free-induction decay in magnetic resonance experiments.

Transient absorption occurs when a two-level system is driven from a condition of equilibrium population difference and negligible polarization to a new state (in a time short relative to the relaxation processes) which contains a macroscopic polarization and a nonequilibrium population difference. During this process, energy is being taken from the radiation to produce a higher energy system. Thus, we refer to this process which has involved a net absorption of energy as transient absorption. The rates and behavior of the system as it moves toward its new state of macroscopic polarization and nonthermal equilibrium are determined by solving the coupled differential equations leading to the extraction (by comparison with experiment) of T_1 and T_2.

Transient emission occurs when the system is taken from a condition of interaction with the radiation where the system is polarized and in nonthermal equilibrium, to a condition where the external radiation is either removed or at least taken far off-resonance and out of interaction with the molecular two-level system. Some of the energy stored in the molecules is released by spontaneous coherent emission. In the process described above, the signal at the detector after the radiation–molecule interaction is terminated arises from a beat between the radiation field coherently emitted from the system with the radiation field of the reference microwave oscillator. The signal obtained can be Fourier transformed to give the spectrum of the original transitions which were polarized. This demonstration of microwave Fourier transform spectroscopy can lead to the same advantages as experienced in nuclear magnetic resonance.

In the last section, we have attempted a microscopic interpretation of T_1 and T_2 in terms of the transition rates between states. In the limit of strong collisions, where relaxation from one state to a large number of states is possible, we find $T_1 = T_2$, which is the most reasonable explanation for the observation that $T_1 = T_2$ in a number of molecular systems. On the other hand, if specific selection rules favor transfer from one to the other state involved in the two-level interaction, T_1 may be shorter than T_2. In order for T_1 to be longer than T_2, the molecules would have to experience collisions which relax the polarization without relaxing the populations. We are hopeful that continued theoretical and experimental study will lead to an improved understanding of molecular relaxation processes.

Structure of Solid Surfaces

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The past decade has witnessed exciting developments in the field of surface science. Much of this advance has been due to new techniques of electron and atom scattering that provide fundamental information on the structural and electronic properties of solid surfaces. In addition, high-speed digital computers have allowed for increasingly realistic calculations to test theoretical models of the surface properties. Surface studies are particularly motivated by the need for a better understanding of the phenomena involved in such important and diverse applications as heterogeneous catalysis, photography, and solid-state devices of high surface-to-volume ratio, to mention only a few. In this Account we shall focus on the characterization of the structure of solid surfaces (or surface crystallography) by the technique of low-energy electron diffraction (LEED), which has been found to be the most powerful method of investigating surface geometry of crystalline solids on an atomic scale.[1-4] Other important surface spectroscopies often utilized in conjunction with LEED include Auger electron spectroscopy (AES) for the characterization of surface chemical composition[5] and ultraviolet photoelectron spectroscopy (UPS) for studies of surface electronic structure.[6]

The structure of solid surfaces is pertinent to virtually all descriptions of surface phenomena and gives LEED a status in surface science analogous to that of x-ray diffraction in the description of bulk atomic structure.

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(1) G. A. Somorjai and L. L. Kesmodel, *MTP Int. Rev. Sci., Phys. Chem., Ser. Two*, 7 (1975).

(2) M. A. Chesters and G. A. Somorjai, *Annu. Rev. Mater. Sci.*, **5**, 99 (1975).

(3) J. A. Strozier, Jr., D. W. Jepsen, and F. Jona, in "Surface Physics of Materials", Vol. I, J. M. Blakely, Ed., Academic Press, New York, N.Y., 1975.

(4) J. B. Pendry, "Low-Energy Electron Diffraction Theory", Academic Press, London, 1974.

(5) See, for example, C. C. Chang, *Surf. Sci.*, **25**, 53 (1971).

(6) See, for example, D. E. Eastman in "Electron Spectroscopy", D. A. Shirley, Ed., North Holland Publishing Co., New York, N.Y., 1972.

As we shall see below, however, the state of our knowledge of surface structures is quite incomplete, although rapidly advancing, and much of what one says today must still be only qualitative. We can underscore the novelty of the field by noting that, although Davisson and Germer performed the first electron diffraction experiments in 1927, the first quantitative determinations of the structure of clean metal surfaces[7] were not carried out until the period 1969–1971. Similar investigations of chemisorbed atoms on surfaces were initially reported[8] for sodium on a nickel substrate in 1972. The first structural determination of molecular chemisorption has been reported only in the past several months for the hydrocarbon acetylene (C_2H_2) on a platinum substrate.[9] The prospects for further significant advances of this kind in the next few years look excellent, and such structural determinations will certainly have considerable impact on our understanding of the nature of the surface chemical bond and of chemical reactions at surfaces.

In this Account we hope to place in perspective the state of surface crystallography on a variety of different surfaces. We limit the discussion to chemically clean crystalline surfaces, the topic of adsorbed gases on surfaces having been discussed very recently in this journal.[10] Following an introduction to essential LEED concepts we consider separately the various surfaces, from metals to molecular crystals. We endeavor to provide quantitative data where available, but emphasis by necessity is placed on qualitative considerations. This is particularly apparent in the case of reconstructed surfaces, which have thus far defied truly quantitative investigation, and insulator surfaces, which pose certain experimental problems due to charging and electron-beam-induced desorption. Finally, we include a brief discussion of stepped surfaces which have received the growing interest of investigators in the field.
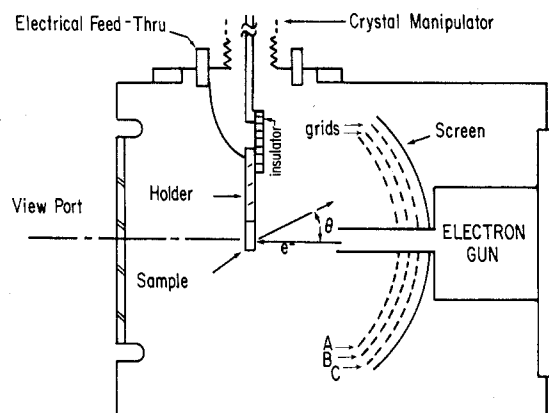
Electron Diffraction from Surfaces

When viewed on a microscopic or submicroscopic scale the surface of a crystal is heterogeneous; various kinds of irregularities are present. Here, however, we are concerned only with those well-ordered domains that commonly span the range of several hundred ångströms with the atoms situated in repeating rows characterized by well-defined interatomic distances. We describe this surface periodicity by a two-dimensional lattice such that a translation $\mathbf{T}$ in the plane of the form

$$\mathbf{T} = n_1\mathbf{a} + n_2\mathbf{b} \tag{1}$$

takes each atom to an equivalent site. Here n_1 and n_2 are integers and $\mathbf{a}$ and $\mathbf{b}$ are the primitive translation vectors defining the surface unit cell.

In LEED we probe this periodicity in the surface plane by scattering a monoenergetic beam of electrons from the surface such that the de Broglie wavelength λ ($= h/(2mE)^{1/2}$) is comparable to the lattice spacing. Strong diffraction occurs, and the elastically backscattered electrons are channeled into a family of discrete beams $\mathbf{g}$ such that

(7) See, for example, the tabulation by Strozier et al.[3]
(8) S. Andersson and J. B. Pendry, *J. Phys. C*, **5**, L41 (1972).
(9) L. L. Kesmodel, P. C. Stair, R. C. Baetzold, and G. A. Somorjai, *Phys. Rev. Lett.*, **36**, 1316 (1976).
(10) J. C. Buchholz and G. A. Somorjai, *Acc. Chem. Res.*, **9**, 333 (1976).

Figure 1. A low-energy electron-diffraction apparatus of the post-acceleration type. Grids A and C are at ground potential for shielding purposes, and a voltage nearly equal to the gun accelerating potential is placed on grid B so that only the elastically backscattered electrons may pass through it. These electrons are then post-accelerated to a phosphor screen for observation through the viewpoint.

$$\mathbf{k}'_\parallel = \mathbf{k}_\parallel + \mathbf{g} \tag{2}$$

where $\mathbf{k}_\parallel$ and $\mathbf{k}'_\parallel$ are respectively the components of the incident and outgoing wavevector of the scattered electron in the direction parallel to the surface. There are precise Laue relations[1,3,4] between the reciprocal lattice defined by the family of beams $\mathbf{g}$ and the direct space lattice so that the process of working back from the observed angles of diffraction to the vectors $\mathbf{a}$ and $\mathbf{b}$ of interest is a straightforward matter.

A typical apparatus used for these experiments is illustrated in Figure 1. Ultrahigh vacuum conditions (base pressure $\sim 10^{-9}$ Torr) are maintained to ensure surface cleanliness. The backscattered electrons are post-accelerated to a fluorescent screen, and the diffraction pattern so produced (Figure 2) is observed through a glass viewport. The condition of the surface under study is quite apparent from the diffraction pattern. Sharp spots are indicative of long-range order (~ 200 Å) on the surface. Diffuse spots probably signal poor ordering or the presence of adsorbed impurities. Extra diffraction spots, meaning those not expected on the basis of simple termination of the bulk lattice structure along the surface plane, indicate either a reordering (reconstruction) of the lattice in the surface region or the presence of ordered impurity structures. AES is routinely used to identify impurities that may be present with about 1% of a monolayer sensitivity.

The energy range $15 \lesssim E \lesssim 200$ eV provides optimal surface sensitivity. The electrons in this range do not penetrate more than a few atomic layers before they undergo inelastic scattering events (absorption) and are lost from the detected (elastic) portion of the beam. Furthermore, they are rather strongly scattered in an elastic fashion by the attractive Coulomb forces of the atomic nuclei and may traverse very complex trajectories (multiple or dynamical scattering) before exiting from the crystal. These considerations are, of course, quite general, and also have some bearing on quantitative interpretations of AES and UPS.
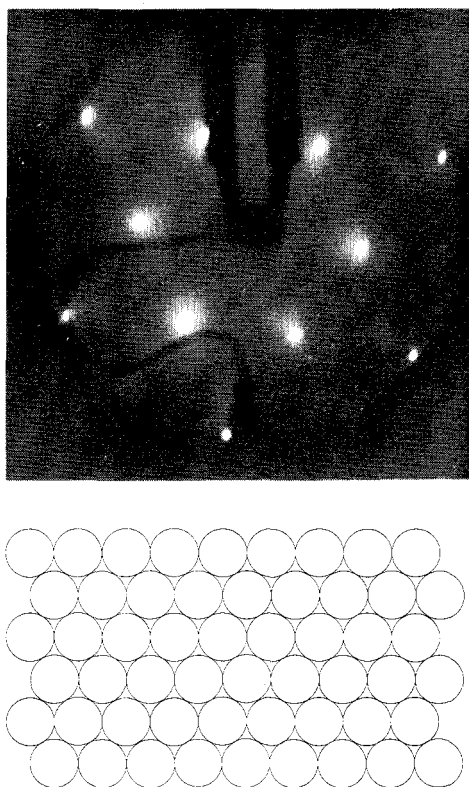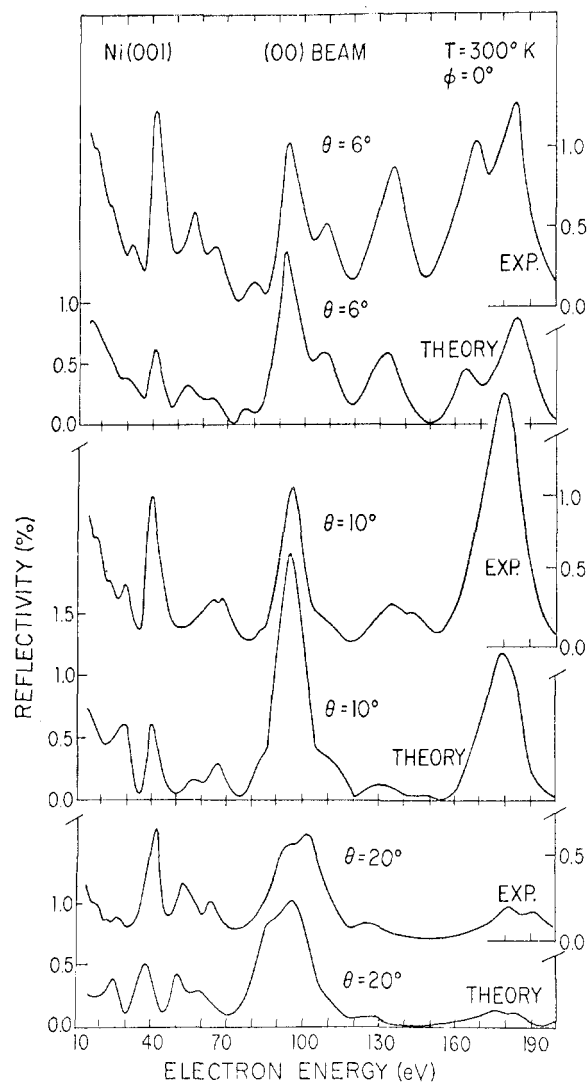
Intensity Analysis

As outlined above, the two-dimensional unit cell vectors are readily found from observation of the diffraction pattern geometry. We cannot in this manner, however, discover the arrangement of atoms or mole-

Figure 2. Low-energy electron-diffraction pattern from the Pt(111) crystal face and a schematic of the surface atomic arrangement.

cules in the basis of the unit cell or information concerning spacings of the atoms in the direction perpendicular to the surface plane (hereafter referred to as the *z* spacing). This essential information can be extracted (although with considerable difficulty!) from analysis of the dependence of the intensity, *I*, of the diffraction spots on the incident beam energy, *V*—so-called *I–V* profiles. These profiles (shown in Figure 3 for the Ni(001) surface[11,12]) exhibit pronounced peaks and valleys which are indicative of constructive and destructive interference of the electron waves scattered from planes parallel to the surface as the electron wavelength is varied. A rather complete quantum mechanical description of this scattering has been achieved through the efforts of a number of theorists in recent years, but the details are outside the scope of this discussion (see, for example, the book by Pendry[4]). We simply mention here that an accurate description of the *I–V* profiles requires, in general, consideration of several orders of multiple scattering (a partial-wave analysis is normally used), absorption due to inelastic events, and vibrational (Debye–Waller) effects.

The analysis proceeds as follows. The diffraction beam intensities are measured, and the intensities are then calculated based on a scattering model in which the essential parameter to be adjusted is the atomic geometry. The assumed geometry is varied until the best fit (principally with regard to peak positions and to a lesser extent with regard to relative intensities) between theory and experiment is reached (Figure 3). Fortunately, the calculated *I–V* profiles are very sensitive to geometrical spacings, so that accuracies of 0.1 Å in atomic positions have been obtained in the better cal-

(11) S. Y. Tong and L. L. Kesmodel, *Phys. Rev. B*, **8**, 3753 (1973).
(12) J. E. Demuth and T. N. Rhodin, *Surf. Sci.*, **42**, 261 (1974).

Figure 3. An example of experimental LEED intensity-voltage profiles[12] and their comparison to theoretical calculations[11] for the specularly reflected beam from the Ni(001) surface at three incident beam angles.

culations. This procedure has been applied to quite a number of clean surfaces[7] and has also provided quantitative bonding information for atomic[10] and molecular adsorbates.[9] Computational limitations presently restrict such analyses to small unit cells or systems with a few atoms per unit cell.

Alternatives to this rather indirect method of analysis have not as yet proven generally applicable.

Metal Surfaces

Metal surfaces are well suited for electron-beam studies because of the absence of space charge buildup during the diffraction experiment and their resistance to electron-beam damage. A variety of cleaning procedures are applicable to metal surfaces, both in and out of the vacuum chamber. Several metal surfaces have been extensively studied with LEED, by simple diffraction pattern observations as well as detailed intensity analysis of the diffraction beams.[7] Indeed the study of metal surfaces provided the testing ground for LEED multiple-scattering theories and placed surface crystallography by the method mentioned earlier on a reasonably firm foundation; this motivated extension to the more complex problem of the surface structures of chemisorbed species.[10]

The thermodynamically favored surfaces are those with densely packed planes of atoms exposed (Figure 2). In conventional crystallographic terms these are the low Miller index planes[13] (e.g., the familiar (100), (110), and (111) planes of a face-centered cubic lattice). The surface unit cell of a low-index face of a clean metal surface has generally been found to be that expected from the projection of the bulk (x-ray) unit cell to the surface (referred to as (1 × 1)), and the uppermost layer z spacing is equal to the bulk value to within the estimated accuracy of about 5%. However, the Al(110) (5–15%),[7] Mo(100) (11–12%),[7] and W(100) (6%)[14] surfaces seem to show substantial contraction in the upper-layer z spacing with respect to the bulk, while retaining the (1 × 1) surface unit cell. A simple contraction or expansion of the interplanar z spacing of this kind is usually termed a *relaxation*. More dramatically, the (100) and (110) faces of Ir,[15] Pt,[16] and Au[17,18] are *reconstructed*, i.e., the two-dimensional surface unit cell is different from that given by the termination of the bulk structure along the plane of interest.

In general, one observes that crystal planes having relatively less dense packing of atoms will be more prone to relaxation or reconstruction, as compared to the most densely packed plane of a given crystal structure. This is consistent with the removal of a larger number of nearest-neighbor atoms in forming a surface of the less densely packed planes. In order to minimize the surface free energy in these cases, a rearrangement (perhaps a subtle one such as a slight buckling of the surface) of surface atoms from bulk positions may, therefore, be quite favorable. The (100) surfaces of Ir, Pt, and Au, for example, exhibit the diffraction pattern illustrated in Figure 4. The spots from a nominal (1 × 1) surface occur at the corners of the squares, but there are extra or "fractional-order" spots in between, indicative of domains of (5 × 1) superstructure.[19] By the designation "(5 × 1) superstructure" we simply mean that the unit cell vectors characterizing the periodicity of the reconstructed surface are respectively five times larger than, and equal to, the corresponding vectors of the (1 × 1) cell. This large apparent unit cell can be due to the superposition of smaller unit cells which are rationally related (so-called coincidence structures), and a plausible, though unproven, suggestion is that the reconstructed surface consists of a hexagonal close-packed layer of atoms lying on top of the undistorted (100) planes.[17]

There is considerable interest in alloy surfaces, due in part to their potential as efficient catalysts. Order–disorder transformations which are well characterized for some bulk alloy systems may also be studied in the surface region. Studies of the surface structure by LEED have been carried out for alloys such as Cu–Au, Cu–Al, and Ag–Pd. The appearance of superlattice beams in the LEED patterns for the $Cu_3Au(100)$ sur-
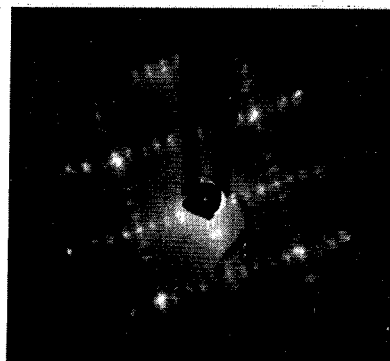

Figure 4. Diffraction pattern from the Pt(100) crystal face exhibiting the (5 × 1) surface structure.

face,[20,21] for example, indicates the presence of long-range order in the alloy surface as in the bulk below the order–disorder transition temperature, t_c = 390 °C. However, the temperature dependence of these beams seems to indicate a different behavior of the long-range order parameter for the surface of this alloy as compared to the bulk.[20]

Semiconductor Surfaces

Several elemental (Si, Ge) and compound (GaAs, InSb, etc.) semiconductor surfaces have been studied by LEED, and in some cases diffraction beam intensities have been analyzed. Whereas surface reconstruction is certainly rare for metals, it seems to be very common for semiconductors.[22] In a general way this behavior can be ascribed to the more localized, directional character of the bonding in semiconductors as opposed to the delocalized bonding picture appropriate for metals. Competing models for the reconstruction of cleaved silicon surfaces involve either periodic displacements of the surface atoms from bulk positions or the formation of ordered surface vacancies. A quantitative LEED intensity analysis to discriminate between these models is presently lacking but will hopefully be soon forthcoming. A complete set of LEED intensity data has been obtained for the (2 × 1) reconstructed surface of Si(100), and its surface structure is currently under theoretical investigation.[23]

We consider the case of the reconstructed silicon(111) surface. Upon cleavage in ultrahigh vacuum, the LEED diffraction pattern shows spots indicative of (2 × 1) superlattice periodicity. This structure is metastable and converts with annealing to the stable (7 × 7) superstructure (Figure 5) which is preceded by an apparent (1 × 1) structure at the phase transition temperature near 400 °C.[24] Rowe and Phillips[25] have argued that, whereas a surface buckling model of the kind proposed by Haneman[26] provides a satisfactory explanation of the metastable (2 × 1) surface, a qualitatively different model such as the one proposed by Lander[27] involving ordered surface vacancies is necessary to explain the properties of the annealed (7 × 7) surface. At present the evidence is inconclusive, and most experi-

(13) For a discussion of bulk crystal structure and Miller indices see, for example, C. Kittel, "Introduction to Solid State Physics", 4th ed, Wiley, New York, N.Y., 1971, Chapter 1.

(14) M. A. Van Hove and S. Y. Tong, *Surf. Sci.*, **54**, 91 (1976).

(15) J. T. Grant, *Surf. Sci.*, **18**, 228 (1969).

(16) S. Hagstrom, H. B. Lyon, and G. A. Somorjai, *Phys. Rev. Lett.*, **15**, 491 (1965); H. B. Lyon and G. A. Somorjai, *J. Chem. Phys.*, **46**, 2539 (1967); A. E. Morgan and G. A. Somorjai, *Surf. Sci.*, **12**, 405 (1968).

(17) D. G. Fedak and N. A. Gjostein, *Surf. Sci.*, **8**, 77 (1967).

(18) P. W. Palmberg and T. N. Rhodin, *Phys. Rev.*, **161**, 586 (1967).

(19) More precisely, the coincidence lattice is (5 × 20) since a splitting of the one-fifth order beams is also observed.

(20) V. S. Sundaram, B. Farrell, R. S. Alben, and W. D. Robertson, *Phys. Rev. Lett.*, **31**, 1136 (1973).

(21) H. C. Potter and J. M. Blakely, *J. Vac. Sci. Technol.*, **12**, 635 (1975).

(22) See, for example, the tabulation of reconstructed surfaces by Chesters and Somorjai.[2]

(23) As cited by S. Y. Tong, *Prog. Surf. Sci.*, **7** (1975).

(24) W. Mönch, *Adv. Solid State Phys.*, **13**, 241 (1973).

(25) J. E. Rowe and J. C. Phillips, *Phys. Rev. Lett.*, **32**, 1315 (1974).

(26) D. Haneman, *Phys. Rev.*, **121**, 1093 (1961).

(27) J. J. Lander and J. Morrison, *J. Appl. Phys.*, **34**, 1403 (1963).

Figure 5. Diffraction pattern from the stable form of the Si(111) surface which exhibits (7 × 7) structure.

ments and theories have focused on the (2 × 1) structure.

The essence of Haneman's model[26] for this surface is as follows. In the bulk material the Si atoms are tetrahedrally coordinated with an sp³ hybrid bonding scheme. The surface atoms, however, have only three nearest neighbors, and the remaining "dangling bond" may have a tendency to become more p-like. If this happens the back bonds will tend toward sp² hybridization or trigonal bonding which is essentially planar. These considerations suggest a movement of the surface atom toward the second plane of atoms (contraction of the back bonds), but this will in turn give rise to lateral forces on the second layer atoms, forces which can be released if other atoms in the upper layer are slightly raised. The net result, of course, is a slight buckling or rumpling of the surface caused by the raising and lowering (∼0.1–0.2 Å) of alternate rows of surface atoms, thereby producing a (2 × 1) periodicity. A number of theoretical calculations for the electronic structure of the idealized Si(111) − (1 × 1) surface have been reported, notably the initial self-consistent one due to Appelbaum and Hamann[28] showing the partially occupied dangling-bond surface state band lying in the semiconductor band gap. Schlüter et al.[29] have subsequently considered the effect of the buckling model for (2 × 1) reconstruction and find that the dangling bond state is split with a transfer of charge from the inwardly relaxed atoms to the outwardly relaxed ones, the surface becoming partially ionic.

Nonstoichiometry is apparently a major factor in the observed reconstruction of the polar faces of the group 3–5 semiconductors such as GaAs (zinc blende structure). The (111) face, for example, would ideally have all Ga atoms at the surface bonded to As atoms immediately beneath the surface, while the reverse would be true of the $(\bar{1}\bar{1}\bar{1})$ face. However the $(\bar{1}\bar{1}\bar{1})$ surface has been found to lose As at elevated temperatures, and this is associated with a $(19^{1/2} \times 19^{1/2})$ surface structure, while the low-temperature (2 × 2) structure is arsenic stabilized.[30,31] Similarly, phosphorus is found to preferentially desorb at high temperatures from the GaP$(\bar{1}\bar{1}\bar{1})$ surface.[32] On the other hand, the GaAs(110) surface which has an equal number of Ga and As surface atoms does not exhibit reconstruction, but LEED in-

tensity analysis does favor outward (inward) movement of As (Ga) surface atoms.[33]

A LEED intensity analysis has been reported for the layered metal dichalcogenide compound MoS_2 by Mrstik et al.[34] These interesting compounds consist of layers of covalently bonded atoms coupled to similar layers by weak van der Waals forces. Each layer has the transition-metal atom sandwiched between planes of chalcogen atoms. The authors found no evidence for surface reconstruction and good agreement resulted between calculated and experimental I–V profiles for the bulk interatomic spacings.

Ionic Crystal Surfaces

Ionic crystals are insulators consisting of a lattice of alternating positively and negatively charged ions (e.g., Na^+ and Cl^-) for which the bulk cohesive energy is due to Coulomb forces between ions. However, at the surfaces of these materials there is a net electric field arising from the ionic half-space beneath the surface which in turn may polarize the ions in the surface layer. These polarization fields affect the anions and cations differently and may cause considerable distortion at the surface. Definitive studies of the surface atomic structure of ionic materials have not yet been made by electron-diffraction techniques. However, McRae and Caldwell[35] did find LEED evidence for a distortion of the (100) surface of LiF, indicating that the top Li and F sublayers do not lie in the same plane, i.e., the surface is periodically buckled. This result is qualitatively consistent with the theoretical predictions of Benson and co-workers[36] and has been further investigated with LEED intensity calculations.[37]

A number of studies have pointed to possible nonstoichiometry of alkali halide crystal surfaces upon cleavage.[38,39] These surfaces may also become charged or damaged under electron beam exposure. In general there is preferential desorption of the halogen atom from the surface by the electron beam with rather high efficiency and the associated formation of F and M color centers.[38,40] Some of these effects may be minimized by working at elevated temperatures to increase conductivity and to permit rapid diffusion of ions from the bulk to recombine with vacancies at the surface. The elementary theoretical models of the surface structure outlined above may have to be modified to include the possibility of varying degrees of nonstoichiometry at the surface.

Oxide Surfaces

The interaction of oxygen with metals to produce various surface oxides is of considerable chemical and technological interest, but relatively few structural studies have been carried out by LEED. Changes in chemical composition have been related to the forma-

(28) J. A. Appelbaum and D. R. Hamann, *Phys. Rev. Lett.*, **31**, 106 (1973).

(29) M. Schlüter, J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, *Phys. Rev. Lett.*, **34**, 1385 (1975).

(30) A. Y. Cho, *J. Appl. Phys.*, **41**, 2780 (1970).

(31) J. R. Arthur, *Surf. Sci.*, **43**, 449 (1974).

(32) H. H. Brongersma and P. M. Mul, *Surf. Sci.*, **35**, 393 (1973).

(33) A. R. Lubinsky, C. B. Duke, B. W. Lee, and P. Mark, *Phys. Rev. Lett.*, **36**, 1058 (1976).

(34) B. J. Mrstik, S. Y. Tong, R. Kaplan, and A. K. Ganguly, *Solid State Commun.*, **17**, 755 (1975).

(35) E. G. McRae and C. W. Caldwell, Jr., *Surf. Sci.*, **2**, 509 (1964).

(36) G. C. Benson, P. I. Freeman, and E. Dempsey, *J. Chem. Phys.*, **39**, 302 (1963); G. C. Benson and T. A. Claxton, *ibid.*, **48**, 1356 (1968).

(37) G. E. Laramore and A. C. Switendick, *Phys. Rev. B*, **7**, 3615 (1973).

(38) See, for example, the series of three papers by T. E. Gallon, I. G. Higginbotham, M. Prutton, and H. Tokutaka, *Surf. Sci.*, **21**, 224 (1970), and references therein.

(39) C. E. Holcombe, Jr., and G. L. Powell, *Surf. Sci.*, **30**, 561 (1972).

(40) P. D. Townsend and J. C. Kelly, *Phys. Lett. A*, **26**, 138 (1968).

tion of new surface unit cells as evidenced for the (0001) surface of α-alumina (Al_2O_3) where reconstruction at elevated temperatures under vacuum was associated with loss of oxygen.[41] The observed transformation from a (1×1) to a $(31^{1/2} \times 31^{1/2})$ unit cell could be reversed by oxidation of the surface in 10^{-4} Torr of oxygen at 1000–1200 °C. The reconstructed surface has been interpreted[41] in terms of a reduced oxide surface layer containing Al^+ or Al^{2+} ions. Fiermans and Vennik[42] have studied the transformation of a $V_2O_5(010)$ surface to one characteristic of $V_{12}O_{26}(010)$ under the influence of the electron beam. The authors found that the transformation proceeds by domain formation, and two different intermediate superstructures of (4×1) and (1×2) periodicity were involved depending on the degree of sample nonstoichiometry. In more recent work leading to quantitative structural determinations Legg et al.[43] have reported LEED intensity data for the (001) surface of MgO.

Molecular Crystal Surfaces

Molecular crystals constitute a large and important group of materials that includes most organic solids, but only very recently have the surface structures of some of these materials been investigated on an atomic scale by LEED. Ice and naphthalene have been grown by vapor deposition on a Pt(111) substrate, and observation of the LEED diffraction patterns have allowed studies of the surface morphologies as a function of substrate structure, temperature, and exposure.[44] The ice structure was obtained by exposing a clean Pt(111) surface to water vapor flux of 10^{14} molecules cm^{-2} s^{-1} at substrate temperatures of from 125 to 155 K for several minutes. The diffraction pattern observed is almost identical with that of domains of a Pt(111)–$(3^{1/2} \times 3^{1/2})$ $R30°$ surface structure, rotated 60° to each other; the domains are of the order of 30 Å in linear dimensions. The pattern is most probably due to domains of the (111) face of fccub ice grown parallel to the Pt(111) surface. Similarly, ordered surface structures of naphthalene were grown between 105 and 200 K, and the observed diffraction pattern is that expected from the monoclinic naphthalene crystals growing with (001) planes parallel to the Pt(111) surface. Several other materials under similar study at this laboratory include benzene, trioxane, *n*-octane, cyclohexane, and methanol.

Ordered films of (Cu, Fe, and metal free) phthalocyanines have recently been grown by vapor deposition on Cu(100), Cu(111), and Pt(111) substrates (monolayer to 500-Å film thickness) and studied by conventional LEED techniques.[45] The diffraction patterns are consistent with a relatively large surface unit cell containing one phthalocyanine molecule with the plane of the molecule parallel to the surface plane. The first layer of molecules is chemically bonded to the substrate; it appears that the central metal atom of the molecule plays only a limited role in this bonding. Other materials presently under study in this laboratory are the amino

a) Pt - ($\bar{1}$11)

b) Pt - ($\bar{5}$57)

c) Pt - ($\bar{6}$79)
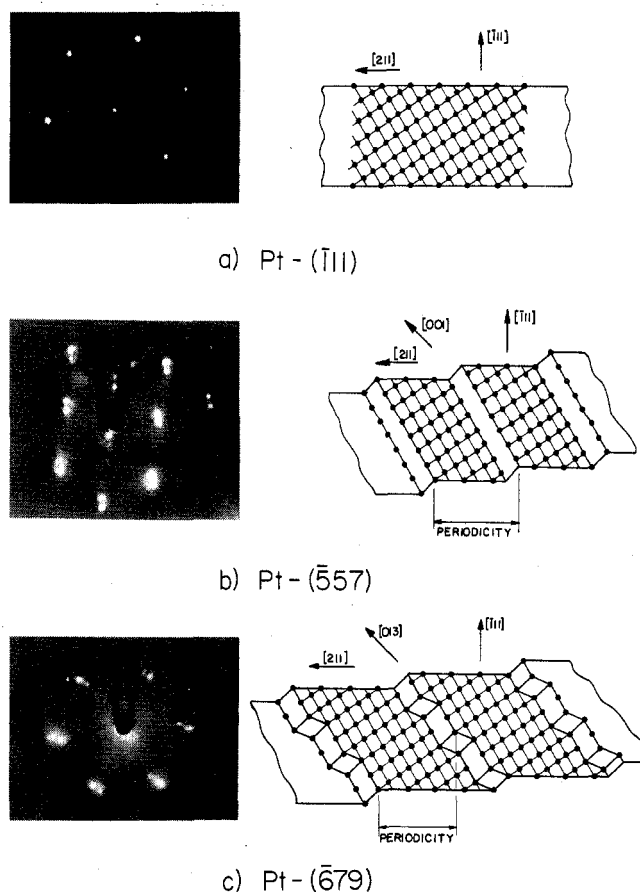
Figure 6. Diffraction patterns and schematic of mean surface configurations for platinum crystal surfaces exhibiting (a) a low defect density, (b) regular step arrays with an average spacing between steps of six atoms, and (c) regular step arrays with kink sites along the steps. Note the spot splittings in (b) and (c) indicative of the regular step arrays.

acids glycine, tryptophan, and alanine grown on metal substrates.

Each of the above studies has indicated that growth of an ordered monolayer phase is essential to ordered growth of the film, and that suitable matching of metal substrate and molecular crystal is of considerable importance in such studies.

General problems encountered in LEED studies of molecular crystals are sample damage and space charging under electron-beam exposure. The vapor pressure of the sample must also be temperature controlled to allow study under ultrahigh vacuum conditions. In the above research, charging effects were largely avoided by vapor growth of suitably thin films on a conducting substrate. This procedure, however, rather severely limits the kinds of surfaces that may be studied, and it is anticipated that LEED systems utilizing much lower beam currents can remedy the charging problem as well as alleviate the problem of electron beam damage. These advances would then allow study of a wide variety of molecular crystal surfaces obtained by suitable cleavage or cutting of bulk crystals.

Stepped Surfaces

To this point we have been concerned with nominally "flat" surface structures which correspond to the close-packed (low Miller index) planes of atoms (neglecting possible surface buckling and a small percentage of surface defects). It is well known, however,

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that surfaces obtained by cleavage contain regions which exhibit a stepped topology, consisting of flat terraces separated by steps or edges typically one atom in height. Regular arrays of such steps were studied with LEED by Ellis and Schwoebel[46] on uranium dioxide crystals by cutting a few degrees off the (111) plane followed by cleaning and annealing in vacuum. The new periodicity introduced by the ordered array of steps (allowing for some variation in terrace width and step height) is readily apparent in the diffraction patterns by the splitting of spots into doublets and sometimes multiplets as quantified by Ellis and Schwoebel[46] and by Henzler,[47] who presented a formula for finding the average step height. Lang et al.[48] examined a number of stepped platinum surfaces prepared by cutting at different angles from a low-index plane. The ordered stepped surfaces were found to be stable under ultra-high vacuum for temperatures up to 1500 K. The appropriate cutting angles are closely related to directions along various high Miller index planes in the crystal, but these sparsely packed, closely spaced planes are of little utility for visualization purposes. More conveniently, we may simply indicate the average terrace width in atoms and the terrace orientation followed by the step orientation, e.g., Pt[6(111) × (100)]. In Figure 6a we show the diffraction pattern and surface topology for an essentially step-free platinum surface and the corresponding diagrams for a high-step density surface (~18%) in Figure 6b. Figure 6c illustrates a stepped surface that also possesses a high density of kinks along the steps.

Stepped surfaces are particularly interesting because of the presence of step and kink sites having lower coordination number than terrace sites and, in fact, these surfaces often exhibit strikingly different chemical behavior from low-index planes. Ibach and co-workers[49] found an exponential increase with step density in the

sticking coefficient for oxygen adsorption on cleaved silicon surfaces. Rowe et al.[50] have reported UPS spectra showing strong dependence on step density for cleaved silicon. Somorjai and associates have found higher reactivity of stepped surfaces as opposed to nominally step-free surfaces in the hydrogen–deuterium exchange reaction[51] and for several hydrocarbon reactions at low pressures.[52] Some theoretical interpretations of the electronic properties of stepped surfaces have been given for metals[53,54] and semiconductors.[55,56] There may indeed be a correspondence in chemical properties between atoms in step and kink sites on single-crystal surfaces and surface atoms on small metal clusters of importance in industrial catalysts, and for this reason alone it is probable that the properties of stepped surfaces will continue to be a topic of lively interest.

Conclusion

Great progress has been made in utilizing low-energy electron diffraction for surface structural analysis as evidenced by several convincing studies of clean metal surfaces and chemisorbed systems, but a vast amount of work obviously remains. We expect that the elucidation of the bonding geometries of various chemisorbed molecules on surfaces by LEED techniques will be one of the foremost challenges. Also of great interest will be the determination of the precise atomic geometries of the many reconstructed surfaces, a topic where much speculation exists, but little is actually known.

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