Surface crystallography with low-energy electron diffraction

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Bragg's 1913 publication of the principles of X-ray crystallography came only a year after von Laue's discovery of X-ray diffraction from crystals. Structure determination (of small molecules) with high-energy electron diffraction followed by just three years the 1927 discovery of electron diffraction by Davisson and Germer. By contrast, low-energy electron diffraction (LEED) would require four more decades before yielding its first structure determinations (of surfaces) around 1970. The delay was primarily due to the need for ultra-high vacuum and to a lesser extent to the need for a suitable theory to model multiple scattering. This review will sketch the development of surface crystallography by LEED and describe its principles and present capabilities.

1. The growth of LEED

Davisson and Germer already realized in 1928, the year of their discovery of electron diffraction, that the kinematic (single-scattering) theory used in X-ray diffraction could not describe low-energy electron diffraction (LEED). The same year, Bethe (1928) published the first 'dynamical theory' of LEED, which was inspired by Ewald's theory of X-ray diffraction. In 1930, Morse applied the first one-electron energy-band theory to LEED, utilizing the Bloch-wave concept introduced in 1928. However, theory could not match the experimental LEED data, because the experiment could not provide the required well-controlled and reproducible surfaces.

For over 30 years thereafter, little experimental or theoretical LEED work was carried out. A notable exception is that of Farnsworth (1930), whose studies introduced lasting concepts and experimental techniques. In particular, he developed methods of sample cleaning that are still very much used today, such as sputtering followed by annealing. Schlier & Farnsworth (1959) also discovered 'surface reconstruction', the deviation of the two-dimensional unit cell of the clean surface from that expected from the bulk structure.

The rise of the semiconductor and aerospace industries in the 1960s spawned renewed interest in surfaces and in LEED, one of the very few surface characterization techniques then in existence. Ultra-high vacuum equipment became commercially available, including Auger electron spectrometers and LEED optics with post-acceleration displays that enabled the reproducible preparation of samples.

McRae (1966) introduced a new theory of LEED, which generalized Darwin's two-beam dynamical X-ray theory to N beams, and in 1968 incorporated the Bloch-wave formalism as well. Different variants of such theories rapidly followed, inspired by band-structure theories. A different approach was the Green's function t-matrix formalism developed by Beeby (1968); it would later present significant advantages

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for complex surface structures. In the same year, Holland (1968) showed how the Debye–Waller factor familiar in X-ray diffraction could be accommodated in this formalism. Duke & Tucker (1969*a*, *b*) introduced an electron mean free path into LEED theory. That year, Pendry (1969) emphasized the importance of ion-core scattering and in 1971 developed the very successful perturbation method called renormalized forward scattering (RFS); he later also popularized the more convergent but computationally slower layer-doubling method (Pendry 1974). In parallel, Jepsen & Marcus (1971) produced their robust layer-KKR method.

Experimental progress was facilitated in the late 1960s by the use of spot photometers for the measurement of the intensity of diffracted electron beams. At long last, theory matched experiment, which was then being performed in the laboratories of Somorjai, Jona, Andersson and others. Around 1970, it thus finally became possible to fit atomic coordinates to experiment with LEED. This was first accomplished for low-Miller-index surfaces of aluminum, copper and nickel and soon thereafter for foreign atoms, like oxygen sulphur, deposited (adsorbed) in ordered arrays on such surfaces.

Since then, many theoretical methods have been introduced to accelerate and generalize the structure determination procedure (Van Hove *et al.* 1986; Van Hove 1988), culminating in recent automated search methods. On the experimental side, more efficient techniques of data acquisition have also been introduced, in particular the photographic method (Kaminska *et al.* 1975), the video camera (Heilmann *et al.* 1976; Lang *et al.* 1979; Ogletree *et al.* 1986) and the position-sensitive detector (Stair 1980; Ogletree *et al.* 1992). Over 300 surface structures have been determined with LEED so far. This represents more than half the structures solved by the dozen techniques that are sensitive to surface structure (the other techniques include various forms of photoelectron diffraction, X-ray diffraction, ion scattering and atom diffraction, among others) (MacLaren *et al.* 1987; Watson 1987, 1990, 1992).

For comparison, X-ray crystallography of surfaces has produced about 60 structures since its inception in the early 1980s; its productivity is limited by the experimental difficulties associated with obtaining a strong signal from the atoms residing within a few atomic diameters of the surface. It must be noted that, compared with bulk X-ray crystallography, a surface structure determination, no matter with which technique, often is a laborious process: sample preparation can take days to weeks, data acquisition hours to days, and the data analysis days to months. Moreover, a structure is often only solved after several independent techniques have been applied to it.

Compared with other techniques of surface structure determination, LEED gives the largest flexibility of application, being suitable for most materials (metals, semiconductors, intermetallic or ionic compounds, with or without atomic or molecular adsorbates of arbitrary kind, etc.) and most structural types (reconstructed or not, with adsorption as an overlayer or an underlayer, ordered or disordered, in submonolayer or multilayer amounts, etc.).

We shall in the following sections first describe the basic experiment and theory of LEED. Then we shall address some of the methods which have allowed the study of different types of structures by LEED, namely those structures that have large two-dimensional unit cells, incommensurate overlayers, disordered overlayers, high-Miller-index (i.e. 'stepped' and 'kinked') surfaces or complex relaxations.

2. The LEED experiment

The high surface sensitivity of LEED (to a depth of a few atomic diameters) requires an ultrahigh vacuum environment to both prepare and measure sample surfaces: 10^{-10} Torr is a typical residual vacuum pressure. Surface cleanliness in essential at the submonolayer level, preferably at the percent-monolayer level, over a period of hours.

In the LEED experiment (Somorjai 1981; Van Hove *et al.* 1986) a well-collimated beam of electrons in the 10–300 eV range is back-scattered from the surface of a crystal. The elastically reflected electrons that carry the surface structural information are then separated from the inelastically scattered electrons by electrostatic retarding grids and detected. Video cameras provide the most common and convenient detection method, in conjunction with a fluorescent display screen. Faraday cups, spot photometers and position-sensitive detectors are currently also used.

Ordered surface structures produce diffracted beams in directions implied by the two-dimensional surface periodicity through Bragg conditions. Disordered surface structures yield diffuse diffraction into all directions. In either case, one needs to measure the probability of diffraction into a collection of appropriate directions to build up an adequate data base.

3. Diffraction theory

The basic physics of the LEED process are well understood and have been harnessed to accurately reproduce experimental data (Pendry 1974; Van Hove & Tong 1979; Van Hove & Somorjai 1979; Clarke 1985; Van Hove *et al.* 1986). We here briefly review the physical ingredients of most theories of LEED. These ingredients are also used in the treatment of related techniques that involve the scattering of low-energy electrons (such as photoelectron and Auger electron emission).

As in electronic band-structure calculations, the muffin-tin model is utilized to represent the scattering potential of the surface atomic lattice felt by low-energy electrons. The muffin-tin model consists of spherically-symmetrical ion-core potentials, surrounded by regions of constant muffin-tin level.

A layered structure is often adopted to describe a surface, by defining atomic layers parallel to the surface. The wavefield is usually expanded in terms of spherical waves within those layers, while it is often expanded in terms of plane waves in the gaps between layers. The plane waves correspond directly to the diffracted beams in LEED.

In the spherical-wave representation within atomic layers it is most common to use free-space Green's functions to describe wave propagation from one atom to another. The electron scattering properties of a single atom are then expressed as partial-wave phase shifts. Important is the fact that this scattering is far from isotropic: instead, it is very dependent on scattering angle. Several approaches exist in the spherical-wave representation to obtain self-consistent solutions of the multiple-scattering problem. Beeby's matrix-inversion method achieves this in a closed form. Suitable perturbation expansions can converge to the same result, when multiple scattering is not too strong, but are rarely competitive in computational efficiency.

Many methods are available in the plane-wave representation to treat multiple

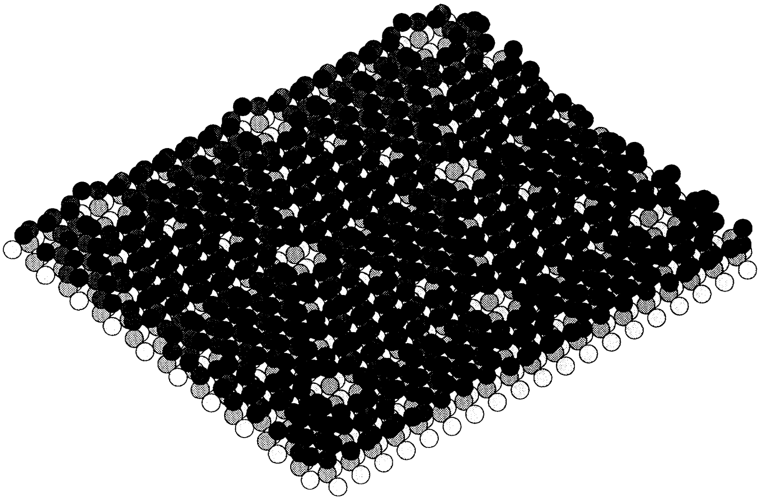

Figure 1. The reconstructed Si(111)-(7 × 7) surface structure. It consists of Si 'adatoms' (black) bonded to four Si atoms in the next bilayer down (identified by the two darkest shades of gray). This bilayer is broken into clearly visible large triangles (7 bulk atoms on a side); one half of the triangles has a lattice rotated 180° with respect to the bulk layer stacking, thereby forming a stacking fault in one half of the (7 × 7) unit cell. The triangles are connected at their seams by rows of three Si 'dimers', while the tips of the triangles meet at deep holes. These holes reveal the next deeper bilayer (two lightest shades of gray), which is bulk-like, but slightly relaxed.

scattering between atomic layers (whose diffraction properties have first been calculated with spherical waves). One method is layer doubling: two layers are joined into a pair, then two pairs are joined into a quartet of layers, etc., until convergence of the diffraction properties. But the most used method is the renormalized forward scattering perturbation expansion, in which the predominance of forward scattering is used to achieve rapid convergence.

The LEED theories outlined above have been very successful when applied to relatively simple surface structures, for example the simple truncation of FCC or BCC metals, and the adsorption thereon of atoms or diatomic molecules which do not affect the substrate structure much. Surfaces of practical interest are rarely that simple, however. Both the computational cost and the complexity of the structural search grow rapidly when the surface reconstructs, relaxes, is disordered, has steps and kinks, is a compound, especially with variable surface stoichiometry, or when molecules of larger size are adsorbed. Furthermore, during its first two decades until about 1990, LEED crystallography has relied on the cumbersome trial-and-error approach to structure search. This permitted the fitting of only four or five parameters, insufficient for most surfaces of interest. We discuss solutions to these limitations in the following sections.

4. Large two-dimensional unit cells

Large 2D unit cells occur frequently when a surface reconstructs, which is common on certain clean surfaces, especially those of many semiconductor and compound materials as well as some metals (e.g. Mo, W, Ir, Pt, Au): the outermost one or two

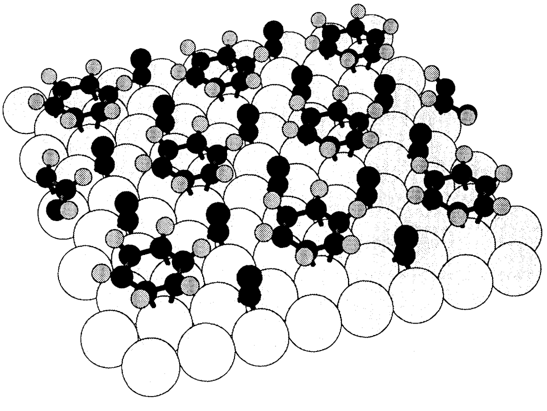

Figure 2. The Rh(111)-(3 × 3)–C_6H_6 + 2CO molecular adsorption structure. Each (3 × 3) unit cell contains one benzene molecule and two CO molecules. The benzene lies parallel to the Rh(111) surface, with expanded C–C bond lengths compared with the gas phase (C atoms are drawn black; the positions of the light-gray hydrogen atoms of the benzene have been guessed for this plot, based on theoretical and experimental information). The CO molecules stand perpendicular to the surface, with the C end (black) bonding to the surface.

surface layers can adopt an atomic arrangement that is quite different from the bulk structure. Reconstructions can also be induced by atomic adsorbates. Similarly, large molecules deposited on any surface also often give rise to large two-dimensional unit cells.

A very effective approach to performing complex structural analyses is to exploit any available symmetries to speed up the calculations. In recent years, quite complex structures have been solved this way (Moritz & Wolf 1985; Tong *et al.* 1988). Even the highly complex Si(111)-(7 × 7) surface reconstruction has thus been analysed in terms of individual bond lengths, despite its 200 displaced atoms in the (7 × 7) unit cell (Tong *et al.* 1988), cf. figure 1 (in this example the bulk unit cell is magnified sevenfold in both surface dimensions).

Alternatively, the 'beam set neglect' method (Van Hove *et al.* 1983) identifies certain classes of weak multiple-scattering paths that can safely be ignored, and thereby gains large factors in computation speed. The method applies particularly to overlayers of atoms and molecules deposited on a substrate.

With beam set neglect a number of complex molecular adsorption structures on metal substrates have been determined. For example, in the structure labelled Rh(111)-(3 × 3)–C_6H_6 + 2CO each (3 × 3) unit cell contains one benzene molecule and two CO molecules, cf. figure 2 (Lin *et al.* 1987).

5. Incommensurate overlayers

An incommensurate overlayer has a two-dimensional periodic lattice which is independent of that of the substrate: it may have a different lattice constant and/or a different crystallographic orientation, such that the combined substrate/overlayer system has no common periodicity. This situation occurs frequently with overlayers (like graphite) and thin films (like oxides) that are strongly cohesive, so that they can ignore the periodicity of the underlying substrate.

From the point of view of diffraction, incommensurate systems create an infinitely dense continuum of diffraction directions. Nevertheless, thanks to the rapid decay of contributions from higher-order multiple scattering, the kinematic pattern dominates, while some double-diffraction spots are also seen, but all higher-order spots are practically undetectable. Beam set neglect has provided a convenient solution to the problem of calculating diffracted intensities from incommensurate overlayers, as in its application to the structure determination of a graphite layer grown on a Pt(111) substrate (Hu *et al.* 1987).

6. Diffuse LEED for disordered overlayers

Many surfaces have disordered phases under certain conditions, or they may never order under any conditions. The LEED theory has been developed to solve the structure of some of these very interesting surfaces, principally those that have lattice-gas disorder (Heinz *et al.* 1985; Saldin *et al.* 1985): an important example is the case of an atomic or molecular overlayer on a perfectly periodic substrate, in which all adsorbates have the same bonding configuration to the substrate atoms. Thus, we have identical short-range order around all overlayer atoms, but no long-range order between them.

In the absence of long-range order, diffraction is possible into all directions, yielding diffuse diffraction patterns (an ordered substrate produces a set of sharp diffraction spots that is superimposed on the diffuse pattern). One may qualitatively view the observed diffuse LEED intensities as the product of a short-range-induced form factor and a long-range-induced structure factor. Most disordered overlayers are close enough to the limit of the dilute lattice gas for this product relation to hold very well. Thus, for a lattice gas, the final diffraction pattern can be viewed as the product of a kinematic structure factor reflecting the long-range disorder and a dynamical form factor reflecting the unique local short-range order. This allows the local structure to be determined in the absence of knowledge about long-range correlations (Saldin *et al.* 1985; Van Hove 1988).

The three-step approach (Saldin *et al.* 1985) for calculating diffuse LEED calculations first allows an incident plane wave to scatter in all possible ways through the substrate until it first reaches a disordered adsorbate. In the second step, the wave that reaches the adsorbate is first allowed to scatter from the adsorbate and then in all possible ways through the surface until it returns to the same disordered adsorbate. Finally, in the third step, this wave propagates in all possible ways through the substrate to the detector. This three-step approach can easily be generalized to other forms of disorder: random vacancies, interstitial or substitutional impurities, etc.

A second method, which is less accurate but speedier, uses the beam-set-neglect approach (Saldin *et al.* 1985; Van Hove 1988). It has been used to study the relatively complex structure of disordered benzene adsorbed on Pt(111) (Wander *et al.* 1991*a*), as illustrated in figure 3.

7. Stepped surfaces

A stepped surface occurs when a crystal is cut along a plane that does not coincide with a low-Miller-index plane. A stepped surface therefore typically consists of close-packed atomic terraces separated by one-atom-high steps. Relatively little structural information is available so far for stepped surfaces, especially when the terraces between steps are wide. This is due in part to the problem that conventional LEED

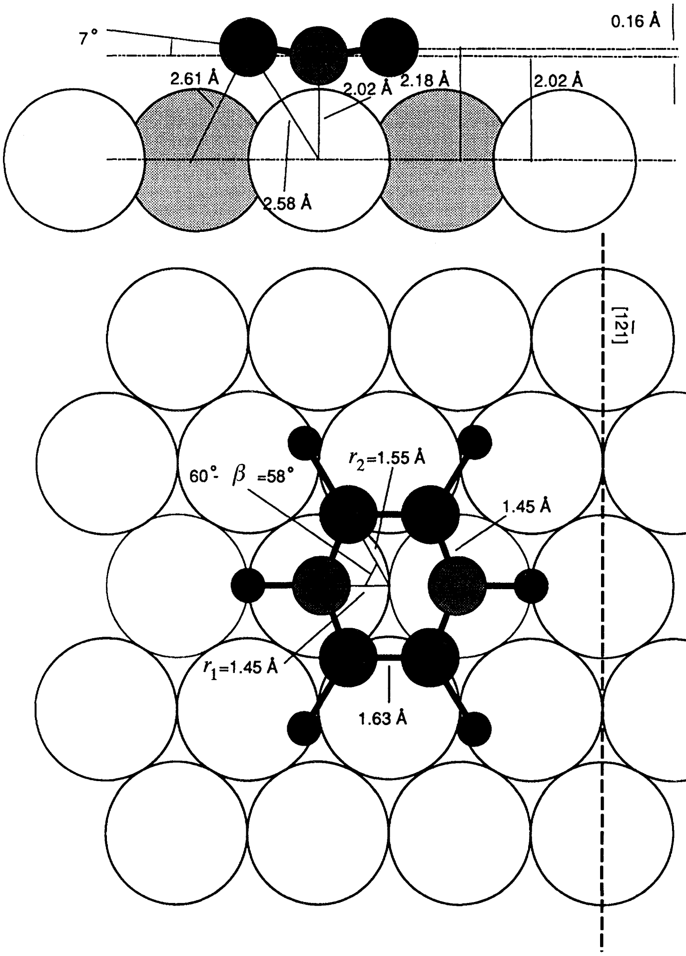

Figure 3. Adsorption structure of disordered benzene on Pt(111), shown in side view parallel to the surface (top panel) and top view perpendicular to the surface (bottom panel). The carbon ring is bent like a butterfly (boat shape). Hydrogen positions are guessed. C–C, metal–C and ring-centre–C distances are labelled, and so are selected interplanar spacings.

theories diverge for stepped surfaces and so cannot be used, and in part to the high reactivity of these surfaces, which makes them difficult to prepare experimentally, but also particularly interesting.

The cause of the divergence in LEED lies in the plane-wave representation of the wavefield between atomic layers, which becomes unsuitable when atomic layers (parallel to the surface) are narrowly spaced, as they are in stepped surfaces. One needs to abandon plane waves in favour of spherical waves. This approach is taken in a recent method (Zhang *et al.* 1990; Pinkava & Crampin 1990) based on a real-space multiple scattering theory. This method exploits the semi-infinite periodicity of the unrelaxed surface, corresponding to the ideal bulk termination of the crystal. As an example, the structure of Pt(210) has been determined in this fashion (Zhang *et al.* 1991).

8. Automation and complex relaxations

For some surfaces, one can guess the approximate structural solution from known bonding behaviour, but it is much harder to accurately fix the detailed coordinates. For instance, most atoms deposited on close-packed metal surfaces are well known to adsorb in high-coordination sites with metal-adatom bond lengths that can be predicted from known atomic radii to an accuracy of no better than 0.1 Å†; in addition, the adatoms most likely induce complex relaxations within the substrate on the scale of 0.1 Å. Even if knowledge of the relaxations were not desired, to obtain the adatom–metal bond length to a better accuracy with LEED requires that the substrate relaxations also be determined to at least the same accuracy.

Thus, there is a need both for efficient methods to compute LEED intensities of the many possible structural relaxations, as well as for automated methods to fit the many corresponding structural parameters. As in X-ray crystallography, R-factors are used in LEED to evaluate the misfit between theory and experiment. It is therefore useful in an automated structural search to rapidly calculate partial R-factor derivatives with respect to all parameters to be fit. Two successful approaches have pursued this idea: tensor LEED (TLEED) is most appropriate for refining the unknown parameters once these are roughly known; a comparably effective method is the nonlinear least squares fit with an improvement first described by Marquardt (1963) for X-ray crystallography, which combines the gradient and the expansion methods.

The optimization methods used in LEED are quite standard numerical algorithms (Press *et al.* 1986). In general, a combination of optimization methods may be most effective, as exemplified by the approach of Marquardt (1963): one method first explores wider areas of parameter space, then another refines parameters closer to the preferred minimum. However, the issue of identifying the global minimum among many local minima will always remain difficult, because of a lack of procedures like the direct methods, Patterson functions and Fourier synthesis of X-ray crystallography (Stout & Jensen 1968).

Linear tensor LEED (LTLEED) provides the partial derivatives of the diffracted amplitudes with respect to changes in the atomic coordinates (Rous & Pendry 1989; Rous 1992). Its more effective generalization, called simply TLEED, in essence produces partial derivatives with respect to the changes in scattering potential induced by changes in atomic coordinates (Rous 1992). The TLEED approximation is good for atomic displacements up to about 0.4 Å.

To date, over a dozen surface structures have been solved with TLEED, coupled with automated search algorithms (Rous *et al.* 1990; Wander *et al.* 1991*b*; Van Hove *et al.* 1993). The Marquardt approach, coupled with the explicit calculation of derivatives, has recently been successfully used in LEED for another dozen surface structure analyses.

Figure 4 illustrates a typical example, Pt(111)-(2 × 2)–C_2H_3 (Starke *et al.* 1993*a*), in which the C_2H_3 ethylidyne specie and the top two metal layers were allowed to relax. Thus, ignoring the hydrogens, 10 atoms within the (2 × 2) unit cell were relaxed fully, represented by 30 coordinates (and the *a priori* unknown muffin-tin zero level). Two features stand out in the resulting structure: the substrate metal layers 'buckle' by about 0.1 Å, i.e. become non-planar, as a result of the molecular bonding to the

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† $1\ \text{Å} = 10^{-10}\ \text{m} = 10^{-1}\ \text{nm}$.

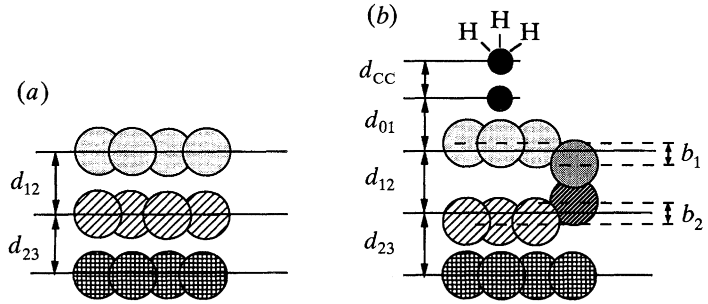


Figure 4. Structure of a quarter monolayer of ethylidyne (C_2H_3) adsorbed on Pt(111), forming a p(2 × 2) superlattice. The side view (*b*) shows admolecule-induced metal relaxations perpendicular to the surface (layer buckling), relative to the clean Pt(111) surface (*a*). A plan view would look similar to that of figure 5*b*, with a lateral inward relaxation r_1 in the top layer of 0.1 ± 0.08 Å. The C–C bond vibrationally tilts on average by about 6° from the drawn normal orientation. Carbon atoms are shown small and black. (*a*) $d_{12} = 2.29 \pm 0.01$ Å, $d_{23} = 2.27 \pm 0.03$ Å, bulk value = 2.26 Å. (*b*) $d_{cc} = 1.49 \pm 0.05$ Å, $d_{01} = 1.21 \pm 0.03$ Å, $d_{12} = 2.30 \pm 0.03$ Å, $d_{23} = 2.26 \pm 0.04$ Å, $b_1 = 0.11 \pm 0.05$ Å, $b_2 = 0.08 \pm 0.09$ Å.

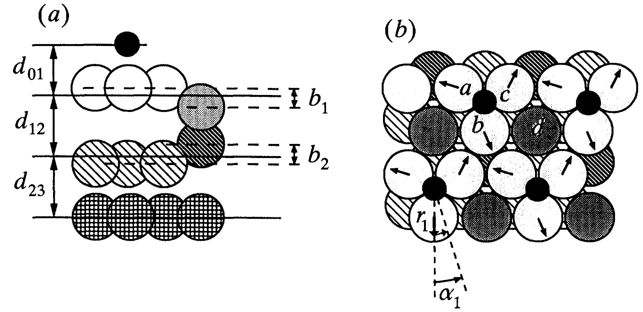


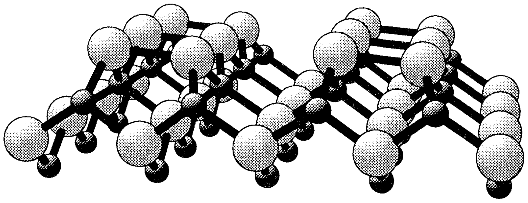
Figure 5. Structure of Pt(111)-(2 × 2)–O, including metal relaxations induced by the oxygen overlayer (for comparison, see interlayer spacings for clean Pt shown in figure 4*a*): (*a*) side view; (*b*) top view. Oxygen atoms are shown small and black. In (*a*) $d_{01} = 1.18 \pm 0.02$ Å, $d_{12} = 2.29 \pm 0.03$ Å, $d_{23} = 2.26 \pm 0.05$ Å, $b_1 = 0.07 \pm 0.03$ Å, $b_2 = 0.09 \pm 0.10$ Å. In (*b*) $r_1 = 0.025 \pm 0.1$ Å, $\alpha_1 = 2.3 \pm 5°$; $r_2 = 0.035 \pm 0.1$ Å, $\alpha_2 = 3.0 \pm 5°$.

surface; in addition, a tilting of the molecule is found by about 6° from the surface normal, which is believed to represent vibrational bending. (Inclusion of the hydrogens does not produce physically acceptable atomic positions, which is assumed to mean that the CH_3 group spins more or less freely about the C–C axis.)

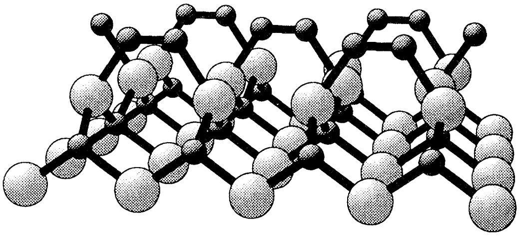
Several similar molecular bending results are obtained with ethylidyne and with CO on Rh(111) (Barbieri *et al.* 1993), as well as with CO on Ru(0001) (Over *et al.* 1993). Substrate layer buckling is also observed in these cases and with atomic adsorbates, e.g. with Pt(111)-(2 × 2)–O (Starke *et al.* 1993*b*), shown in figure 5, and Re(0001)-(2 × 2)–S (Jentz *et al.* 1993). The consistency of these results is very encouraging, and begs for a theoretical explanation of the underlying relaxation and bonding mechanisms.

To illustrate the applicability of these methods to other materials, figure 6 shows the case of the reconstructed SiC(100) surface (Powers *et al.* 1991, 1992): despite the non-tetrahedral interbond angles in the top two layers, the rigidity of this compound prevents significant relaxations from propagating into the subsurface region.

X-ray crystallography is blessed with direct methods that allow one to solve



SiC(100) - p(2×1)



SiC(100) - c(2×2)

Figure 6. Two different reconstructions of SiC(100), one prepared Si-rich and forming a p(2 × 1) superlattice (shown at top), the other prepared C-rich and forming a c(2 × 2) superlattice (shown at bottom). Si pairs and C pairs form at the surface of the respective structures, but the Si atoms in these pairs bond to three neighbours, while the C atoms bond to two. The views are nearly parallel to the surface; C atoms are drawn small and dark, Si atoms large and light.

certain structures in a single non-iterated step. This capability is sorely lacking in LEED. The closest to such a direct method in LEED is based on the TLEED idea (Heinz *et al.* 1990; Pendry & Heinz 1990). The TLEED expansion leads to a set of linear equations in the unknown atomic displacements from a guessed structure. If the linear expansion from guessed structure to actual structure is accurate, the structure can be solved in one step. In practice, the procedure can be iterated to the required accuracy, but it is still necessary to make an initial guess accurate to within 0.1 Å.

One may also in TLEED expand and retain terms to all orders, rather than only the linear terms. Then a series is obtained in the powers of the displacement components (Pendry & Heinz 1990), thus delivering the moments of the probability distribution of the atomic locations. These provide additional information to describe thermal and other site disorder, including anharmonic vibrational effects, diffusion and multi-site adsorption. In fact, the probability distribution of the atomic locations can be related to the potential energy function within which the surface atoms move, thus determining it.

A new approximate method called linear LEED (LLEED) has been developed recently (Wander *et al.* 1992), which has not yet been applied in a structural determination. LLEED is aimed particularly at exploring *combinations* of atomic displacements, where several atoms or rigid groups of atoms are displaced simultaneously, but independently. The effects of these displacements are also treated as independent and therefore with great computational advantage. This linear independence allows computer time savings of many orders of magnitude, similar to LTLEED and TLEED.

9. Conclusions and outlook

LEED is a very mature technique that has been generalized to determine a variety of complex surface structures. The structures that have benefited most from the advances in LEED have been reconstructions of clean surfaces, relaxations induced by adsorbates and molecular adsorption. Important structural determinations that are becoming routine include adsorption on semiconductor surfaces, which before were generally too complex to solve. Other applications that are becoming more accessible are surfaces of compounds and stepped surfaces, including atoms and molecules deposited thereon.

The recent developments in LEED theory have pushed the technique close to the level of automation of surface structure determination known in X-ray crystallography (with the major exception of the lack of more or less direct methods in LEED to obtain good structural guesses before refinement). It is now routine to fit 30 unknown structural parameters overnight on a workstation.

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