Bonding at Surfaces [and Discussion]

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Bonding at surfaces

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Surface crystallography is a rapidly growing subject in terms of both its scope and capabilities. Some surface structures are examined in detail and their interesting features stressed. We go on to examine new developments in the field, and conclude with a review of possibilities for studying thermal motion at surfaces of both harmonic and anharmonic nature, and of thermal diffusion across the surface.

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1. Overview of structures

Surface crystallography has come of age and the atomic arrangement of a surface can now be reliably determined for all but the most complex situations. Something like 500 surface structures are reported in the Surface Crystallographic Information Service catalogue (MacLaren *et al.* 1987) and with recent additions to the literature close to 1000 structures have now been determined, most of these by low-energy electron diffraction, but with a wide variety of other techniques contributing: surface X-ray diffraction, Rutherford back scattering, surface extended X-ray absorption fine structure, to name the major contenders. Enough is now known that some patterns are emerging which are unique to surface crystallography, and relevant to a host of phenomena from semiconductor growth to catalysis.

The plan of this article is to review a few of the known surface structures, to outline how LEED functions (the major technique of surface determination) and then to speculate about future directions which surface crystallography may explore.

Figure 1 shows the structure formed when Ni is deposited on a Si (111) surface, as might be the case in making a Schottky diode. The structure, determined by Van Loenen *et al.* (1985), clearly shows that the interface consists of a chemical compound, $NiSi_2$, not of pure metal. This simple structural fact explains the many anomalies in diode performance, which early theories predicted on the basis of the barrier height given by a pure metal–semiconductor interface.

Figure 2 is another overlayer structure: that of C adsorbed on Ni (100) (Onuferko *et al.* 1979). For obvious reasons this has been christened 'the clock structure'. It illustrates a very common situation in adsorbate systems, namely that the substrate is not simply a passive template but itself responds to the presence of an adsorbate. Sometimes the response is a simple one with substrate inter layer spacing relaxations, sometimes it can be extremely complex as in the case of N adsorbed on W (100). Here we see a beautifully symmetrical structure. The eye is naturally drawn to the alternate rotation of four Ni atoms about the carbon sites, but the driving force is almost certainly to be found on the sites holding no C atoms. Here four substrate Ni atoms are rearranging themselves from a square structure to an hexagonal structure, packing closer together in the process, and releasing more space around the C sites.

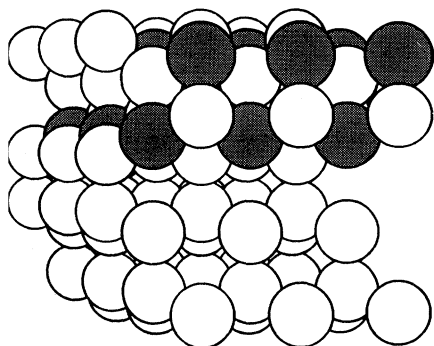The C on Ni (100) structure is a example of an extremely important class of

Figure 1

Figure 2

Figure 1. The NiSi$_2$ (111)–Si (111) interface as determined by Rutherford back scattering (Van Loenen *et al.* 1985). Si atoms are shown as open circles. This structure is formed when Ni is deposited on Si (111) at 300 K followed by annealing.
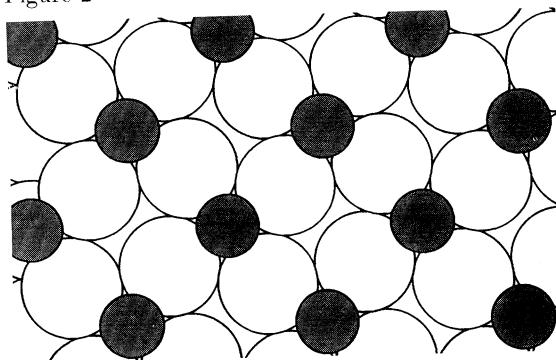
Figure 2. The 'clock structure' of P(2 × 2)C/Ni (100) as determined by Onuferko *et al.* (1979). Note the distortion of the top layer of Ni: the clock-like rotation about the C sites, and the hexagonal distortion about the empty sites.

systems: carbidic carbon adsorbed on transition metal surfaces. Billions of dollars worth of organic chemicals are formed in processes involving similar structures. We are taking the first steps in producing a detailed understanding of these systems.

Figure 3 shows a structure which is also relevant to the catalysis industry, that of CO adsorbed on Cu (100). The major catalyst for methanol formation from CO is Cu. This structure, determined by Andersson & Pendry (1980), is typical of the molecular phase of interaction with surfaces. The CO molecule is relatively weakly bound, sits well clear of the substrate atoms in contrast to C on Ni. Many molecules have such weak interactions with substrates, preserving their vibrational frequencies except for small shifts. This means that they are highly mobile at the surface, and can easily desorb, a most desirable characteristic in a reaction product.

The structure shown in figure 4 (Van Hove *et al.* 1986) is a tour de force representing the state of the art for surface structure determination. It shows two adsorbates, CO and C$_6$H$_6$, adsorbed on a Rh (111) surface. Several interesting points are raised here. It is observed that neither CO nor C$_6$H$_6$ form separate structures on this surface. Only when both are present does a well-ordered surface structure form. The reason appears to be that charge transfer occurs from C$_6$H$_6$ to CO and electrostatic forces stabilize the resulting surface ionic compound. Similar structures are seen when CO is coadsorbed with alkali metals. Look carefully at the C$_6$H$_6$ and you will see that it is no longer six-fold symmetric. The C atoms now cluster in three acetylene pairs on top of each of the three Rh atoms. This distortion of the six-fold ring is about the largest observed without the molecule fragmenting. Could we have caught the molecule on the verge of a reaction?

All the systems above form ordered structures, and conventional methods require this before experiments can be analysed to give the atomic coordinates. Two methods are capable of side stepping this restriction: surface EXAFS and diffuse LEED. The latter method has been applied to disordered O adsorbed on W (100) by Rous *et al.* (1986). The structure is shown in figure 5a and compared with the structure of the reconstructed clean W (100) surface in figure 5b (Barker *et al.* 1978). The clean
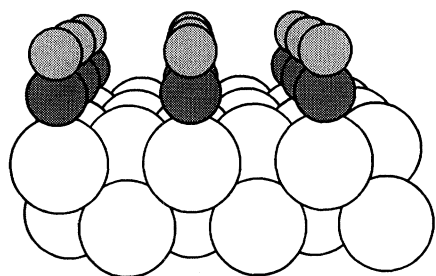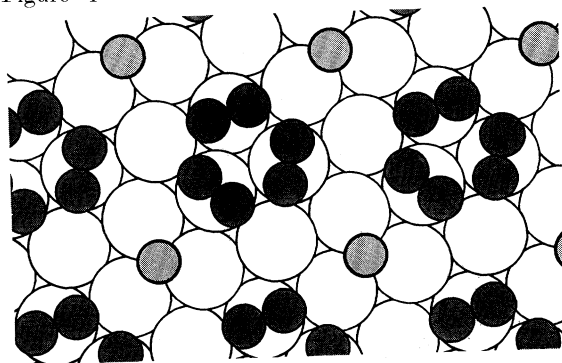
Figure 3

Figure 4

Figure 3. C(2×2)CO/Cu (100) determined by Andersson & Pendry (1980). The open circles represent Cu, the black circles C, and the half-shaded circles O. Contrast the location of C atoms in this structure at on-top sites, with that in figure 2 where isolated C atoms bury into the four-fold hollows.

Figure 4. A complex surface structure determined by Van Hove *et al.* (1986) containing a mutually stabilizing arrangement of CO and C_6H_6 molecules on the Rh (111) surface. H atoms are not shown, and the C in the CO molecules is hidden by the terminal O. Note the restructuring of C_6H_6 induced by the underlying Rh atoms.
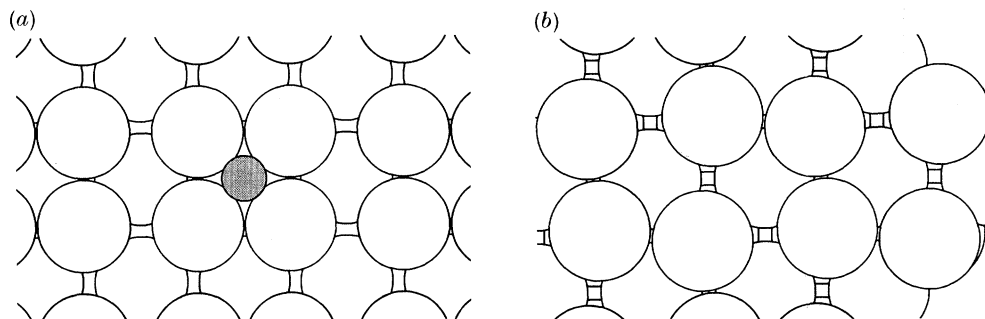
(*a*)   (*b*)

Figure 5. O adsorbs on W (100) in a disordered state at low temperatures, but its structure can still be determined by diffuse LEED (Rous *et al.* 1986). Note how in (*a*) the top layer of W atoms reconstructs around the O, in contrast to the clean surface reconstruction shown in (*b*), as determined by Barker *et al.* (1978).

surface forms zig-zag chains running across the surface in an effort to acquire some in-plane coordination for the surface W atoms. O acts as a nucleus around which these chains can wrap themselves. In this way the W atoms keep two in-plane W neighbours, but in addition acquire some energy from bonding to O. Once again an adsorbate has radically changed the substrate structure. It is almost as if each adsorbate atom is elastically screened by substrate movement, just as an adsorbed ion is electronically screened by substrate electrons. How much energy is involved, and whether screening can play a role in smoothing the course of chemical reactions remains to be investigated.

These structures illustrate the uniqueness of the surface environment. Surfaces are not simply a corner of the bulk solid. In the bulk atoms are strongly confined by the geometry. The consequence of weak bonds tends to be melting or evaporation, but at the surface it is only necessary to confine the atoms normal to the surface. The
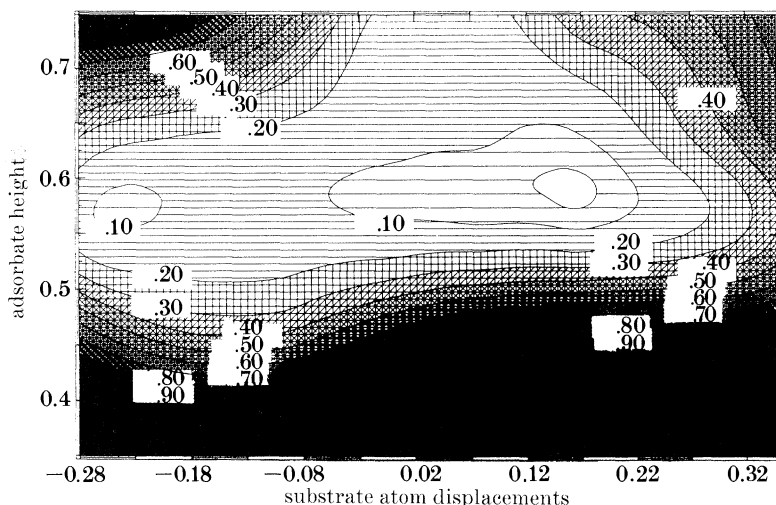
Figure 6. A typical *R*-factor map. This one is for the O/W (100) system shown in figure 5*a*. The *R*-factor summarizes agreement between theory and experiment for a trial structure: zero for perfect agreement, 1 for perfect disagreement. The trial variables are: the height of the O above the surface, and the magnitude of the top layer W displacements. A clear minimum is seen indicating the correct structure.

parallel motion can be harmonic, anharmonic, or gas like. Thus the surface is not simply a two-dimensional crystal, but is more analogous to a two-dimensional world, encompassing gas, liquid as well as solid phases.

2. Developments in methods of structural analysis

Traditional surface structure determination has been made by trial and error analysis of experimental data (see, for example, Pendry 1974; Van Hove & Tong 1979; Heinz & Mueller 1982). For example, in the case of low-energy electron diffraction, intensities of reflected beams are collected as functions of incident energy: perhaps six different beams over an energy range 50–250 eV. A large quantity of data is important because a great deal of surface structure information is encoded in the data, and a large data-set is essential before all this information can be reliably extracted. Because of the well-known complications of multiple scattering of electrons, the connection between structure and diffraction data is not trivial, and extraction of information is done by postulating a trial structure, calculating the spectra implied by that structure, and comparing to experiment to test how close a guess we have made. It is usual to sum up the theory–experiment agreement for a trial in a single number called the *R*-factor (Zannazzi & Jona 1977; Pendry 1980) which is defined to be 0 for perfect agreement, and 1 for perfect disagreement. Figure 6 shows an example for the disordered O on W (100) structure taken from Rous *et al*. (1986). The *R*-factor is plotted as a function of the trial vertical height of the O and of the size of the W reconstruction. There is a clearly identifiable minimum which represents the true structure. Complications arise when data are of poor quality, or of small quantity. Then several trial structures may fit the data equally well and confusion has sometimes arisen in the past for these reasons.

Another major difficulty arises when there are many unknown coordinates in a surface structure. Suppose that we wish to try 10 possible values for each of six
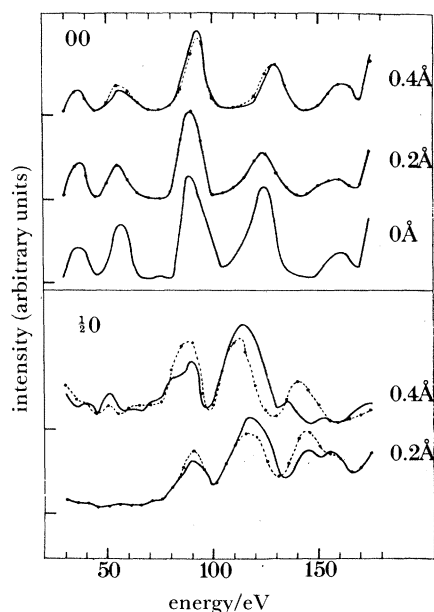
Figure 7. A test of the accuracy of tensor LEED taken from Rous *et al.* (1986): full dynamical (——) and tensor LEED (– – –) calculations for an artificial P(2 × 2) reconstruction of the Ni (100) surface in which every fourth atom is raised by 0, 0.2, 0.4 Å in the three curves shown. The method appears to be accurate for displacements as large as 0.4 Å.

coordinates. The number of trials is 10^6 and grows exponentially with the number of coordinates to be determined. The consequence is that for complex structures there is nearly always an inadequate search of parameter space. To combat this difficulty some new ideas were introduced into the theoretical calculations which are the most time-consuming step in data analysis (Rous *et al.* 1986; Rous & Pendry 1989*a*, *b*).

The idea is to introduce a reference structure which is a best guess at the true structure. One calculation of LEED intensities is made for the reference structure and closely related structures are then handled by first-order perturbation theory. It is easy to show that the change in diffracted amplitude of the gth beam can be written,

$$\delta A(\boldsymbol{g}) \approx \Sigma_j \boldsymbol{M}(\boldsymbol{g}, j)\, S(j, \delta \boldsymbol{R}), \tag{1}$$

where S is purely a geometrical function of the displacements, $\delta \boldsymbol{R}$, away from the reference structure; the tensor $\boldsymbol{M}$ is calculated once and for all for a given reference structure. Obviously matrix multiplication is made very rapidly and many trials can be made at little cost. In many cases the whole procedure is speeded by a factor of 1000 and the analysis can be made on a personal computer for relatively simple systems. The name given to the methodology is 'tensor LEED'.

In figure 7 we show a trial of the new method for a hypothetical structure taken from Rous *et al.* (1986). The trial structure is an unreconstructed Ni (100) surface. The perturbation is a reconstruction of this surface formed by raising every fourth atom in the surface in a P (2 × 2) array. The integer order beams, present also in the unreconstructed case, show excellent agreement with the exact calculation for displacements of up to 0.4 Å†, and even the fractional order beams which are unique to the reconstructed surface show acceptable agreement out to this magnitude of

† 1 Å = 10^{-10} m.

displacement. Displacements of this magnitude encompass most adsorbate induced surface reconstructions. When the atoms concerned are very light ones such as C or O, then the method works even better because of their weak scattering nature and light atoms can in fact be displaced anywhere on the surface and still be treated by perturbation theory.

3. Direct methods

Tensor LEED is a very effective way of analysing more complex structures, based on very straightforward concepts. However, the next step examines the new concept introduced and makes serious analysis of the possibilities which it holds (Pendry & Heinz 1990).

Suppose that, as before, we have defined a reference structure, and that the true structure is displaced from the reference by a small distance, δR. Then the potential of the surface changes by

$$\delta V \approx \delta R \cdot \nabla V(r - R). \tag{2}$$

Provided that δR is sufficiently small we can use first-order perturbation theory to calculate,

$$\delta A(g) \approx \langle k + g; \text{out} | \delta R \cdot \nabla V | k; \text{in} \rangle$$
$$= \Sigma_j M'(g, j) \, \delta R_j. \tag{3}$$

Hence if we take this equation seriously, and if we can measure enough values of $\delta A(g)$, then equation (3) can be inverted to give,

$$\delta R_j \approx \Sigma_g M'^{-1}(j, g) \, \delta A(g). \tag{4}$$

There is the question of how to measure $\delta A(g)$, but we can obtain this easily for small $\delta A(g)$,

$$|A(g) + \delta A(g)| = |A(g)|^2 + (A^*(g) \, \delta A(g) + A(g) \, \delta A^*(g)) + |\delta A(g)|^2$$
$$\approx |A(g)|^2 + (A^*(g) \, \delta A(g) + A(g) \, \delta A^*(g)), \tag{5}$$

and hence with a knowledge of $A(g)$ we have the information we require.

In principle, when δR_j is small, we can solve for the structure by a direct inversion procedure without having to use trial and error at all. Obviously if this were possible all the difficulties of having to make good guesses and to make huge numbers of trial calculations would be circumvented. The problem is that matters are not quite so simple: equation (2) is a very bad approximation for all but very small values of δR_j, essentially because the wavelength of 150 eV electrons is of the order of 1 Å. We can get around the problem as follows by using the exact atomic t-matrix,

$$\delta A(g) \approx \langle k + g; \text{out} | t(R + \delta R) - t(R) | k; \text{in} \rangle$$
$$= \Sigma_n M(g, n) \, \delta R^n, \tag{6}$$

that is, we have made a polynomial expansion in powers of δR. The interpretation of (6) is clearer if we recognize that we are determining, not the location of a single atom, but an average location of many atoms at the surface, relative to the reference structure. Thus after inversion we find,

$$\langle \delta R^n \rangle \approx \Sigma_g M^{-1}(n, g) \langle \delta A(g) \rangle, \tag{7}$$

where the brackets $\langle \ \rangle$ denote an average. Now we see that our first shot at theory though equation (4) merely gave the average location of atoms. Although we now
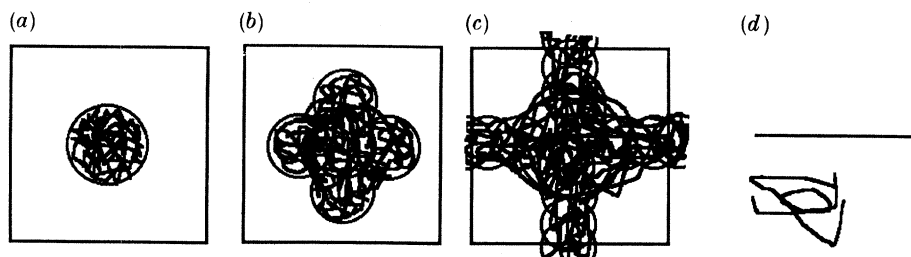
(a)   (b)   (c)   (d)

Figure 8. Diffusion of an adsorbed atom around the unit cell of a surface. Note how the motion can be expected to change in character as the amplitude of motion increases, first becoming anharmonic, and then diffusive, as the atom breaks loose from its site. (a) Low temperature, spherical distribution, harmonic vibrations; (b) intermediate temperature, non-spherical distribution, anharmonic vibrations; (c) high temperature, distribution overlaps cell sides, surface diffusion; (d) unit surface, adsorbate trajectory.

pay the price of a more complex theory, the reward is that we retrieve not just the atom positions but the moments of their distribution, $P(\delta R)$. If we know,

$$\langle \delta R^n \rangle = \int \delta R^n P(\delta R) \, d\delta R, \tag{8}$$

then we can reconstruct $P(\delta R)$ by standard methods.

Developing the direct methods has given us more than we hoped for. Diffraction measurements can now give information not just about static locations of atoms, but also about their distribution.

4. Thermal motion of atoms at surfaces

We have already discussed how surfaces are differentiated from the bulk of a solid by the freedom they allow to adsorbed atoms in the plane parallel to the surface. This unique property is almost entirely without an experimental probe. Currently surface crystallography studies averaged atom positions. Surface vibrations are accessible through probes which lose energy to the phonons, but study mainly high-frequency harmonic vibrations of strong bonds which anchor the atom or molecule firmly in place. Much more interesting are the very-low-frequency vibrations of molecules about to dissociate, or the diffusive motion of a molecule moving from one reaction site to the next. In figure 8 we show examples of various types of thermal motion at a surface.

Direct methods hold the potential for extending experimental surface studies to the fascinating and vital area of low-frequency vibration and diffusion.

The idea is a simple one. If we can assume that the atoms and molecules at a surface are disordered but in thermal equilibrium, then if the motion is classical and not quantum (a complication with H) we can apply the Boltzmann formula,

$$P(\delta R) = \text{const.} \times \exp\left(-V_A(\delta R)/k_B T\right), \tag{9}$$

where $V_A(\delta R)$ is the potential in which the atom migrates across the surface. Our prescription for finding $V_A(\delta R)$ is to apply direct methods to the surface at several different temperatures and extract $P(\delta R)$ at each temperature. This will enable us to infer $V_A(\delta R)$. Several temperatures must be used because at any given temperature (9) only gives good sensitivity when $V_A(\delta R)$ is of the order,

$$V_A(\delta R) \approx k_B T. \tag{10}$$

[153]

Once in possession of $V_A(\delta \boldsymbol{R})$ some elementary molecular dynamics simulation will give the harmonic and anharmonic vibrations, and also tell us about the diffusion of atoms across a surface: what path they take, where the blockages to diffusion occur and, in the case of a molecule, in what orientation they diffuse.

The method is unproven as yet, but experiments and the associated theory are in hand for a serious attempt to extract this elusive information.

5. Conclusions

Surface crystallography is providing structures which are relevant to work at the forefront of surface technology. We are not limited to simplistic surfaces of only academic interest, though obviously many complex surface structures still elude us. For the future a host of new ideas are being put forward. Those presented in this paper represent very largely my own viewpoint, but many researchers are actively seeking to widen the field and to make the study of surfaces as rich and diverse as that of the bulk.

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Discussion

R. HAYDOCK (*Materials Science Institute, U.S.A.*). I am intrigued by Professor Pendry's method of finding a structure by linear methods applied to a distribution of structures. This seems a general way of solving nonlinear equations by linear methods. Does he know of other applications?

J. B. PENDRY. I am not aware that this 'nonlinear inversion' procedure has been used before, but would imagine that it has wide application wherever there is a complex function whose global minimum has to be found.

L. M. FALIVOC (*University of California, Berkeley, U.S.A.*). Together with Professor Pendry's reported advances in the theoretical interpretation of LEED there has been

enormous progress in the experimental methods which aim at visualizing the position of atoms at surfaces. In particular the proposed electron holographic methods based on photoelectron diffraction seem to be on the threshold of a major breakthrough in 'real space' surface-structure determination.

J. B. PENDRY. Yes I agree. However, the correct interpretation of LEED or PE hologram depends on *future* development of theoretical methods as well as the direct methods discussed here.

J. D. C. McCONNELL (*The University of Oxford, U.K.*). Does the absorbed benzene continue to resonate?

J. B. PENDRY. Probably not, as the distortion is considerable, several tenths of an ångström.