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THE STRUCTURE OF SURFACES

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THE STRUCTURE OF SURFACES

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1. INTRODUCTION

The past several years have seen a virtually explosive development of structural surface science. The techniques of low-energy electron diffraction and electron spectroscopy have found a multitude of applications in investigations of various surface and interfacial phenomena. Studies of the atomic structure of clean solid surfaces of low Miller index by low-energy electron diffraction, LEED, are being expanded to high Miller index or stepped surfaces as well as to studies of the structure of adsorbed gases. There are recent LEED studies of catalysts and of electrode surfaces that were examined before and after surface reactions.

Among the various techniques of electron spectroscopy, Auger electron spectroscopy is the most widely applied to studies of surfaces. The composition of the surface can be determined with a sensitivity of about 1% of a monolayer (about 10^{13} atoms/cm^2), all elements being detectable this way except hydrogen and helium.[1] Auger electron spectroscopy, (AES), has also been utilized to determine the valency of surface atoms, i.e. the oxidation state of the same element in various compounds.[2] More recently, other techniques such as ultraviolet photoelectron spectroscopy,[3] electron loss spectroscopy[4,5] and X-ray photoelectron spectroscopy[6] have all been utilized in surface studies to determine surface composition and valency. These techniques are based on one-electron processes and, therefore, the experimental data may be analyzed more easily than in the case of AES, which involves a two electron process. In this report, we shall review the recent advances made in surface crystallography and in studies of surface structure of solids and of adsorbed layers. This

field is developing so rapidly that by the time this review is published, most of the information reported here from the various areas of structural surface science will need updating.

We shall first consider those surfaces for which there have been attempts at obtaining an exact structural analysis from LEED measurements. These are unreconstructed metal surfaces and simple layers of chemisorbed atoms. We shall go on to review the present state of understanding of more complex surfaces of metals, semiconductors and insulators where a complete structural analysis is not yet possible.

2. SURFACE CRYSTALLOGRAPHY

During the past four years, rapid advances have been made in developing the theory of low-energy electron diffraction. The purpose of this effort was to develop a viable physical model of the low-energy electron surface interaction that permits computation of the diffraction beam intensities monitored at various electron energies in the range of 20-200 eV (intensity profiles). The computed intensities should accurately predict peak positions and shapes and relative diffraction beam intensities that are observed by experiments and the only adjustable parameter in the theory should be that of the positions of surface atoms. A multiple scattering theory has been successfully developed that allows accurate computation of the diffraction beam intensity profiles from clean low Miller index metal surfaces (with the only adjustable parameter of the surface geometry itself). Thus, the field of surface crystallography has been born and work is being carried out in many laboratories to determine the surface structure of solids of ever-increasing structural

complexity. The development of the multiple scattering theory has been reviewed recently[7,8] and the discussion of its main features is outside the scope of this review. However, review of the results of its applications to determine the atomic surface structure is in order.

2.1 Clean Surfaces

The structure of solid surfaces studied so far are very similar to the bulk structures expected from the projection of the bulk unit cell to the surface. This is deduced from inspection of the diffraction pattern. The possibility of expansion of contraction of the topmost layer with respect to the underlying layer in the direction perpendicular to the surface was studied by surface crystallography. For the most closely packed (111) crystal face of fcc metals, there appears to be no change in the interlayer spacing, certainly not with any degree of significance, for copper[9,10,11] silver,[9,12] and platinum.[13] There may be a very small, 1% contraction for nickel,[16,15] and a small expansion for aluminum.[9,17,18,19] The outer layer spacing in the (100) face of copper remains unchanged, but there is a 2.5% expansion for Nickel(100). Since the precision in the experimentally reported diffraction beam positions allows the determination of atomic distances only to within 0.1 Å, or approximately 5%, the small changes reported are certainly within the accuracy of the reported intensity data.

However, much larger changes in the interlayer spacing have been reported for the more open crystal faces. Atoms in the top layer of the Aluminum(110) crystal face are contracted by 5-15% of the bulk interlayer spacing,[20] and in Nickel(110) by 5%.[15] For bcc solids, there is a substantial

contraction of the top layer reported, approximately 11% in the (001) crystal face of molybdenum.[8,21] Preliminary calculations on the LiF(100) face indicate[22] that the top fluorine layer is contracted by 0.1 Å, and that the top lithium layer by 0.35 Å toward the back. Thus, the two ions do not lie in the same plane, as predicted by several theoretical calculations in the past. As surface structure analyses of other metals, semiconductors and ionic crystal surfaces become available, it will be possible to uncover trends in the interlayer spacing at surfaces with varied atomic density.

2.2 Chemisorbed Layers

There are several surface structure analyses of adsorbed layers which have been reported. The substrates were fcc metals in all cases, either the (100) orientation with fourfold, or the (111) orientation with threefold rotational symmetries, while the adsorbates were small atoms: Sodium, iodine, sulfur, oxygen, and selenium. These atoms appear to occupy those atomic positions (fourfold or threefold) that are expected from the overlayer, if it were the continuation of the substrate. Sodium on the Nickel(100) occupies a fourfold coordination site[23] at a distance of 2.87 Å from the nickel layer; iodine occupies a threefold coordination site 2.25 Å above the silver surface layer;[24] and oxygen, sulfur, selenium, and tellurium all occupy fourfold sites on Nickel(100) at distances of 0.90 Å, 1.30 Å, 1.45 Å, and 1.90 Å respectively, from the top layer of nickel atoms.[25]

Using different sets of experimental data, Duke et al.[26] concluded that sulfur does indeed occupy a fourfold position, but at an elevation

of 1.7 Å, instead of 1.3 Å. Using another set of experimental data, Anderson et al.[27] conclude a similar structure for the adsorbed oxygen, but at an elevation of 1.5 Å, instead of 0.9 Å. Duke et al.[26] conclude that the Nickel(100) surface is reconstructed with both nickel and oxygen atoms at an elevation of 1.75-1.90 Å above the nickel substrate.

Although there is uncertainty in the predicted atomic positions for atoms in the adsorbed layer, this, we believe, is not due to computational problems, or to the inadequacy of the multiple scattering theory. The disagreements are due to the lack of a large base of intensity data, i.e. to the availability of reproducible intensity profiles taken at a wide range of scattering angles. Both oxygen and sulfur can chemically interact with the metal substrate, and it is likely that the various investigators obtained their diffraction data at various stages of chemical interaction. It is entirely possible that all of the structure determinations are correct, that the chemical state of the surface was undefined. At present, the lack of availability of accurate intensity data on a large number of diffraction beams for the various overlayer systems is the obstacle in further development of surface structure analysis.

2.3 Time-Saving Methods

A new photographic method has been developed[28] to measure diffraction beam intensity profiles rapidly and precisely. Since low-energy electron diffraction experiments are carried out at reduced pressures, where surface contamination is time-dependent, and on structures whose ordering is time-dependent, it is necessary to measure intensities rapidly and obtain all of the diffraction beam intensities simultaneously.

Using this new technique, the fluorescent screen is photographed and the film is machine developed for uniformity. The optical densities are converted to integrated intensities by a computer-assisted scanner, and the relative intensities of all of the diffraction beams are determined simultaneously. It is hoped that a great deal of experimental intensity data will become available in the near future, and this will accelerate the development of surface crystallography. Such a rapid photographic technique will also make it possible to study reconstructed surfaces or coincident lattices that give rise to diffraction patterns with many diffraction beams; for example, the (7x7) structure exhibited by the (111) face of silicon.

In its present form, the multiple scattering theory is quite cumbersome to use for the purposes of surface structure analysis. The computer time necessary to solve more complex surface structures can become excessive and the cost prohibitive. There is a great deal of theoretical and experimental effort being expended to develop a pseudo-kinematic theory that is adequate for the purposes of surface crystallography, and averaging, or other data reduction methods, to convert the intensity profiles to a form useful for such simplified theoretical calculations.

Both theoretical and experimental efforts are justified by the predominance of single-scattering features in the I vs. eV curves (intensity profiles) obtained in low-energy electron diffraction studies. Lagally et al.[29,30] and Bucholz et al.[31] have applied the data averaging method of analysis to the Silver(111) and Nickel(111) surfaces. Clarke et al.[32] have used the Fourier transform of the intensities to examine the Platinum(100) surface. The theoretical framework for the application of

pseudo-kinematical theories to structure analysis has been developed,[33,34] and such an approach is viable to analyze more complex surface structures where computation by multiple scattering theory is too expensive.

The central problem in the application of simplified pseudo-kinematic theory is the requirement of a large body of intensity data, I vs. eV data, to eliminate data truncation errors, and multiple scattering. Nevertheless, the transformation methods could provide a fast automated procedure for surface structure analysis.

3. MORE COMPLEX SURFACE STRUCTURES

The preceding section has been concerned with the surface crystallography of clean, low index metal surfaces and simple chemisorbed layers of atoms. It is rapidly becoming feasible to analyze such systems by LEED and obtain a complete solution for the structure of the surface unit mesh. There remains a vast majority of surfaces of more complex structures for which complete structure analysis is a little further off. For example, surfaces which have large unit meshes containing several atoms of more than one element or which adopt different structure to that of the bulk, or become chemically non-stoichiometric through selective evaporation or solution of one component.

A more qualitative application of LEED has provided much useful information on such systems particularly when combined with other analytical tools such as electron spectroscopy, ion scattering, i.v. spectroscopy, etc. It will be convenient to outline the present state of understanding of the structure of complex surfaces with reference to; Reconstructed surfaces, alloy surfaces, and stepped (high Miller index) surfaces.

3.1 Reconstructed Surfaces

As pointed out in section 2, most metals expose a surface which arises from a simple truncation of the bulk crystal structure along a given plane, although slight relaxation of the outer layers might occur. A reconstructed surface is one which does not retain the geometry of the bulk; this may arise through a complete redistribution of surface atoms or by a more subtle distortion of the surface layer. Reconstruction of surfaces of compounds may also involve selective evaporation or solution of one component producing a non-stoichiometric surface.

Some reconstructed surfaces which have been identified by LEED are listed in the Table. In most cases these structures are thought to represent equilibrium or metastable states of the clean surface, e.g. Si(111)-(7x7) or (2x1), but some have been shown to be impurity stabilized, e.g. Si(111)-($19^{\frac{1}{2}}$x$19^{\frac{1}{2}}$).[37] This question of impurity stabilization can only be settled within the present limits cf detection of Auger electron spectroscopy. Probably the test of time is most reliable; structures which have been observed reproducibly in several laboratories using different preparation techniques, are most likely to represent clean surfaces.

It is clear from the table that reconstruction is most common semiconductor and insulator surfaces, but is known on only three metals - iridium, platinum, and gold. This may be rationalized in a very simple way. When a surface of any material is instantaneously created, there will exist unstable electronic surface states. In the case of a metal these may relax into more stable states without disturbing the position of the nuclei, due to the delocalized nature of the bonding. The surface

states (dangling bonds) of a covalently bonded crystal may only be stabilized by a rehybridization of the surface atoms which requires a relocation of its nuclei due to the directional nature of the bonding.

Although the driving force for reconstruction is understood in a general way, the details of the process remain unknown. It has been proposed that a semiconductor surface is stabilized by a large concentration of surface vacancies (of the order of 20-50%) followed by rearrangement into an aromatic-like structure.[62,63] Alternatively, a surface buckling might arise from a rehybridizaton of the surface layer without generation of vacancies.[44] Both viewpoints have been considerably refined, see recent review by Mönch.[71]

These arguments apply equally to the reconstruction of compound semiconductors but here surface non-stoichiometry may exist. Crystals of III, V compounds (zinc blende structure) possess a polar axis, <111>, such that an ideal (111) surface consists of a layer of group III atoms with group V atoms immediately beneath and the $(\bar{1}\bar{1}\bar{1})$ plane is the reverse. Non-stoichiometry has been observed for GaAs$(\bar{1}\bar{1}\bar{1})$[42,65] and GaP$(\bar{1}\bar{1}\bar{1})$[55] surfaces. The (2x2) structure of cleaved GaAs$(\bar{1}\bar{1}\bar{1})$ converts to a $(19^{\frac{1}{2}} \times 19^{\frac{1}{2}})$ structure on heating in vacuum at 800°K and this has been correlated with evaporation of arsenic.[42,65] The (2x2) structure is restored at the elevated temperature in a flux of arsenic molecules and is stable to 650-700°K in this flux. The sticking probability of arsenic or phosphorus molecules was found to be low on the 'arsenic stabilized' (2x2) surface and high on the gallium stabilized $(19^{\frac{1}{2}} \times 19^{\frac{1}{2}})$ surface which accounts for the fact that stoichiometric GaAs films may be grown by vapor deposition. It has been

suggested that a further driving force causing reconstruction of compound surfaces is the reduction of surface charge.[66] Due to the partial ionic character of the bonding, ideal polar surfaces of III,V and II,VI semiconductors will possess high surface charge densities; surfaces which contain equal numbers of each ion (neutral surfaces) generally display (1x1) LEED structures, e.g. ZnO$(10\bar{1}0)$[51] and GaAs(110).[36]

The reduction of surface charge density will also be important for insulating compounds. The (100) cleavage planes of alkali halide crystals on neutral surfaces usually display (1x1) LEED patterns;[64] in contrast, an ideal (111) surface plane should have one type of ion in the top layer and the ion of opposite charge in the second layer, unfortunately such surfaces have not, as yet, been studied by LEED. A surface reconstruction has been suggested for AgBr(111), on the basis of film nucleation experiments, in which half of the top layer Ag^+ ions are removed to produce an electrically neutral surface.[67]

The interplay of forces resulting in the reconstruction of the α alumina(0001) surface is probably more complex. The $(31^{\frac{1}{2}}x31^{\frac{1}{2}})$ structure observed at above 800°C[48,49] probably results from a reduced surface layer containing Al^{1+} or Al^{2+} ions, fig. 1. It was found possible to reverse this transformation by oxidizing the surface in 10^{-4} torr of oxygen at 1000°-1200°C.

As mentioned previously, only gold, platinum, and iridium of the metals have been consistently reported to reconstruct. The (5x20) structure observed on the (100) faces has been correlated with a hexagonally close-packed surface layer[56,57] thus the surface is stabilized by an

increased atom density in contrast to semiconductor and insulator surfaces. It has been suggested that the anomolous behavior of gold, iridium, and platinum arises from the high polarizibility of these metal atoms which intensifies the driving force towards reconstruction under the action of the surface electric field.[62]

The large number of possible models for reconstructed surfaces will make rigorous crystallographic analysis lengthy and tedious but clues to the most likely structures are being gathered by a variety of techniques.

A pseudo-kinematic LEED analysis of the Pt(100)-(5x20) surface has indicated that the surface adopts a buckled, hexagonal, close-packed structure.[32] Electronic surface states of silicon and germanium have been detected by ion neutralization spectroscopy[68] and by photoemission and electron energy loss spectroscopy.[5] On the basis of the latter study it was suggested that the metastable Si(111)-(2x1) surface is likely to be a 'buckled' rehybridized structure while the equilibrium Si(111)-(7x7) surface probably involves vacancies to a considerable extent. Thus, it appears that, under different conditions, both the Haneman[44] and Lander[63] models of reconstruction may be applicable.

3.2 Alloy Surfaces

The characterization of alloy surfaces has received a great deal of attention mainly through attempts at understanding chemisorption and catalysis by observing trends with alloy surface composition. Since neither the surface composition nor structure can be predicted from the bulk parameters they have to be determined independently in much the same way as for the other reconstructed surfaces.

In the case of a binary alloy solid solution, of components A and B, the bulk crystal structure may be determined (the lattice constant is commonly a linear function of composition - Vegard's Law), but the probability of any lattice point being an A atom is simply x_A/x_B (where x = mole fraction), i.e. the crystal is substitutionally disordered. At the surface of such a crystal the concentrations of A and B may differ from those in the bulk due to the forces tending to reduce the surface energy, generally the component with the lowest surface tension will be concentrated in the surface and the problem is to determine the degree of surface enrichment.

At the other extreme we have an ordered alloy or metallic compound. Now the crystal structure is made up of lattice points which are uniquely A or B sites, e.g. $AuCu_3$.[82] At the surface of this crystal there will again be a tendency for surface enrichment in A or B, but this driving force will be modified by the force tending to order the crystal (the A-B binding energy). Clearly surface order and surface composition may differ from the bulk and both will have to be determined by surface sensitive techniques.

Almost all studies of alloy surfaces to date have been concerned only with surface chemical composition, mostly of disordered alloys. It will be helpful in discussing them to write down some important equations. The monolayer ideal solution model has been discussed in a recent review.[72] In this model there is enrichment in the top surface layer only, and the surface composition is related to that in the bulk by

$$\frac{x^s_A}{x^s_B} = \frac{x^b_A}{x^b_B} \exp\left(\frac{(\sigma_A - \sigma_B)a}{RT}\right) \qquad (1)$$

where x = mole fraction, σ = surface tension, and a = surface area per gram atom which is assumed to be the same for A and B.

A measure of the deviation from ideal behavior is given by the regular solution parameter, Ω.

$$\Omega = z E_{AB} - \frac{E_{AA} + E_{BB}}{2} \qquad (2)$$

where E_{AB} is the bond energy between atoms A and B, etc, and z is the number of nearest neighbors. As Ω becomes negative, the system tends to order while large positive values of Ω lead to phase separation.

Because of the distinct change in surface chemical properties in passing from group VIII_3 to group I_b metals, alloys of these two components have received most attention.[72] Unfortunately, these systems are generally not simple. The system Cu/Ni segregates into two bulk phases below 322°C,[72] one copper-rich and one nickel-rich. It has been shown, for polycrystalline alloy films, that the copper-rich phase forms an outer shell on the alloy crystallites, thus producing a constant surface composition for a range of alloy compositions. However this is a somewhat secondary problem since the surface composition of the copper-rich phase still needs to be determined.[73]

A direct measurement of the surface composition of binary alloys became possible with the advent of Auger electron spectroscopy (AES). This technique is, as yet, not fully quantitative, see recent review;[1] the main difficulties are (1) the depth sampled is a function of Auger electron energy, and (2) the sensitivity is a function of the electron scattering properties of the material. Broadly speaking, two to four atom layers are sampled and it is not possible to deduce a concentration profile over

these layers in systems where surface enrichment is occurring. It has often been shown[75,76,77] that the relative Auger signals of two components of a binary alloy are a linear function of bulk alloy composition, but this may not be regarded as evidence against surface enrichment.

It should be possible to detect surface enrichment by recording Auger spectra at varying angles of incidence of the exciting electron beam or by comparing compositions measured with low-energy and high-energy Auger peaks, but these techniques have produced negative results for the Ag/Au[83], Cu/Ni[78] and Ag/Pd[75] systems.

It is probably significant that surface enrichment has been positively identified by AES for an alloy equilibrated in the liquid phase[79] and for an ordered alloy.[76]

Experiments carried out on Pb/In alloys, brought to equilibrium in the liquid phase, showed considerable surface enrichment in lead as expected from the relative surface tensions of the components.[79] The temperature dependence of x_{Pb}/x_{In} showed that the system behaved as an ideal solution (equation (1)), although the surface enrichment in lead was higher than predicted by the monolayer model. Another important parameter affecting surface composition was found to be the nature of the gas phase, surface enrichment in tin resulted in an oxygen atmosphere while excessive carbon contamination produced surface enrichment in lead. Similar effects have been reported for the platinum/tin system where changing from oxidizing to reducing conditions greatly reduced the surface enrichement in tin.[76]

Studies on the ordered alloys Pt_3Sn and PtSn have revealed a more complex pattern of surface enrichment.[76] A combination of AES (probing

2-4 monolayers), and X-ray photoelectron spectroscopy, XPS (probing 4-8 monolayers) produced a qualitative concentration profile which showed the expected first layer enrichment in tin, but also second layer enrichment in platinum. This situation has been predicted theoretically for alloys with negative values of the regular solution parameter, Ω. For ordered alloys, where $-\Omega >> kT$, both surface structure and composition may change, as outlined above.

Sachtler[81] has recently discussed the interplay between ordering forces and surface enrichment forces using Pt_3Sn as an example. The (111) plane of this crystal, figure 2, has tin atoms surrounded by platinum atom near neighbors; Sachtler predicts that surface tin enrichment will occur by place exchange between second layer tin atoms and top layer platinum atoms. A sharp increase in surface tin enrichment is predicted above the critical temperature at which the alloy becomes disordered.

Clearly ordered alloy surfaces should provide a rich area for further research, although it will only be possible to follow surface order changes with LEED if the atomic scattering factors of the components are sufficiently different. This is illustrated by the fact that substitutionally disordered single crystal alloy surfaces of Cu/Ni[78] and Ag/Pd[75] gave sharp (1x1) LEED patterns with low background intensities. If the atomic scattering factors of the components are similar, the effective surface unit mesh will not take account of substitutional disorder, fig. 3.

It is also likely that ion scattering experiments will be useful in studying surface order-disorder transitions on alloy surfaces, particularly in the intermediate stage where short range ordering or clustering may occur.

3.3 High Miller Index or Stepped Surfaces

When surfaces are produced by the cleavage process, a series of monatomic steps commonly results which may be ordered over a long range[84]

or disordered.[53] Such steps have long been known to be important in the nucleation and growth of surface films this being the basis of the surface decoration technique in electron microscopy. It has been shown that surface defects produced by electron bombardment damage assist the development of epitaxial films.[86] A more detailed investigation of this phenomenon has become possible through the use of high-energy ion scattering. Randomly oriented steps on a cleaved NaCl(100) surface have been observed by this technique[85] and it proved possible to distinguish between sodium ion steps and chloride ion steps; it was also shown that copper atoms are captured preferentially at chloride ion steps which suggest that the first stage in nucleation is formation of a surface compound.

Steps are also important in evaporation processes, particularly for molecules larger than diatomic. Evaporation of arsenic in the form of As_4 tetrahedral molecules has been shown to require a certain step geometry in which the tetrahedral configuration is already present at the step[87] edge. This suggests that the molecule breaks away from the step as a whole and is not generated from mobile fragments on the surface.

Long range ordered arrays of monatomic steps may also be generated by cleavage[84] and in the majority of cases are the stable form of high Miller index or vicinal surfaces independent of their mode of preparation. Cabrera[88] has developed the thermodynamics of vicinal surfaces which can be used to predict their free energy and relative stability.

Surfaces of this kind may be studied by LEED and their step and terrace dimensions determined by a kinematic analysis.[84] When a face

centered cubic metal, for example, is cut at 9.5° away from the (111) face in the direction of the (100) face, a (755) Miller index surface is obtained. The LEED pattern observed from such a surface indicates a structure in which atomic terraces of (111) orientation, six atom rows wide are separated by periodic atomic steps, one atom in height, fig.4. This structure may be identified by a shorthand notation [6(111)x(100)], e.g. for the stepped platinum surface Pt(S)-[6(111)x(100)]. This notation provides a more graphic description of the surface than the Miller index. In this way monatomic step structures have been found to be stable on metals,[89,90] semiconductors,[84] oxides,[91] and there is indirect evidence for their stability on ionic surfaces.[92]

Restructuring of a stepped surface may occur during chemisorption[93] with changes in step height and width, but this is reversible on desorption or cleaning. Crystal faces with four or less atom wide terraces, such as the (211) face of platinum, have been found to facet.[94] Clearly more research has to be carried out to explore the structure and stability of vicinal surfaces in various crystallographic orientations and in the presence of overlayers.

Special importance has been given to stepped surfaces by the discovery of their great significance in chemical reactions on metals. The chemisorption characteristics of stepped platinum surfaces are very different from those of low Miller index surfaces. It has been found that atomic steps play a controlling role in dissociating hydrogen and oxygen molecules on platinum surfaces.[95] Atoms at steps in various stages of coordination control the rates of breaking of C-H and C-C bonds

on platinum[94] in the absence of steps, adsorbed hydrocarbon molecules tend to remain essentially intact below 300°C and produce ordered surface structures.[96] Hydrocarbon layers on stepped surfaces at low temperature tend to be disordered.

The catalytic activity of platinum in hydrocarbon reactions is controlled by surface atoms in or near steps. The product distribution in several competing organic reactions is markedly dependent on the surface structure of platinum.[97] Thus, it appears that, in addition to their importance in crystal growth, condensation and vaporization, atomic steps play an important role in heterogeneous catalysis.

The unique properties of atoms at steps may be due to their charge densities which are different from high coordination number atoms in low Miller index planes. There is evidence for increased charge density on atoms at steps from measurements of the work function of various crystal planes[98] and from theory.[99] Thus, a stepped surface is multifunctional, containing atoms with different charge densities and therefore different strengths to break or form chemical bonds.

It is not necessarily true that atomic steps play an important role in chemical reactions on all surfaces with every molecule. On gold, for example, atomic steps do not enhance chemisorption of various hydrocarbon molecules.[100] Conrad et al.[101] have shown that while stepped surfaces exhibit an enhanced initial heat of adsorption for hydrogen on palladium, the heat of adsorption of carbon monoxide on both (111) and stepped palladium surfaces was the same.[102]

Thus, it is likely that the adsorption characteristics of strongly chemisorbed species, particularly atoms, will be more affected by atomic steps and that this effect will be most important on surfaces of intermediate activity. If adsorption is very strong, e.g. on tungsten, it should readily occur on low Miller index surfaces. It is significant that surfaces which form chemisorption bonds of intermediate strength are the best candidates for heterogeneous catalysis.

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TABLE

RECONSTRUCTED SURFACES

Pt(100)-(5×20) [56] Pt(110)-(1×2) [61]	Ir(100)-(5×20) [58]	Au(100)-(5×20) [57] Au(110)-(1×2)
Bi(11$\bar{2}$0) [69]	Sb(11$\bar{2}$0) [69]	Te(0001) [70]
Si(111)-(7×7), (2×1), (19$^{\frac{1}{2}}$×19$^{\frac{1}{2}}$) Si(100)-(2×1), (4×2) Si(110)-(4×5), (5×1) [35,36,37,39]		Ge(111)-(2×8), (1×2) Ge(100)-(2×2), (4×4) Ge(110)-(2×1) [35,36, 39]
GaAs(111)-(2×2) GaAs($\bar{1}\bar{1}\bar{1}$)-(3×3), (2×2), (19$^{\frac{1}{2}}$×19$^{\frac{1}{2}}$) GaAs(100)-(6×1), R45°, (2×8), R45° [40,41,42]		GaP(111)-(2×2) [55]
lnSb(111)-(2×2) lnSb($\bar{1}\bar{1}\bar{1}$)-(2×2), (3×3) lnSb(100)-(2×1) [41,43,44]		GaSb(111)-(2×2) GaSb($\bar{1}\bar{1}\bar{1}$)-(2×2), (3×3) [40,44]
ZnO(0001) Reconstructed [51] ZnO(000$\bar{1}$) Not reconstructed [53,59,60]		CdS(0001)-(2×2) CdSe(0001)-(2×2) [60]
Al_2O_3(0001)-(31$^{\frac{1}{2}}$×31$^{\frac{1}{2}}$) Al_2O_3($\bar{1}$012)-(2×1) Al_2O_3(11$\bar{2}$3)-(4×5) [48,49]		V_2O_5(010)-(4×1), (1×2) [47] $BaTiO_3$(001)-(3$^{\frac{1}{2}}$×3$^{\frac{1}{2}}$) [50]
Diamond(111)-(2×2) [45,46]		Diamond(100)-(2×1) [45,46]

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LIST OF FIGURES

Fig. 1. (a) The hexagonal unit cell of the (0001) substrate and the (b) square unit cell of the oxygen-deficient overlayer which together generate the (c) unit cell corresponding to the rotated $(\sqrt{31} \times \sqrt{31})$ by coincidence.

Fig. 2. (111) plane of the ordered alloy Pt_3Sn.

Fig. 3. (100) plane of an f.c.c. crystal of a disordered alloy. $x_A = x_B = 0.5$.

Fig. 4. (b) Pt(S)-[6(111)×(100)] stepped surface. (a) LEED pattern.

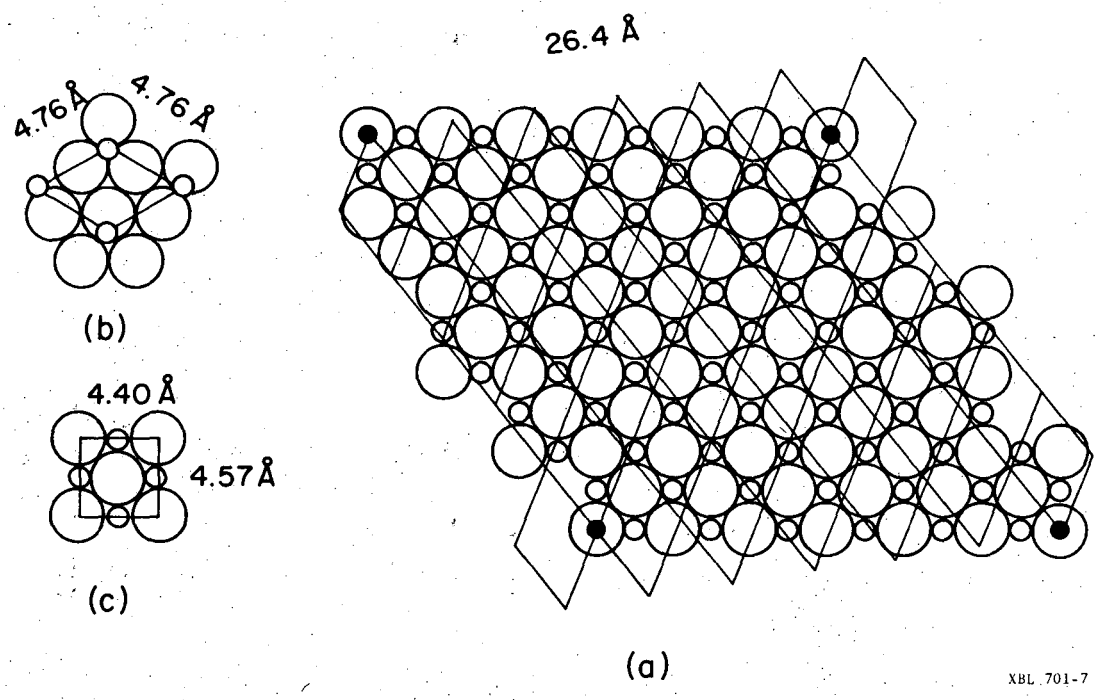
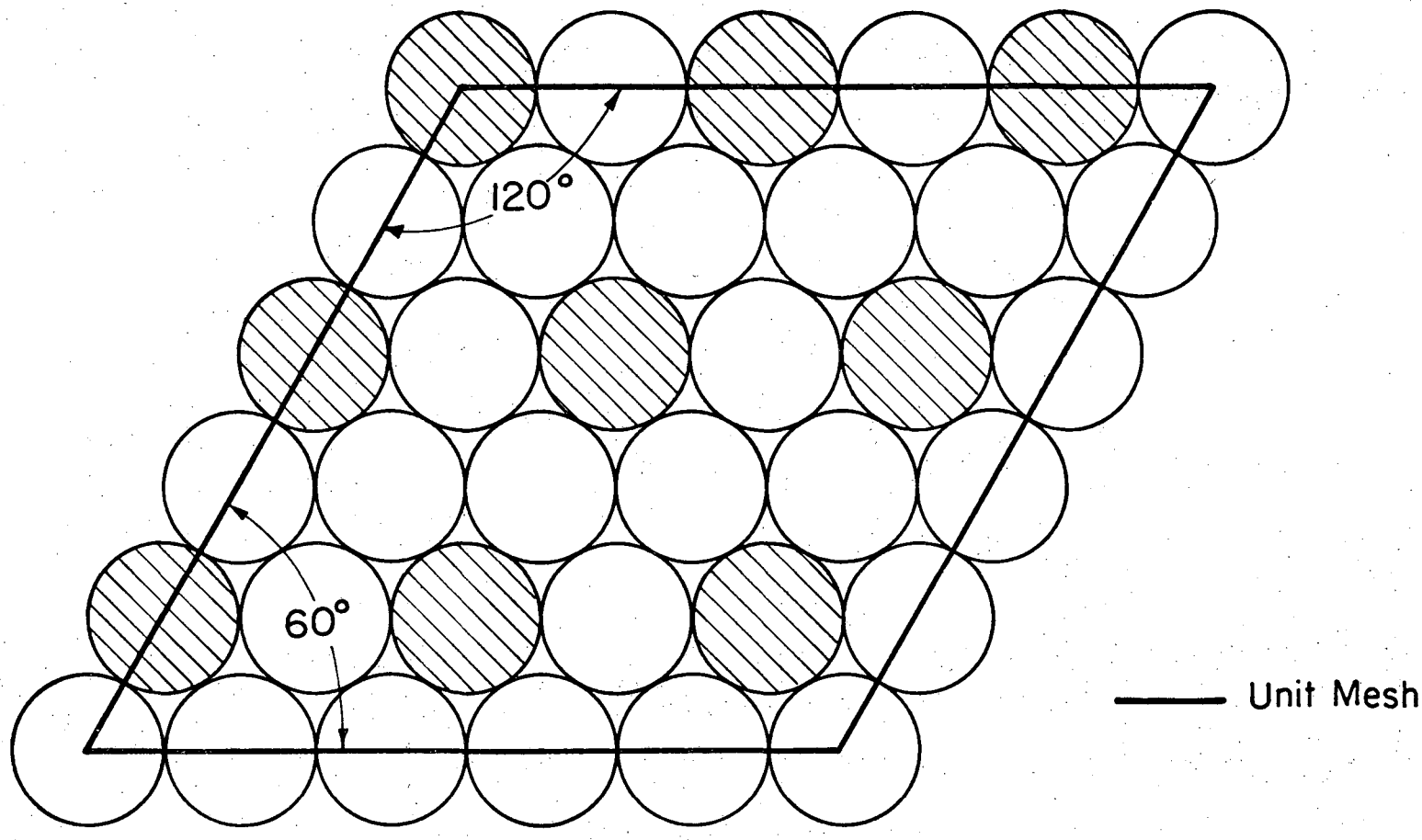


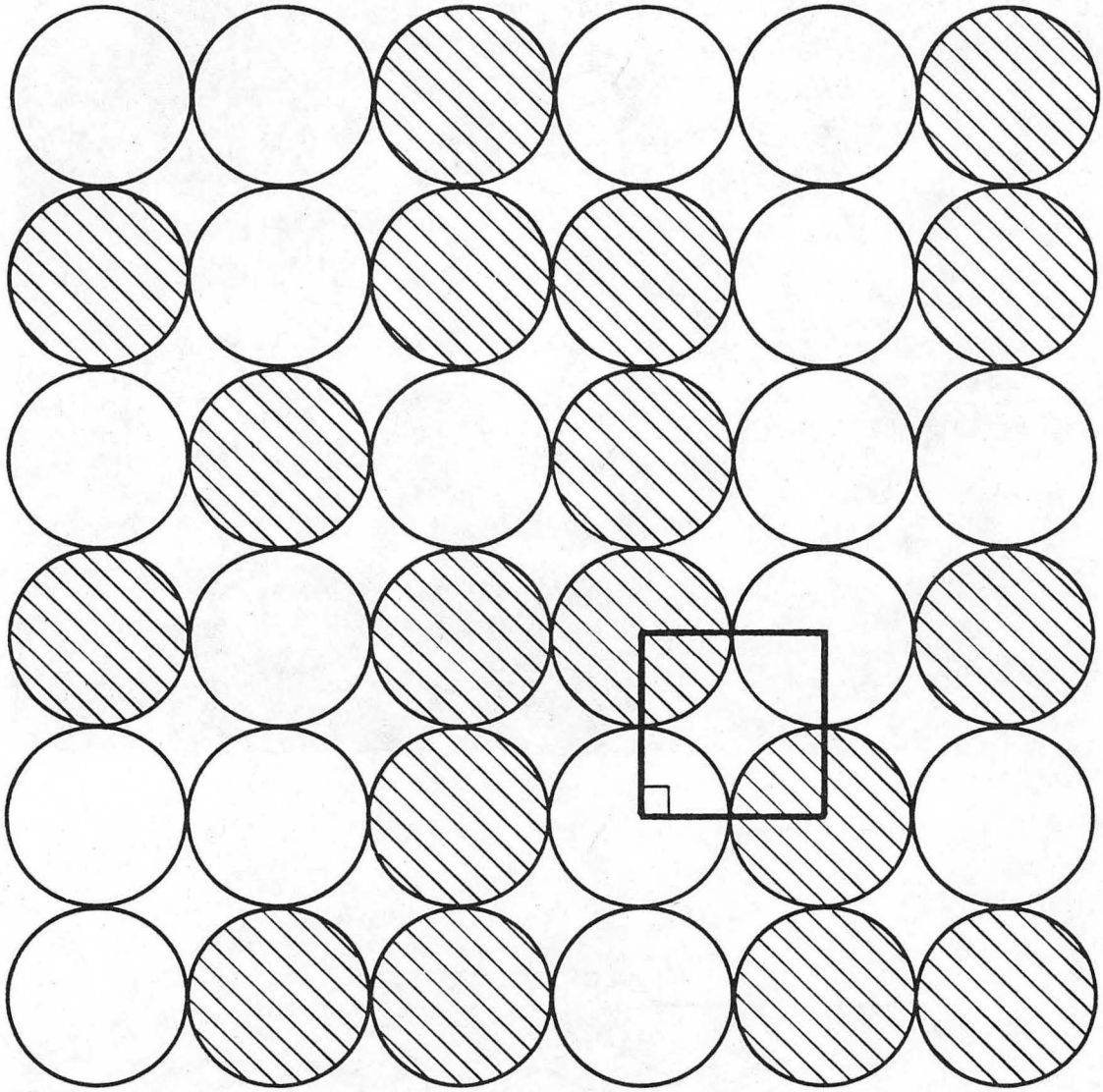
Figure 1



XBL 749-7220

Figure 2

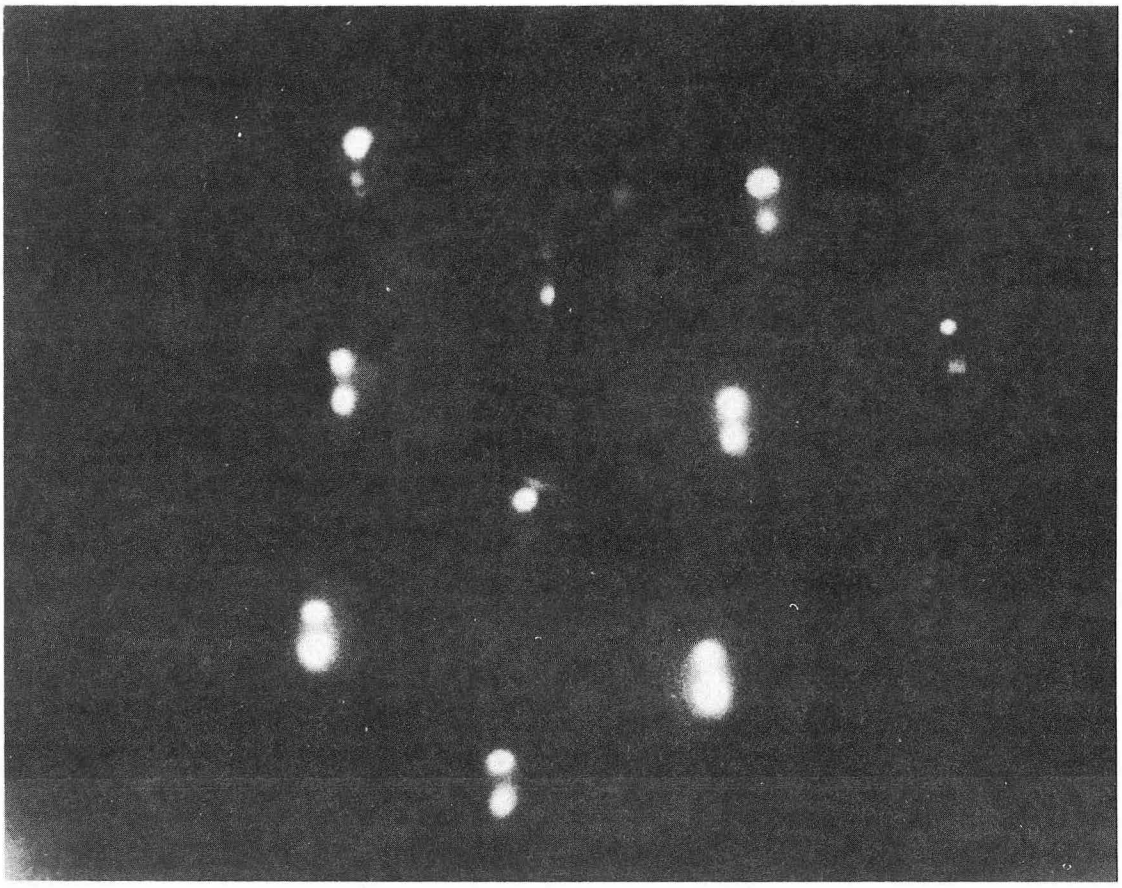
0 0 0 0 4 2 0 1 9 4 7



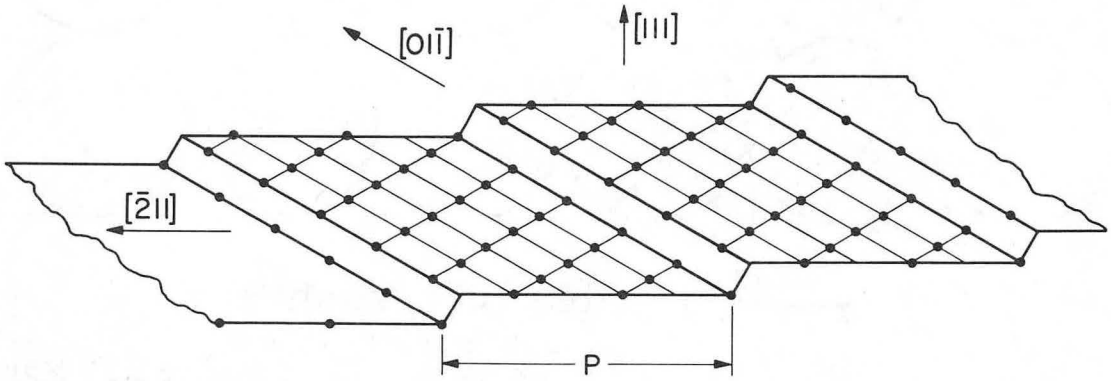
—— Effective Unit Mesh

XBL 749-7221

Figure 3



(a)



XBB 733-2083

(b)

FIGURE 4

0 0 0 0 4 2 0 1 9 4 8

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