SURFACE PHYSICS

The geometry of surface layers

Various experimental techniques show that atoms adsorbed onto a crystal surface form two-dimensional arrays with a structure that depends on their density, the temperature and the substrate.

Peder J. Estrup

If we wish to understand the properties of a solid surface, we must begin with some picture of the geometrical arrangement of atoms in the outermost layers of the solid. Such a structural model represents an essential ingredient in any microscopic description of a material.

A variety of methods are available for the experimental exploration of the composition and the electronic structure of the surface. These are discussed in other articles in this issue of PHYSICS TODAY, by Robert Park, by Dean Eastman and Marshall Nathan, and by Ward Plummer, David Penn and John Gadzuk. For those cases in which the identity and positions of the surface atoms are known, it is now becoming also possible to calculate the energy spectrum of the electrons in the surface layer, as described by J. Robert Schrieffer and Paul Soven. However, with rare exceptions, the atomic arrangement at the surface cannot be predicted theoretically, and structural models must be built almost exclusively on the basis of experimental evidence.

Most of our knowledge of surface geometry to date has been obtained by two techniques, electron diffraction[1] and field-ion microscopy.[2] Unfortunately, these techniques rather severely restrict the types of systems that can be studied. Electron diffraction requires a flat, smooth sample while, in field-ion microscopy, the sample must have the form of a fine needle tip. A model of such a tip is shown in figure 1. For either technique to be applicable, the substrate must be a single crystal, and the experiments must be carried out in an ultrahigh vacuum. It is clear that measurements of this type cannot be made directly on, say, a catalyst operating under the conditions used in practice. On the other hand, it is only by working with "idealized" systems, in which the number of variables has been drastically reduced, that one can hope to understand the complex interactions taking place in the surface region. Some of the results that have been obtained by this approach are discussed here and illustrated by selected samples. Questions having to do with the macroscopic surface structure, that is, the surface topography, have been surveyed recently[3] and will not be taken up here.

If the solid is a single crystal free of impurities we expect, and find, the surface layers to differ little from the parallel layers in the bulk. There are important exceptions, however, some of which are indicated schematically in figure 2. The surfaces of many covalent materials and of a few metals exhibit "reconstruction," in which the surface atoms are displaced from their expected lattice position. In non-elemental solids, alloys for example, segregation of one component at the surface may occur. Furthermore, the concern of current research in surface physics is not primarily the clean surface but rather a class of phenomena that depend on the interaction of a solid surface with foreign atoms or molecules. Examples are chemisorption, epitaxial growth, oxidation and heterogeneous catalysis. All of these involve the formation of overlayers, which typically differ in both composition and structure from the initial substrate surface. The precise characterization of such layers has turned out to be a very difficult, so far unsolved, problem.

Field-ion microscopy

The direct observation of surface geometry became feasible with the development in the 1950's of field-ion microscopy by Erwin Müller and his coworkers.[2] In this technique the sample is placed opposite a fluorescent screen, in an imaging gas such as helium and a very large electric field, about 3–6 V/Å, is applied. Helium atoms in the vicinity of the crystal tip become ionized when they pass through a region of high local field above a protruding surface atom, and the ions are then repelled by the positive tip and projected radially towards the screen to produce a micrograph. By cooling the tip with liquid helium, a resolution of a few angstroms can be achieved so that individual surface atoms can be imaged.

Above a certain value, which depends on the substrate material, the electric field will cause field evaporation, the ionization and removal of surface atoms from the crystal itself. This phenomenon is used routinely to prepare clean and well-ordered surfaces, and it allows the gradual examination, layer by layer, of the regions below the original surface. Although the occurence of field evaporation thus may be put to great advantage, it also limits the applicability of this technique to those materials for which the imaging field is smaller than the evaporation field. The majority of field-ion microscopy studies have therefore involved refractory metals such as tungsten, tantalum and rhenium.

The capability of field-ion microscopy to provide information about the arrangement of surface atoms is illustrated by some remarkable results recently obtained by William Graham and Gert Ehrlich.[4] This work aimed to define the lateral position of an adsorbed atom in relation to the atoms of the underlying substrate. This identification of the *adsorption site* for an isolated atom had not been achieved previously.

The specific system selected for investigation was the adsorption of a tungsten atom on the (111) plane (see figure 1) of a tungsten crystal. Figure 3

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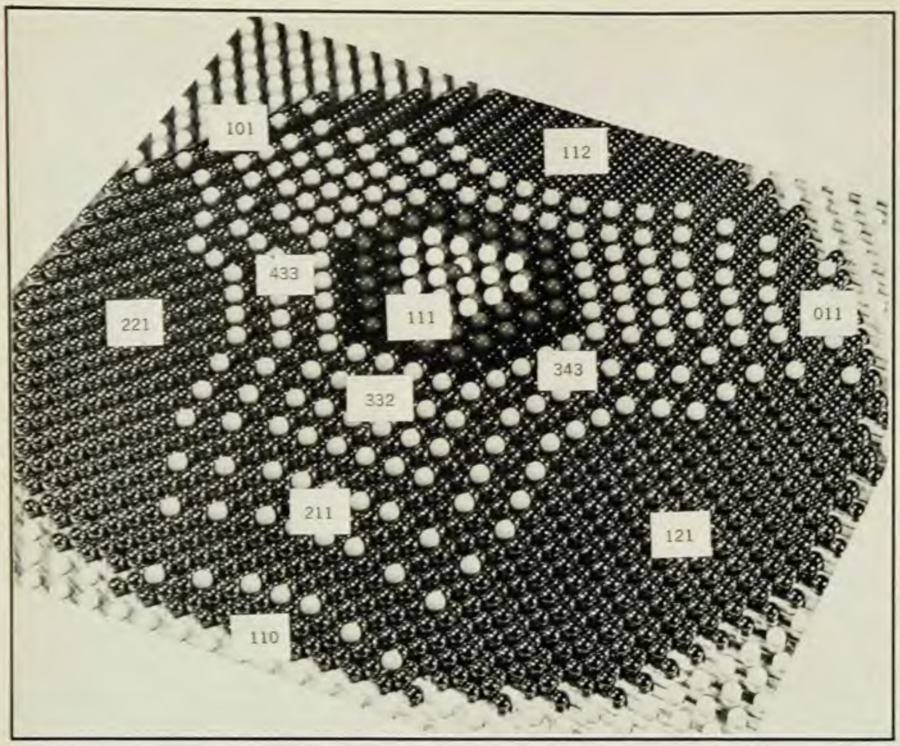


Hard-sphere model of a tungsten tip oriented along the [111] direction. The model has been scaled to have the same number of atoms in the (111) surface as are present in the specimen used to produce the micrographs shown in figure 4. (Courtesy of Gert Ehrlich.) Figure 1

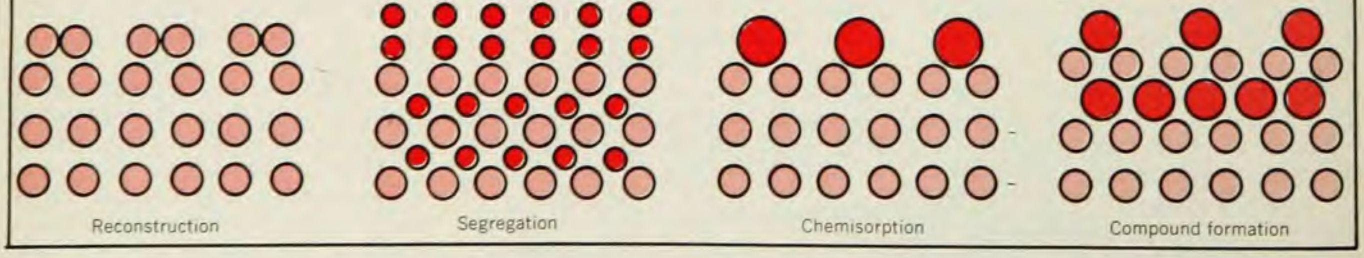
shows a model of the atomic arrangement on this surface. A number of different possible sites for an adatom can be imagined—right on top of a substrate atom, or in a bridged position between two atoms in the first layer. However, one intuitively expects the adatom to choose a site of high coordination, and on the (111) surface there are two such possibilities, both with trigonal symmetry: one above the atom labelled 2 and one above atom 3 in the unit cell. When the experiment was carried out, the field-ion micrographs, some of which are reproduced in figure 4, showed clearly that this expectation is correct; only the trigonal sites become occupied and in almost all cases (94% of the runs) the site above atom 3 in figure 3 was found to be chosen. Since a layer started by placing an adatom above atom 2 would constitute a stacking fault in the body-centered cubic substrate, this result does not come as a surprise; what is surprising is the fact that direct determinations of this type can be made. The application of the method to other systems should be most interesting.

Among other results obtained by field-ion microscopy,[2] mention should be made of the determination of surface diffusion rates and the measurements of the binding energy of adatoms to the substrate. For technical reasons that have already been alluded to, most of the data obtained by this method concern adatoms such as Ta, W, Rh and other heavy-metal atoms. As is clear from the model in figure 1, the surface planes of the tips studied have a very small area and the technique is therefore best suited for the investigation of the behavior of single adatoms, that is, of the adatom–substrate interaction. Lateral adatom–adatom interactions between two or more adsorbed species are more difficult to explore, but data relevant to this problem have nevertheless been obtained in some cases. For example, the correlated motion[5] of *pairs* of tungsten atoms has been observed on the (211) surface of tungsten. We will refer to some of these results again below.

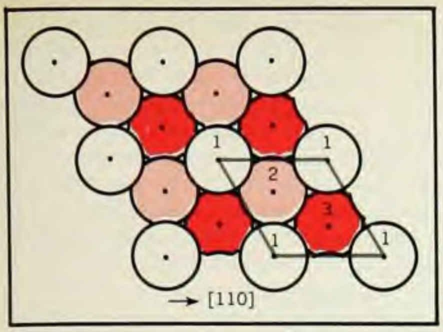
Low-energy electron diffraction

The oldest and most versatile tool for the investigation of surface structures is electron diffraction. Whereas field-ion microscopy gives a direct image of the surface atoms, diffraction—by its nature—provides information about the *distance* between atoms.[1]

The initial discovery of the wave nature of the electron soon led to the realization that a method for the study of surface crystallography had become available. Discussing the technique now referred to as LEED (low-energy electron diffraction), Lester Germer wrote[6] in 1929: "The circumstance that electron waves are scattered very efficiently by the surface atoms of the crystal and are consequently extinguished on penetrating into the crystal at a very rapid rate, opens to us the possibility of the use of electron diffraction as a means of studying surfaces." Germer's paper describes the diffraction pattern from a clean Ni(111) surface and reports the appearance of a new lateral periodicity, twice that of the substrate, caused by the adsorption of an unidentified gas. Harry Farnsworth made very similar observations[7] at about the same time for Cu(100) and Ag(100), and in each case models of the surface layers were proposed. Significant experimental and theoretical advances have been made in the intervening four decades; nevertheless, much of the LEED work carried out at present is only slightly more sophisticated than those pioneering investigations. The development of LEED as a tool of surface crystallography comparable to x-ray diffraction in the study of solids is still in progress.



The surface of a crystal can differ from the bulk structure in a number of ways, some of which are illustrated here. The surface atoms may be displaced to give **(a)** a contraction of the interlayer spacing and a new lateral periodicity. At the surface of an alloy, segregation of one of the components may occur, as in **b.** Foreign atoms, shown in diagram **c** as colored circles, may be chemisorbed into an overlayer. Following the adsorption of a reactive species, a three-dimensional compound may begin to form, as in **d.** Figure 2



Atomic arrangement of the (111) plane of a body-centered cubic crystal, such as tungsten. The colored line marks a unit cell of the surface atoms, shown in white. The layer shown in light color is $\sqrt{3}/6$ lattice parameters below, and that in dark color twice that distance below, the surface. Arrow shows [110] direction. Figure 3

In a LEED experiment, a monoenergetic beam of electrons is directed towards the crystal surface and the elastic component of the backscattered electrons is observed, as diagrammed in figure 5. The electron energy is usually in the range 20–500 eV, making the corresponding wavelengths about 3–0.5 Å. If the surface atoms are arranged in a periodic lattice they act as a grating for the electron waves and diffract them. Discrete electron beams will therefore appear at angles that depend on the electron energy, the incident polar and azimuthal angles and the two-dimensional periodicity of the surface. These beams may be detected with a movable Faraday cup, or a fluorescent screen on which each beam gives rise to a bright spot. The resulting spot pattern can be observed through a viewing port.

Some examples of LEED patterns are shown in figure 6. From the positions of the spots in such patterns, the space group and the translation vectors that define the two-dimensional unit cell may be deduced. Absolute measurements of the lateral dimensions are rarely needed because it is usually assumed that the lattice parameters of the substrate are known. It is sufficient, therefore, to determine the relative *changes* in the surface periodicity that take place during the experiment. These changes may be quite simple; the adsorption of carbon monoxide on Ni(100), for example, produces initially a doubling of the substrate periodicity, an inference made from the appearance of extra, "half-order" spots in the pattern, as can be seen in figure 6.

Intensity profiles

To determine the location of the atoms within the unit cell of the surface we need additional information; specifically, the *intensity* of the diffracted beams. The measurements, usually made for fixed angles of incidence, are of the variation of the intensity I with electron energy E. In practice these "intensity profiles" or "spectra" are taken for only a few beams. In the approach that so far has given the best results, the experimental data are then compared with the intensity calculated for a model surface. In the trial-and-error procedure, the coordinates of the atoms are adjusted until the predictions agree with the experimental profiles.

Calculations of this sort have received much attention during the last five or ten years, but it is only very recently that a surface structure analysis has been carried out successfully. Theoretical difficulties related to the very strong scattering, both elastic and inelastic, of the electrons by the surface atoms had to be overcome. A kinematical (single-scattering) treatment, which is useful in the case of x-ray and neutron diffraction, is inadequate for LEED, and the calculations require a self-consistent dynamical (multiple-scattering) theory that takes proper account of the rapid electron attenuation.

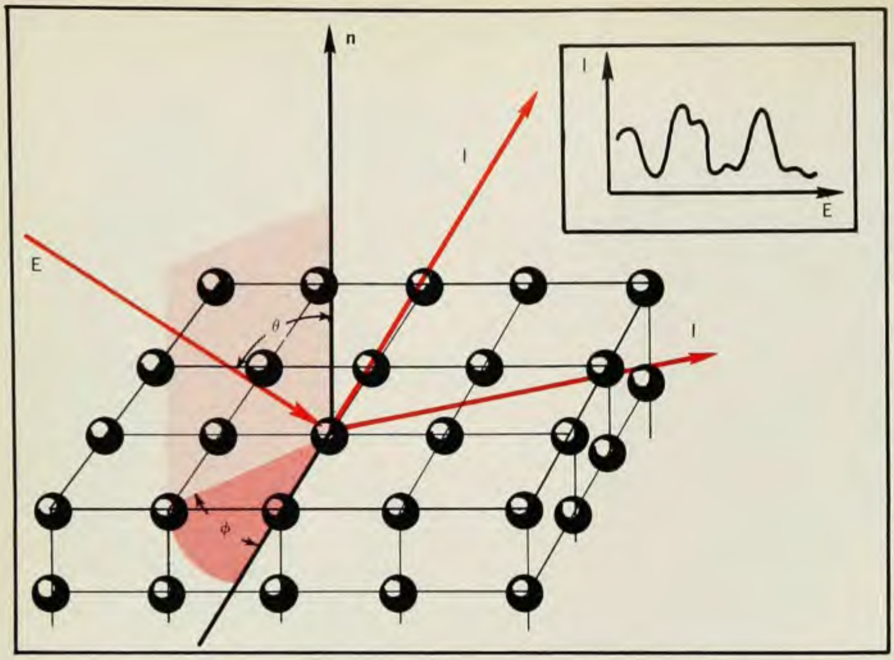
The state of the art is illustrated by the results for a clean nickel(110) surface shown in figure 7, in which a comparison is made between the calculated and measured[10] intensity for the 00 beam (the specular beam) in the diffraction pattern. In the calculations,[11] done by Joseph Demuth, Paul Marcus and Donald Jepsen, the procedure was to apply the Korringa–Kohn–Rostoker method of band theory to a single atomic layer to obtain the scattering properties of that layer, and then to use the result to solve the multiple scattering problem between layers. A number of input parameters were needed; the scattering potential of a nickel atom was described in terms of eight phase shifts, and a value for the "inner potential" was chosen to reference the scattering potential relative to the vacuum level. Electron attenuation in the solid was taken into account by adding to the crystal potential an imaginary part dependent on energy. The model also includes lattice motion characterized by an effective surface Debye temperature. Finally, the diffracted intensity was calculated for a series of values of the first interlayer spacing.

As seen in figure 7, they obtained an excellent fit to the experimental data. The calculations reproduce not only the peak positions but also the line shapes of the experimental intensity–energy curve. The best match occurs for a model that has the first interlayer spacing 5% smaller than the bulk value. The agreement extends to I–E curves for various angles of incidence and diffracted beams from Ni(110). Furthermore, the parameters describing the electron–solid interactions produce an equally satisfactory agreement for the LEED intensity from the (100) and (111) surfaces. No contraction perpendicular to the surface plane appears to take place in these two cases.

A similar structure analysis for a surface containing an overlayer is substantially more difficult, because additional parameters must be included to describe the properties and locations of the foreign atoms. Nevertheless, an encouraging measure of success has recently been achieved for systems of this kind as well.[12] Surfaces of nickel have again provided the best test cases; in particular, the Ni(100) plane with adsorbed chalcogen atoms (O, S, Se or Te) has been the subject of a number of calculations.

The spot patterns show that the adsorption can produce several new surface structures; for example, when half a monolayer of adatoms are present, a structure designated c(2 × 2) is formed. The geometry of this structure, shown

The location of an adatom. The field-ion micrograph on the left is that of a [111] oriented tungsten surface, as in the model of figure 1. Every atom in the outermost layer of the (111) plane (in the center of the photograph) is shown. The photo on the right shows the superposition of two micrographs, one with a single adatom on the (111) plane and the other, of a clean surface, as on the left. The adatom is located in the center of the (111) plane. It occupies a site above one of the dark-colored atoms (3) in figure 3. Figure 4



Schematic illustration of LEED. The energy of the incident electron beam is *E*; its direction is defined by polar angle *θ* and azimuthal angle *φ*. Two diffracted beams are shown; the inset shows the intensity *I* of one of them versus *E*. Adapted from reference 8. Figure 5

in figure 6, may be visualized by thinking of the square array of nickel atoms as a checkerboard on which each black square is occupied by an adatom. As already mentioned, this identification of the unit cell is only a first step in the structure determination, and even qualitative features of the atomic arrangement are left in doubt unless an intensity analysis can be done. The chalcogen atoms might occupy a variety of sites on top of the substrate plane, or some sort of reconstruction could have occurred, consisting for example of a replacement of every other Ni atom in the top layer by a chalcogen atom to initiate the formation of a three-dimensional compound.

The comparison of calculated and experimental intensity data did not at first lead to a clear choice between these possibilities. Different investigators obtained markedly different structures, creating some uncertainty about the validity of the approach in general. However, it now appears that computational details rather than any fundamental flaws in the method were responsible and, after refinements are made, the calculations converge on a single geometrical model.[12] In a c(2 × 2) structure formed by adsorption of S on the Ni(100) plane, for example, the sulfur atoms are located 1.3 Å above the nickel surface in sites of high coordination, namely in the hollows between four nickel atoms. The calculated Ni–S bond distance is 2.18 Å and confidence in the model is enhanced by the fact that this same bond length is found in millerite, a metastable bulk phase of nickel sulfide in which the coordination of sulfur is very similar. Furthermore, the set of surface models constructed for different chalcogens adsorbed on different planes of nickel shows trends that appear entirely consistent with concepts of crystal chemistry.[12]

It would be important to apply microscopic model calculations to other transition metals such as molybdenum, palladium, tungsten and platinum, on which a large number of studies of chemisorption and catalysis have been done, and for which complementary information is available from field-ion microscopy. However, there are practical difficulties associated with an extension of the present procedures to materials with high atomic number; the task may exceed the computer capacity available in all but a few laboratories—it will be very expensive, and additional complications may set in. Computations have recently been carried out for the Mo(100) surface, with and without a c(2 × 2) layer of adsorbed nitrogen.[13] A model gives convincing agreement between the calculated and observed *I–E* curves for four different diffracted beams. Unfortunately, the same structure fails badly in accounting for the intensity profiles of several other beams. This paradox is not yet resolved.

The analysis of surface structures that have a large unit cell is also beyond present capabilities. An example is the (7 × 7) structure[1] of Si(111); it is formed in a spontaneous reconstruction of a clean silicon(111) surface at a temperature below 800°C and it has a two-dimensional unit cell in which both translation vectors are seven times larger than the corresponding vectors in the bulk. (Practically all LEED experimentalists have observed the resulting spot pattern because commercial diffraction equipment used to come with a free silicon sample!) Significant progress has been made in the understanding of the electronic structure and bonding of this surface.[14] A direct determination of the coordinates of the surface atoms would be very useful in the establishment of a definite model.

These difficulties have spurred a search for an alternative way to extract structural information from the intensity data. A Fourier inversion, as is done in x-ray crystallography to obtain the pair-distribution function, has been attempted, but the multiple scattering of the electrons creates several difficulties. It has yet to be demonstrated that the method will lead to the correct structure in the case of a surface with an overlayer of foreign species.[15]

A different approach is the so-called "Constant Momentum Transfer Averaging" procedure.[1,15] The idea underlying this approach is that the low-energy electron diffraction intensity consists of single-scattering and multiple-scattering contributions and that these depend differently on the diffraction angles. If a series of intensity measurements for a selected beam are made in such a manner that the electron *momentum transfer is the same* but the *incident angle varies*, then the multiple-scattering contribution will tend to average out. Curves of intensity versus energy can therefore be obtained for which the modulation is determined largely by the single-scattering component, and an analysis by a kinematical treatment, as for x-rays, should be valid. Complicated model calculations can thus be avoided, being, however, replaced by difficult experimental problems that at this time can be handled in only a few laboratories because of instrumental limitations. Nevertheless, preliminary results obtained for overlayer structures are promising.[15]

A specific system that has been investigated in this way is the interaction of oxygen with the (110) plane of tungsten. The results suggest that, contrary to previous speculations,[16] the initial chemisorption occurs without reconstruction of the tungsten surface. The sites of the oxygen atoms have not yet been determined.

Related techniques

Since no single experimental method can provide a complete characterization of a surface, the usual strategy is to combine several techniques,[17] preferably within the same vacuum system. LEED, for instance, is almost always augmented with Auger-electron spectroscopy, electron-loss spectroscopy and work-function measurements—and may also be combined with photoelectron spectroscopy (ultraviolet or x-ray) and optical (for example, infrared) spectroscopy. Although the main purpose of these additions is the investigation of the composition and electronic properties of the surface, they may indirectly yield information about the surface geometry. For example, Auger-electron spectroscopy data can be used to establish the density of adatoms (the "coverage") corresponding to a given overlayer structure; the change in the work function determines the dipole moment associated with an adsorbed species, and ultraviolet photoelectron or IR spectra may settle a question of whether or not a diatomic molecule dissociates upon adsorption.

Among methods that are used less frequently but are directly applicable to structural studies are HEED (high-energy electron diffraction) and ion scattering. HEED typically employs electrons of $E > 10$ keV, which makes it possible to observe diffraction of transmitted as well as reflected electrons. This ability is a significant advantage, particularly for studies of epitaxial growth. For precise measurements of surface lattice parameters, HEED is also the superior technique.[17]

Ion scattering is the newest addition to the collection of surface crystallographic tools, and so the method has not yet come into general use. In a typical experiment,[18] the surface is bombarded with a beam of noble-gas ions with incident energy of about 1 keV and the energy spectrum of the scattered ions at a particular angle is measured. The collisions with the surface atoms can be treated by means of billiard-ball mechanics and the spectrum at once gives an identification (in terms of mass) of the atoms in the surface. For a substrate with an adsorbed layer of atoms, two peaks are therefore expected, their ratio depending on the extent to which a substrate atom is "shadowed" by an adatom. Thus, by varying the direction of the primary ion beam, the surface geometry can be explored. It is gratifying that when observations were made on the Ni(100) c(2 × 2)-S surface[18] mentioned above, the results were consistent with the model determined by LEED.

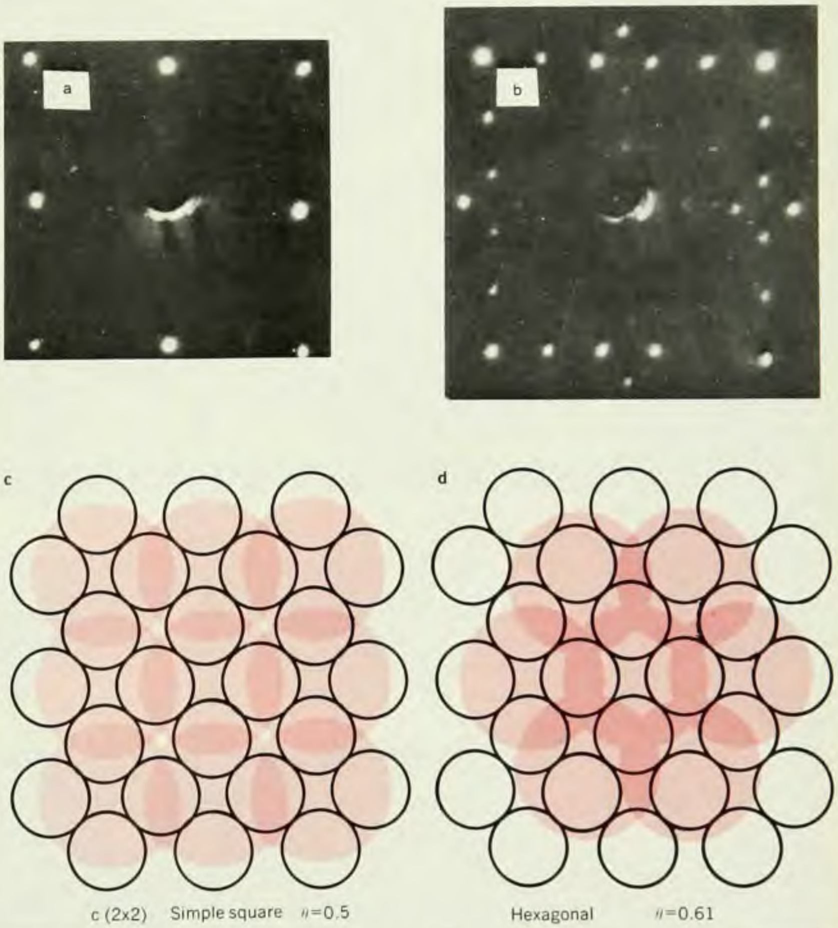
Clean surfaces

Structural investigations of clean surfaces are done in order to correlate the surface geometry with other physical properties such as lattice dynamics and electronic structure and as a preliminary step to studies of adsorption and surface reactions. As stated at the beginning of this article, if a detailed characterization is to be given, the available techniques limit the experiments to substrate surfaces with an atomic arrangement close to that of the bulk crystal lattice, or to surfaces in which the deviations from this arrangement are of a particularly simple nature. I have already mentioned the contraction of the interlayer spacing in Ni(110) and the surface reconstruction on silicon, and will now give a few additional examples.

Regularly spaced steps on a surface represent a structural feature that can be analyzed in some detail. The steps, which appear on crystals that are cut to expose a high-Miller-index plane, are surprisingly stable. The LEED pattern from such a surface has a characteristic appearance, with diffraction spots that are split into multiplets, and in favorable cases both the width of the terraces and the step height may be determined from the LEED data. This has been used by Gabor Somorjai and his coworkers in a study[19] of the catalytic activity of platinum(111); they found that the adsorption of gases such as oxygen and hydrogen occurs more readily on a stepped than on a flat surface; there appears to be a correlation between terrace width and catalytic activity for certain reactions.

Studies of clean surfaces have produced some examples of order–disorder transformations.[1,16] A LEED pattern from a NiO crystal shows an additional periodicity due to its antiferromagnetic ordering, the extra diffraction spots disappearing as the temperature is raised above the Néel point. Other experiments[20] revealed the reversible disordering of the (100) surface of Cu_3Au. The superlattice that exists in the bulk crystal is found to extend to the surface layers, and its gradual disappearance with temperature can be followed with low-energy electron diffraction. For both of these surface transformations, the temperature dependence of the order parameter is different from that in the bulk.

The disorder due to the thermal vibrations of the surface atoms always affects LEED measurements. Theory



Carbon-monoxide overlayer in two different surface structures on the (100) face of a nickel crystal. At a coverage (adatom density) of 0.5 monolayer, the LEED pattern **(a)** shows five of the spots present in the clean-surface pattern: the zero-order center spot and the four first-order beams in the corners. The additional spots in the middle of the sides of the square, produced by the overlayer, indicate that it has the c(2 × 2), or simple square, structure diagrammed in **c.** Here the open black circles represent nickel atoms and the colored circles, CO molecules. When the coverage is increased to 0.61, the diffraction pattern changes to that of **b,** corresponding to the hexagonal structure **(d).** (Courtesy of J. C. Tracy.) Figure 6 predicts that the values of the mean-square displacements of atoms in layers near the surface will be considerably larger than in the solid, and this is confirmed by experiments.[1] In the analysis of the Ni(110) data shown in figure 7, the observed temperature dependence of the intensity was found to be describable by an effective surface Debye temperature $\Theta_D = 335$ K. Thus, the lattice near the surface is much "softer" than in the bulk where $\Theta_D \approx 430$ K.

While field-ion microscopy readily detects structural defects on the atomic scale, electron diffraction is not nearly as sensitive to surface imperfections. LEED data are usually obtained as an average over a relatively large surface area, and if the surface layer consists of ordered domains larger than about 100 Å in diameter, a sharp pattern will be observed. Random defects will contribute only to background intensity.

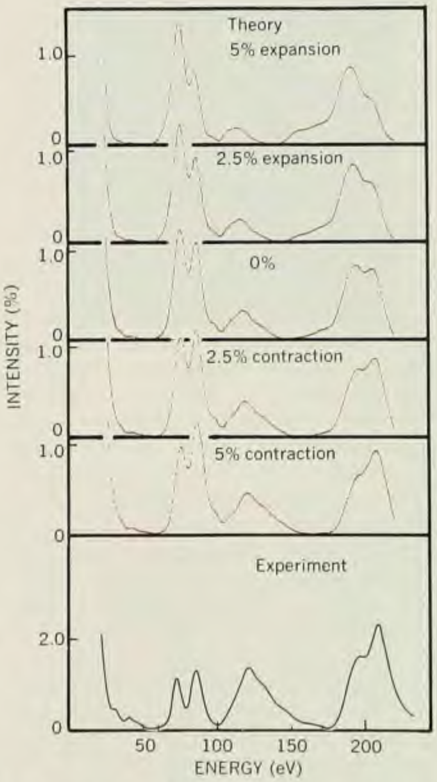
Adsorbed layers

A striking result of experimental studies of adsorbed layers is the large number of well-ordered periodic arrangements that may be formed.[16] As was pointed out by James Lander some years ago, the potential total of such structures is larger in two dimensions than in three. The discovery and recording of overlayer structures on well-defined surfaces represent a considerable achievement that has set the stage for a more fundamental inquiry into the underlying interactions.

The forces between a single atom and a substrate can be thought of in terms of a potential-energy surface with valleys and hills, which defines the equilibrium position and the binding energy for adsorption, as well as the barriers against lateral migration. The details of the energy contours are usually not known, but they must reflect the spacing and symmetry of the substrate structure so that the adatom site will be simply related to the positions of the substrate atoms. As it has already been seen in connection with the data of figure 4, field-ion microscopy provides a direct confirmation of these ideas. A particular bond geometry is thus indicated—this is a prerequisite for a frequently used model that treats the act of chemisorption as the formation of a "surface molecule" consisting of the adatom and one or more substrate atoms.

When many atoms are adsorbed, this picture must be modified. In addition to the adatom–substrate interactions the potential energy will depend on the lateral interactions between the adatoms. LEED measurements on adsorbates usually become possible when 0.1–0.2 monolayers have been adsorbed; the observations, of necessity, concern overlayers in which both types of interaction are involved. Some of the overlayer structures that have been seen are clear evidence that the adatom–adatom interactions can produce large changes in the potential energy surface.

The two-dimensional geometry of an overlayer generally will depend on the relative strength of the two types of interaction. If the adatom–adatom interactions are negligible, the adsorption will proceed by random occupation of the sites. If there is one site per substrate surface atom, the result at saturation will be an overlayer with two-dimensional lattice parameters identical with those of the substrate, that is, a (1 × 1) structure. Since no new periodicity is created, the LEED pattern will remain the same throughout (except for changes in the intensity). On the other hand, if the adatoms have sufficient mobility, a lateral interaction will give rise to ordered structures during the adsorption. For instance, a strong repulsion between adatoms on neighboring sites will tend to produce the c(2 × 2) structure, which is formed by many adsorption systems at a coverage of about half a monolayer. Overlayers with a much larger two-dimensional unit cell have also been observed, suggesting that long-range forces can be involved. The nature of these interactions is discussed in the accompanying article by Schrieffer and Soven.



The experimental intensity profile obtained from LEED (bottom curve) is here compared with model calculations for various values of interlayer spacing. These vary from 5% expansion (top curve) to 5% contraction relative to the bulk spacing; the latter gives the best fit. The surface here is Ni(110) with diffraction angles $\theta = 4$ deg and $\phi = 90$ deg; the specularly diffracted beam is used. The parameters of the model calculation include a surface Debye temperature of 335 K, an electron-attenuation parameter $\beta = 0.85E^{1/3}$ and an inner potential $V_0 = 11$eV (From Demuth, Marcus and Jepsen, ref. 11.) Figure 7

Overlayer structures sometimes show a periodicity that is weakly or not at all related to the substrate periodicity; such structures are called "incoherent" or "incommensurate" layers. The adsorbed species do not occupy crystallographic sites and the geometry of the layer is determined almost completely by adatom–adatom interactions. In these cases, the substrate contribution to the hills and valleys of the potential-energy surface has evidently become negligible. Under such conditions the concept of a "surface molecule" has little meaning, and a different approach to the bonding appears necessary.

Results obtained by Charles Tracy for the adsorption of carbon monoxide on the nickel (100) surface[8,21] provide examples of these structures. Figure 6 shows two different LEED patterns that are obtained as the coverage θ increases, together with proposed models of the surface geometry. For θ not greater than 0.5 the CO molecules occupy lattice sites and form an ordered c(2 × 2) overlayer that gives rise to characteristic new features, "½ ½ spots," in the LEED pattern. The model of the c(2 × 2) structure drawn in figure 6 places each CO molecule on a "four-fold" site. The possibility that the CO molecules occupy a bridged position, with bonds to just two Ni atoms, is discarded, even though no LEED intensity analysis has been done for this surface. The reason is that sites of low symmetry permit a type of structural mistake in the formation of the c(2 × 2) layer that cannot happen if four-fold sites are used.[1] The distinction was therefore made by examining the LEED patterns from partially disordered structures.[21]

Lateral interactions

When the CO coverage becomes larger than half a monolayer, the c(2 × 2) arrangement is no longer possible. The ½ ½ spots are observed to split into four new spots and, when the overlayer is nearly completed at θ greater than 0.6, a pattern of approximately hexagonal symmetry is observed. These results show that the initial registry with the substrate gradually is lost as the overlayer is "compressed," and at saturation it is the interactions between the CO molecules that dominate the overlayer geometry. The lack of strong substrate effects also become evident in a comparison of the adsorption of carbon monoxide on the (100) and (110) faces of nickel.[22] When the adsorption stops, the CO layers on the two different substrates are almost identical in regard to

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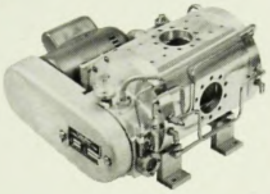
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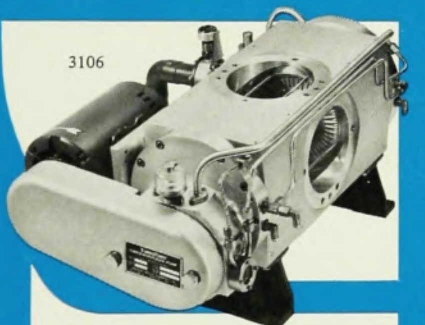
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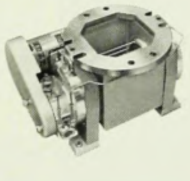
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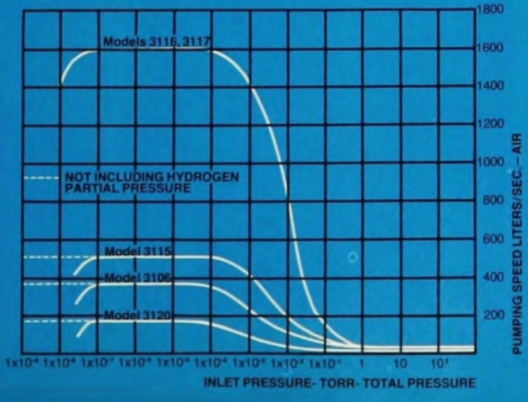

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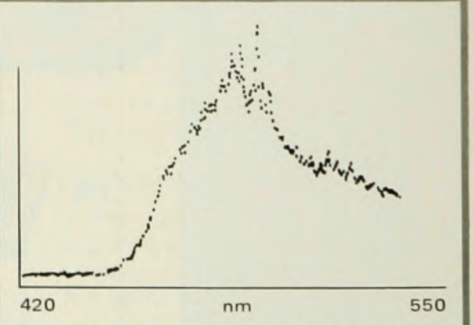

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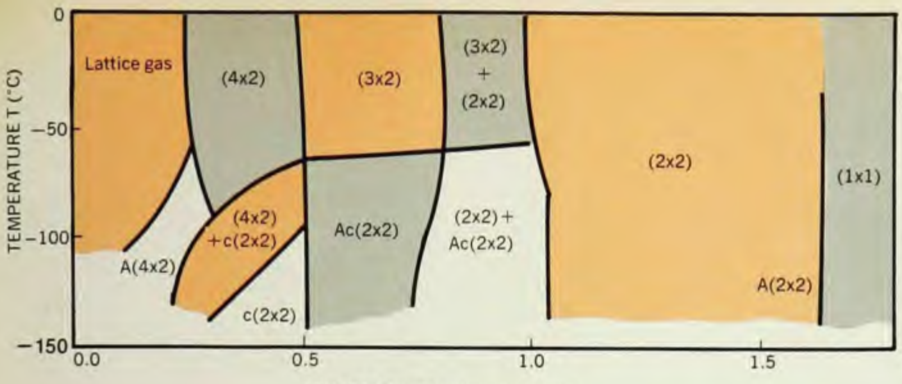

This phase diagram for hydrogen overlayers on the (100) surface of molybdenum shows the approximate regions on the temperature-coverage plane in which a particular two-dimensional structure is observed. The structures are labelled by the dimensions of the unit cell, with an A denoting the occurrence of antiphase domains. At $T = -130$ °C and $\theta = 0.45$, for example, the c(2 × 2) structure is stable, but if the temperature is raised (from the white region to the gray in the figure), a reversible transition to a (4 × 2) structure takes place, in which at least half of the hydrogen atoms must change position. (From reference 27.) Figure 8

their density as well as their structure.

A similar insensitivity to the substrate geometry has been reported for other systems, as for example CO adsorption on palladium.[23] However, it should not be concluded that this behavior is the rule; the overlayers formed on tungsten surfaces, for example, almost always maintain a strong substrate specificity even at the highest coverages.[16,24] In these cases the structural changes observed during adsorption is often ascribed to an inherent heterogeneity.[25] It is assumed that the substrate provides several types of site differing in symmetry and in adatom-binding energy. The sites are filled in the order of their binding energy and a characteristic LEED pattern may result upon completion of each binding state. This model also gives a rationale for the rather large and abrupt decreases that can occur in the binding energy as the coverage increases. However, as already indicated, adatom–adatom forces are rarely negligible and statistical-mechanical calculations suggest that the "induced heterogeneity" due to these lateral interactions can give rise to an equally strong coverage dependence of the binding energy.[25]

A measurement of the binding energy at low coverage provides an indication of the strength of the adatom–substrate interaction. It is more difficult to obtain quantitative data for the adatom–adatom interactions. One method is to examine the effect of temperature on the overlayer structure.[26] Assuming that no desorption occurs, an increase in temperature will tend to randomize the adatom arrangement; the stronger the lateral interactions are, the higher is the critical temperature for the order–disorder transition. This procedure has been used with some success for a c(2 × 2) overlayer of hydrogen on tungsten(100). As discussed by Schrieffer and Soven, the forces between the adatoms will depend on the electronic structure of the substrate, and similar experiments on the c(2 × 2) structure of hydrogen atoms on Mo(100) were therefore interesting to do. Surprisingly enough, no order–disorder transition was observed for this structure; instead, a reversible transformation to another ordered structure was observed.[27] Further investigations in different regions of coverage and temperature revealed a number of other transitions for hydrogen overlayers on this surface. It was found, for example, that at low θ the hydrogen atoms form a lattice gas from which an ordered structure will "precipitate" when the coverage exceeds about 0.25. The richness of two-dimensional structural phenomena is illustrated by the phase diagram in figure 8. The nature of the different transformations is not well understood but it is clear that they deserve additional study.

A promising beginning

The present discussion has emphasized the simplest possible surface layers. Powerful experimental techniques are now being applied to studies of surface structures, but so far accurate models have been established in only a few cases. However, the overlayer structures can be characterized sufficiently well to allow rather detailed conclusions to be made about the nature of the atomic interactions at the surface. The result has been a rapidly growing contact between experimental and theoretical work that holds promise for the development of a microscopic description of surface phenomena.

* * *

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