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Surface structural determination: Diffraction methods

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List of Symbols and Abbreviations [IF NEEDED]

\mathbf{a} , \mathbf{b} = two-dimensional unit cell vectors in direct space

\mathbf{a}^* , \mathbf{b}^* = two-dimensional unit cell vectors in reciprocal space

α = rotation angle in Wood notation

γ = angle between vectors \mathbf{a} , \mathbf{b}

\mathbf{g}, \mathbf{k} = two-dimensional reciprocal-lattice vectors

hkl = Miller indices of a surface

\hbar = Planck constant

λ = inelastic electronic mean free path

m_{ij} = i,j matrix element in the matrix notation for unit cells

\mathbf{M} = matrix of the matrix notation for unit cells

ML = monolayer

\mathbf{n} = surface normal

θ = polar angle of incidence (from surface normal)

10 Ångström = 1 nanometer

AD = atom diffraction

AED = Auger electron diffraction

ARPEFS = angle-resolved photoelectron emission fine structure

ARUPS = angle-resolved ultraviolet photoemission spectroscopy

ARXPD = angle-resolved x-ray photoelectron diffraction

ED = electron diffraction

GIXD = grazing-incidence x-ray diffraction

GIXS = grazing-incidence x-ray scattering

HEIS = high-energy ion scattering

HREELS = high-resolution electron energy loss spectroscopy

IS - ion scattering

LEED = low-energy electron diffraction

LEIS = low-energy ion scattering
LEPD = low-energy positron diffraction
MEED = medium-energy electron diffraction
MEIS = medium-energy ion scattering
ND = neutron diffraction
NEXAFS = near-edge x-ray absorption fine structure
NMR = nuclear magnetic resonance
NPD = normal photoelectron diffraction
OPD = off-normal photoelectron diffraction
PD = photoelectron diffraction
PED = photoelectron diffraction
RHEED = reflection high-energy electron diffraction
SEELFS = surface extended energy loss fine structure
SEXAFS = surface extended x-ray absorption fine structure
STM = scanning tunneling microscopy
TED = transmission electron diffraction
TOF-SARS = time-of-flight scattering and recoiling spectrometry
XAFS = x-ray absorption fine structure
XANES = x-ray absorption near-edge spectroscopy
XRD = x-ray diffraction
XSW = x-ray standing waves

B1.21 SURFACE STRUCTURAL DETERMINATION: DIFFRACTION

METHODS

B1.21.1 INTRODUCTION

Diffraction methods have provided the large majority of solved atomic-scale structures for both the bulk materials and their surfaces, mainly in the crystalline state. Crystallography by diffraction tends to filter out defects and focus on the periodic part of a structure. By adding contributions from very many unit cells, diffraction gives results that are, in effect, averaged over space and time. This is excellent for investigating stable states of solid matter as they occur in well-crystallized samples; some forms of disorder can also be analyzed reasonably well. Diffraction, however, is much less appropriate for examining inhomogeneous and time-dependent events such as transition states and pathways in chemical reactions.

For bulk structural determination (see section B1.9), the main technique used has been x-ray diffraction (XRD). Several other techniques are also available for more specialized applications, including: electron diffraction (ED) for thin film structures and gas-phase molecules; neutron diffraction (ND) and nuclear magnetic resonance (NMR) for magnetic studies (see sections B1.12 and B1.13); x-ray absorption fine structure (XAFS) for local structures in small or unstable

samples (see section B1.6); and other spectroscopies to examine local structures in molecules, etc. Electron microscopy also plays an important role, primarily through imaging (see section B1.18).

At surfaces, the primary challenge is to obtain the desired surface sensitivity. Ideally, one wishes to gain structural information about those atomic layers which differ in their properties from the underlying bulk material. This means in practice extracting the structure of the first few monolayers, i.e. atoms within about 5 to 10 Å (0.5 - 1 nm) of the vacuum above the surface. The above-mentioned bulk methods, if applied unchanged, do not easily provide sensitivity to this very thin slice of matter. The challenge becomes even greater when dealing with an interface between two materials, including solid/liquid and solid/gas interfaces. A number of mechanisms are available to obtain surface sensitivity on the required depth scale. We shall describe some of them in the next subsection, with emphasis on the solid/vacuum interface.

However, it is necessary to first discuss the meaning of “diffraction”, because this concept can be interpreted in several ways. After these fundamental aspects are dealt with, we will take a statistical and historical view of the field. It will be seen that many different diffraction methods are available for surface structural determination.

It will also be useful to introduce concepts of two-dimensional ordering, and the corresponding nomenclature used to characterize specific structures. Next, we can then describe how the surface diffraction pattern relates to the ordering, and thus provides important two-dimensional structural information.

We will, in the latter part of this discussion, focus our discussion only on those few methods that have been the most productive, with low-energy electron diffraction (LEED) receiving the most attention. Indeed, LEED has been the most successful surface structural method in two quite distinct ways. First, LEED has become an almost universal characterization technique for single-crystal surfaces: the diffraction pattern is easily imaged in real time and is very helpful in monitoring the state of the surface in terms of the ordering, and hence also density, of adsorbed atoms and molecules. Second, LEED has been quite successful in determining the detailed atomic positions at a surface (e.g., interlayer distances, bond lengths and bond angles), especially for ordered structures. This relies primarily on simulating the intensity (current) of diffracted beams as a function of electron energy in order to fit assumed model structures to measured data. Because of multiple scattering, such simulation and fitting is a very different and much more difficult task than looking at a diffraction pattern.

We will close with a description of the state of the art and an outlook on the future of the field.

B1.21.2 FUNDAMENTALS OF SURFACE DIFFRACTION METHODS

B1.21.2.1 Diffraction

diffraction and structure

Diffraction is based on wave interference, whether the wave is an electromagnetic wave (optical, x-ray, etc.), or a quantum-mechanical wave associated with a particle (electron, neutron, atom, etc.), or any other kind of wave. To obtain information about atomic positions, one exploits the interference between different scattering trajectories among atoms in a solid or at a surface, since this interference is very sensitive to differences in path lengths and hence to relative atomic positions (see section B1.9).

It is relatively straightforward to determine the *size and shape of the three- or two-dimensional unit cell* of a periodic bulk or surface structure, respectively. This information follows from the *exit directions* of diffracted beams relative to an incident beam, for a given crystal orientation: measuring those exit angles determines the unit cell quite easily. But no *relative positions* of atoms within the unit cell can be obtained in this manner. To achieve that, one must measure *intensities* of diffracted beams and then computationally analyze those intensities in terms of atomic positions.

With XRD applied to bulk materials, a detailed structural analysis of atomic positions is rather straightforward and routine for structures that can be quite complex (see B1.9): *direct methods* in many cases give good results in a single step, while the resulting atomic positions may be refined by iterative fitting procedures based on simulation of the diffraction process.

With electron diffraction, by contrast, the task is more complicated due to *multiple scattering* of the electrons from atom to atom (see B1.18). Such multiple scattering is especially strong at the relatively low energies employed to study surfaces. This dramatically restricts the application of direct methods, and strongly increases the computational cost of simulating the diffraction process. As a result, an iterative *trial-and-error fitting* is the method of choice with electron diffraction, even though it can be a slow process when many trial structures have to be tested.

Also, the result of any diffraction-based trial-and-error fitting is not necessarily unique: it is always possible that there exists another untried structure that would give a better fit to experiment. Hence, a multi-technique approach that provides independent clues to the structure is very fruitful and common in surface science: such clues include chemical composition, vibrational analysis, and position restrictions implied by other structural methods. This can greatly restrict the number of trial structures which must be investigated.

non-periodic structures

Diffraction is not limited to periodic structures [1]. Non-periodic imperfections such as defects or vibrations, as well as sample-size or domain effects, are inevitable in practice but do not cause much difficulty or can be taken into account when studying the ordered part of a structure. Some other forms of disorder can also be handled quite well in their own right, such as *lattice-gas* disorder in which a given site in the unit cell is randomly occupied with less than 100% probability. At surfaces, lattice-gas disorder is very common when atoms or molecules are adsorbed on a substrate. The local adsorption structure in the given site can be studied in detail.

non-planar initial waves

More fundamental is the distinction between planar and spherical initial waves. In x-ray diffraction, for instance, the incident x-rays are well described by plane waves; this is generally true of probes that are aimed at the sample from macroscopic distances, as is the case also in most forms of electron and neutron diffraction. However, there are techniques in which a wave is generated locally within the sample, for instance through emission of an x-ray (by fluorescence) or an electron (by photoemission) from a sample atom. In such *point-source emission*, the wave which performs the useful diffraction initially has a spherical

rather than planar character; it is centered on the nucleus of an atom, with a rapidly decaying amplitude as it travels away from the emitting site. (Depending on the excitation mechanism, this initial wave need not be spherically symmetrical, but may also have an angular variation, as given by spherical harmonics, for instance, or combinations thereof).

This spherical outgoing wave can diffract only from atoms that are near to the emitting atom, mainly those atoms within a distance of a few atomic diameters. In these circumstances, the crystallinity of the sample is of less importance: the diffracting wave sees primarily the *local* atomic-scale neighborhood of the emitting atoms. As long as the same local neighborhood predominates everywhere in the sampled part of the surface, information about the structure of that neighborhood can be extracted. It also helps very much if the local neighborhood has a constant orientation, so that the experiment does not average over a multitude of orientations, since these tend to average out diffraction effects and thus wash away structural information.

variety of diffraction methods

From the above descriptions, it becomes apparent that one can include a wide variety of techniques under the label "diffraction methods". Table B1.21.1 lists many techniques used for surface structural determination, and specifies which can be considered diffraction methods due to their use of wave

interference (Table B1.21.1 also explains many technique acronyms commonly used in surface science). The diffraction methods range from the classic case of x-ray diffraction (XRD) and the analogous case of low-energy electron diffraction (LEED) to much more subtle cases like x-ray absorption fine structure (XAFS, listed as both SEXAFS and NEXAFS in the table).

XAFS is a good example of less obvious diffraction [2, 3]. In XAFS, an electron is emitted by an x-ray locally within the sample. It propagates away as a spherical wave, which is allowed to back-scatter from neighboring atoms to the emitter atom. The back-scattered electron wave interferes at the emitting atom with the emitted wave, thereby modulating the probability of the emitting process itself when the energy (wavelength) is varied: as one cycles through constructive and destructive interferences, the emission probability oscillates with a period that reflects the interatomic distances. This emission probability is however measured through yet another process (e.g. absorption of the incident x-rays, or emission of other x-rays or other electrons), which oscillates in synchrony with the interference. Thus, the structure-determining diffraction is in such a case buried relatively deeply in the overall process, and does not closely resemble the classic plane-wave diffraction of XRD.

B1.21.2.2 Surface sensitivity

There are several approaches to gain the required surface sensitivity with diffraction methods. We review several of these here, emphasizing the case of solid/vacuum interfaces; some of these also apply to other interfaces.

short mean free path

One obvious method to obtain surface sensitivity is to choose probes and conditions that give shallow penetration. This can be achieved through a short *mean free path* λ , i.e. a short average distance until the probe (e.g., x-ray or electron) is absorbed by energy loss or is otherwise removed from the useful diffraction channels. For typical x-rays, λ is of the order of micrometers in many materials, which is too large compared to the desired surface thickness [4].

But for electrons of low kinetic energies, i.e. $E \approx 10 - 1000$ eV, the mean free path λ is of the order of 5 - 20 Å [5]. The mean free path has a minimum in the 100 - 200 eV range, with larger mean free paths existing both below and above this range.

Such ideal low mean free paths are the basis of LEED, the technique that has been used most for determining surface structures on the atomic scale. This is also the case of photoelectron diffraction (PD): here, the mean free path of the emitted electrons restricts sensitivity to a similar depth (actually double the depth

of LEED, since the incident x-rays in PD are only weakly attenuated on this scale).

grazing incidence and/or emergence

Another approach to limit the penetration of the probe into the surface region is to use *grazing incidence* and/or *grazing emergence*; this works for those probes that already have a reasonably small mean free path λ . A grazing angle θ (measured from the surface normal, i.e., θ close to 90°) then allows the probe to penetrate to a depth of only about $\lambda \cos(\theta)$. This approach is used primarily for higher-energy electrons above about 1000 eV in a technique called reflection high-energy electron diffraction (RHEED) [6].

With XRD, however, the mean free path is still too long to make this approach practical by itself [4]: as an example, to obtain even 100 Å penetration, one would typically need to use a grazing angle of about 0.05° , which is technically extremely demanding. The penetration depth is proportional to the grazing angle of incidence at such small angles, so that a 10 times smaller penetration depth requires a further tenfold reduction in grazing angle. In addition, such small grazing angles require samples with a flatness that is essentially impossible to achieve, in order that the x-rays see a flat surface rather than a set of ridges that shadow much of the surface.

total external reflection

In XRD, surface sensitivity can, however, be achieved through another phenomenon [4]: *total external reflection*. This also occurs at grazing angles of incidence, giving rise to the technique acronym of GIXS for grazing-incidence x-ray scattering. At angles within approximately 0.5° of $\theta = 90^\circ$, x-rays cannot penetrate by refraction into materials: the laws of optics imply that the wave velocity of refracted waves in the material would have to be larger than the speed of light under those circumstances, which is impossible for propagating waves.

Instead, the incident wave is totally reflected. However, this is accompanied by a shallow penetration of waves that decay exponentially into the bulk while propagating parallel to the surface. Under such conditions, the decay length into the surface is of the order of 10-30 Å, as desired. This penetration depth depends on the material, and not on the wavelength of the x-rays. Note that total external reflection does not require vacuum: it can occur at various kinds of interfaces, depending on the relative optical constants of the phases in contact.

high-surface area materials

None of the above methods is sufficient for neutrons, however. Neutrons penetrate matter so easily that the only effective approach is to use materials with a very high surface-to-volume ratio. This can be accomplished with small

particles and exfoliated graphite, for instance, but the technique has essentially been abandoned in surface studies. [7, 8]

superlattice diffraction

One further method for obtaining surface sensitivity in diffraction relies on the presence of two-dimensional *superlattices* on the surface. As we shall see further below, these correspond to periodicities that are different from those present in the bulk material. As a result, additional diffracted beams occur (often called fractional-order beams), which are uniquely created by and therefore sensitive to this kind of surface structure. XRD, in particular, makes frequent use of this property [4]. Transmission electron diffraction also has used this property, in conjunction with ultrathin samples to minimize bulk contributions [9].

hybrid methods

As we have seen, the electron is the easiest probe to make surface sensitive. For that reason, a number of hybrid techniques have been designed that combine the virtues of electrons and of other probes. In particular, electrons and photons (x-rays) have been used together in techniques like photoelectron diffraction (PD) [10] and surface extended x-ray absorption fine structure (SEXAFS or EXAFS, which is the high-energy limit of XAFS) [2, 11]. Both of these rely on diffraction by electrons, which have been excited by photons. In

the case of PD, the electrons themselves are detected after emission out of the surface, limiting the depth of "sampling" to that given by the electron mean free path.

elemental and chemical-state resolution

With some techniques, another mechanism can give high surface sensitivity, namely *elemental resolution* through spectroscopic filtering of emitted electrons or x-rays. In this approach, one detects, by setting an energy window, only those electrons or x-rays that are emitted by a particular kind of atom, since each electronic level produces a line at a particular energy given by the level energy augmented by the excitation energy.

Thus, if a "foreign" element is present only at the surface, one can detect a signal that only comes from that element, and therefore only from the surface. Given sufficient energy resolution, one can even differentiate electrons coming from the same atoms in different bonding environments, e.g., in the case of a clean surface, atoms of the outermost layer vs. bulk atoms [10]. This *chemical-state resolution* is due to the fact that electronic levels are shifted by bonding to other atoms, resulting in different emitted lines from atoms in different bonding situations.

Elemental and chemical-state resolution affords the possibility of detecting only a monolayer or even a fraction of a monolayer. This approach is prevalent in photoelectron diffraction and in methods based on x-ray fluorescence.

It is also used in SEXAFS [11]: as we have seen, photoexcited electrons are back-reflected to the photoemitting atoms, thereby modulating the x-ray absorption cross-section through electron wave interference, after which a secondary electron or ion or fluorescent x-ray is ejected from the surface and finally detected. This latter ejection process provides surface sensitivity, through the electronic mean free path or the shallowness of ionic emission. However, elemental and chemical-state selection by energy filtering is essentially universal here, and again can give monolayer resolution with emission from foreign surface atoms different from the bulk atoms.

A similar device can be applied to a form of x-ray diffraction called the x-ray standing wave (XSW) method [12, 13], as detected by fluorescence. Here, x-ray waves reflected from bulk atomic planes form a standing wave pattern near the surface. The maxima and minima of this standing wave pattern can be arranged to fall at different locations on the atomic scale, by varying the energy and incidence angles. Thereby, the induced fluorescence varies with the location of those maxima and minima. Since the fluorescence is element-specific, one can thus determine positions of foreign surface atoms relative to the extended bulk lattice (it remains difficult, however, to locate those substrate atoms that are

close to the fluorescing surface atoms, because they are drowned by the bulk signal).

B1.21.3 STATISTICS OF FULL STRUCTURAL DETERMINATIONS

Many methods have been developed to determine surface structure: we have mentioned several in the previous subsection, and there are many more. To get an idea of their relative usage and importance, we here examine historical statistics. We also review the kinds of surface structure that have been studied to date, which gives a feeling for the kinds of surface structures that current methods and technology can most easily solve. This will provide an overview of the range of surfaces for which detailed surface structures are known, and those for which very little is known.

As source of information we use the Surface Structure Database [14], a critical compilation of surface structures solved in detail, covering the period through the end of 1997. It contains 1113 structural determinations, with on average 2 determinations for each structure: thus there are approximately 550 distinct solved structures available.

In terms of individual techniques, Table B1.21.1 lists the breakdown totaled over time, counting from the inception of surface structural determination in the early 1970s. It is seen that LEED has contributed altogether about 67% of all

structural determinations included in the database. The annual share of LEED was 100% until 1978, and has generally remained over 50% since then. In 1979 other methods started to produce structural determinations, especially PD, IS and SEXAFS. XRD and then XSW started to contribute results in the period 1981-83.

As the table shows, a host of other techniques have contributed a dozen or fewer results each. It is seen that diffraction techniques have been very prominent in the field: the major diffraction methods have been LEED, PD, SEXAFS, XSW, XRD, while others have contributed less, such as NEXAFS, RHEED, LEPD, HREELS, MEED, AED, SEELFS, TED and AD. The major non-diffraction method is ion scattering (IS), which is described in section B1.23.

The database provides interesting perspectives on the evolution of surface structural determination since its inception around 1970. Not surprisingly, there is a clear temporal trend toward more complex and more diverse materials, such as compound substrates, alloyed bimetallic surfaces, complex adsorbate-induced relaxations and reconstructions, epitaxial and pseudomorphic growth, alkali adsorption on semiconductor and transition metal substrates, and molecular adsorbates as well as coadsorbates on metal surfaces. The complexity of some solved structures has grown to about 100 times that of the earliest structures. The range of structure types can also be gauged, for instance, from the list of substrate lattice categories included in the SSD database: bcc, CdCl₂, CdI₂,

corundum, CsCl, CuAu I, Cu₃Au, diamond, fcc, fluorite, graphite, hcp, hexagonal, NaCl, perovskite, rutile, spinel, wurtzite, zincblende, 2H-MoS₂, 2H-NbSe₂, and 6H-SiC.

Nonetheless, when counting all structures solved over time, one finds a strong predominance of studies in certain narrow categories, as exhibited by the following uneven statistics:

- fcc metals far outdistance any other substrate lattice type, with 60% of the total;
- the diamond lattice (C, Si and Ge) forms the next most numerous lattice category, about 10%, followed by the bcc (9%) and hcp (7%) lattices;
- elemental solids (with or without foreign adsorbates) form 85% of the substrates examined, the rest being metallic alloys (7%) or other compounds (8%);
- the surfaces of *non-reconstructed* elemental metal substrates (with or without adsorbates) constitute about 77% of the results; the remainder are *reconstructed*, i.e. have undergone a substantial structural change from the ideal termination of the bulk lattice, involving bond breaking and/or bond making;
- looking at electronic properties, metals again dominate heavily, with 81% of the total, followed by semiconductors (16%), insulators (3%) and semimetals (less than 1%);

- atomic overlayers comprise about 54% of all types of adsorption, as opposed to interstitial (1%) or substitutional (5%) underlayers, molecular overlayers (10%), multilayers (9%) or mixes of these adsorption modes.

There is much room for further studies of various important categories of materials: one prominent example is oxides and other compounds (carbides, nitrides, ...); another is all types of adsorption on oxides and other compounds.

However, recent advances in techniques will ensure further diversification and complexification of solved surface structures. The present maturity of techniques will thus increasingly allow the analysis of structures chosen for their practical interest rather than for their simplicity.

B1.21.4 TWO-DIMENSIONAL ORDERING AND NOMENCLATURE

In diffraction, the degree and kind of structural ordering is an important consideration, since the diffraction reflects those structural properties. As a result, diffraction methods are ideal for characterizing the degree and type of ordering that a surface exhibits. In particular, at surfaces, LEED has always been a favorite tool for "fingerprinting" a particular state of ordering of a surface, enhancing experimental reproducibility. It is therefore useful to first briefly examine the forces that are responsible for the variety of ordering types that occur at surfaces. Then, we can introduce standard notation to succinctly

describe specific forms of ordering that occur at surfaces.

B1.21.4.1 Two-dimensional ordering

A large number of ordered surface structures can be produced experimentally on single-crystal surfaces, especially with adsorbates [15]. There are also many disordered surfaces. Ordering is driven by the interactions between atoms, ions, or molecules in the surface region. These forces can be of various types: covalent, ionic, Van der Waals, etc. And there can be a mix of such types of interaction, not only within a given bond, but also from bond to bond in the same surface. A surface could, for instance, consist of a bulk material with one type of internal bonding (say, ionic). It may be covered with an overlayer of molecules with a different type of intramolecular bonding (typically covalent). And the molecules may be held to the substrate by yet another form of bonds (e.g., Van der Waals).

Strong adsorbate-substrate forces lead to *chemisorption*, in which a chemical bond is formed. By contrast, weak forces result in *physisorption*, as one calls non-chemical “physical” adsorption.

The balance between these different types of bonds has a strong bearing on the resulting ordering or disordering of the surface. For adsorbates, the relative strength of adsorbate-substrate and adsorbate-adsorbate interactions is

particularly important. When adsorbate-substrate interactions dominate, well-ordered overlayer structures are induced that are arranged in a *superlattice*, i.e. a periodicity which is closely related to that of the substrate lattice: one then speaks of *commensurate* overlayers. This results from the tendency for each adsorbate to seek out the same type of *adsorption site* on the surface, which means that all adsorbates attempt to bond in the same manner to substrate atoms.

An example of commensurate overlayers is provided by atomic sulfur chemisorbed on a Ni(100) surface: all S atoms tend to adsorb in the *four-fold coordinated hollow sites*, i.e., each S atom tries to bond to four Ni atoms. At typical high coverages and moderate temperatures, this results in an ordered array of S atoms on the Ni(100) surface. However, high temperatures will disorder such overlayers; also this layer may be kinetically disordered during its formation, as a result of gradual addition of sulfur atoms before they manage to order. The same is often true of molecular adsorption. Although intramolecular bonding can be strong enough to keep an adsorbed molecular species intact despite its bonding to the substrate, there is usually only a relatively weak mutual interaction among adsorbed molecular species.

Relatively strong adsorbate-adsorbate interactions have a different effect: the adsorbates attempt to first optimize the bonding between them, before trying to satisfy their bonding to the substrate. This typically results in close-packed

overlayers with an internal periodicity that it is not matched, or at least is poorly matched, to the substrate lattice. One thus finds well-ordered overlayers whose periodicity is generally not closely related to the substrate lattice: this leads to so-called *incommensurate* overlayers. Such behavior is best exemplified by very cohesive overlayers like graphite sheets or oxide thin films that adopt their own preferred lattice constant regardless of the substrate material on which they are adsorbed.

B1.21.4.2 Coverage and monolayer definitions

It is useful to define the terms *coverage* and *monolayer* for adsorbed layers, since different conventions are used in the literature. The surface coverage measures the 2-dimensional density of adsorbates. The most common definition of coverage sets it to be equal to one monolayer (1 ML) when each 2-dimensional surface unit cell of the unreconstructed substrate is occupied by one adsorbate (the adsorbate may be an atom or a molecule). Thus, an overlayer with a coverage of 1 ML has as many atoms (or molecules) as does the outermost single atomic layer of the substrate.

However, many adsorbates cannot reach a coverage of 1 ML, as defined in this way: this occurs most clearly when the adsorbate is too large to fit in one unit cell of the surface. For example, benzene molecules normally lie flat on a metal surface, but the size of the benzene molecule is much larger than typical

unit cell areas on many metal surfaces. Thus, such an adsorbate will saturate the surface at a lower coverage than 1 ML; deposition beyond this coverage can only be achieved by starting the growth of a second layer on top of the first layer.

It is thus tempting to define the first saturated layer as being one monolayer, and this often done, causing some confusion. One therefore also often uses terms like *saturated monolayer* to indicate such a single adsorbate layer that has reached its maximal two-dimensional density. Sometimes, however, the word “saturated” is omitted from this definition, resulting in a different notion of monolayer and coverage. One way to reduce possible confusion is to use, for contrast with the saturated monolayer, the term *fractional monolayer* for the term that refers to the substrate unit cell rather than the adsorbate size as the criterion for the monolayer density.

B1.21.4.3 Two-dimensional crystallographic nomenclature

Miller indices

Single-crystal surfaces are characterized by a set of Miller indices that indicate the particular crystallographic orientation of the surface plane relative to the bulk lattice [5]. Thus, surfaces are labeled in the same way that atomic planes are labeled in bulk x-ray crystallography. For example, a Ni(111) surface has a surface plane that is parallel to the (111) crystallographic plane of bulk

nickel. Thus, the Ni(111) surface exposes a hexagonally close-packed layer of atoms, given that nickel has a face-centered close-packed (fcc) cubic bulk lattice, cf. Figure B1.21.1(a). Some authors use the more correct notation $\{111\}$ instead of (111), as is common in bulk crystallography to emphasize that the (111) plane is only one of several symmetrically-equivalent plane orientations, like $(11\bar{1})$, $(\bar{1}11)$, etc. The $\{111\}$ notation implicitly includes all such equivalent planes.

FIGURE B1.21.1 (a-h) NEAR HERE

Figure B1.21.1 shows a number of other clean unreconstructed low-Miller-index surfaces. Most surfaces studied in surface science have low Miller indices, like (111), (110) and (100). These planes correspond to relatively close-packed surfaces that are atomically rather smooth. With fcc materials, the (111) surface is the densest and smoothest, followed by the (100) surface; the (110) surface is somewhat more "open", in the sense that an additional atom with the same or smaller diameter can bond directly to an atom in the *second* substrate layer. For the hexagonal close-packed (hcp) materials, the (0001) surface is very similar to the fcc(111) surface: the difference only occurs deeper into the surface, namely in the fashion of stacking of the hexagonal close-packed monolayers onto each other (ABABAB... vs. ABCABC..., in the convenient layer-stacking notation). The hcp($10\bar{1}0$) surface resembles the fcc(110) surface to some extent, in that it

also presents open troughs between close-packed rows of atoms, exposing atoms in the second layer. With the body-centered cubic (bcc) materials, the (110) surface is the densest and smoothest, followed by the (100) surface; in this case, the (111) surface is rather more open and atomically “rough”.

high-Miller-index or stepped surfaces

The atomic structures of high-Miller-index surfaces are composed of *terraces*, separated by *steps*, which may have *kinks* in them [5]. Examples are shown in Figure B1.21.2. Thus, the (755) surface of an fcc crystal consists of (111) terraces, six atoms deep (from one step to the next), separated by straight steps of (100) orientation and of single-atom height. The fcc(10,8,7) has “kinks” in its step edges, i.e. the steps themselves are not straight. The steps and kinks provide a degree of roughness that can be very important as sites for chemical reactions or for nucleation of crystal growth.

FIGURE B1.21.2 NEAR HERE

The step notation [5, 16] compacts the terrace/step information into the general form $w(h_t k_t l_t) \times (h_s k_s l_s)$. Here $(h_t k_t l_t)$ and $(h_s k_s l_s)$ are the Miller indices of the terrace plane and the step plane, respectively, while w is the number of

atoms that are counted in the width of the terrace, including the step-edge atom and the in-step atom. Thus, the fcc(755) surface can be denoted by $6(111) \times (100)$, since its terraces are 6 atoms in depth. A kinked surface, like fcc(10,8,7), can also be approximately expressed in this form: the step plane ($h_s k_s l_s$) is a stepped surface itself, and thus has higher Miller indices than the terrace plane. However, the step notation does not exactly tell the relative location of adjacent steps, and it is not entirely clear how the terrace width w should be counted. A more complete microfacet notation is available to describe kinked surfaces generally [5].

superlattices

Many surfaces exhibit a different periodicity than expected from the bulk lattice, as is most readily seen in the diffraction patterns of LEED: often additional diffraction features appear which are indicative of a *superlattice*. This corresponds to the formation of a new two-dimensional lattice on the surface, usually with some simple relationship to the expected "ideal" lattice [5]. For instance, a layer of adsorbate atoms may occupy only every other equivalent adsorption site on the surface, in both surface dimensions. Such a lattice can be labeled (2x2): in each surface dimension the repeat distance is doubled relative to the ideal substrate. In this example, the unit cell of the original bulk-like surface is magnified by a factor 2 in both directions, so that the new surface unit cell has dimensions (2x2) relative to the original unit cell. For instance, an

oxygen overlayer on Pt(111), at a quarter-monolayer coverage, is observed to adopt an ordered (2x2) superlattice: this can be denoted as Pt(111)+(2x2)-O, which provides a compact description of the main crystallographic characteristics of this surface. This particular notation is that of the Surface Structure Database [14]; other equivalent notations are also common in the literature, such as Pt(111)-(2x2)-O or Pt(111)2x2-O.

This (2x2) notation can be generalized. First, it can take on the form $(m \times n)$, where the numbers m and n are two independent stretch factors for the two unit cell vectors. These numbers are often integers, but need not be. In addition, this new stretched unit cell can be rotated by any angle about the surface normal: this is denoted as $(m \times n)R\alpha^\circ$, where α is the rotation angle in degrees [5, 17, 18, 19]; the suffix $R\alpha^\circ$ is omitted when $\alpha=0$, as is the case for Pt(111)+(2x2)-O. This *Wood notation* [5, 19] allows the original unit cell to be stretched and rotated; however, it conserves the angle between the two unit cell vectors in the plane of the surface, therefore not allowing "sheared" unit cells.

As a particular case, a surface may be given the Wood notation (1x1), as in Ni(111)-(1x1): this notation indicates that the two-dimensional unit cell of the surface has the same size as the two-dimensional unit cell of the bulk (111) layers. Thus, an ideally terminated bulk lattice without overlayers or reconstructions will carry the label (1x1).

The Wood notation can be generalized somewhat further, by adding either the prefix "c" for centered, or the prefix "p" for primitive. For instance, one may have a c(2x2) unit cell or a p(2x2) unit cell, the latter often abbreviated to (2x2) because it is identical to it. In a centered unit cell, the center of the cell is an exact copy of the corners of the cell; this makes the cell non-primitive, i.e., it is no longer the smallest cell that, when repeated periodically across the surface, generates the entire surface structure. Nonetheless, the centered notation is often used because it can be quite convenient, as the next example will illustrate.

The c(2x2) unit cell can also be written as $(\sqrt{2} \times \sqrt{2})R45^\circ$. Here, the original unit vectors of the (1x1) structure have both been stretched by factors $\sqrt{2}$ and then rotated by 45° . Thus, sulfur on Ni(100) forms an ordered half-monolayer structure that can be labeled as Ni(100)+c(2x2)-S or, equivalently, Ni(100)+ $(\sqrt{2} \times \sqrt{2})R45^\circ$ -S. The c(2x2) notation is clearly easier to write and also easier to convert into a geometrical model of the structure, and hence is the favored designation.

A more general notation than Wood's is available for all kinds of unit cells, including those that are sheared, so that the superlattice unit cell can take on any shape, size and orientation. It is the *matrix notation*, defined as follows [5]. We connect the unit cell vectors **a'** and **b'** of the superlattice to the unit cell vectors **a** and **b** of the substrate by the general relations:

$$\mathbf{a}' = m_{11} \mathbf{a} + m_{12} \mathbf{b}$$

$$\mathbf{b}' = m_{21} \mathbf{a} + m_{22} \mathbf{b}$$

The coefficients m_{11} , m_{12} , m_{21} and m_{22} define the matrix $\mathbf{M} = \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix}$, which

serves to denote the superlattice. The (1x1), (2x2) and c(2x2) lattices are then

denoted respectively by the matrices $\mathbf{M} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$, $\mathbf{M} = \begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}$ and $\mathbf{M} = \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}$.

This allows the Ni(100)+c(2x2)-S structure to be also written as Ni(100)+ $\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}$ -

S. Clearly, this notation is not as intuitive and compact as the c(2x2) Wood

notation. However, when the Wood notation is not capable of a clear and

compact notation, use of the matrix notation is necessary. Thus, a structure

characterized by a matrix like $\mathbf{M} = \begin{pmatrix} 4 & -3 \\ 2 & 5 \end{pmatrix}$ could not be described in the Wood

notation.

In LEED experiments, the matrix \mathbf{M} is determined by visual inspection of the diffraction pattern, thereby defining the periodicity of the surface structure: the relationship between surface lattice and diffraction pattern will be described in more detail in the next subsection.

A superlattice is termed *commensurate* when all matrix elements m_{ij} are integers. If at least one matrix element m_{ij} is an irrational number (not a ratio of

integers), then the superlattice is termed *incommensurate*. A superlattice can be incommensurate in one surface dimension, while commensurate in the other surface dimension, or it could be incommensurate in both surface dimensions.

A superlattice can be caused by adsorbates adopting a different periodicity than the substrate surface, or also by a reconstruction of the clean surface. In Figure B1.21.3 several superlattices that are commonly detected on low-Miller-index surfaces are shown with their Wood notation.

FIGURE B1.21.3 NEAR HERE

B1.21.5 SURFACE DIFFRACTION PATTERN

The diffraction pattern observed in LEED is one of the most commonly used “fingerprints” of a surface structure. With XRD or other non-electron diffraction methods, there is no convenient detector that images in real time the corresponding diffraction pattern. Point-source methods, like photoelectron diffraction, do not produce a convenient spot pattern, but a diffuse diffraction pattern that does not simply reflect the long-range ordering.

So it is essential to relate the LEED pattern to the surface structure itself. As mentioned earlier, the diffraction pattern does not indicate relative atomic positions within the structural unit cell, but only the size and shape of that unit cell. However, since experiments are mostly performed on surfaces of materials with a known crystallographic bulk structure, it is often a good starting point to assume an ideally terminated bulk lattice; the actual surface structure will often be related to that ideal structure in a simple manner, e.g. through the creation of a superlattice that is directly related to the bulk lattice.

In this subsection, we concentrate on the relationship between diffraction pattern and surface lattice [5]. In direct analogy with the three-dimensional bulk case, the *surface lattice* is defined by two vectors **a** and **b** parallel to the surface (defined already above), subtended by an angle γ ; **a** and **b** together specify one unit cell, as illustrated in figure B1.21.4. Within that unit cell atoms are arranged according to a *basis*, which is the list of atomic coordinates within that unit cell; we need not know these positions for the purposes of this discussion. Note that this unit cell can be viewed as being infinitely deep in the third dimension (perpendicular to the surface), so as to include all atoms below the surface to arbitrary depth.

FIGURE B1.21.4 NEAR HERE

There are several special shapes of the surface lattice, forming the five two-dimensional Bravais lattices shown in Figure B1.21.4. The Bravais lattices form the complete list of possible lattices. They are characterized by unit cell vectors of equal length (in the case of the square and hexagonal lattices), and/or a subtended angle of 90° or 60° (for the square, rectangular and hexagonal lattices), or by completely general values (for the oblique lattice). The rectangular lattice comes in two varieties: primitive and centered. The centered lattice has the particularity that its atomic basis is duplicated: each atom is reproduced by displacement through the vector $\frac{1}{2}(\mathbf{a} + \mathbf{b})$. The main value of the centered rectangular lattice is its convenience: it is easier to think in terms of the rectangle (with duplicated basis) than to think of the rhombus with arbitrary angle γ . One could also center any of the other lattices, but one would only produce another instance of a square, rectangular or oblique lattice, i.e. nothing more convenient.

The diffraction of low-energy electrons (and any other particles, like x-rays and neutrons) is governed by the translational symmetry of the surface, i.e. the surface lattice. In particular, the directions of emergence of the diffracted beams are determined by conservation of the linear momentum parallel to the surface, $\hbar\mathbf{k}_\parallel$. Here \mathbf{k} denotes the wave vector of the incident plane electron wave that represents the incoming electron beam. This conservation can occur in two ways. After the diffractive scattering, the parallel component of the momentum

$\hbar\mathbf{k}'_{\parallel}$ can be equal to that of the incident electron beam, i.e. $\hbar\mathbf{k}'_{\parallel} = \hbar\mathbf{k}_{\parallel}$; this corresponds to *specular* (mirror-like) reflection, with equal polar angles of incidence and emergence with respect to the surface normal, and with a simple reversal of the perpendicular momentum $\hbar\mathbf{k}'_{\perp} = -\hbar\mathbf{k}_{\perp}$.

Alternatively, the electron can exchange parallel momentum with the lattice, but only in well-defined amounts given by vectors $\hbar\mathbf{g}$ that belong to the *reciprocal lattice* of the surface. That is, the vector \mathbf{g} is a linear combination of two reciprocal lattice vectors \mathbf{a}^* and \mathbf{b}^* , with integer coefficients. Thus, $\mathbf{g} = h\mathbf{a}^* + k\mathbf{b}^*$, with arbitrary integers h and k (note that all the vectors \mathbf{a} , \mathbf{b} , \mathbf{a}^* , \mathbf{b}^* and \mathbf{g} are parallel to the surface). The reciprocal lattice vectors \mathbf{a}^* and \mathbf{b}^* are related to the “direct-space” lattice vectors \mathbf{a} and \mathbf{b} through the following non-transparent definitions, which also use a vector \mathbf{n} that is perpendicular to the surface plane, as well as vectorial dot and cross products:

$$\mathbf{a}^* = 2\pi \left(\frac{\mathbf{b} \times \mathbf{n}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{n})} \right) \text{ and } \mathbf{b}^* = 2\pi \left(\frac{\mathbf{n} \times \mathbf{a}}{\mathbf{b} \cdot (\mathbf{n} \times \mathbf{a})} \right).$$

These two equations are a special case of the corresponding three-dimensional definition, common in XRD, with the surface normal \mathbf{n} replacing the third lattice vector \mathbf{c} .

Figure B1.21.4 illustrates the “direct-space” and reciprocal-space lattices for the five two-dimensional Bravais lattices allowed at surfaces. It is useful to realize that the vector \mathbf{a}^* is always perpendicular to the vector \mathbf{b} and that \mathbf{b}^* is always perpendicular to \mathbf{a} . It is also useful to notice that the length of \mathbf{a}^* is inversely proportional to the length of \mathbf{a} , and likewise for \mathbf{b}^* and \mathbf{b} . Thus, a large unit cell in direct space gives a small unit cell in reciprocal space, and a wide rectangular unit cell in direct space produces a tall rectangular unit cell in reciprocal space. Also, the hexagonal direct-space lattice gives rise to another hexagonal lattice in reciprocal space, but rotated by 90° with respect to the direct-space lattice.

The reciprocal lattices shown in figures B1.21.3 and B1.21.4 correspond directly to the diffraction patterns observed in LEED experiments: each reciprocal-lattice vector produces one and only one diffraction spot on the LEED display. It is very convenient that the hemispherical geometry of the typical LEED screen images the reciprocal lattice without distortion; for instance, for the square lattice one observes a simple square array of spots on the LEED display.

One of the spots in such a diffraction pattern represents the specularly reflected beam, usually labeled (00). Each other spot corresponds to another reciprocal-lattice vector $\mathbf{g}=h\mathbf{a}^*+k\mathbf{b}^*$, and is thus labeled (hk) , with integer h and k .

When a superlattice is present, additional spots arise in the diffraction pattern, as shown in Figure B1.21.3 in terms of the reciprocal lattice: again, each reciprocal lattice point corresponds to a spot in a diffraction pattern. This can be easily understood from the fact that a larger unit cell in direct space imposes a smaller unit cell in reciprocal space. For instance, a (2x1) superlattice has a unit cell doubled in length in one surface direction relative to the (1x1) lattice, i.e. \mathbf{a} is replaced by $2\mathbf{a}$. According to the above equations, this has no effect on \mathbf{b}^* , but halves \mathbf{a}^* . This is equivalent to allowing h to be a half-integer in $\mathbf{g}=h\mathbf{a}^*+k\mathbf{b}^*$, thus doubling the number of spots in the diffraction pattern. These additional spots are therefore often called half-order spots in the (2x1) case, or fractional-order spots in the general case.

With some practice, one can easily recognize specific superlattices from their LEED pattern. Otherwise, one can work through the above equations to connect particular superlattices to a given LEED pattern. A number of examples are given and discussed in some detail in [5]. A discussion can also be found there of the special case of stepped and kinked surfaces.

B1.21.6 DIFFRACTION PATTERN OF DISORDERED SURFACES

Many forms of disorder in a surface structure can be recognized in the LEED pattern. The main manifestations of disorder are *broadening* and *streaking* of diffraction spots and *diffuse* intensity between spots [1].

Broadening of spots can result from thermal diffuse scattering and island formation, among other causes. The thermal effects arise from the disorder in atomic positions as they vibrate around their equilibrium sites; the sites themselves may be perfectly crystalline.

Islands occur particularly with adsorbates that aggregate into two-dimensional assemblies on a substrate, leaving bare substrate patches exposed between these islands. Diffraction spots, especially fractional-order spots if the adsorbate forms a superlattice within these islands, acquire a width that depends inversely on the average island diameter. If the islands are systematically anisotropic in size, with a long dimension primarily in one surface direction, the diffraction spots are also anisotropic, with a small width in that direction. Knowing the island size and shape gives valuable information regarding the mechanisms of phase transitions, which in turn permit one to learn about the adsorbate-adsorbate interactions.

Lattice-gas disorder, in which adatoms occupy a periodic lattice of equivalent sites with a random occupation probability, produces diffuse intensity distributions between diffraction spots. For complete disorder, one observes such diffuse intensity throughout the diffraction pattern. If there is order in one surface direction, but disorder in the other, one observes streaking in the diffraction pattern: the direction of the streaks corresponds to the direction in

which disorder occurs. In principle, the diffuse intensity distribution can be converted into a direct-space distribution, including a pair-correlation function between occupied sites, e.g. by Fourier transformation. However, the diffuse intensity is too much affected by other diffraction effects (like multiple scattering) to be very useful in this manner. It nonetheless can be interpreted in terms of local structure, i.e. bond lengths and angles, by a procedure that is very similar to the multiple-scattering modeling for solving structures in full detail [20].

LEED has found a strong competitor for studying surface disorder: scanning tunneling microscopy, STM (see section B1.20). Indeed, STM is the ideal tool for investigating irregularities in periodic surface structures. LEED (as any other diffraction method) averages its information content over macroscopic parts of the surface, giving only statistical information about disorder. By contrast, STM can provide a direct image of individual atoms or defects, enabling the observation of individual atomic behavior. By observing a sufficiently large area, STM can also provide statistical information, if desired.

B1.21.7 FULL STRUCTURAL DETERMINATION

In the previous subsections we have emphasized the two-dimensional information available through the diffraction pattern observed in LEED. But, as mentioned before, one can extract the detailed atomic positions as well, including interlayer spacings, bond lengths, bond angles, etc. Here we sketch how this

more complete structural determination is accomplished. We focus on the case of LEED, since this method has produced by far the most structural determinations [5, 17, 18, 21]. The procedures employed to analyze photoelectron diffraction data are in fact very similar to those for LEED, in many details. With XRD, the kinematic (single-scattering) nature of the problem makes the analysis simpler, but still considerable for complex structures: there also, a trial-and-error search for the solution is common.

To obtain spacings between atomic layers and bond lengths or angles between atoms, it is necessary to measure and analyze the *intensity* of diffraction spots. This is analogous to measuring the intensity of XRD reflections.

The measurement of LEED spot intensities is nowadays mostly accomplished by digitizing the image recorded by a video camera that observes the diffraction pattern, which is visibly displayed on a fluorescent screen within an ultra-high vacuum system [22]. The digitized image is then processed by computer to give the integrated spot intensity, after removal of the background. This is repeated for different incident electron energies. Thereby, the intensity of each spot is obtained as a function of the incident electron energy, resulting in an *IV-curve* (intensity-voltage curve) for each spot. Computer codes for this purpose are available, and are normally packaged together with the required hardware [23]. The resulting IV-curves form the experimental database to which theory can fit

the atomic structure. It typically takes between minutes and an hour to accumulate such a database, once the sample has been prepared.

Since electron diffraction by a surface is a complicated process, there is no routine method available to *directly* and accurately extract atomic positions from the experimental data. Direct holographic methods have been proposed [24], but have not yet become routine methods, and in any case they yield only approximate atomic positions (with uncertainties on the scale of 0.2 – 0.5 Å) and work only for relatively simple structures; when they do work they have to be followed up by refinement using the same trial-and-error approach that we discuss next.

A detailed structural determination proceeds by modeling the full multiple scattering of the electrons that are diffracted through the surface structure. The multiple scattering means that an electron can bounce off a succession of atoms in an erratic path before emerging from the surface. Various theoretical and computational methods are available to treat this problem to any degree of precision: a compromise between precision and computing expense must be struck, with progress moving toward higher precision, even for more complex structures.

The modeling of the multiple scattering requires input of all atomic positions, so that the *trial-and-error approach* must be followed: one guesses reasonable

models for the surface structure, and tests them one by one until satisfactory agreement with experiment is obtained.. For simple structures, and in cases where structural information is already known from other sources, this process is usually quite quick: only a few basic models may have to be checked, e.g. adsorption of an atomic layer in hollow, bridge or top sites at positions consistent with reasonable bond lengths. It is then relatively easy to refine the atomic positions within the best-fit model, resulting in a complete structural determination. The refinement is normally performed by some form of *automated steepest-descent optimization*, which allows many atomic positions to be adjusted simultaneously [21]. Computer codes are also available to accomplish this part of the analysis [25]. The trail-and-error search with refinement may take minutes to hours on current workstations or personal computers.

In more complex cases, and when little additional information is available, one must test a larger number of possible structural models. The computational time grows rapidly with complexity, so that it may take hours to check a single model. More time-consuming, however, is often the human factor in guessing what are reasonable models to test. This is a much more difficult problem, which is the issue of finding the "global optimum", not just a "local optimum". At present, several approaches to *global optimization* are being examined, such as *simulated annealing* [26] and *genetic algorithms* [27]. In any event, these will require larger amounts of computer time, since a wide variety of surface models must be tested in such a global search.

B1.21.8 PRESENT CAPABILITIES AND OUTLOOK

Surface crystallography started in the late 1960s, with the simplest possible structures being solved by LEED [14]. Such structures were the clean Ni(111), Cu(111) and Al(111) surfaces, which are unreconstructed and essentially unrelaxed, i.e. very close to the ideal termination of the bulk shown in Figure B1.21.1(a): typically, only one unknown structural parameter was fit to experiment, namely the spacing between the two outermost atomic layers.

Progress in experiment, theory, computational methods and computer power has contributed to the capability to solve increasingly complex structures [28, 29]. Figure B1.21.5 quantifies this progress with three measures of complexity, plotted logarithmically: the achievable two-dimensional unit cell size, the achievable number of fit parameters and the achievable number of atoms per unit cell per layer: all of these measures have grown from 1 for simple clean metal surfaces, like Ni(111) (cf. Figure B1.21.1(a)), to about 50 to 100 in the case of the reconstructed Si(111)-(7x7) surface, the most complicated structure examined to date [30] (note that the basic model which solved the Si(111)-(7x7) surface was mainly derived from another diffraction study, using TED [9]). All these measures thus exhibit a progression by about two orders of magnitude over less than 25 years.

FIGURE B1.21.5 NEAR HERE

Figures B1.21.6 through B1.21.9 show several of the more complex structures solved by LEED in recent years. They exhibit various effects observed at surfaces:

- clustering of adatoms in $\text{Re}(0001)-(2\sqrt{3}\times 2\sqrt{3})R30^\circ-6S$ [31], cf. Figure B1.21.6;
- hollow-site adsorption and adsorbate-induced relaxations of substrate atoms both in $\text{Re}(0001)-(2\sqrt{3}\times 2\sqrt{3})R30^\circ-6S$ [31] and in $\text{Mo}(100)-c(4\times 2)-3S$ [32], cf. Figure B1.21.7;
- adsorbate-induced reconstruction as well as substitutional adsorption in $\text{Cu}(100)-(4\times 4)-10\text{Li}$ [33], cf. Figure B1.21.8; note that this is the most complex surface structural determination by LEED to date, involving far more adjustable structural parameters than were fit in the $\text{Si}(111)-(7\times 7)$ structure [30];
- compound ionic surface with a large bulk unit cell and very large surface relaxations in $\text{Fe}_3\text{O}_4(111)$ [34], cf. Figure B1.21.9.

FIGURES B1.21.6 - B1.21.9 NEAR HERE

Further progress towards solving more complex surface structures is possible. The biggest challenge on the computational and theoretical side is the identification of the globally optimum structure. Holographic and other methods have not yet provided a convenient way to accomplish this, and would actually fail with structures that have the complexity of Cu(100)-(4x4)-10Li and Si(111)-(7x7). Global-search algorithms, like simulated annealing and genetic algorithms, may provide workable, if perhaps not cheap, solutions.

On the experimental side, a larger measured database is required than is commonly available to determine the large number of structural parameters to be fit. For instance, LEED calculations for the Si(111)-(7x7) surface have been attempted to fit the many tens of unknown structural parameters; however, the amount of experimental data was insufficient for the task, resulting in a multitude of locally-optimum structures, without the ability to discriminate between them. Increasing the database size can be achieved by extending the energy range to higher energies, or by acquiring data at a number of different incidence directions: either way, the calculations become disproportionately more time-consuming, because the computing effort rises quickly with energy and non-symmetrical off-normal incidence directions.

Acknowledgments

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Table Captions

Table B1.21.1

Surface structural determination methods. The second column indicates whether a technique can be considered a diffraction method, in the sense of relying on wave interference. Also shown are statistics of surface structural determinations, extracted from the Surface Structure Database [14], through 1997. Counted here are only "detailed" and complete structural determinations, in which typically the experiment is simulated computationally and atomic positions are fit to experiment. (Some structural determinations are performed by combining two or more methods: those are counted more than once in this table, so that the columns add up to more than the actual 1113 structural determinations included in the database.)

Surface structural determination method	Diffraction method?	Number of structural determinations	Percent of structural determinations
LEED - low-energy electron diffraction	yes	751	67.5
IS - ion scattering (incl. LEIS, MEIS and HEIS for low-, medium- and high-energy ion scattering)	no	102	9.2
PD - photoelectron diffraction (covers a variety of other acronyms, like ARPEFS, ARXPD, ARXPS, ARUPS, NPD, OPD, PED, ...)	yes	88	7.9
SEXAFS - surface extended x-ray absorption fine structure	yes	67	6.0
XSW - x-ray standing wave	yes	52	4.7
XRD - x-ray diffraction (also GIXS, GIXD, ...)	yes	40	3.6
TOF-SARS - time-of-flight scattering and recoiling spectrometry	no	13	1.2
NEXAFS - near-edge x-ray absorption fine structure (also called XANES)	yes	11	1.0
RHEED - reflection high-energy electron diffraction	yes	10	0.9
LEPD - low-energy positron diffraction	yes	5	0.4
HREELS - high-resolution electron energy loss spectroscopy	yes	4	0.4
MEED - medium-energy electron diffraction	yes	3	0.3
AED - Auger electron diffraction	yes	3	0.3
SEELFS - surface extended energy loss fine structure	yes	2	0.2
TED - transmission electron diffraction	yes	1	0.1
AD - atom diffraction	yes	1	0.1
STM - scanning tunneling microscopy	no	1	0.1

Figure Captions

Figure B1.21.1

Atomic hard-ball models of low-Miller-index bulk-terminated surfaces of simple metals with face-centered close-packed (fcc), hexagonal close-packed (hcp) and body-centered cubic (bcc) lattices: (a) fcc(111); (b) fcc(100); (c) fcc(110); (d) hcp(0001); (e) hcp(10-10), usually written as hcp($10\bar{1}0$); (f) bcc(110); (g) bcc(100); and (h) bcc(111). The atomic spheres are drawn with radii that are smaller than touching-sphere radii, in order to give better depth views. The arrows are unit cell vectors. These figures were produced by the software program BALSAC [35].

Figure B1.21.2

Atomic hard-ball models of “stepped” and “kinked” high-Miller-index bulk-terminated surfaces of simple metals with fcc lattices, compared with an fcc(111) surface: fcc(755) is stepped, while fcc(10,8,7) and fcc(25,10,7) are “kinked”. Step-edge atoms are shown singly-hatched, while kink atoms are shown cross-hatched.

Figure B1.21.3

“Direct” lattices (at left) and corresponding reciprocal lattices (at right) of a series of commonly occurring two-dimensional superlattices. Black circles correspond to the ideal (1x1) surface structure, while grey circles represent

adatoms in the direct lattice (arbitrarily placed in “hollow” positions) and open diamonds represent fractional-order beams in the reciprocal space. Unit cells in direct space and in reciprocal space are outlined.

Figure B1.21.4

“Direct” lattices (at left) and reciprocal lattices (middle) for the five two-dimensional Bravais lattices. The reciprocal lattice corresponds directly to the diffraction pattern observed on a standard LEED display. Note that other choices of unit cells are possible; e.g. for hexagonal lattices, one often chooses vectors **a** and **b** that are subtended by an angle γ of 120° rather than 60° . Then the reciprocal unit cell vectors also change: in the hexagonal case, the angle between **a*** and **b*** becomes 60° rather than 120° .

Figure B1.21.5

Evolution with time of the complexity of structural determination achievable with LEED. The unit cell area is measured relative to the the unit cell area of the simple (1x1) structures studied in the early days: thus a (nxn) superstructure (due to reconstruction and/or adsorption) has a unit cell size of n^2 . A (7x7) structure gives a complexity of 49 on this scale. The number of fit parameters measures the number of coordinates fit to experiment in any given structure: a value of 1 was typical of many early determinations, when only one interlayer spacing was fit to experiment. The Si(111)-(7x7) structure has over 100 fit parameters, if one allows only those structural changes in the top two double

layers and the adatom layer that maintain the $p3m1$ symmetry of the substrate. The number of atoms per unit cell refers to so-called composite layers, which are groups of closely-spaced layers: this number dramatically affects computation time in multiple scattering methods. It has grown from 1 in the simplest structures to about 100 in the $\text{Si}(111)-(7 \times 7)$ structure.

Figure B1.21.6

Side and top views of the best-fit structure of the $\text{Re}(0001)-(2\sqrt{3} \times 2\sqrt{3})R30^\circ-6S$ surface structure (with a half-monolayer coverage of sulfur), as determined by LEED [31]. A $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ unit cell is outlined in the top view. Sulfur atoms are drawn as small open circles, Re atoms as large gray circles. Sulfur-sulfur distances in a ring of 6 alternate between 2.95 and 3.32 Å, expanded from the unrelaxed distance between hollow sites of 2.75 Å. Arrows represent lateral relaxations in the topmost metal layer, with the scale of displacements indicated by the lone arrow at right. The bulk interlayer spacing in $\text{Re}(0001)$ is 2.23 Å. Shades of gray identify atoms that are equivalent by symmetry in the sulfur and outermost rhenium layers. The darkest-gray rhenium atoms forming a triangle within a sulfur ring are pulled out of the surface by the adsorbed sulfur, relative to the lighter-gray rhenium atoms in the same layer.

Figure B1.21.7

Top and side views of the best-fit structure of the $\text{Mo}(100)-c(4 \times 2)-3S$ surface structure (with a $3/4$ -monolayer coverage of sulfur), as determined by LEED [32].

A $c(4 \times 2)$ unit cell is outlined in the top view. The sulfur sizes (small black and dark gray circles) have been reduced from covalent for clarity, while the molybdenum atoms (large circles) are drawn with touching radii. The same cross-hatching has been assigned to molybdenum atoms that are equivalent by symmetry in the topmost two metal layers. Two thirds of the sulfur atoms are displaced away from the center of the hollow sites in which they are bonded: these displacements by 0.13 \AA are drawn exaggerated. Arrows in the top view also indicate the directions and relative magnitudes of molybdenum atom displacements (these substrate atoms are drawn in their undisplaced positions, except for the buckling seen in the second molybdenum layer in the side view). The bulk interlayer spacing in Mo(100) is 1.575 \AA .

Figure B1.21.8

Perspective view of the structure of the Cu(100)-(4x4)-10Li surface structure (with a 10/16-monolayer coverage of lithium), as determined by LEED [33]. The atoms are drawn with radii that are reduced by about 15% from covalent radii. The surface fragment shown includes four (4x4) unit cells. Lithium atoms are shown as larger spheres. In each unit cell, four lithium atoms (dark gray) form a flat-topped pyramid (as outlined): the lithium atoms rest in hollow sites on a 3x3 base of nine Cu atoms (lighter gray). Around each pyramid 12 lithium atoms occupy substitutional sites, i.e. have taken the place of Cu atoms: these lithium atoms are shown linked by an octagon. Since the lithium atoms are about 15% larger than the copper atoms that they replace, fewer lithium atoms can fit in the

troughs evacuated by the copper atoms; they, thus, do not fill the troughs completely, and leave a hole at each intersection between troughs (e.g. at the exact center of the fragment). The lightest-gray atoms underneath are the bulk Cu(100) termination: some small local distortions in the atomic positions are also detected by LEED there. This and the following figure were produced with the SARCH / LATUSE / PLOT3D / BALSAC software, available from the author.

Figure B1.21.9

Perspective side and top view of the best-fit structure of $\text{Fe}_3\text{O}_4(111)$, as determined by LEED [34]. A unit cell is outlined in the top view, in which all atoms are drawn with nearly touching radii, while smaller radii are used in the side view. This iron oxide was grown as an ultrathin film on a Pt(111) substrate, in order to prevent electrical charging of the surface. The free surface is at the top end of the side view, exposing 1/4 monolayer of "external" iron ions (shown as small light-gray circles in both views). Large circles represent oxygen ions, forming hexagonally close-packed layers. In each such layer, one fourth of the oxygen ions (drawn in darkest gray) is not coplanar with the others: in particular, in the outermost oxygen layer, these ions are raised outward by a large amount (0.42 Å, compared to 0.04 Å in the opposite direction in the bulk). Small circles below the surface represent iron ions in tetrahedral or octahedral interstitial positions between the O layers: the lightest-gray of these are in tetrahedral positions. Interlayer spacings as determined by LEED are given at right with error bars, and with corresponding bulk values between parentheses.

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A full description of the principles of low-energy electron diffraction (LEED) as of 1974, containing all the basic physics still in use today

2. Van Hove M A, Weinberg W H and Chan C-M 1986 LEED experiment, theory and structural determination (Heidelberg: Springer)

Covers in great detail the practical application of low-energy electron diffraction (LEED) for structural studies, excepting more recent techniques like tensor LEED and holography.

3. Van Hove M A, Determination of Complex Surface Structures with LEED 1997 *Surf.Rev.Lett.* **4** 479-488

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5. Rehr J J Multiple-scattering approach to surface EXAFS - theory versus experiment 1995 *Surf.Rev.Lett.* **2** 63-69

Addresses the need for advanced methods in surface extended x-ray absorption fine structure (SEXAFS) for accurate structural determination.

6. Feidenhans'l R Surface structure determination by x-ray diffraction 1989 *Surf.Sci.Rep.* **10** 105-188

Covers the experiment and analysis of surface x-ray diffraction, excepting the x-ray standing wave method.

Keywords

adsorption site
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diffuse diffraction
direct methods
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genetic algorithms
global optimization
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incommensurate lattice
kink
lattice gas
low-Miller-index surface
matrix notation
mean free path
monolayer
multiple scattering of electrons
physisorption
point-source emission of electrons
reciprocal lattice
simulated annealing
spot broadening in diffraction
steepest-descent optimization
step
streaking in diffraction
superlattice
surface reconstruction
surface structure
terrace
total external reflection
trial-and-error fitting
unit cell
Wood notation