
<td>-1.25 (0.03)</td>
<td>1.06 (-0.09)</td>
</tr>
<tr>
<td>Cu4</td>
<td>-1.807 (0)</td>
<td>1.278 (0)</td>
<td>1.17 (0.02)</td>
</tr>
<tr>
<td>Cu5</td>
<td>-5.421 (0)</td>
<td>-1.278 (0)</td>
<td>1.30 (0.16)</td>
</tr>
<tr>
<td>Cu6</td>
<td>0 (0)</td>
<td>0 (0)</td>
<td>2.50 (-0.06)</td>
</tr>
<tr>
<td>Cu7</td>
<td>3.615 (0)</td>
<td>2.556 (0)</td>
<td>2.56 (-0.01)</td>
</tr>
<tr>
<td>Cu8</td>
<td>-0.10 (-0.10)</td>
<td>2.66 (0.11)</td>
<td>2.60 (0.04)</td>
</tr>
<tr>
<td>Cu9</td>
<td>0.10 (0.10)</td>
<td>-2.66 (-0.11)</td>
<td>2.60 (0.04)</td>
</tr>
<tr>
<td>Cu10</td>
<td>1.82 (0.01)</td>
<td>1.41 (0.14)</td>
<td>3.79 (-0.03)</td>
</tr>
<tr>
<td>Cu11</td>
<td>-1.82 (-0.01)</td>
<td>-1.41 (-0.14)</td>
<td>3.79 (-0.03)</td>
</tr>
<tr>
<td>Cu12</td>
<td>-1.807 (0)</td>
<td>1.278 (0)</td>
<td>3.84 (0.02)</td>
</tr>
<tr>
<td>Cu13</td>
<td>-5.421 (0)</td>
<td>-1.278 (0)</td>
<td>3.86 (0.04)</td>
</tr>
</tbody>
</table>

bulk repeat 1.807 1.278 1.278
vector
2D repeat 3.615 -2.556 0
vectors 7.230 5.112 0
Figure 6.2 The Cu(110)-($\begin{pmatrix} 2 & 2 \\ -1 & 1 \end{pmatrix}$)-p surface structure: (a) one domain, (b) designation of atoms within the unit mesh.
Table 6.3 Some individual P-Cu and averaged Cu-Cu bond lengths (in Å); the latter are averaged over all neighboring bonds and the number of such neighbors is given in parenthesis in each case.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Neighbors</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1-Cu1</td>
<td>2.35</td>
<td></td>
</tr>
<tr>
<td>P1-Cu2</td>
<td>2.21, 2.43</td>
<td></td>
</tr>
<tr>
<td>P1-Cu4</td>
<td>2.35</td>
<td>Cu2-Cu 2.67 (x8)</td>
</tr>
<tr>
<td>P1-Cu5</td>
<td>2.43</td>
<td>Cu5-Cu 2.57 (x9)</td>
</tr>
<tr>
<td>P1-Cu8</td>
<td>2.21</td>
<td></td>
</tr>
<tr>
<td>Cu1-Cu</td>
<td>2.60 (x5)</td>
<td></td>
</tr>
<tr>
<td>Cu2-Cu</td>
<td>2.67 (x8)</td>
<td>Cu6-Cu 2.59 (x11)</td>
</tr>
<tr>
<td>Cu4-Cu</td>
<td>2.60 (x7)</td>
<td>Cu7-Cu 2.57 (x12)</td>
</tr>
<tr>
<td>Cu5-Cu</td>
<td>2.57 (x9)</td>
<td>Cu8-Cu 2.58 (x11)</td>
</tr>
<tr>
<td>Cu6-Cu</td>
<td>2.59 (x11)</td>
<td></td>
</tr>
<tr>
<td>Cu7-Cu</td>
<td>2.57 (x12)</td>
<td></td>
</tr>
<tr>
<td>Cu8-Cu</td>
<td>2.58 (x11)</td>
<td></td>
</tr>
</tbody>
</table>

* Due to the two-fold rotational symmetry, P2 has equivalent bonding situations as P1; similarly for the (Cu2, Cu3) and (Cu8, Cu9) groups.
Cu bond length is 2.33 Å. Information is sparse for assessing whether the P-Cu bond distances found by TLEED are reasonable, but the following argument gives some support.

As discussed in Chapter 1, surface bond lengths in many systems, where an electronegative atom X chemisorbs on a metal (M) surface, can often be related quite well to Eq. (1.15). No other surface structures are known to us for P on Cu, and the only established bulk compound appears to be Cu$_3$P [102]. The latter has a relatively complex structure, but from it a value of 2.04 Å can be deduced for r(1), and this in turn allows an estimation of the average P-Cu bond length expected for the P on Cu(110) surface structure. Using an average bond order, by taking s as the valency of P divided by its coordination number (i.e., as 3/6), Eq. (1.15) allows an estimate for the P-Cu bond length equal to 2.30 Å, which satisfactorily matches the average value of 2.33 Å given by the TLEED analysis for model type 8.

Another consideration is whether the structure identified appears reasonable in relation to the plausible alternatives. If P is to bond to the Cu(110) surface without subjecting it to a substantial reconstruction, this chemisorption would most likely occur on the center site, where its coordination number could in principle be four or five, depending on whether the distance between P and the second layer Cu atom directly below is beyond a normal bonding distance, or is within it. These possibilities can be assessed with Eq. (1.15), which can immediately rule out the four-fold coordination. Thus P bonding to four neighboring Cu atoms, with average bond order of 3/4 for each, and with r(1) of 2.04 Å, would require the P-Cu distance to equal 2.15 Å. This is even less than the value of 2.21 Å applying if P is co-planar with the topmost Cu atoms when, without considering metallic relaxations, P is only 1.28 Å from the Cu atom below in the second metal layer. The latter distance is unacceptably short in relation to the single bond value of 2.04 Å, and therefore it necessarily negates the initial assumption of four-fold coordination.
The next possibility is P bonded to the center site with 5-fold coordination. For this case, there are two different types of bonds, four of equal length to neighboring top layer Cu atoms, and one to the second layer Cu atom directly below P. These lengths are constrained by the metallic structure, and should not be varied independently, although Eq. (1.15) can be used to estimate the height above the surface at which P is consistent with its regular trivalency. For the ideal Cu(110) structure, that requires four bonds at 2.32 Å and one at 1.99 Å. The latter is still 0.05 Å less than the single bond distance, which again seems unlikely given that the Cu atom involved is itself already bonding to 11 other Cu atoms. For the somewhat similar case of S on Rh(110) [93], the short S-Rh bond is longer than the single bond distance by 0.23 Å, and this points to the 5-coordination arrangement being less likely for P on Cu(110). In turn, these arguments provide some background for the coordination number of six, for which, as noted above, the predicted bond lengths match in a broad sense to those found for P on Cu(110) in model type 8.

An alternative possibility extending from the favored model is that its missing rows are filled by Cu atoms. The P atoms would then be seven-fold coordinate, and Eq. (1), assuming all Cu atoms are in regular bulk positions, would require P-Cu bonds at 2.09 (1), 2.36 (4) and 2.60 Å (2). The first value still seems far too short, although it can be increased by metallic relaxation, as indeed occurs in the structure indicated here by TLEED for P on Cu(110). A more serious problem with the 7-coordinate model is that the translational symmetry is incorrect; it would likely revert to the c(2x2) form, or to (2x1) if the neighboring Cu-P-Cu-P rows are in phase.

In summary, we feel that model type 8, which is favored by the TLEED analysis, seems to provide the most "chemically plausible" model for the Cu(110)-\[
\begin{pmatrix}
2 & 2 \\
-1 & 1
\end{pmatrix}
\]-P surface structure. In essentials, the 0.5 ML of P reconstructs the original Cu(110) surface by adding 0.25 ML of Cu
atoms in rows parallel to the \([\bar{1}12]\) direction, and these in turn appear to be stabilized by bonding to the six-fold coordinate P atoms.

6.5 Refined structural analysis

6.5.1 Tests for further minimization in \(R_p\)

To ensure that the optimal geometry attained from the initial TLEED analysis for the favored model type 8 (Table 6.2) is not corresponding to some "local \(R_p\) minima", further tests were conducted. A range of initial reference structures were considered for model 8, as shown in Fig. 6.2, based on hard sphere models and plausible bond length arguments, and each was taken through several full dynamic/TLEED (FD/TL) analysis cycles until the atomic coordinates converged to a "final structure" (differences in atomic coordinates between the final structure and the closest reference structure were never more than 0.02 \(\text{Å}\)). Whenever a minimum in \(R_p\) was indicated, several manual "disturbances" in atomic coordinates were made, to provide new starting points for the TL analysis, in order to try to "displace" the \(R_p\) minimum to a lower value. Two particular initial reference structures, in which all Cu atoms are at their normal bulk positions, are specified as follows: (i) each P atom is placed exactly above hollow sites at 0.9 \(\text{Å}\) above the second Cu layer (this corresponds closely to the Cu-P distance from the sum of the Cu metallic radius and the P single-bond covalent radius); and (ii) compared with the situation in (i), the P atoms are laterally shifted towards the nearest top layer Cu atom by 0.3 \(\text{Å}\) and down by 0.1 \(\text{Å}\) (this makes the average Cu-P distance equal to 2.31 \(\text{Å}\), basically fitting expectation according to the bond length - bond order argument given previously). Despite there being a 0.32 \(\text{Å}\) difference in the initial P positions, after several FD/TL cycles both starting points led to the same \(R_p\) minimum, and the corresponding set of optimized atomic coordinates are the same as those given in Table 6.2 (the maximum displacement in the final atomic positions from those in the initial reference structure is 0.34 \(\text{Å}\)).
third initial reference structure (iii) is now chosen by doubling the displacements obtained from the second reference structure, that is the coordinates for each atom \((x, y, z)\) are set to equal \((x_{op}+(x_{op}-x_{ii}), y_{op}+(y_{op}-y_{ii}), z_{op}+(z_{op}-z_{ii}))\), where \((x_{ii}, y_{ii}, z_{ii})\) and \((x_{op}, y_{op}, z_{op})\) correspond respectively to atomic coordinates for the initial starting reference structure (ii) and the optimized structure.

Starting from the reference structure (iii), four FD/TL cycles were required to minimize \(R_p\) so that the atomic positions converged consistently; again they converged to the very same structure indicated in Table 6.2. Taking all this experience and information into account, we conclude that this structure does indeed appear to give the lowest value in \(R_p\) (0.255) attainable with the particular non-structural parameters and calculation procedures used here. The correspondence between the experimental and calculated I(E) curves for 13 beams is shown in Fig. 6.3.

6.5.2 Structural features of the favored model

The features for the \(\begin{pmatrix} 2 & 2 \\ -1 & 1 \end{pmatrix}\) structure formed by a half monolayer of \(P\) at the \(Cu(110)\) surface can be summarized as (Fig. 6.2): (i) Each \(P\) atom occupies an identical 6-coordinated site created by the reconstructed \(Cu(110)\), which itself corresponds to a quarter ML of "added Cu" atoms at hollow sites, each bonding to two neighboring \(P\) atoms and five other bulk-like \(Cu\) atoms.

(ii) Both the \(P\) and "added Cu" atoms line up along the \([1\bar{1}2]\) direction, which gives rise to the particular LEED pattern observed (with contributions from two equally probable domains, one being a mirror image of the other, each domain having a two-fold rotation symmetry).

(iii) Significant relaxations occur in both the vertical and lateral dimensions: each \(P\) atom displaces laterally by about 0.33 Å from the "ideal" center site to be closer to the neighboring "added Cu" atom; the maximum lateral displacements for \(Cu\) atoms in the second, third and fourth metal layers
Figure 6.3 \( I(E) \) curves for 13 diffracted beams for normal incidence on the Cu(110)-\( \begin{pmatrix} 2 & 2 \\ -1 & 1 \end{pmatrix} \) surface: the dot-dashed lines are from experiment, and the solid lines are from calculation for the favored geometry according to the tensor LEED analysis.
are indicated to equal 0.26, 0.14 and 0.14 Å respectively; vertically, the first four Cu-Cu interlayer spacings (on a "center of mass" basis) are: 1.15, 1.42, 1.25 and 1.27 Å, corresponding to changes of -10%, +11%, -1.8% and -0.5% compared with the bulk spacing (1.278 Å). Additionally, bucklings in the metal atom positions (Table 6.2) show reduced amplitudes with depth, being 0.24, 0.10 and 0.06 Å for the second, third and fourth layers.

The effects of the relaxations show up in the bond length information given in Table 6.3. The average Cu-Cu bond distances for the first three metal layers are 2.60, 2.63 and 2.58 Å, respectively; the first two appear significantly longer than the bulk value of 2.556 Å. Overall this increase is reasonable insofar as each of the Cu atoms in the first two metal layers additionally bonds to two P atoms, while only half of the third layer Cu atoms bond to one P atom (consistently the averaged Cu-Cu bond distance for the third layer Cu atoms is a little shorter). Such considerations suggest that the details in the metallic part of this surface structure are broadly plausible, and are not obviously artifacts introduced by the tensor LEED analysis finding a physically unreasonable minimum in $R_p$.

6.5.3 Rationalization of structural details

This section considers the degree to which the details of the structure from the TLEED analysis fit the emerging framework of principles for surface structural chemistry. All comments relate to the optimized atomic coordinates in Table 6.2, for 15 atoms per unit mesh, and the associated displacements in each coordinate from an "ideal" position ($\Delta x$, $\Delta y$ refer to lateral displacements from the symmetrical (i.e., center) site, while $\Delta z$ gives the vertical displacement from the center of mass plane for the appropriate layer). As a result of the two-fold rotation axis, and the diperiodic translational symmetry, all P atoms have the same vertical height, and the same
statement can be made for the "added Cu" atoms (i.e., Cu1 in Fig. 6.2). Additionally, the lateral coordinates are fixed for the copper atoms labelled 1, 4, 5, 6, 7, 12 and 13; therefore these atoms can relax only in a vertical sense.

In the following we attempt to rationalize details of the relaxations indicated by this tensor LEED analysis: (i) First, the driving force for the relaxations appears to be associated with the need to ensure sufficient P-Cu bonding, particularly to stabilize the "added Cu" atoms (which bond to only five other Cu atoms), and in turn that requires the Cu1 atoms to relax downwards (to reduce the vertical distance between P1 & Cu1), as seen by the overall contraction in the spacing between the first and second metal layers. (ii) This downward movement in the "added Cu" atoms, compared with the bulk positions, leads to distortions in the second metal layer; inevitably the atoms Cu2/Cu3, Cu4 and Cu5 displace differently because of their different local bonding environments. The atoms designated Cu5 are constrained to displace in the vertical direction only, and therefore they reasonably move downwards given that the Cu1 atoms move down. By contrast Cu2/Cu3 can relax laterally, and a natural displacement is towards the short-bridge site formed by Cu6 and Cu8/Cu9, which in turn requires the Cu2/Cu3 atoms to "ride" up. Therefore, compared with Cu4, which is not directly affected by the movement of Cu1, the vertical relaxations experienced by the second layer metal atoms (Table 6.2) are readily understood: the atoms Cu2/Cu3 are lifted up, while Cu5 is lowered. (iii) The optimizing of the P1-Cu1 bonding also requires P1 to move towards Cu1 along the y direction (by 0.25 Å according to the TLEED analysis), but a further component along the -x direction (by 0.20 Å) is encouraged by the bonding to the laterally displaced atoms Cu2. These two components combine to give a net lateral displacement of 0.33 Å for P1 (similarly for P2). (iv) In the third metal layer, the atoms Cu8/Cu9 are directly under P atoms, and they are consequently displaced down compared with Cu6 (otherwise the P1-Cu8 and P2-Cu9 bond lengths would be too short as has been discussed in other contexts); in an
intermediate position is Cu7, which is pushed down by Cu5 from the second metal layer. This therefore provides some rationalization of the vertical heights in the third metal layer, namely Cu6 is above Cu7, which in turn is above the atoms Cu8/Cu9. (v) The vertical displacements indicated for atoms in the fourth metal layer appear as a response to the displacements noted for the atoms directly above in the second layer (Table 6.4); the senses are the same although the magnitudes reduce with depth. (vi) Further, for lateral relaxations in the third layer, the atoms Cu8/Cu9 show the same type of movements as the P atoms to which they are bonded, although the magnitudes are less as expected given the inevitable constraints from the neighboring Cu atoms. In the fourth layer, the atoms Cu10/Cu11 (directly underneath Cu2/Cu3) could be expected to couple to Cu8/Cu9 above, but with the significant downward displacement in the latter, the atoms Cu10/Cu11 seem limited to relax only along the y-directions (although the uncertainty in the indicated value of Δy will be large, as noted further below).

6.6 Comparison with related structures

As indicated in Chapter 1, when electronegative atoms react with a metal surface to give a coverage of the order of 1 ML or less, the structural arrangement formed may correspond to (i) simple chemisorption; (ii) absorption; (iii) surface compound formation; or (iv) an independent reconstruction. Possibility (iv) is to be expected when the conditions do not match those required for (i)-(iii). This may be the case for the subject of this study since, from the arguments in the previous sections, the bonding arrangements for P on Cu(110) structure are not apparently conducive for coordination numbers of four or five when P bonds to the regular center site of the Cu(110) surface. Also the complex bulk structure Cu3P does not obviously have an orientation which matches to this metal surface. By contrast, the (100) plane of the simpler Cu3N structure does match to the Cu(110) surface in the (2x3) arrangement [97], and it is clear that this model
Table 6.4 Comparison of z-coordinates (in Å) for atoms in the second and fourth Cu layers.

<table>
<thead>
<tr>
<th>atoms</th>
<th>z</th>
<th>atoms</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu2</td>
<td>1.06</td>
<td>Cu10 (directly under Cu2)</td>
<td>3.79</td>
</tr>
<tr>
<td>Cu3</td>
<td>1.06</td>
<td>Cu11 (directly under Cu3)</td>
<td>3.79</td>
</tr>
<tr>
<td>Cu4</td>
<td>1.17</td>
<td>Cu12 (directly under Cu4)</td>
<td>3.84</td>
</tr>
<tr>
<td>Cu5</td>
<td>1.30</td>
<td>Cu13 (directly under Cu5)</td>
<td>3.86</td>
</tr>
<tr>
<td>buckling</td>
<td>0.24</td>
<td>buckling</td>
<td>0.06</td>
</tr>
</tbody>
</table>
accounts for the high stability of the Cu(110)-(2x3)-N surface structure. Similarly, both (2x1) and c(6x2) structures formed by O on Cu(110) have some relationship to the bulk Cu$_2$O structure (Chapter 5).

The bonding of S to the Cu(110) surface also differs from that for P; this is shown both by the differently observed LEED patterns and by the following argument. The known structural arrangement and bond lengths for S on Cu(100) [103], when used in Eq. (1.15), give r(1) = 2.00 Å for the length of the S-Cu bond of unit bond order, and when that value is applied to bonding at the Cu(110) surface, with S at the regular center site of 5-fold coordination, the divalency of S is readily accommodated with S-Cu bond lengths: one of 2.18 Å (to second layer Cu atom) and four of 2.39 Å (to first layer Cu atoms). This would appear to indicate the basics of a natural bonding arrangement, which could be accommodated in the c(2x2) 0.5 ML structure observed, although a SEXAFS study reported five S-Cu bonds at 2.37 Å [104]. Also, this surface is not well ordered; possibly with some heterogeneity, local regions of higher S coverage may restructure to give a (100) layer of the surface compound Cu$_2$S, as suggested by Domange and Oudar for 0.6 ML [105].

6.7 Summary

This TLEED study reveals an ordered surface structure formed by P chemisorbed on the Cu(110) surface with \( \begin{pmatrix} 2 & 2 \\ -1 & 1 \end{pmatrix} \) transitional symmetry. Detailed analysis of the measured I(E) curves indicates a new type of structural model in which a half-monolayer of P reconstructs the original metal surface, in effect by adding a 0.25 ML of Cu atoms which form rows parallel to the [\ddbar{1} 12] direction. All P atoms occupy identical six-coordinate sites while each metal atom in the top two Cu layers bonds to two neighboring P atoms. Appreciable relaxations, both vertical and lateral, are identified for individual atoms in the first four layers, but they appear to follow trends that are
broadly consistent with reasonable structural chemical principles. In summary, this novel surface reconstruction seems to be dominated by the need for the P atoms to attain a six-fold coordination arrangement with respect to neighboring Cu atoms.
Chapter 7 Structural analysis for the Rh(111)-($\sqrt{7} \times \sqrt{7}$)R19.1°-P surface

7.1 Introduction

Surface structures with the ($\sqrt{7} \times \sqrt{7}$)R19.1° translational symmetry are providing considerable interest, in part because they represent the upper end of complexity for current LEED structural analyses, when no other information is available, and they can show distinctive chemistries compared with simpler systems. Examples include the $\sqrt{7}$ structures formed by I on Pt(111) and S on Ru(0001) which have been indicated respectively by STM [106] and LEED crystallography [107] to have simple chemisorption arrangements without substantial modifications to the metallic structure; but in contrast the $\sqrt{7}$ structures formed by S on Pd(111) [108], Cu(111) [109] and Ag(111) [110] appear much more challenging. There have been frequent suggestions that the latter systems involve mixed sulfur-metal overlayers, and, in particular, that the structures for the S/Cu(111) and S/Ag(111) cases relate to the (111) plane of the bulk compounds Cu$_2$S and Ag$_2$S [109,110], but confirmation has proven hard to obtain. Another case in point is the Rh(111)-($\sqrt{7} \times \sqrt{7}$)R19.1°-P surface, which is highly stable and the work described here shows it has a novel structural arrangement. Discussions of this structure, its implications to other $\sqrt{7}$ systems, and possible links between this structural type and chemical properties provide the subject of this chapter.

7.2 Experiment

The experiment was conducted in a UHV chamber as described in Chapter 3 (base pressure $2 \times 10^{-10}$ Torr). The sample was cut and polished to within 1° of the (111) plane following standard procedures [62]. Typical cleaning and ordering cycles (Chapter 3) were
repeated until AES showed no evidence for residual contamination, and LEED showed a sharp (1x1) diffraction pattern with low background. After cleaning, PH₃ (99.9% purity) was introduced through a leak valve, and the adsorption process was monitored by measuring the Auger intensity ratio $R = \frac{A_{120}}{A_{302}}$, where $A_{120}$ and $A_{302}$ are Auger peak-to-peak heights respectively for phosphorus at 120 eV and rhodium at 302 eV. Figure 7.1 shows a typical Auger spectrum for the P-chemisorbed Rh(111) surface.

Only one ordered LEED pattern, associated with the $(\sqrt{7}x\sqrt{7})R19.1^\circ$ surface structure, was observed over a range of PH₃ exposures (to 13.3 L) and annealing temperatures (to 1100°C). This diffraction pattern is shown in Fig. 7.2 and illustrated schematically in Fig. 1.4. No ordering was observed prior to annealing, but a blurred $\sqrt{7}$ pattern could be seen at room temperature after annealing to 200°C. Generally it seemed that the higher the PH₃ exposure, the higher the annealing temperature required for getting a good diffraction pattern. The annealing also reduced the R value and it appears to be relatively constant after annealing to 1000°C for a range of PH₃ exposures between 5 and 9 L, as indicated in Fig. 7.3. Similar observations have been reported by other groups for Pd(111)-(\sqrt{7}x\sqrt{7})R19.1°-S [108c]. The sharpest $\sqrt{7}$ pattern (for which the LEED measurements were made) was obtained by dosing PH₃ at $1.6 \times 10^4$ Torr for 5 min (~ 4.8 L) on to the clean and well-ordered Rh(111) surface, followed by flash annealing to 1000°C (R drops from about 0.83 to 0.55).

The Rh(111)-(\sqrt{7}x\sqrt{7})R19.1°-P LEED pattern is very sharp and stable: in fact, it can last for days without any significant deterioration (a similar observation has also been reported for the corresponding S/Pd(111) surface [108d]), and considerable effort (more than four bombardment/annealing cycles) was needed for recovering the clean (1x1) surface after creation of the $\sqrt{7}$ structure. Two sets of diffracted beams from the individual domains (Fig. 1.4), which have a
Figure 7.1 Auger spectrum taken on the P-chemisorbed Rh(111) surface.
Figure 7.2 LEED pattern observed at 114 eV from the Rh(111)-($\sqrt{7}x\sqrt{7}$)R19.1°-P surface.
Figure 7.3 Plot of the Auger ratio $R = A_{120}/A_{302}$ as a function of $\text{PH}_3$ dosage before and after annealing (to $1000^\circ\text{C}$).
mirror symmetry relationship to one another, can be distinguished by one set having systematically stronger intensities than the other (this may reflect some small misorientation of the sample surface). Nevertheless, intensity-versus-energy (I(E)) curves measured from those symmetrically equivalent beams showed identical peaks and shapes, which indicates that the two domains have equivalent structures.

I(E) curves were measured for normal incidence with the video LEED system for 12 inequivalent diffracted beams and for energies up to 252 eV (total energy range 1438 eV). These diffracted beams are designated as (1 0), (0 1), (1 1), (2 0), (5/7 -4/7), (4/7 1/7), (6/7 -2/7), (2/7 4/7), (9/7 -3/7), (3/7 6/7), (10/7 -1/7) and (1/7 9/7), using the notation shown in Fig. 1.4. Independent sets of I(E) curves were measured from separately prepared surfaces, and they showed good reproducibility (Fig. 3.9); these data served as a solid base for the following structural analysis.

7.3 Calculation

The analysis was done with multiple-scattering calculations in the context of tensor LEED [31] using the R-factor (R_P) introduced by Pendry [54]; the potential of the solid was approximated with the muffin-tin model with the electron scattering by the Rh and P cores described by phase shifts (l_{max} = 7) as used in another study [99]. The real part of the constant potential (V_{0r}) between all muffin-tin spheres was initially set at -8.5 eV, although this was continuously refined during the calculations; the imaginary part of the constant potential (V_{0i}) was fixed throughout at -5.0 eV. The bulk Debye temperature (480 K) was used for all Rh atoms, while that for P (875 K) was chosen so all vibrating atoms probed by LEED have a constant root-mean-square amplitude [29].
7.4 Structure analyses:

7.4.1 Initial view of model types

Over 50 structural types consistent with the $\sqrt{7}$ translational symmetry were tested, and for convenience we classify into four groups: (I) simple P overlayer models; (II) mixed Rh/P overlayer models; (III) pseudo-Rh$_2$P(111) layer models; (IV) reconstructed models with eight-coordinated P atoms. Figure 7.4 shows some representative examples from each group (whenever applicable, in each case, both fcc and hcp adsorption sites were tested for topmost layer Rh and/or P atoms). Some factors related to these various structural types are briefly described in the following.

The simple P overlayer models (Fig. 7.4 I(a)-I(k)) need to be considered for completeness, particularly since S is reported to form such a structure on the Ru(0001) surface [107], although with these model types it is hard to see why the $\sqrt{7}$ structure is favored over other possibilities. Also, in these models, each P bonds only to two or three Rh atoms, which does not seem compatible with the large bonding capacity for this electronegative element, nor do they obviously explain the high stability of this surface structure. Among these models, the P coverage ranges from 1/7 to 6/7 ML, although coverages of 3/7 or 4/7 ML have been proposed by others for related $\sqrt{7}$ surface structures [108c,d & 109b,c]. In Fig. 7.4, model I(e) is analogous to that proposed for the I/Pt(111) system by STM study [106], and model I(f) corresponds to that of S/Ru(0001) from a recent LEED analysis [107]. TLEED analyses made in this work for the simple overlayer models generally gave minimum $R_P$ values greater than 0.50 (the one exception was for model I(h) for which minimum $R_P = 0.42$ but the calculation showed poor convergence). No evidence could be found in this work to support the P overlayer type of model for the Rh(111)-(\$\sqrt{7}$x$\sqrt{7}$)R19.1°-P surface structure.
Figure 7.4 Some models considered in TLEED analyses for the Rh(111)-(\(\bar{f}\times\bar{f}\))R19.1\(^\circ\)-P surface.
Figure 7.4, continued
The group II models considered in the TLEED analysis involve mixed Rh/P overlayers (Fig. 7.4 II(a)-II(p)). Again these models give the required translational symmetry without clear reasons for why any of them should be chosen as structures of high stability. The variations in models II(m)-II(p) have some P atoms embedded into the substrate Rh layer, which is consistent with the observed drop in the Auger ratio $R$, and followed earlier suggestions for the $\sqrt{7}$ structure formed by S chemisorbed on Pd(111) surface [108c]. The detailed TLEED analyses conducted on these models gave minimum $R_P$ values greater than 0.43; consistently the visual $I(E)$ curve comparison was always poor, and no support could therefore be provided for these possibilities.

The group III models considered are provided by the so-called “pseudo-Rh$_2$P(111) layer” models (Fig. 7.4 III(a)-III(c)). The idea of such models was initially proposed in 1968 [109a] in an attempt to interpret the $\sqrt{7}$ structure observed for the S/Cu(111) system. Basically, the topmost layers of these models with mixed Rh and P atoms resemble the atomic arrangements corresponding to the (111) plane of bulk Rh$_2$P [111], but these can be fitted onto the Rh(111) substrate in various ways: (i) Model III(a) contains three P and three Rh atoms per unit mesh with P atoms sitting on on-top, fcc and hcp sites; the misfit in dimensions of the two (111) faces is less than 6%. (ii) III(b) has a more densely-packed overlayer with P atoms adsorbing on either on-top or bridge sites. The misfit is slightly larger (~ 9%), but the shorter bond lengths in the surface region can fit the reduced coordination numbers for the surface atoms. (iii) Model III(c) simply switches Rh and P atoms in model III(a), but now some Rh atoms stay at on-top sites and therefore bond to just one other Rh atom. Intensive effort with TLEED analyses were devoted to these models, with a number of different starting reference structures tested for each model type.
However, the minimized $R_p$ values were always greater than 0.60, and no evidence could be found to support any of the "pseudo-Rh$_2$P(111) layer" models.

The group IV models (Fig. 7.5) involve a novel type of reconstruction: the topmost layer Rh atoms rearrange and form pentagons and triangles while simultaneously creating eight-coordinated holes for hosting P atoms. Two possible registries of the topmost layer exist with respect to the third Rh layer: model IV(a) with four Rh atoms (Rh1, Rh3, Rh4 and Rh5) occupying the regular fcc sites and one (Rh2) at a hcp site, while model IV(b) has these groups of Rh atoms occupying hcp and fcc sites respectively. The initial TLEED analysis immediately favored model IV(a), and reduced $R_p$ to below 0.33. By contrast, model IV(b) proved less favorable with $R_p$ always in excess of 0.40. Further structural refinement was accordingly conducted on model IV(a), as described in the next section.

7.4.2 Structural refinement for model IV(a)

The refined TLEED calculations for the Rh(111)-($\sqrt{7}$x$\sqrt{7}$)R19.1°-P surface structure allowed variations in the positions for 22 atoms (over three metal layers). With this large number of structural parameters, there is concern that the analysis may misleadingly identify a local, rather than global, minimum in $R_p$. To minimize this possible problem, extra caution was taken throughout the analysis. Firstly, as many as nine different initial starting points were used, and each individually included three to eight FD/TL cycles until varied atomic coordinates converged to within 0.02 Å at the final FD/TD cycle. Secondly, the bond length - bond order relation (Eq. (1.15)) was used to construct the initial starting points, and to check the general plausibility for the structures at the attained minima. Thirdly, whenever a $R_p$ minimum was reached, a number of different restarting points were tested (at least 0.2 Å away from the minimum reached) for the next TL searching step. It was found that disturbances of amplitude 0.3 Å to 0.4 Å (close to the
Figure 7.5 The Rh(111)-(\sqrt{7} \times \sqrt{7})R19.1°-P surface structure with an indication of atom designations used in the text. The 3-fold rotation axes are located at the centers of atoms Rh₁, Rh₂ and Rh₉.
validity range of current TL direct searching schemes according to Rous [31]) for some key atomic coordinates (e.g., z coordinates for atoms in the topmost layer) can help the minimization process escape from local minima in some instances. In short, a lot of effort was devoted to minimize any negative effects due to the involvement of a large unit mesh and a substantial number of atoms to be varied. This exhaustive I(E) curve analysis finally gave a minimized $R_p$ value as low as 0.235, which appears as a very high level of correspondence for such a relatively complex surface structure. The specific I(E) curves comparisons are shown in Fig. 7.6, while the atomic coordinates for the optimized geometry are listed in Table 7.1 (the notation for labeling atoms is given in Fig 7.5).

7.4.3 Structural features

The structural features identified for the Rh(111)-(\(\sqrt{7}\times\sqrt{7}\))R19.1°-P surface (Fig. 7.5) are summarized in the following: (i) The structure has three-fold rotational symmetry axes, and the P coverage corresponds to three atoms per unit mesh. (ii) Each P atom occupies an identical site created by the reconstructed Rh structure, and is within the bonding distance of eight Rh atoms (Table 7.2). (iii) The topmost Rh layer is characterized by a packed arrangement of pentagons and triangles at a density of five Rh atoms per unit mesh (those designated Rh1, Rh3, Rh4 and Rh5 remain close to their bulk-like fcc hollow sites with respect to the lower layers, while Rh2 is at a hcp hollow site), so that the densely-packed Rh-P mixed layer (with a P atom incorporated into the center of each pentagon) consists of eight surface atoms per seven for the Rh(111) substrate. (iv) Relaxations occur which are much more significant laterally than vertically (the largest lateral displacements from the "ideal" 3-fold symmetrical sites are about 0.66 Å for P atoms and about 0.28 Å for Rh atoms, while vertical displacements among the top three layers are 0.08 Å or less). Without relaxations, a "first-approximation" estimate for the first-layer Rh atoms in three-fold sites
Figure 7.6   Comparison of experimental I(E) curves (dot-dashed lines) with those calculated (solid lines) for the favored geometry.
Table 7.1 Atomic coordinates in Å for the TLEED-determined structure of the Rh(111)-($\sqrt{7}\times\sqrt{7}$)R19.1°-P surface. The atomic labels are defined in Fig. 7.5.

<table>
<thead>
<tr>
<th>Atomic label</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Rh1</td>
<td>4.035</td>
</tr>
<tr>
<td>Rh2</td>
<td>0</td>
</tr>
<tr>
<td>Rh3</td>
<td>1.46</td>
</tr>
<tr>
<td>Rh4</td>
<td>2.41</td>
</tr>
<tr>
<td>Rh5</td>
<td>4.20</td>
</tr>
<tr>
<td>P1</td>
<td>1.91</td>
</tr>
<tr>
<td>P2</td>
<td>4.79</td>
</tr>
<tr>
<td>P3</td>
<td>5.41</td>
</tr>
<tr>
<td>Rh6</td>
<td>2.65</td>
</tr>
<tr>
<td>Rh7</td>
<td>3.99</td>
</tr>
<tr>
<td>Rh8</td>
<td>5.47</td>
</tr>
<tr>
<td>Rh9</td>
<td>2.690</td>
</tr>
<tr>
<td>Rh10</td>
<td>1.41</td>
</tr>
<tr>
<td>Rh11</td>
<td>1.30</td>
</tr>
<tr>
<td>Rh12</td>
<td>5.36</td>
</tr>
<tr>
<td>Rh13</td>
<td>2.71</td>
</tr>
<tr>
<td>Rh14</td>
<td>4.08</td>
</tr>
<tr>
<td>Rh15</td>
<td>5.31</td>
</tr>
<tr>
<td>Rh16</td>
<td>1.32</td>
</tr>
<tr>
<td>Rh17</td>
<td>2.73</td>
</tr>
<tr>
<td>Rh18</td>
<td>4.02</td>
</tr>
<tr>
<td>Rh19</td>
<td>0</td>
</tr>
<tr>
<td>bulk repeat vector</td>
<td>1.345</td>
</tr>
<tr>
<td>2D repeat vectors</td>
<td>1.345</td>
</tr>
<tr>
<td></td>
<td>5.380</td>
</tr>
</tbody>
</table>
would require an irregular pentagon with a 15% variation in side lengths, but the structure from the tensor LEED analysis shows that this variation is reduced to less than 3%. (v) Vertically, the topmost Rh atoms are almost coplanar (the rumpling is 0.06 Å) with P sitting 0.13 Å below the center-of-mass plane for the first Rh layer, but 2.15 Å above the second Rh layer. The Rh-Rh interlayer spacings are only slightly changed from the bulk value of 2.196 Å (the percentage changes correspond to +3.7, -1.3 and +0.7 for the first, second and third spacings, respectively).

(vi) The P-Rh distances range from 2.17 to 2.97 Å (Table 7.2); for each P atom there are two short (2.17-2.22 Å), three medium (2.30-2.48 Å) and three longer (2.71-2.97 Å) bonds to the neighboring Rh atoms. (vii) The determined atomic positions show an approach to a mirror symmetry within the topmost Rh-P layer, although this is not required by the overall symmetry. A consequence of this close approach to the mirror symmetry ("pseudo" mirror lines are indicated in Fig. 7.5) is that each P has two "short", two "medium" and one "long" bond to its neighbors in the Rh pentagon.

7.5 Discussion

7.5.1 About the structure

This structure shows a completely new bonding arrangement for P at a transition metal surface. The eight-coordination for P matches the situation in bulk Rh2P (anti-fluorite) [111], although other details differ. For example, the average P-Rh bond length in Rh(111)-($\sqrt{7}\times\sqrt{7}$)R19.1°-P (2.52 Å) is slightly longer than the distance in Rh2P (2.38 Å); in part this increase arises from the limited "free valencies" available for the neighboring Rh atoms, given that they are themselves each bonding to between six and eleven other Rh atoms (and sometimes other P atoms as well). Additionally this structure is constrained by the need to maintain an appropriate local coordination around P while simultaneously maintaining, in a continuous structure, the diperiodicity to match the substrate. The high density of the topmost Rh-P layer, its flatness, and its
possibilities for maintaining high total bonding by P, appear as major factors contributing to the generally high stability of this surface. In addition, with the assumption that P atoms are sitting on top of the topmost Rh layer before annealing, the drop of Auger ratio R after annealing may result from the fact that P atoms are below the surface Rh layer (0.13 Å) so they were partially hidden (this is especially significant since a glancing Auger electron gun was used in this work).

Table 7.2 shows some important P-Rh and Rh-Rh bond lengths for the atoms in the top two layers. While the diversity of P-Rh bond lengths may be explained by the geometric constraints, the variations of average Rh-Rh bond lengths around an individual Rh atom are clearly associated with the number of P-Rh bonds and their relative strength. For example, each of the Rh atoms in the topmost layer (Rh1-Rh5) bonds with three P atoms, and hence show weaker bonding to the neighboring Rh atoms (ave Rh-Rh bond length 2.77 - 2.85 Å). By contrast, those Rh atoms in the second layer (Rh6-Rh12) have shorter Rh-Rh distances (2.71 - 2.68 Å) since they either bond weakly with neighboring P atoms or do not have any P neighbors. Indeed, for Rh9, which has no P neighbors and bonds to twelve Rh atoms like in the bulk metal, the average Rh-Rh distance (2.68 Å) is essentially equal to that in the metal (2.69 Å). Also, for those Rh atoms on 3-fold rotation sites (i.e., Rh1, Rh2 and Rh9), the individual Rh-Rh bond lengths are closer to each other than those Rh atoms on asymmetrical sites (i.e., Rh3-5, Rh6-8 and Rh10-12), which show a more diversified range of Rh-Rh bond lengths.

Figure 7.7 shows that two pairs of Rh-P bonds in each pentagon are related by the pseudo-mirror symmetry, while the other Rh-P bond (the longest) is closely parallel (to within 0.15°) to the unit mesh vector. These features are remarkable since they are not required by the space group symmetry, but they may help contribute to the high stability of the structure. It is almost as if the Rh-P bond dipoles orient themselves to minimize electrostatic interactions. Figure 7.7 also shows that the surface Rh atoms relax to make the Rh pentagons more regular:
Table 7.2 Some important bond lengths (in Å) in the Rh(111)-(√7x√7)R19.1°-P surface structure. Note that Rh4 and Rh5 are related to Rh3 by a 3-fold rotation symmetry, so their bonding situations correspond exactly to those of Rh3; a similar statement applies for the (Rh6, Rh7, Rh8) and (Rh10, Rh11, Rh12) groups.

<table>
<thead>
<tr>
<th></th>
<th>P1</th>
<th>Rh1</th>
<th>Rh2</th>
<th>Rh3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN=8 (8Rh)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1-Rh1 - 2.17</td>
<td>Rh1-P1 - 2.17</td>
<td>Rh2-P1 - 2.22</td>
<td>Rh3-P1 - 2.48</td>
<td></td>
</tr>
<tr>
<td>P1-Rh2 - 2.22</td>
<td>Rh1-P2 - 2.17</td>
<td>Rh2-P2 - 2.22</td>
<td>Rh3-P2 - 2.71</td>
<td></td>
</tr>
<tr>
<td>P1-Rh3 - 2.48</td>
<td>Rh1-P3 - 2.17</td>
<td>Rh2-P3 - 2.22</td>
<td>Rh3-P3 - 2.40</td>
<td></td>
</tr>
<tr>
<td>P1-Rh4 - 2.71</td>
<td>Rh1-Rh3 - 2.82</td>
<td>Rh2-Rh3 - 2.85</td>
<td>Rh3-Rh1 - 2.82</td>
<td></td>
</tr>
<tr>
<td>P1-Rh5 - 2.40</td>
<td>Rh1-Rh4 - 2.82</td>
<td>Rh2-Rh4 - 2.85</td>
<td>Rh3-Rh2 - 2.85</td>
<td></td>
</tr>
<tr>
<td>P1-Rh6 - 2.30</td>
<td>Rh1-Rh5 - 2.82</td>
<td>Rh2-Rh5 - 2.85</td>
<td>Rh3-Rh4 - 2.78</td>
<td></td>
</tr>
<tr>
<td>P1-Rh10 - 2.93</td>
<td>Rh1-Rh6 - 2.81</td>
<td>Rh2-Rh10 - 2.84</td>
<td>Rh3-Rh5 - 2.78</td>
<td></td>
</tr>
<tr>
<td>P1-Rh11 - 2.97</td>
<td>Rh1-Rh7 - 2.81</td>
<td>Rh2-Rh11 - 2.84</td>
<td>Rh3-Rh8 - 2.81</td>
<td></td>
</tr>
<tr>
<td>Rhl-P - 2.17</td>
<td>Rhl-Rh - 2.82</td>
<td>Rhl-Rh - 2.82</td>
<td>Rhl-Rh - 2.82</td>
<td></td>
</tr>
<tr>
<td>ave</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1-Rh - 2.52</td>
<td>ave Rh1-P - 2.17</td>
<td>ave Rh2-P - 2.22</td>
<td>ave Rh3-P - 2.53</td>
<td></td>
</tr>
<tr>
<td>ave</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rh6-Rh - 2.71</td>
<td>ave Rh2-Rh - 2.85</td>
<td>ave Rh3-Rh - 2.77</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rh6</th>
<th>Rh10</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN=12(1P&amp;11Rh)</td>
<td>CN=13(2P&amp;11Rh)</td>
</tr>
<tr>
<td>Rh6-P1 - 2.30</td>
<td>Rh10-P1 - 2.93</td>
</tr>
<tr>
<td>Rh6-Rh1 - 2.81</td>
<td>Rh10-P3 - 2.97</td>
</tr>
<tr>
<td>Rh6-Rh5 - 2.81</td>
<td>Rh10-Rh2 - 2.84</td>
</tr>
<tr>
<td>Rh6-Rh7 - 2.82</td>
<td>Rh10-Rh4 - 2.61</td>
</tr>
<tr>
<td>Rh6-Rh8 - 2.82</td>
<td>Rh10-Rh6 - 2.69</td>
</tr>
<tr>
<td>Rh6-Rh9 - 2.60</td>
<td>Rh10-Rh7 - 2.58</td>
</tr>
<tr>
<td>Rh6-Rh10 - 2.69</td>
<td>Rh10-Rh8 - 2.70</td>
</tr>
<tr>
<td>Rh6-Rh11 - 2.70</td>
<td>Rh10-Rh9 - 2.67</td>
</tr>
<tr>
<td>Rh6-Rh12 - 2.58</td>
<td>Rh10-Rh11 - 2.78</td>
</tr>
<tr>
<td>Rh6-Rh13 - 2.67</td>
<td>Rh10-Rh12 - 2.78</td>
</tr>
<tr>
<td>Rh6-Rh14 - 2.68</td>
<td>Rh10-Rh13 - 2.61</td>
</tr>
<tr>
<td>Rh6-Rh17 - 2.64</td>
<td>Rh10-Rh16 - 2.68</td>
</tr>
<tr>
<td>Rhl-Rh - 2.58</td>
<td>Rh10-Rh19 - 2.71</td>
</tr>
<tr>
<td>ave</td>
<td></td>
</tr>
<tr>
<td>Rh6-P - 2.30</td>
<td>ave Rh10-P - 2.95</td>
</tr>
<tr>
<td>ave</td>
<td></td>
</tr>
<tr>
<td>Rh6-Rh - 2.71</td>
<td>ave Rh10-Rh - 2.69</td>
</tr>
</tbody>
</table>
Figure 7.7 Another view of the topmost layer in the Rh(111)-($\overline{7}x\overline{7}$)R19.1° P surface structure with associated bond lengths (in Å).
the maximum difference in the pentagon side length drops from 0.42 Å (for unrelaxed bulk-like positions) to 0.07 Å (i.e., less than 3% variation). However a perfect pentagon is not possible since the 3-fold rotation symmetry requires that at least one of the inner angles has to be exactly 120°.

7.5.2 Implications to other \( \sqrt{7} \) structures

It seems likely that the \( \sqrt{7} \) structures formed by S on Cu(111), Ag(111) and Pd (111) have similar structures to that identified for P on Rh(111) given that there have been reports that the former may have mixed S-metal overlayers [108-110], and indeed the elements involved all form cubic bulk compounds (i.e., Cu₂S, Ag₂S and Pd₄S) [111] in which the S atoms are eight-coordinate. That the four \( \sqrt{7} \) examples mentioned here may have similar structures is also suggested by some approach to constancy in the ratio of the neighboring interatomic distance from M to S (or P) in the bulk compound (where S or P is eight-coordinate) to the neighboring M-M distance on the fcc metal (111) surface. All examples fit within 0.92 ± 0.05. But the combinations P/Rh and S/Pd are particularly close (both 0.88), as are S/Cu and S/Ag (0.97 and 0.95 respectively). In particular, the \( \sqrt{7} \) S/Pd(111) surface is also reported to have very high stability, and to be flat with a S coverage of 3/7 ML [108]. Indeed STM images taken on this surface match exactly with the structural model in Fig. 7.5 if the bright spots are interpreted as metal atoms [108b,c].

That the Pd(111)-(\( \sqrt{7} \times \sqrt{7} \))R19.1°-S surface is likely to have a different bonding environment for S from that in the lower-coverage (\( \sqrt{3} \times \sqrt{3} \))R30° form is suggested by their different chemical reactivities [112]. For the cyclization reaction of acetylene to thiophene, carried out on these two sulfided Pd(111) surfaces, the former (after heating to 1050 K) appears approximately five times more effective than the more-regular \( \sqrt{3} \) chemisorption structure [108d],
a factor that has already been alluded to by Gellman [112a]. With the probability that the \(\sqrt{7}\) structure for S/Pd(111) is analogous to that in Fig. 7.5, the reaction scheme outlined in Fig. 7.8 suggests how the novel arrangement of S, nearly coplanar with the pentagonally-arranged neighboring Pd atoms, may help accelerate the reaction compared with that in the \(\sqrt{3}\) form, where S is held above the regular Pd(111) surface [108d]. Like the conversion of \(\text{C}_2\text{H}_2\) to \(\text{C}_6\text{H}_6\) on the clean Pd(111) surface [113], the formation of thiophene may also proceed through the \(\text{C}_4\text{H}_4\) intermediate (Fig. 7.8(a)), and Fig. 7.8(b) indicates how the cyclization to thiophene may be facilitated by a neighboring S atom bound to the center of a Pd pentagon. Indeed with the expected tilting [113c,d], the \(\text{C}_4\) unit could approach coplanarity with the S. Figure 7.8(c) outlines an extension of this situation to a step edge where the S is bound to a smaller number of Pd atoms, and hence should be more easily removed. In summary, it seems that while the pentagonal reconstruction for the topmost layer encourages the formation of thiophene, the presence of steps helps the desorption; together these points indicate a rationalization of observations that the yield of desorbed thiophene increases with the step density for the \(\sqrt{7}\) structure [108b].

7.6 Summary

The tensor LEED crystallographic analysis reported in this chapter finds a novel reconstruction for the Rh(111)-(\(\sqrt{7}\times\sqrt{7}\))R19.1°-P surface with the topmost metal layer involving a packed arrangement of Rh pentagons and triangles. In this surface, each P atom has an identical environment and bonds to eight neighboring Rh atoms. The nearly flat, densely-packed Rh-P mixed layer (at a density of five Rh and three P atoms per seven substrate atoms in the unit mesh) appears to be the major factor in giving the surface a high general stability. A number of similarities are noted between this surface and the corresponding ones formed by S on Pd(111),
Figure 7.8 Schematic indication of a possible route for the formation of thiophene from the cyclization of acetylene on Pd(111)-(7x7)R19.1°-S structures: (a) and (b) are for a flat terrace, and (c) is for a step edge. The small circles represent C atoms of the C₄H₄ intermediate; the open ones are expected to be tilted away from the surface, while the filled circles are closer and bond initially with surface Pd atoms as indicated (the H atoms are not shown, but one bonds to each C atom).
Cu(111) and Ag(111), and it is suggested that they may all have the same structure type. Given the new structural information from this work, suggestions are also made in relation to previous observations of the cyclization reaction of acetylene to thiophene on the $\sqrt{7} S/Pd(111)$ surface.

As well as introducing a completely new surface structure, this study additionally indicates how modern surface structure determinations can help add insight for surface stability and reactivity. Also, given the constraints associated with both short-range coordination and long-range crystal matching, that are present in such diperiodic systems, the details of this structural type should have significance to much broader aspects of structural chemistry. The interest in establishing structure-reactivity relationships has been alluded to for many years [114], but it is clear that the recent rapid developments in surface structure determination are now strengthening such efforts in relation to significant catalytic processes [115].
8.1 Further studies

8.1.1 Structures formed by O and P on copper surfaces

A particularly interesting future direction in surface science is to extend quantitative structural studies to stepped surfaces. Of relevance to the work reported in this thesis is the (410) surface of copper (Fig. 8.1), which is based on (100) terraces and (110) steps. Therefore studies of O chemisorbed on this surface should provide an important test ground for the principles identified in Chapter 5 for the construction of O/Cu superstructures on the (100) and (110) substrates. Although some studies [83,90] have been conducted on the O/Cu(410) system, there is still much uncertainty on the O adsorption site, and on whether the metallic structure reconstructs. In fact, based on the common features extracted from this work, two main possibilities seem likely for the O/Cu(410) structures: (i) at low coverage, O may simply stay at the [001] step edge sites between two edge Cu atoms without substrate reconstruction (Fig. 8.2); and (ii) at higher coverage, as proposed by Robinson et al. [83], the Cu structure may reconstruct with a missing row at the base of each step (Fig.8.3). In both cases, the O atoms retain the favorable four-coordinate status with the basic three atom O-Cu-O construction unit. Currently, we are participating in an international research team engaged in structural study of the O/Cu(410) surface [116] with SXRD at the Daresbury synchrotron source in England. The analysis is still in progress, but it is hoped that this project will give insight into various other experimental observations, such as: (i) why is the O-chemisorbed Cu(410) surface after annealing more ordered than the clean surface? and (ii) why does the Cu(100) surface on heating in the presence of oxygen give Cu(410) facets [117]?
Figure 8.1 Structure of the Cu(410) surface. The dashed line shown is parallel to a (410) plane.
Figure 8.2 A possible low-coverage structural model for O adsorbed at the Cu(410) surface. The small, black circles represent O atoms, while the larger circles are Cu atoms.
Figure 8.3 A possible high-coverage structural model for O adsorbed at the Cu(410) surface; the arrows indicate the missing Cu rows.
An examination of the arrangements of Cu atoms at step edges in the Cu(410) surface shows six-coordinate sites that resemble very closely the adsorption sites adopted by P at the Cu(110)-\( \begin{pmatrix} 2 & 2 \\ -1 & 1 \end{pmatrix} \)P surface (Fig. 6.2). The difference is that in the latter case those adsorption sites are created by the reconstruction ("added Cu row") while on Cu(410) surface they exist naturally. There is therefore an expectation that a P-adsorbed Cu(410) surface will give the structure indicated in Fig. 8.4. Such a structure, with P bonding to Cu atoms in both the upper and lower terraces, is likely to stabilize this stepped Cu arrangement, and, as well as establishing its structural details, it will be interesting to determine the effect of P on the disordering temperature of the Cu(410) surface.

8.1.2 \( \sqrt{7} \) structures on fcc(111) surfaces

Similarities between the \( \sqrt{7} \) surfaces of the P/Rh(111), S/Pd(111), S/Cu(111) and S/Ag(111) systems have been noted in Chapter 7, and this opens a possibility that they may all have the same type of reconstruction as Rh(111)-(\( \sqrt{7} \times \sqrt{7} \))R19.1°-P. That needs checking. Equally, structural studies for such systems should establish new trends in details for the different systems (e.g., in bond lengths, deviations from top layer coplanarity) and in turn help develop basic principles guiding the formation of this type of reconstructed surface, particularly since the S/Ru(0001) and I/Pt(111) systems apparently form \( \sqrt{7} \) structures based on overlayer (non-reconstructed) models [106,107]. Assessments of linkages between these \( \sqrt{7} \) structures and surface reactivity are also of interest. For example, the proposal in Fig. 7.8 for the cyclization reaction of acetylene on the \( \sqrt{7} \) S/Pd(111) surface needs testing with other probes, including
Figure 8.4 A possible structural model for P adsorbed at the Cu(410) surface.
HREELS and TDS, in order to establish structure for reaction intermediates and thereby lead to a fuller understanding of the reaction mechanism.

8.2 Estimation of error bars in LEED crystallography

An important but poorly understood issue in LEED crystallography relates to the uncertainties in structural analyses. So far this issue has not been considered explicitly in this thesis, although the philosophy throughout has been to assess whether the indicated details fit a consistent framework; accordingly this provides a more empirical, rather than absolute, test of reasonableness or otherwise for the results obtained. Several schemes have been proposed to determine the statistical error bars in LEED analysis, but none of them really solve this problem completely, in part because they emphasize the random errors without consideration of the systematic errors (resulting from aspects of both the experiment and the calculations). Two of the most commonly used methods for error bar estimation are briefly outlined here.

Andersen et al. [118] proposed that the uncertainty \( \sigma_i \) in the optimal value of a certain coordinate \( x_i \) from a LEED analysis can be estimated by

\[
\sigma_i^2 = \frac{\varepsilon R_{\text{min}}}{N}
\]  

(8.1)

where the R-factor is assumed to be a quadratic function of \( x_i \), \( 1/\varepsilon \) is the curvature at the minimum (\( R_{\text{min}} \)) with respect to \( x_i \), and \( N \) is the number of independent data points (e.g., number of \( I(E) \) curve peaks over the energy range of measurement). In an alternative approach, Pendry [54] suggested that the uncertainty caused by random errors can be calculated by the variance of \( R \) at its minimum, which can be expressed in terms of his double-reliability factor \( RR \) as

\[
\text{var} R_{\text{min}} = RR \times R_{\text{min}} = \sqrt{\frac{8V_0}{\Delta E}} \times R_{\text{min}}
\]  

(8.2)
where $V_{\text{im}}$ is the imaginary part of the muffin-tin potential used in the calculations, and $\Delta E$ is the total energy range for intensity data. The associated error bar for coordinate $x_i$ is then deduced directly from the $R$ versus $x_i$ plot.

No independent checks of the validity of these approaches are available, but those of Anderson et al. and Pendry have been seen as over-optimistic and over-conservative respectively [64,74a]. For example, the error bar in the vertical coordinate for the topmost Cu atoms in the Cu(110)-$\left(\begin{array}{cc} 2 & 2 \\ -1 & 1 \end{array}\right)$-P structure is about 0.02 Å using Anderson's method, but 0.05 Å with Pendry's approach. An average of the error bars from these two approaches may give a better guide for uncertainties at the current time, although an optimal solution is still needed. There is also a need for completely independent studies (e.g., different measurement systems and computational packages) to be made on (nominally) the same surface in order to assess questions of precision in LEED structural determinations, perhaps following the philosophy of an earlier project for clean Cu(100) [119].

In summary, even though no definite answers are available for the uncertainty problem in LEED crystallography at the current time, the best estimation of the error bars for vertical coordinates appears to be in the range of 0.02 - 0.03 Å, while for lateral coordinates the uncertainties may be as much as 0.06 Å. Larger values would be appropriate for deeper atoms, for example those in the third or fourth layers for which the LEED intensities are less sensitive.

8.3 **Challenges and future prospects for surface crystallography**

The development of tensor LEED [31] has opened a new era for LEED crystallography: it not only provides an efficient way to calculate diffracted beam intensities over a range of atomic positions, but it also appears to reduce possibilities of error due to subjective human judgment in
the evaluation of model types and the optimization of geometrical parameters. The analysis of simple surface structures (e.g., (2x1) overlayer structure) now can be routinely accomplished within a day or two, while the structural determination for complex surfaces (e.g., those involving larger unit meshes with substantial reconstruction) become tractable. Undoubtedly, the availability of effective codes for tensor LEED applications represents a giant leap for surface structural determination.

Even so, to make LEED crystallography as successful and effective as its counterpart, X-ray diffraction crystallography, some areas need improvement, including the problem of how to efficiently find “global minima” in TLEED structural searches. Currently, there is no working direct method to solve this problem, at least for anything other than the very simplest surface structures. Therefore there is still a large reliance on human judgment to choose model types, as has been addressed in previous chapters. Also attempts are being made to apply different approaches to the automatic searching scheme, for example with the genetic algorithms [120]. Other challenges include how to apply LEED crystallography to study ordered, stepped surfaces (e.g., Cu(410)) for which the interlayer spacings are 0.5 Å or less, and how to analyze low symmetry surfaces with large unit mesh size (e.g., (5x5)) for which many more atoms will have to be included in the calculations? Solutions to these problems may provide directions for future developments in LEED crystallography.

Another point of relevance concerns the advantages of combining complementary techniques in surface structure study. As previously noticed, the tedious searching out of the correct model type for a surface still remains a substantial obstacle for LEED analysis, although that can be greatly helped by having information from other structural techniques, including STM, SXRD, HREELS and ion scattering. That was seen in this thesis in relation to the successful determination for the Cu(110)-c(6x2)-O surface structure (Chapter 4). Equally the
existence of detailed information from a range of techniques applied to the same system should greatly help assessments of "error bars" for the individual techniques, including LEED. At this time, the combinations of LEED, AES, HREELS, STM, SXRD and ion scattering would seem to provide the best approach for solving surface structure with complexity beyond that for \( \sqrt{7} \) system studied in Chapter 7.

Further, with the accumulation of new and detailed surface structure knowledge [30], it becomes increasingly important to classify such information in terms of basic chemical principles. That is needed both to improve understanding of structural chemistry more generally (ranging from individual molecules, through surfaces to bulk solids), and to provide the framework with which to assess surface chemical bonding. In turn, knowledge of the latter is needed to provide an important component of models which attempt to understand surface reactivity and processes, for example in heterogeneous catalysis, corrosion, crystal growth and semiconductor fabrication.
References

     (c) G. Dorenbos, Ph.D. Thesis, Groningen University, 1994.


78 Some results of W. Moritz et al. quoted in Ref. 67.


80 J. Wever, D. Wolf and W. Moritz, to be published.


116 K.A.R. Mitchell (UBC), I.K. Robinson (U. Illinois), E. Vlieg (FOM Institute, Amsterdam) and D.P. Woodruff (U. Warwick) et al.


List of publications

LEED Crystallographic Studies for the Rh(100)-p(2x2)-S and Rh(100)-c(2x2)-S Surface Structures

A Structural Study of Pd/Cu(100) Surface Alloys

Structural Details for the Cu(110)-c(6x2)-O Surface Determined by Tensor LEED

LEED Crystallographic Determination for the Restructured Surface Formed by Phosphorus Bonded at Cu(110)

A Novel Surface Structure: Rh(111)-(√7x√7)R19.1°-P

What Determines the Structures Formed by Oxygen at Low Index Surfaces of Copper?

XPS Studies for an Iron-Zirconium Interface in an Oxidizing Environment

Tensor LEED Analysis for the Rh(110)-(3x2)-S Surface Structure

Tensor LEED Analysis for the (√3x√3)R30° and c(4x2) Structures Formed by Sulphur Chemisorbed on the (111) Surface of Rhodium

An Investigation of Structural Details for the Cu(110)-\begin{pmatrix} 2 & 2 \\ -1 & 1 \end{pmatrix}P Reconstructed Surface

LEED Crystallographic Analysis for the Rh(111)-(2x1)-O Surface Structure