Title
THE SURFACE STRUCTURE OF AND CATALYSIS BY PLATINUM SINGLE CRYSTAL SURFACES

Permalink
https://escholarship.org/uc/item/7m35416t

Author
Somorjai, G.A.

Publication Date
1971-12-01

Submitted to Catalysis Reviews

LBL-455
Preprint c.2

THE SURFACE STRUCTURE OF AND CATALYSIS BY PLATINUM SINGLE CRYSTAL SURFACES

G. A. Somorjai

December 1971

AEC Contract No. W-7405-eng-48

25

DISCLAIMER

The Surface Structure of and Catalysis by Platinum Single Crystal Surfaces

G. A. Somorjai

Inorganic Materials Research Division, Lawrence Berkeley Laboratory,
and Department of Chemistry; University of California
Berkeley, California 94720

Introduction

The importance of the atomic structure of solid surfaces and of adsorbed molecules in heterogeneous catalysis has been advocated by many scientists throughout the years. Early studies by Balandin,[1] for example, have suggested the presence of close-packed structures of adsorbed molecules that are intermediates in catalytic reactions. In his view both the atomic structure of the substrate metal surface and the structure of the adsorbed molecules were of primary importance in carrying out certain types of catalytic reactions. In the past, however, the difficulties of determining the atomic structure of catalyst surfaces proved to be almost insurmountable, mostly because of the configuration of the catalyst systems. In the case of metal catalysts most commercial catalyst systems consist of finely dispersed metal particles that are deposited on a high surface area support, most frequently silica or alumina. Even at present the atomic structure of such polydispersed systems cannot be ascertained unambiguously, although the application of several techniques, for example x-ray diffraction, small angle x-ray scattering, electron microscopy and the electron microprobe have helped to define many of its structural and chemical characteristics. The difficulties of unraveling the role of surface structures in surface reactions were compounded by the variable active surface area of catalyst systems that also markedly influences the rates of catalytic reactions. The effects of surface area, particle size distribution and structure had to be separated before the role of atomic surface structure in heterogeneous catalysis could be explored by definitive studies.

Many investigators have turned to evaporated thin films that are oriented in certain crystallographic directions to study the role of surface structure in catalysis. Beeck and Ritchie,[2] and most recently Anderson et al.[3] are among those who have found correlation between crystal orientation and reactivity. Even single crystals have been used in catalytic studies of different types. Gwathmey et al.[4] and others have reported marked differences in reactivity on the different crystal faces.

Careful measurements in several laboratories revealed that changes in surface area or particle size distribution had marked effects on some of the catalytic reactions, while it had no effect on others. Recently, Boudart had suggested[5] that there are classes of structure-sensitive and structure-insensitive reactions. Compilation of the experimental data indicated that many oxidation and isomerization reactions and, as we shall see, dehydrocyclization reactions as well, are structure-sensitive, while many hydrogenation, dehydrogenation and hydrogenolysis reactions are structure-insensitive. The conclusion that some catalytic reactions are sensitive to the atomic surface structure while others are not, was not the result of actual experimental studies of the correlation of the reactivity to atomic structure, but came from careful elimination of the effects of other experimental variables. Indeed, reading papers of many outstanding workers whose suggestions of various catalytic reaction mechanisms, based on intuition and deductive reasoning, have been proven correct by experiments, sometimes only decades later, is a humbling and thrilling experience.

In recent years studies, using well-defined single crystal surfaces, have obtained definitive information on the atomic structure and chemical composition of solid surfaces and adsorbed layers. One can determine the surface structure of single crystal surfaces using low-energy electron diffraction,[6] and the surface composition by Auger electron spectroscopy.[7] The surface area of the crystal under study using these techniques could be small, in the range of 0.01-1 cm^2. We have learned a great deal about the atomic surface structure of the clean surfaces, their possible rearrangement in the presence of adsorbed gases about impurities at the surface, and the structures of adsorbed gases.[8] It became apparent to us that complex catalytic reaction studies using well-defined single crystal surfaces of such small surface area are feasible utilizing techniques that are available presently and that these studies should reveal the relationship between the atomic surface structure and the catalytic activity. Combining Auger spectroscopy and low-energy electron diffraction with mass spectrometry, we have been able to monitor catalytic reactions on one face of a single crystal of area less than 1 cm^2 and examine the relationship between the structure and the composition of the surface and its reactivity. We have found that the rate of dehydrocyclization of n-heptane to form toluene on platinum crystal surface has been structure-sensitive and depends markedly on the atomic surface structure of platinum.[9]

In this review we shall concentrate on discussing the surface structure of platinum, which was the focus of attention and the subject of many of our studies during the past six years. First, the experimental techniques utilized in studies of single crystal surfaces will be briefly reviewed. Then the structure and cleaning of platinum surfaces will be discussed, along with the structure of chemisorbed gases on the various platinum surfaces. Then, the evidence for the reconstruction of platinum surfaces in the presence of adsorbed atoms of certain type will be discussed. We shall briefly review the solubility of hydrogen and carbon in platinum, as surface reactions may be catalyzed by the platinum-hydrogen and platinum-carbon systems. Finally, the dehydrocyclization of n-heptane to toluene on the various platinum crystal surfaces will be described.

Techniques to Study Catalysis by Single Crystal Surfaces: Low-Energy Electron Diffraction, Auger Electron Spectroscopy, and Mass Spectrometry

1. Low-Energy Electron Diffraction

In order to carry out low-energy electron diffraction experiments to study the atomic structure of surfaces, one needs ultra high vacuum ($\leq 10^{-8}$ torr), one face of a single crystal, and a well-focused electron beam in the energy range of 1-500 eV. In the present state of our technology, such an experiment can be carried out with relative ease. Low-energy electron diffraction (LEED) is essentially an electron back-scattering technique.[6] Low-energy electrons are produced by heating a metal or an oxide filament cathode in vacuum. The emitted electrons are drawn off by a suitable accelerating potential, then are focused electrostatically, and allowed to impinge on the surface of a single crystal. The approximate electron beam size is 1 mm^2. Figure 1 shows schematically the apparatus most frequently used in LEED studies. The crystal in most experiments is maintained at a ground potential with respect to the negative cathode. The majority of the electrons back-scattered from the crystal have lost energy in the scattering process (inelastic scattering). These electrons contain no diffraction information and have to be separated from the elastically scattered electrons which are back-diffracted by the solid surface. After allowing the scattered electrons to drift radially away from the crystal surface, the separation of the elastically and the inelastically scattered electrons is made by using a retarding potential applied to a grid that repels all electrons that have lost energy in the scattering process, thus allowing only the elastically scattered electrons to penetrate. The elastically scattered electrons, after passing through the retarding field, are post-accelerated by a large positive potential and impinge on a spherical fluorescent screen where the diffraction pattern is displayed. A typical diffraction pattern from the (111) face of platinum that is observed at different electron energies is shown in Figure 2. Ultra high vacuum, pressures below 10^{-8} torr, has to be maintained in a LEED chamber in order to assure that the single crystal surface remains clean, i.e., free of adsorbed ambient gases during the time of the experiment. Since typical surface densities are on the order of 10^{15} atoms/cm^2, the surface is covered by a monolayer of gas in about 10^2-10^3 seconds at that pressure, assuming the worst case, a sticking probability near unity for the incident gas. The relative distances of the diffraction spots in the diffraction pattern and their symmetry can be used to determine the size of the surface unit cell which characterizes the arrangement of surface atoms. However, this information alone is insufficient to determine the unique position of atoms in the unit cell, since a given diffraction pattern can be obtained from several different ordered arrangements of atoms on the surface.[6] In order to determine the exact position of atoms in the unit cell, the intensities of the diffraction spots have to be analyzed based on a model which takes into account the nature of diffraction. For low-energy diffraction, calculations to determine the unique surface structure involve consideration of the dominant scattering characteristics, multiple scattering events, the low penetration of the electron beam (few atomic layers), and the very large amount of inelastic scattering.

2. The Technique of Auger Electron Spectroscopy (AES)

The analysis of inelastically back-scattered electrons from the surface that have characteristic energy losses can provide us with qualitative and quantitative analysis of the surface chemical composition.[7] Auger electron spectroscopy analyzes the energy distribution of electrons emitted from the surface following the creation of electron vacancies in the inner shells of atoms by incident electron beams of moderate energy (1000-5000 eV). The peaks in the energy spectrum which appear at characteristic energies (independent of the incident energy) identify the various surface atoms, and from the intensity of the peaks the concentration of a given type of surface atom can be obtained. The electrons that are back-scattered from the surface can be energy-analyzed using an assembly of three or four grids and a collector plate (retarding field energy analyzer) as shown in Figure 3. In LEED experiments the collector plate is the fluorescent screen, while the grids are used to retard the inelastically scattered electrons. As the electrons pass through the grids they are modulated by an a.c. signal of known frequency and amplitude and using suitable lock-in phase-sensitive detection, one can produce the derivative of the collector current d^2I/dV^2, as a function of the variable d.c. retarding potential at the grid. These derivative signals allow one to distinguish the characteristic Auger peaks easily from the background of many other types of electron loss processes. Typical Auger spectra from a clean platinum surface and from a platinum surface that is covered with CO are shown in Figure 4.

Auger electron spectroscopy can readily be combined with low-energy electron diffraction studies and provides us with a sensitive experimental tool for surface chemical analysis. It is sensitive to the presence of surface atoms in quantities of less than 1% of a monolayer, approximately 10^{13} atoms/cm^2. The analysis is non-destructive, and unlike low-energy electron diffraction, it can be carried out in relatively poor vacuum equally well using thin polycrystalline foils, powders, or liquids. Quantitative and qualitative surface chemical analysis may be carried out directly on all elements in the periodic table except hydrogen and helium. The technique is sensitive to low atomic number for which x-ray methods such as x-ray fluorescence cannot provide detailed chemical information. The oxidation states of atoms may also be identified by the energy shift of the Auger electron distributions (chemical shift).[10] In general, Auger electron spectroscopy appears to be sensitive to the chemical environment about surface atoms.

3. The Reaction Chamber for Catalytic Studies using Single Crystal Surfaces

The scheme of the apparatus used in the low pressure catalytic studies is shown in Figure 5. The reactant gases are incident on a single crystal surface through a needle so that their contact with the platinum surface is assured before any collisions with the wall chamber could occur.[9] The stainless steel diffraction chamber which is also used as a reaction chamber in this study is coated with a thin gold film to reduce the rate of wall reactions that might compete with the surface reactions that take place on the platinum sample of much smaller surface area. A gate valve that separates the reaction chamber from the vacuum pumps (vac ion and/or sublimation pumps) permits one to carry out the chemical reactions as in a batch-type reactor or under steady-state conditions. The ambient pressures were in the range of 10^{-9} torr before the introduction of n-heptane and the ambient gases in largest abundance are CO, H_2O and H_2. The crystal sample is heated by resistance through the polycrystalline platinum holder and the temperature was monitored by a thermocouple that was spot welded to the back of the crystal sample. A quadrupole mass spectrometer is used to analyze the reactants and the products. The ionizer of the mass spectrometer is about 5 cm from the crystal surface. The sensitivity and other characteristics of the quadrupole mass spectrometer are discussed elsewhere.[11]

A Simple Nomenclature of Surface Structures

In most cases studies are carried out on low index, highest density crystal surfaces of monatomic solids. These surfaces exhibit six-fold, four-fold and two-fold rotational symmetry. In considering the structure of adsorbed molecules on surfaces of high symmetry, we can use a simple notation which has been applied widely in the literature.[6,8] If the surface structure which forms in the presence of an adsorbed gas is characterized by a unit cell which is identical to the primitive unit cell of the substrate (the underlying solid surface), the surface structure is denoted (1 x 1). This is shown in Figure 6a. The magnitude of the unit cell vector, in this case $(\sqrt{2}/2)a$, is defined in terms of the magnitude of the x-ray unit cell vector $\vec{a}$. A (2 x 2) surface structure is formed if the unit cell dimensions of the new surface structure are twice as large as the substrate unit cell (Figure 6b). The appearance of the diffraction pattern which is characteristic of this structure often indicates that the adsorbed atoms occupy every second lattice site on the substrate. If every third lattice site on a hexagonal face is distinguished from the other sites by selective adsorption, then a ($\sqrt{3} \times \sqrt{3}$)R-30° surface structure may arise (Figure 6c). The angle afterh (n x n) notation and the latter R indicate that the orientation of the new unit cell is rotated relative to the substrate unit cell. If every other lattice site on a square face is unique and occupied by an adsorbed atom, a ($\sqrt{3} \times \sqrt{3}$)R-45° surface structure could be formed (Figure 7b). The surface structures that occur most frequently on surfaces with six-fold, four-fold and two-fold rotational symmetry are depicted in Figures 6-8. Often surface structures will exist that have the dimensions of the substrate unit cell along one translation of the surface but larger dimension along the other translation direction. These structures are frequently denoted as being (1 x n) where the 1 indicates the usual bulk unit cell dimension or substrate unit cell dimension along the x direction, while the n indicates n times the substrate unit cell dimension along the y direction. When both unit cell vectors of the substrate are of the same magnitude, it is possible to have two types of domains, one set, the (1 x n), and one set of the (n x 1) kind. The diffraction pattern arising from the surface which exhibits both (1 x n) and (n x 1) domains is, in most cases, distinguishable from the diffraction pattern arising from the (n x n) surface structure. On substrates which are characterized by unit cell vectors of unequal magnitude (for example an fcc (110) surface, Figure 8a), surface structures of the (n x m) type (with $n \neq m$) are formed most frequently. If the surface structure is known to be associated with the adsorbed gas or condensate, it is customary to denote the adsorbate material in the description of the surface structure as (n x m)-S, where S is a chemical symbol or formula for the adsorbate. Perhaps one of the simplest examples of this would be a surface structure of chemisorbed oxygen on molybdenum, where the oxygen atoms or molecules on the surface of the metal have the same unit mesh as the clean metal surface. This structure would be denoted as the Mo(100)-(1 x 1)-O structure, the chemical symbol and crystallographic face of the substance being given first, then the unit mesh of the surface structure relative to that of the substrate, and finally the chemical symbol of the adsorbate is denoted.

Recent studies[12,13] indicate that the surfaces of crystals cut to expose a crystal plane of high Miller index, consist of terraces of low index planes linked by steps of often monatomic height. Since the rearrangement to ordered low index terraces seems to take place regardless of the chemical bonding in the crystal,[14,15] it may be regarded as a general structural property of high index surfaces. One such stepped surface is shown schematically in Figure 9. The standardized nomenclature to identify stepped surface structures is as follows.[12] A stepped surface is indicated by the postscript (S), so that Pt(S) indicates a stepped platinum surface. The ordered step array can then be completely designated by the width and orientation of the terraces and the height and orientation of the steps. This information can be presented as Pt(S)-[m(111) x n(100)] where m(111) designates a terrace of (111) orientation, m atomic rows in width, and n(100) indicates a step of (100) orientation and n atomic layers high. For example the stepped surface shown in Figure 9 is designated as Pt(S)-[6(111) x 1(100)].

The Structure and Cleaning of Platinum Surfaces

1. The Pt(111) Surface

LEED studies have shown[16] that this face has the surface structure expected from the bulk unit cell (see Figure 2). The surface unit cell is a rhombus of side of 2.77 Å. The Pt(111) surface is the highest atomic density, lowest free energy of platinum surfaces, and LEED studies as well as twin boundary measurements of McLean and Mykura[17] indicate that it is stable close to the platinum melting point.

2. The Pt(100) Surface

Projection from the bulk unit cell suggests that this face should have a square unit cell of side 2.77 Å. However, early studies by Lyon and Somorjai[18] suggested that this was not so and that the actual unit cell was a rectangle of approximate size (5 x 1) with respect to that predicted (Figure 10a). Similar anomalous surface structures were reported for the (100) surfaces of gold[19] and iridium.[20] These metals are neighbors of platinum and also possess fcc bulk structure. Since these studies predated the wide application of Auger electron spectroscopy for analyzing the surface composition, it was inevitable that the cleanliness of the anomalous structures be called into question.[21] A great deal of investigation has been carried out to understand the nature of this surface phase transformation. Palmberg and Rhodin[22] examined the epitaxial growth of gold on a (100) silver crystal. After deposition of three monolayers of gold, the LEED pattern assumed the (5 x 1) structure. Palmberg[23] subsequently used Auger electron spectroscopy to demonstrate the cleanliness of the Pt(100)-(5 x 1) surface. Similar evidence has been obtained in our laboratory. Grant and Haas[24] suggested that the (5 x 1) surface structure is stabilized by oxygen and that the Pt(100)-(1 x 1) surface structure is representative of the clean surface. Their arguments are not in agreement with the AES observation which indicates that the (1 x 1) diffraction pattern is associated with the presence of carbon, while the Auger spectrum from the (5 x 1) surface structure does not indicate the presence of any impurity, including oxygen. The adsorption of CO and hydrocarbons causes rapid disappearance of the (5 x 1) surface structure, changing the diffraction to a Pt(100)(1 x 1).[25] The (5 x 1) structure that is shown in Figure 10a may be regenerated by the desorption of gases if no carbon is deposited in the desorption process. It is clear that the surface structure is atomically clean. The interpretation of the structure is, however, a more complex question. Fedak and Gjostein[21] analyzed the diffraction pattern as being due to a hexagonal overlayer forming a (5 x 20) coincidence lattice with the underlying square unit mesh. This structure is shown schematically in Figure 10b. Palmberg[23] indicates that the coincidence unit cell is not rectangular but is a parallelogram with dimensions close to those suggested by Fedak and Gjostein. It is possible to divide the hexagonal overlayer within the coincidence cell outlined by Palmberg so that the analysis of Fedak and Gjostein does not have to be changed. Rhodin, Palmberg and Plummer[26] have argued convincingly that the rearrangement of gold and platinum may be explained in terms of enhanced surface valency. A phase transformation of the Pt(100) surface is therefore considered to occur along with the

(100) surface of its neighbors, iridium and gold, in which the surface atoms adopt a hexagonal unit mesh resulting in small out-of-plane displacement (buckling) of the atoms in the outermost layer. The reason for the rearrangement is likely to be a reduced free electron density at the surface and a reduction in the surface free energy by an increase in close packing.[27]

Several other metals and most semiconductor or insulating surfaces exhibit rearranged surface structures that are characterized by unit cells that are integral multiples of the unit cell dimensions in the bulk. These surface structures are described in detail elsewhere.[6,28] In general, studies of the structures of clean metal and non-metal surfaces indicate that the stable surface may be characterized by one of several possible ordered surface structures. The various surface structures must have only slightly different free energies of formation. Thus, as a function of temperature or due to changes in the surface chemical environment, one surface structure may become more stable than another one. Surface structural rearrangement must play an important role in several surface phenomena, oxidation, chemisorption, and catalysis.

3. The Platinum (110) Surface

A recent study by Bonzel[29] indicates that the Pt(100) crystal face is thermodynamically stable. It exhibits a (1 x 2) surface structure that has chemical properties similar to the Pt(100)-(5 x 1) surface. Although Bonzel has not been able to ascertain that this surface is completely clean, the surface structure of this rearranged platinum surface was reproducible in all conditions of the experiment and has been used to carry out studies of the catalytic oxidation of carbon monoxide. The same surface structure was found on the (110) face of gold.[21] In the absence of the Auger technique this gold surface structure was not studied in detail. The remarkable stability of the (110)(1 x 2) surface structure indicates that it is most likely characteristic of the clean Pt(110) surface.

4. The Structure of Stepped Surfaces

When a platinum crystal is cut to expose a high index plane (by cutting a low index crystal face at a small angle, 5-15° to the crystal plane) a doubling of the diffraction spots and the appearance of new diffraction features is often observed.[12] Analysis of the diffraction features of crystals cut along the high index planes indicate that the structure of these surfaces consist of terraces of low index planes linked by steps often of monatomic height (see Figure 9). Low-energy electron diffraction investigations of platinum,[12] copper,[13] germanium,[14] gallium arsenide[15] and UO_2[30] showed ordered step arrays with terraces of constant width and steps of constant height. The ordered stepped surfaces can display varying degrees of thermal stability. Stepped surfaces of metals, particularly Pt and Cu, exhibited remarkable thermal stability. A diffraction pattern of such a stepped surface of platinum and a schematic diagram of this stepped surface structure are shown in Figures 10a and 11b. Since ordered steps have been noted on other metals and semiconductors, the stepped surfaces must be a general property of high index surfaces of all types of crystalline material. The thermodynamic stability of these surfaces with respect to that of the lowest free energy low index surfaces have also been examined.[12] The stepped surfaces may not be thermodynamically stable with respect to the (111) and (100) surfaces of platinum. The remarkable thermal stability, however, which has been observed, is likely to be due to the difficult route which the crystal must take to develop an equilibrium shape. There are only two ways in which the ordered surface can transform into a low free energy (111) or (100) face: by thermal faceting or by rearrangement by surface diffusion. Both of these rearrangements require considerable activation energy and there does not seem to be any energetically feasible route by which an array of ordered steps may rearrange to a thermodynamically more favorable structure. A detailed analysis and calculations indicate that even under conditions of appreciable surface diffusion the array of constant step height and terrace width is time-independent and must be stable under conditions of surface diffusion.

5. Cleaning of Platinum Surfaces[16]

A metal surface has a number of possible sources of contamination. The metal may possess a layer of impurities resulting from pretreatment before the experimental study. This layer, in the case of platinum, is always carbonaceous and is easy to remove. Other sources of contamination may come from the ambient atmosphere or by diffusion of impurities from the bulk of the platinum to the surface. Significant non-metallic impurities in platinum are oxygen, silicon, chlorine, sulfur and carbon.[16] Oxygen does not easily adsorb at low index platinum surfaces[25] but readily chemisorbs on stepped surfaces.[31] Platinum oxides are thermodynamically unstable at high temperatures[32] and oxygen diffusing to the surface is likely to undergo instantaneous desorption. Palmberg[23] has reported reversible segregation of silicon at platinum surfaces. However, silicon may be removed irreversibly by heating the sample in oxygen. Little is known about the chlorine impurity in platinum. In the platinum samples that were studied in our laboratory chlorine has not been present. Sulfur that is a remarkably efficient poison of catalytic activity in platinum surfaces also has not been encountered in our studies. However, the effect of sulfur and the likely mechanism of platinum catalyst poisoning by sulfur will be discussed below. The remaining intrinsic impurity is carbon, and since it is the major impurity in platinum, it will occupy a greater part of our attention. Carbon diffuses readily onto a clean platinum surface from the bulk at around 1000°C or at even lower temperatures, and can be easily detected by AES by its Auger peak at 276 v. Of the three principal techniques for generating clean ordered surfaces that are currently in use,[16] ion bombardment, chemical cleaning, and vaporization, chemical cleaning is the most effective way of removing carbon from platinum surfaces. The removal of carbon from the freshly prepared crystal can take place by heating the sample in oxygen at 1000°C for six hours at a pressure of 5×10^{-6} torr of oxygen.[16] After this treatment a LEED pattern that indicates the presence of a clean platinum surface and an Auger spectrum characteristic of a clean platinum surface are obtained. Although the carbon removal is not as rapid, heating platinum crystals at 400°C in 5×10^{-7} torr of oxygen will also remove carbon from the surfaces after 3-4 hours of such treatment. Polycrystalline or randomly oriented single crystal platinum should be cleaned by the same method since the effectiveness of oxygen treatment for removing carbon has been well studied not only on low index but also on stepped crystal surfaces of platinum.[16,31]

Turning now to other impurities which may adsorb at the surface from the ambient, we consider four major species, carbon monoxide, oxygen, hydrogen, and hydrocarbons. CO is well known as a major constituent of the ambient in an ultra high vacuum system and is known to adsorb readily on platinum surfaces. Carbon monoxide also forms ordered surface structures of many types on platinum crystal faces.[33] Recent work in this laboratory indicates that CO, although it forms ordered structures on low index surfaces, does not form ordered structures on stepped platinum surfaces with (111) terraces. There is also evidence that CO adsorbed at these steps dissociates into carbon and oxygen, the carbon not being desorbed.[31] The chemisorption characteristics of various stepped platinum surfaces are markedly different from those of low index platinum surfaces and they are also different from each other. There appears to be a much stronger interaction of chemisorbed gases with stepped surfaces than with low index planes that must be caused by the differing nature of the atomic structure at the steps.

Heating stepped platinum surfaces in oxygen yields new surface structures as well as the formation of platinum dioxide at higher temperatures (800°C).[31] The oxide structure is readily removable by heating platinum in hydrogen. Oxygen adsorbs only weakly on low index crystal faces of platinum and there is no indication of the formation of ordered surface structures. Oxygen readily desorbs from these crystal faces upon heating in hydrogen or in vacuum.[25]

Hydrogen adsorbs very poorly on low-index platinum crystal faces[25] although room temperature adsorption is observed readily on stepped platinum surfaces.[31] Hydrogen adsorption gives rise to the appearance of new diffraction patterns that indicate the formation of new surface structures with a (2 x 2) unit cell on the (100) crystal face and a (2 x 2) diffraction pattern on the (111) surface. The adsorption of hydrogen on the Pt(100) surfaces has been examined at temperatures up to 1000°C and hydrogen pressures up to 10^{-7} torr. No change of the (5 x 1) diffraction pattern was observed. Increasing the hydrogen pressure to 2×10^{-5} torr resulted in the removal of the (5 x 1) pattern and the appearance of a (2 x 2) unit cell.[34] This structure can be removed in vacuum only by heating to 1200°C, a convincing evidence that this structure was due to the presence of hydrogen at the platinum surface and not to impurities. The (2 x 2) diffraction pattern could be removed by heating the crystal in 2×10^{-8} torr oxygen at 500°C. The hydrogen-induced diffraction pattern on platinum surfaces may be interpreted in various ways. New, atomic scattering cross section data indicate[35] that backscattering of low-energy electrons from hydrogen atoms is about two orders of magnitude weaker than that to be expected from metal atoms, so that adsorbed hydrogen at the surface is not likely to give rise to the high intensity new diffraction pattern. It is more likely that the platinum surface atoms rearrange by periodic out-of-plane buckling in the presence of hydrogen, although at present it is not possible to make a clear distinction between strong forward scattering of the electron beams emerging from the crystal by the adsorbed hydrogen and a possible rearrangement of the metal atoms in the surface in the presence of hydrogen.[16]

The interaction of hydrogen with stepped platinum surfaces has also been studied. At 300°K hydrogen adsorption may occur along the monatomic steps that yield new surface structures which are stable to heat treatment in vacuum and to mild oxygen treatment. The controlling step in the formation of a new surface structure in the presence of hydrogen or in the dissolution of hydrogen in the platinum lattice appears to be the atomization of the hydrogen molecules. Dissociation may take place readily at the atomic step and subsequent diffusion into the bulk is likely to be rapid at most temperatures of catalytic interest.[31]

The Structure of Chemisorbed Gases on Platinum Surfaces

In the past several years the surface structures of many gases on platinum single crystal surfaces have been studied in detail. The chemisorption of hydrocarbons and carbon monoxide has been studied.[25,33] The surface structures that have been found upon chemisorption at 25°C are listed in Table I. A (2 x 2) surface structure was produced on the (111) face by all of the unsaturated hydrocarbons studied, with the exception of iso-butylene, which exhibited a larger unit mesh. Ethylene and acetylene produced a $(\sqrt{2} \times \sqrt{2})R\text{-}45°$ surface structure on the (100) face of platinum, while the adsorption of other hydrocarbons was disordered. The necessity of close-packing of the olefins appears to be responsible for the presence of ordered structures on the Pt(111) surface and for their absence on Pt(100). The chemisorption of CO resulted in the appearance of several ordered surface structures. Three flash desorption peaks of CO were apparent on the (100) face of platinum, while only one was detected on the (111) face. More recently, the structures of aromatic hydrocarbons have also been studied on platinum surfaces.[36] Naphthalene forms an ordered surface structure, (3 x 3), on the platinum surface, and this surface structure is consistent with a flat close-packed arrangement of naphthalene molecules on the (111) surface. Other molecules, benzene, aniline, etc., do not seem to form ordered structures at 300°K, while pyridine forms a one-dimensional surface structure. The results of low-energy electron diffraction studies of the chemisorption of aromatic molecules on platinum surfaces will be reported in detail elsewhere.[36]

Low-energy electron diffraction studies have shown that chemisorption predominantly yields ordered structures on single crystal surfaces of various types.[8] The surface structure that forms depends to a great extent on the symmetry of the substrate, the chemistry, the size of the adsorbed gas molecules, and in some cases, the surface concentration of the adsorbate which may be controlled by the gas partial pressure over the surface. The accumulated experimental data indicate several trends that are operative in the formation of surface structures of adsorbed gases on high density crystal planes. It is possible to propose a set of rules of ordering[8] that appear to govern the formation of ordered surface structures. Judicious application of these rules to other substrate-adsorbate systems that have not been studied allows one to predict the surface structures that should form. These rules, although empirical, are formulated from the correlation of existing surface structural data and are based on strong physical-chemical foundation. It appears that chemisorption leads to the formation of surface structures that exhibit maximum adsorbate-adsorbate and adsorbate-substrate interactions. These rules are discussed in detail elsewhere.[8,37] The rule of close packing indicates that adsorbed atoms of molecules tend to form surface structures characterized by the smallest unit cell permitted by the molecular dimensions and adsorbate-adsorbate and adsorbate-substrate interactions.[8,37] The molecules adsorbed on the surface that form ordered surface structures, prefer close-packing arrangements. The rule of rotational symmetry says that the adsorbed atoms or molecules are likely to form ordered structures that have the same rotational symmetry as the substrate, and the rule of similar unit cell vectors indicates that adsorbed atoms or molecules in monolayer thickness tend to form ordered surface structures characterized by unit cell vectors closely related to the substrate unit cell vectors. Thus, the surface structure bears a greater similarity to the substrate structure than to the structure of the bulk condensate. This rule is of little interest where chemisorption terminates at monolayer coverage; it may be very important, however, at multilayer coverage or under conditions of epitaxial growth of films on various substrates.

Low-energy electron diffraction studies have also uncovered surface structures that would form during the simultaneous adsorption or co-adsorption of two gases,[6] but would not form during the adsorption of one or the other of the gas components. The formation of these mixed surface structures seems to be a general property of adsorbed gas layers on many surfaces. For example, hydrogen and carbon monoxide form such a co-adsorbed structure on the (100) surface of platinum.[25] The appearance of such surface structures indicates that there is strong attractive interaction within the adsorbed layers between the unlike molecules which arrange themselves in a mixed structure where both molecules appear to be part of the surface unit cell.[8] These surface structures appear most frequently when both gases that are being adsorbed have approximately equal probability of accommodation. If one gas adsorbs more strongly than the other, one finds that the more tenacious species will replace and displace the other species adsorbed on the surface. In this case the co-adsorbed structures are unlikely to form.

The chemisorption and the formation of ordered structures on stepped surfaces are markedly different from those of low-index platinum surfaces. Hydrogen and oxygen which do not chemisorb easily on the (111) and (100) crystal faces, chemisorb readily and at relatively low temperatures (300°K) and pressures on the stepped platinum surfaces. In contrast to the ordered adsorption of carbon monoxide and ethylene on low index platinum surfaces, the adsorption of CO was disordered on the stepped surfaces and there is evidence for the dissociation of the molecule. Carbon forms several ordered surface structures and caused faceting on the stepped platinum surface, which are not observed on low index platinum surfaces.[31] There appears to be a much stronger interaction of chemisorbed gases on stepped surfaces than with low index planes that must be caused by the differing atomic structures at the steps. There is evidence for differing reactivities of the various stepped surfaces depending on the step geometry.

Reconstruction of Platinum Surfaces in the Presence of Adsorbed Atoms

It has been reported from several studies that a strongly exothermic surface reaction such as chemisorption of oxygen on nickel or on other metal surfaces can dislodge the substrate atoms from their equilibrium positions and cause rearrangements of the surface structure.[6] This is commonly called surface reconstruction. The reconstructed surface structures could best be interpreted as composed of both metal and chemisorbed atoms in periodic arrays. In other cases the reconstructed surface structures were more likely a new surface structure composed solely of the metal atoms that had formed in the presence of the impurity. The adsorbed impurity had the effect of lowering the surface free energy and apparently had stabilized a new surface structure different from that characteristic of the clean solid surface. Although changes in the diffraction pattern during chemisorption can be analyzed in several different ways, complementary experimental evidence seems to indicate that reconstruction is the most likely interpretation of the structural changes observed during the oxidation of many metal surfaces. There is evidence that other gases when adsorbed on the surface can also cause changes of the atomic structure of the solid surface. For example, hydrogen adsorption on platinum causes the appearance of new diffraction features that can be interpreted assuming a reconstruction of the platinum surface structure.[31]

Reconstruction of the surface may be looked upon in some cases as a precursor for oxidation reactions or other chemical reactions which proceed from the surface into the bulk. Hydrogen diffusion can also be initiated from such a reconstructed surface. Since reconstruction displaces or rearranges metal atoms at the surface, these structures may be stable to much higher temperatures than two-dimensional surface structures which are solely due to adsorbed gases. Although reconstructed surfaces may persist to higher temperatures than those due to adsorbed gases only on top of the surface, they can also be removed by well-chosen surface chemical reactions. Oxide structures or structures induced by oxygen chemisorption could be removed by heating in hydrogen. Ion bombardment, high temperature heat treatment in vacuum which causes the vaporization of the topmost atomic layer can also be used to restore the surface to its original unreconstructed state.

There is increasing evidence that in the presence of impurity atoms that are adsorbed on surfaces the surface free energies of the different crystal faces can be changed in such a way that a crystal face which in its clean state had a higher surface free energy and therefore was less stable, may become more stable in the presence of impurities. For example, in the presence of sulfur on the surface, the chromium (100) crystal face appears to be more stable than the highest density, lower surface free energy (110) face of chromium.[38] Similarly, sulfur that was present in small concentrations on platinum surfaces caused recrystallization of platinum[39] to a structure which consisted of predominantly (100) crystal faces, even though in the clean state the Pt(111) crystal face was the one with the lowest surface free energy. Thus it appears that changes of surface free energy caused by the adsorption of impurity atoms can stabilize surface structures that would have higher surface free energies in the absence of these foreign atoms and therefore would not necessarily be thermodynamically stable. Surface reconstruction processes which have been discovered by LEED studies provide a new insight into the mechanism of chemisorption, recrystallization and other surface chemical reactions.

It is most likely that the poisoning of polydispersed platinum catalysts by sulfur is due to the recrystallization of the small platinum particles induced by the presence of a minute amount of sulfur. Once the sulfur is removed it takes a long time before the original surface structure of the platinum surface can be, if at all, reestablished.

Stepped crystal faces have also shown signs of reconstruction in the presence of adsorbed impurities.[31] For example, in the presence of carbon a stepped platinum crystal face rearranges into atomic terraces of different widths and the height of the steps are multiplied with respect to the original stepped surface. The crystal surface could be restored to its original structure by eliminating the carbon from the surface. In the presence of carbon, faceting to form new crystal surfaces of platinum, has also been detected. The adsorption of oxygen has disordered the atomic steps at the surface and has also changed the step height. After removal of oxygen from the stepped platinum surfaces the initial clean platinum surface that exhibits steps of monatomic height could be restored.

If the platinum surface structure is reconstructed in the presence of adsorbed gases or impurities such as H_2 and C, catalysis is carried out not by the clean platinum surface, but by the reconstructed platinum surface which is stable in the presence of these adsorbed gases or impurities. Thus one should consider catalysis not only by the clean platinum surface but by the platinum-hydrogen system or by the platinum-carbon system. In order to complete the description of such a system, the solubilities and diffusion rates of hydrogen and carbon in platinum will be briefly discussed below.

It should be noted that the surface composition, just like the surface structure, does not remain the same during chemisorption. Sachtler et al.[40] have reported changes in surface composition for platinum-gold and silver-palladium alloys upon the adsorption of carbon monoxide. The platinum or the palladium concentration at the surface increases in the presence of CO. On desorption of CO the palladium excess at the surface diffuses back into the bulk. Thus adsorption can change the surface free energy and therefore change the surface composition in binary systems or in general in multicomponent systems.

The Solubilities of Hydrogen and Carbon in Platinum

The solubility and diffusion of hydrogen in (100) platinum disks has been examined.[4] The diffusion coefficient is given by $D = 6 \times 10^{-3} \exp[-5.9 \text{ kcal}/RT] \text{ cm}^2/\text{sec}$, and the solubility at one atm pressure is calculated as $S = 1.2 \times 10^{-3} \exp[-11 \text{ kcal}/RT]$ g-atom H/ g-atom Pt. To calculate the solubilities at lower hydrogen pressures, the pressure dependence of the hydrogen solubility also has to be taken into account. Since the solubility increases with increasing temperature, dissolved hydrogen diffuses to the surface and can accumulate there once the temperature has fallen in the range where the desorption rate is slow. A random walk argument would predict a mean diffusion distance of 0.6 mm within 300 sec at 200°C. Since the crystal in our studies is about 1 mm thick, all the hydrogen contained in the bulk could reach the surface. The solubility at 1 atm is about 1 hydrogen atom in 10^{11} platinum atoms at 25°C, and 3 hydrogen atoms for about every 10^6 platinum atoms at

650°C, which would supply several monolayers of hydrogen to the surface of our crystal at this high temperature. Although the permeation method that determines these values gives average values of bulk solubility, it will not detect local variations such as may exist close to the surface of the metal. The LEED studies suggest that crystals exposing stepped surfaces have a higher solubility for hydrogen, at least near the surface, than that reported by Ebisuzaki et al.[41] for a platinum crystal with a (100) surface plane. Hydrogen forms ordered surface structures on both the (100) and (111) faces of platinum, but only at elevated temperature (about 1000°C) and higher hydrogen pressures ($>10^{-5}$ torr). On the other hand, hydrogen forms ordered one-dimensional surface structures and causes reconstruction of the platinum surface at room temperature or at slightly elevated temperatures (200-300°C).[31] It appears that in dehydrocyclization reactions where the presence of hydrogen is necessary to carry out the chemical reactions with high efficiency, the catalytic reactions take place on such reconstructed surfaces that appear in the presence of hydrogen.

The solubility of carbon in platinum has also been studied.[42] The solubility is about 2.0 atomic % carbon at 1245°C. Another group[43] claims much lower carbon solubility and also note rapid rates of diffusion of carbon in platinum. The heat of solution of carbon in platinum was reported to be 8.3 kcal/mole. Carbon forms ring-like diffraction patterns on the low index platinum surfaces that could be indexed as due to the basal plane of graphitic carbon that is parallel to the platinum crystal planes. This carbon can be readily removed by heating the platinum surfaces in oxygen under conditions that were described above. On various stepped crystal faces of platinum carbon forms several ordered surface structures that are not observed on the low index crystal faces of platinum.[31] On heating these carbon deposits that formed due to coking of adsorbed hydrocarbons on stepped platinum surfaces form the graphitic overlayer that seems to be the most stable carbon surface structure on platinum surfaces. In addition, carbon induces faceting at the surface. All of the new surface structures due to carbon can be removed from the stepped surfaces of platinum by heating the crystal in oxygen. Heat treatment using about 1 x 10^{-6} torr oxygen at 800°C for 10 minutes is usually adequate to remove the carbon from platinum surfaces.[16]

The Dehydrocyclization of n-Heptane on Platinum Crystal Surfaces[9]

n-Heptane exhibits the well-known fragmentation pattern upon electron impact ionization in a quadrupole mass spectrometer that is published in the AIP tables. Toluene, that is a product of the dehydrocyclization of n-heptane, can be easily recognized in the mass spectrometer, by the appearance of the (m/e) = 91 and 92 peaks that have the known intensity ratio, since at these masses there are no peaks due to the fragmentation of n-heptane. The mass peaks that could be attributed to n-heptane and toluene are shown in Figures 12a and 12b. The surface reaction of n-heptane on platinum yields several other products (methylcyclopentane and n-heptane isomers) and the appearance of some of these is apparent from the mass spectra. We shall concentrate on the appearance of toluene, however, which is the only surface reaction of interest in this study.

n-Heptane and n-heptane-hydrogen mixtures were used in studying the dehydrocyclization on platinum single crystal surfaces. In the mixtures the ratio of n-heptane to hydrogen was varied from 1:1 to 1:5, while the total reactant pressures were maintained in the range 10^{-4} -10^{-3} torr.

a) n-Heptane dehydrocyclization on the Pt(111) and Pt(100) crystal faces.

When n-heptane was adsorbed at 300°K on the (111) face of platinum, a (2 x 2) surface structure formed. Such a diffraction pattern indicates the presence of an ordered surface structure that is characterized by unit cell vectors that are two times that of the platinum unit cell vectors (2 x 2.77 Å) and parallelwith them. The n-heptane molecules would be much longer if adsorbed as a straight chain and would not fit into a periodic structure that is characterized by such a unit cell. It appears that the (2 x 2) surface structure is due to the appearance of atomic hydrogen on the surface as a result of the partial dehydrogenation of the n-heptane at the (111) surface. Upon adsorption of n-heptane on the Pt(111) crystal face at 300°K, the sample was heated to 600°K. The 91 and 92 peaks that are characteristic of the appearance of toluene could be detected in the quadrupole mass spectrometer in about 10 minutes. The peak intensities increased for about 10 minutes, then remained unchanged until beginning to decrease after about 60 minutes. When the vacuum chamber was evacuated, the Auger electron spectrum indicated the presence of carbon deposits on the Pt(111) surface. It is apparent that the slow reduction of the toluene yield as a function of time is due to the build-up of the carbon deposit on the Pt(111) surface.

An interesting "template" effect that indicates the formation of surface intermediates that may be necessary for the dehydrocyclization of n-heptane was detected first during the dehydrocyclization studies on the (111) crystal face. It was found that the preadsorption of n-heptane on the (111) crystal face at 300-400°K was necessary for the subsequent production of toluene at 600°K. When the (111) crystal face was heated in vacuum to 600°K and the n-heptane was introduced when the crystal was already hot, the formation of toluene could not be detected within the usual or even longer reaction times. There was also no indication of enhanced coking of the Pt(111) surface under these conditions. Using the various platinum crystal surfaces in every case the pre-adsorption of n-heptane at 300°K was a necessary condition for the production of toluene at 600°K.

Adsorption of n-heptane on the Pt(100) surface caused the immediate disappearance of the (5 x 1) surface structure that is characteristic of the clean platinum surface. However, the formation of toluene has not been observed on this crystal face under various conditions of the experiments. It appears that this surface does not detectably catalyze the dehydrocyclization of n-heptane to toluene. The reaction was studied both with pure n-heptane and in the presence of different n-heptane-hydrogen mixtures. There was no indication of the formation of toluene under the conditions of these experiments which were identical to those employed using the other ((111) and stepped) platinum crystal faces.

b) Dehydrocyclization of n-heptane on various stepped surfaces of platinum.[9]

Adsorption of n-heptane on any of the stepped surfaces in the absence of hydrogen at 300°K did not lead to the formation of ordered surface structures that could be detected by LEED. When the stepped surfaces were heated to 600°K, after the adsorption of n-heptane at 300°K, in n-heptane in the pressure range of 10^{-4}-10^{-3} torr, the formation of toluene could not be detected. Instead, the surfaces became coated rapidly with a heavy carbon deposit (2-3 minutes) that could be readily monitored by AES. It appears that the rates of dissociation and dehydrogenation of n-heptane that yield a carbon deposit is much too rapid when compared to the rates of dehydrocyclization of n-heptane on these surfaces.

However, the dehydrocyclization of n-heptane readily takes place on stepped surfaces that exhibit (111) orientation terraces in the presence of hydrogen using the same, 1:1 to 1:5 gas mixtures. Upon exposure of the stepped (111) surfaces to the n-heptane-hydrogen mixture at 300°K, heating to 600°K resulted in the production of toluene within 1-3 minutes. When the stepped surface was pretreated in hydrogen at 900°K at 10^{-5} torr H_2, that is readily chemisorbed in the stepped surface and gives rise to a characteristic new diffraction pattern, adsorption of n-heptane at 300°K and subsequent heating of the sample to 600°K have produced toluene as well. It is apparent that chemisorbed hydrogen retards the reactions that lead to the coking of n-heptane on the stepped surface, thus allowing the slower dehydrocyclization reaction to take place.

After about 15 minutes of continuous reaction at 600°K a $(\sqrt{3} \times \sqrt{3})R\text{-}30°$ surface structure appeared on the stepped (111) surface. This structure did not appear to influence the dehydrocyclization noticeable. The thermal stability of this structure indicates that it is likely to be associated with the presence of ordered carbon on the surface that is very different from the graphite overlayer that forms readily on the low index surfaces of platinum. The same surface structure is detectable during the co-adsorption of H_2 + CO on the same surface. However the co-adsorbed surface structure can readily be removed by heating to 600°K while the structure that forms during the dehydrocyclization of n-heptane in an n-heptane-hydrogen mixture is stable to much higher temperatures (1000°K).

The same "template" effect was found in studied of n-heptane dehydrocyclization on stepped (111) surfaces as on low index crystal faces of platinum. The preadsorption of the n-heptane-hydrogen mixture at 300°K was necessary to produce toluene at 600°K. Exposure of the clean stepped (111) surface to the n-heptane-gas mixture at 600°K did not yield toluene.

The stepped surfaces that exhibit (111) orientation terraces have been found to be the most efficient in producing toluene in the presence of hydrogen. When a stepped surface that exhibits atomic terraces of (100) orientation was inserted into the reaction chamber to study the dehydrocyclization of n-heptane, the formation of toluene could not be detected. Regardless of the partial pressure of hydrogen that was used in the reactant mixture the formation of toluene could not be detected in the presence of stepped surfaces with (100) terraces. It appears that the dehydrocyclization of n-heptane is extremely sensitive to the platinum surface structure; while the reaction is taking place efficiently in the presence of hydrogen on the stepped or low index (111) crystal surfaces of platinum, it does not take place on either the stepped or low index (100) crystal faces of platinum.

Studies of the dehydrocyclization of n-heptane on various low index and stepped surfaces of platinum that are in progress indicate that this catalytic reaction is very sensitive to the atomic structure of the platinum surface. There is a strong correlation between the atomic structure of the surface and the reactivity of that surface in the dehydrocyclization surface reaction. The reaction proceeds slowly on the Pt(111) crystal face, but it takes place even in the absence of hydrogen. The dehydrocyclization reaction does not take place either on the (100) surface of platinum or on stepped crystal faces with atomic terraces of (100) orientation. There must be orders of magnitude differences in the rates of dehydrocyclization on these two different crystal orientation at 600°K according to the experimental observations. On platinum surfaces that exhibit a characteristic stepped surface structure with atomic terraces of (111) orientation, the rate of dissociative chemisorption that yields carbon deposits must be orders of magnitude faster than the rate of dehydrocyclization. Thus in the absence of hydrogen the dehydrocyclization of n-heptane to toluene cannot take place. The presence of chemisorbed hydrogen has the effect of reducing the rate of coking on all surfaces so that the dehydrocyclization reaction can now more successfully compete with it. This effect is particularly dramatic for stepped (111) surfaces where dehydrocyclization occurs only in the presence of hydrogen. This is a clear demonstration of the role of hydrogen that is commonly used during dehydrocyclization on polydispersed platinum catalysts. On stepped surfaces that have atomic terraces of (100) orientation, however, dehydrocyclization does not take place at a detectable rate under similar conditions.

These investigations also give evidence that the pre-adsorption of the reactant induces the formation of surface species or a surface structure that play an important role in catalytic surface reactions. It has been a general feature of the dehydrocyclization of n-heptane on the various platinum surfaces that the presence of adsorbed n-heptane was prerequisite for the successful conversion of the molecule to toluene. n-Heptane had to be pre-adsorbed at 300°K under conditions where adsorption can readily occur before subsequent conversion to toluene at 600°K could take place. This "template" effect suggests that the surface structure of adsorbed n-heptane or an adsorbed reaction intermediate may be important in forming the product toluene molecule. Wise[44] has reported similar template effects during studies of the isomerization of _cis_ or _trans_ butene on palladium surfaces. The pre-adsorption of one particular isomer was a necessary prerequisite for the _cis_-_trans_ or _trans_-_cis_ isomerization.

This study of a complex catalytic reaction using one face of a single crystal sample of small surface area demonstrates the feasibility of carrying out surface reaction studies at low pressures on well-defined surfaces under well-controlled experimental conditions. Such studies allow one to select and investigate those variables that are to be significant in heterogeneous catalysis. The thermal stability of ordered stepped surfaces indicates that they are likely to be present on small metal particles that are commonly used as catalysts in surface chemical reactions. The presence of atomic steps changes the nature of chemisorption and thus plays an all-important role in subsequent surface reactions.[31] Adsorption occurs preferentially at the steps, and ordering of the adsorbed atoms or molecules may also be nucleated at the steps. The catalytic behavior of stepped surfaces with (111) orientation atomic terraces are very similar to the behavior of polydispersed platinum particles in dehydrocyclization reactions. The atomic structure of small platinum particles dispersed on alumina or silica carriers are thus likely to have atomic structures similar to that of stepped surfaces. Thus investigations of catalytic reactions on stepped surfaces should shed light on the chemical and structural properties of polydispersed metal systems which are catalysts for many surface chemical reactions.

Catalytic Studies Using Single Crystal Surfaces at High Pressures

Low pressure studies of catalytic surface reactions on single crystal surfaces allow us to select and investigate those variables (structure, composition, etc.) that are significant in heterogeneous catalysis. It would be of importance, however, to compare the results of these investigations to those results obtained in catalytic reactions studied at high pressures (1 atm or higher) but otherwise similar reaction conditions. This would involve the use of single crystal surfaces at high pressures. Such studies are feasible and are in progress in our laboratory. One may use a set of platinum single crystal surfaces and gas chromatographic detection instead of the mass spectrometer to monitor the catalytic surface reactions. The design features of such a single crystal catalytic reactor will be described elsewhere.

Acknowledgement

This work was performed under the auspices of the U. S. Atomic Energy Commission.

REFERENCES

1. A. A. Balandin, Adv. Catalysis 10, 96 (1958).
2. O. Beeck and A. W. Ritchie, Disc. Faraday Soc. 8, 159 (1950).
3. J. R. Anderson, R. J. MacDonald and Y. Shimoyama, J. of Catalysis 20, 147 (1971).
4. A. T. Gwathmey and R. E. Cunningham, Adv. Catalysis 10, 57 (1958).
5. M. Boudart, Adv. in Catalysis 20, 153 (1969).
6. G. A. Somorjai and H. H. Farrell, Advan. Chem. Phys. 20, 215 (1971).
7. G. A. Somorjai and F. J. Szalkowski, Advan. High Temp. Chem., 4, in press (1971).
8. G. A. Somorjai and F. J. Szalkowski, J. Chem. Phys. 54, 389 (1971).
9. R. W. Joyner, B. Lang and G. A. Somorjai, J. of Catalysis, to be published (1972).
10. F. J. Szalkowski and G. A. Somorjai, J. Chem. Phys., to be published (1972).
11. J. E. Lester, Ph.D. Thesis, Univ. of California, Berkeley, 1967.
12. B. Lang, R. W. Joyner and G. A. Somorjai, Surface Sci., to be published (1972).
13. J. Perdereau and G. E. Rhead, Surface Sci. 24, 555 (1971).
14. M. Henzler, Surface Sci. 19, 159 (1970).
15. M. Henzler, Surface Sci. 22, 12 (1970).
16. R. W. Joyner, J. L. Gland and G. A. Somorjai, Surface Sci., to be published (1972).
17. M. McLean and H. Mykura, Surface Sci. 5, 466 (1966).

18. H. B. Lyon and G. A. Somorjai, J. Chem. Phys. 46, 2539 (1967).

19. A. B. Mattera, R. M. Goodman and G. A. Somorjai, Surface Sci. 7, 26 (1967).

20. J. T. Grant, Surface Sci. 18, 228 (1969).

21. D. G. Fedak and N. A. Gjostein, Surface Sci. 8, 77 (1969).

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

23. P. W. Palmberg in Structure and Chemistry of Solid Surfaces, G. A. Somorjai, ed., Wiley, New York, 1969.

24. J. T. Grant and T. W. Haas, Surface Sci. 18, 457 (1969).

25. A. E. Morgan and G. A. Somorjai, Surface Sci. 12, 405 (1968).

26. T. N. Rhodin, P. W. Palmberg and E. W. Plummer, in Structure and Chemistry of Solid Surfaces, G. A. Somorjai, ed., Wiley, New York, 1969.

27. G. A. Somorjai, J. de Physique Cl, 31, 139 (1970).

28. G. A. Somorjai, Principles of Surface Chemistry, Prentice-Hall Inc., Englewood Cliffs, N. J., 1972.

29. H. P. Bonzel, R. Ku, J. Vac. Sci. Tech., in press (1972).

30. W. P. Ellis and R. L. Schwoebel, Surface Sci. 11, 82 (1968).

31. B. Lang, R. W. Joyner, G. A. Somorjai, Surface Sci., in press (1972).

32. M. N. Lewis and M. Randall, Thermodynamics, K. S. Pitzer and L. Brewer, eds., McGraw-Hill, New York, 1961.

33. A. E. Morgan and G. A. Somorjai, J. Chem. Phys., 51, 3309 (1969).

34. T. M. French, A. E. Morgan, and G. A. Somorjai, Surface Sci. 22, 486 (1970).

35. M. Fink, M. Martin and G. A. Somorjai, Surface Sci., submitted for publication.

36. J. L. Gland and G. A. Somorjai, Surface Sci., to be published.

37. B. Lang and G. A. Somorjai, J. de Chim. Phys. 7-8, 1223 (1971).

38. R. Kaplan, private communication.

39. L. D. Schmidt, J. of Catalysis 22, 269 (1971).

40. R. Bouwman and W. M. H. Sachtler, J. of Catalysis 19, 127 (1970).

41. Y. Ebisuzaki, W. J. Kass and M. O'Keefe, J. Chem. Phys. 49, 3329 (1968).

42. R. H. Siller, W. A. Oates and R. B. McLellan, J. Less Common Metals, 16, 71 (1968).

43. G. L. Selman, P. J. Ellison and A. S. Darling, J. Materials Sci., 4, 14 (1969).

44. H. Wise, private communication.

TABLE I

	Pt(111)-(1 x 1)	Pt(100)-(5 x 1)
CO	C(4 x 2)	C(4 x 2)
	(2 x 2)	$(\sqrt{2} \times \sqrt{5})$R-45°
C_2H_2	(2 x 1)[a]	$(\sqrt{2} \times \sqrt{2})$R-45°
C_2H_4	(2 x 1)[a]	$(\sqrt{2} \times \sqrt{2})$R-45°
C_3H_6	(2 x 1)[a]	(1 x 1)
cis-2-butene	(2 x 2)	(1 x 1)
trans-2-butene	(2 x 2)	(1 x 1)
1,3-butadiene	(2 x 2)	(1 x 1)
isobutylene	$(\sqrt{7} \times \sqrt{3})$R-13.9°	none
H_2	(2 x 2)	(2 x 2)
H_2 + CO	$(\sqrt{3} \times \sqrt{3})$R-30°	$(\sqrt{2} \times \sqrt{2})$R-45°
carbon	graphite (basal plane)	graphite (basal plane)
naphthalene	(3 x 3)	(1 x 1)
pyridine	(3 x 1)	$(\sqrt{2} \times \sqrt{2})$R-45°
nitrobenzene	(2 x 2)	(1 x 1)
pyrrole	(4 x 2) or (4 x 4)	$(\sqrt{2} \times \sqrt{2})$R-45°

---

[a] The diffraction pattern indicates a (2 x 2) surface structure due to the presence of 60° rotated (2 x 1) domains.

FIGURE CAPTIONS

Figure 1. Scheme of the low-energy electron diffraction apparatus.

Figure 2. Diffraction patterns from the (111) face of platinum at different electron energies: a) 51 volts, b) 63.5 volts, c) 160 volts, d) 181 volts.

Figure 3. Scheme of an Auger electron spectroscopy apparatus.

Figure 4. Auger spectra of clean and carbon monoxide covered platinum surfaces.

Figure 5. Scheme of the reaction chamber for low pressure (10^{-9}-10^{-4} torr) catalytic studies using single crystal surfaces.

Figure 6. Schematic diagrams of the most common surface structures appearing on substrates with six-fold rotational symmetry.

Figure 7. Schematic diagrams of the most common surface structures appearing on substrates with four-fold rotational symmetry.

Figure 8. Schematic diagrams of the most common surface structures appearing on substrates with two-fold rotational symmetry.

Figure 9. Schematic representation of a stepped surface.

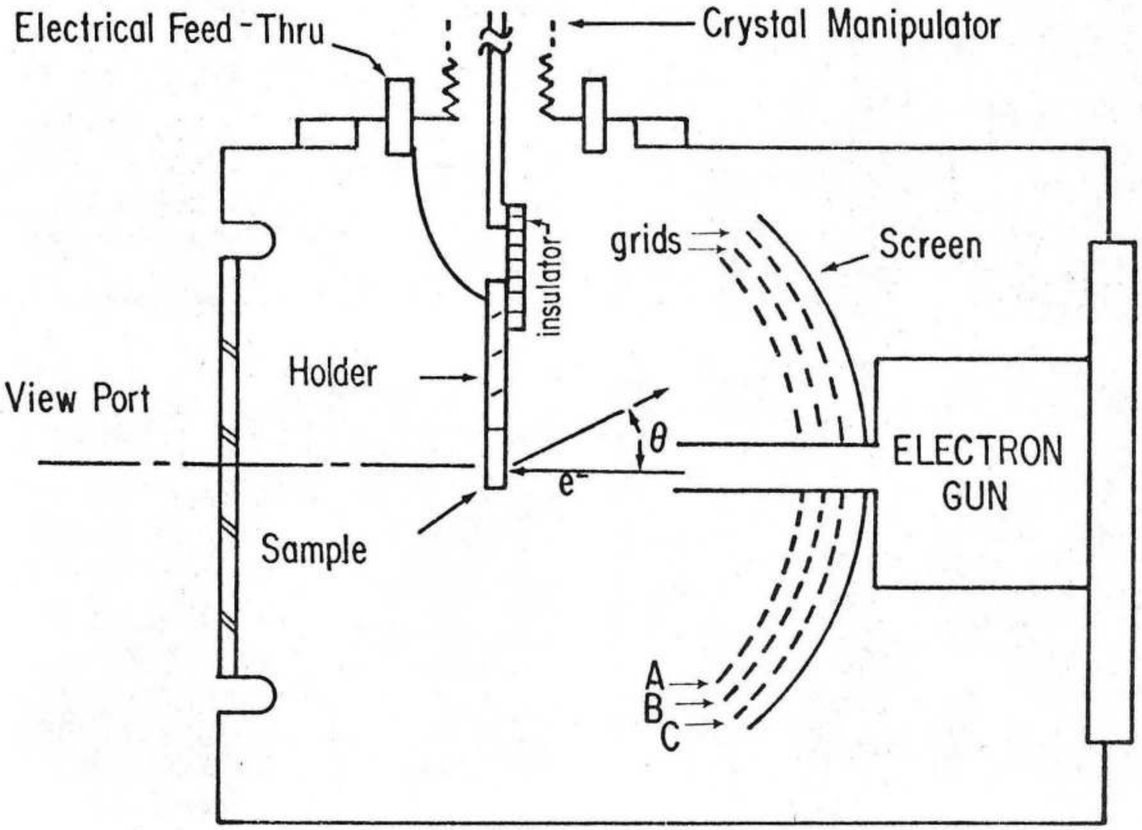
Figure 10. a) Diffraction pattern of the Pt(100)-(5 x 1) surface structure that is characteristic of clean platinum.

b) Schematic representation of the hexagonal distortion of the topmost layer in the (100) surface that forms the (5 x 1) coincidence lattice with the underlying square unit mesh.

Figure 11. a) Diffraction pattern at 140 volts and b) schematic representation of the atomic structure of the stepped Pt(S)[9(111) x (111)] surface.

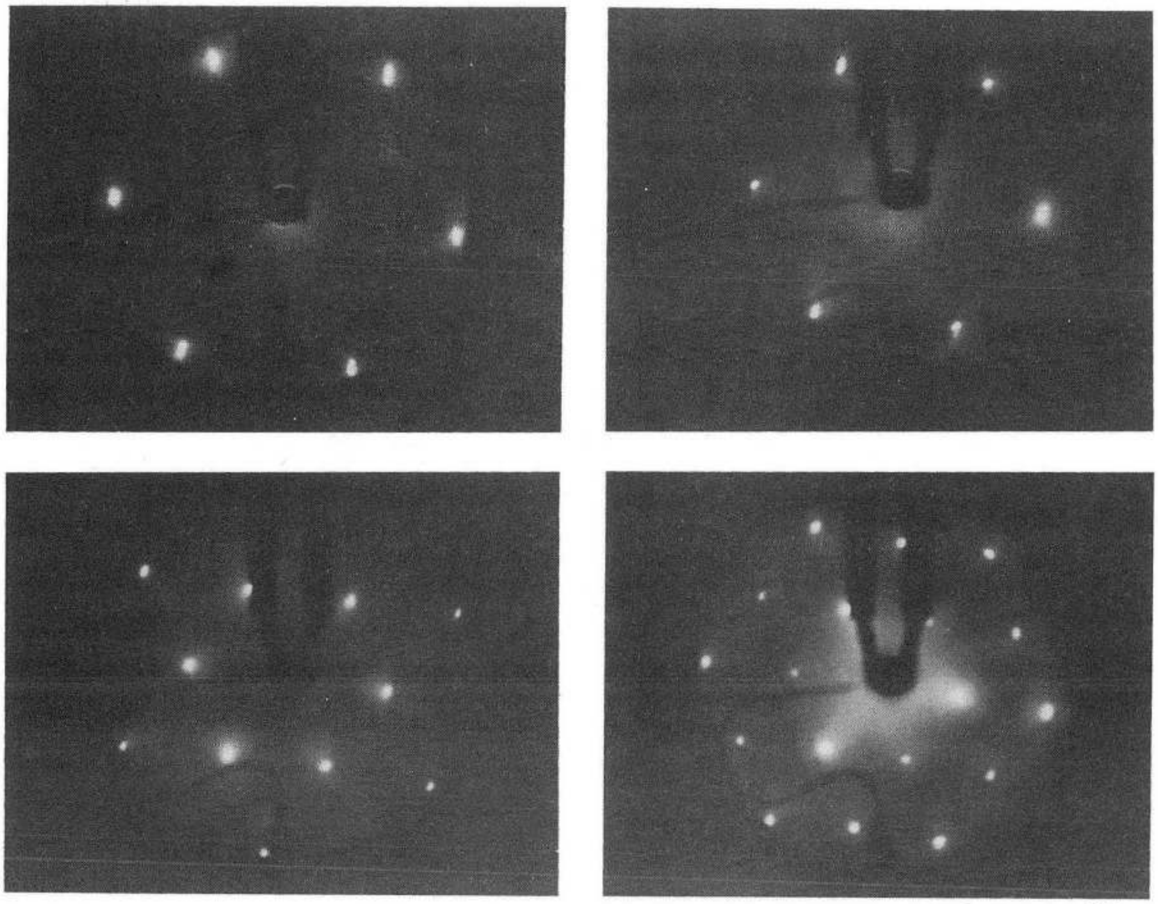
Figure 12. Mass spectra of a) n-heptane and b) toluene.

Table I. Surface structures that formed during the adsorption of various molecules on the (111) and (100) crystal faces of platinum.



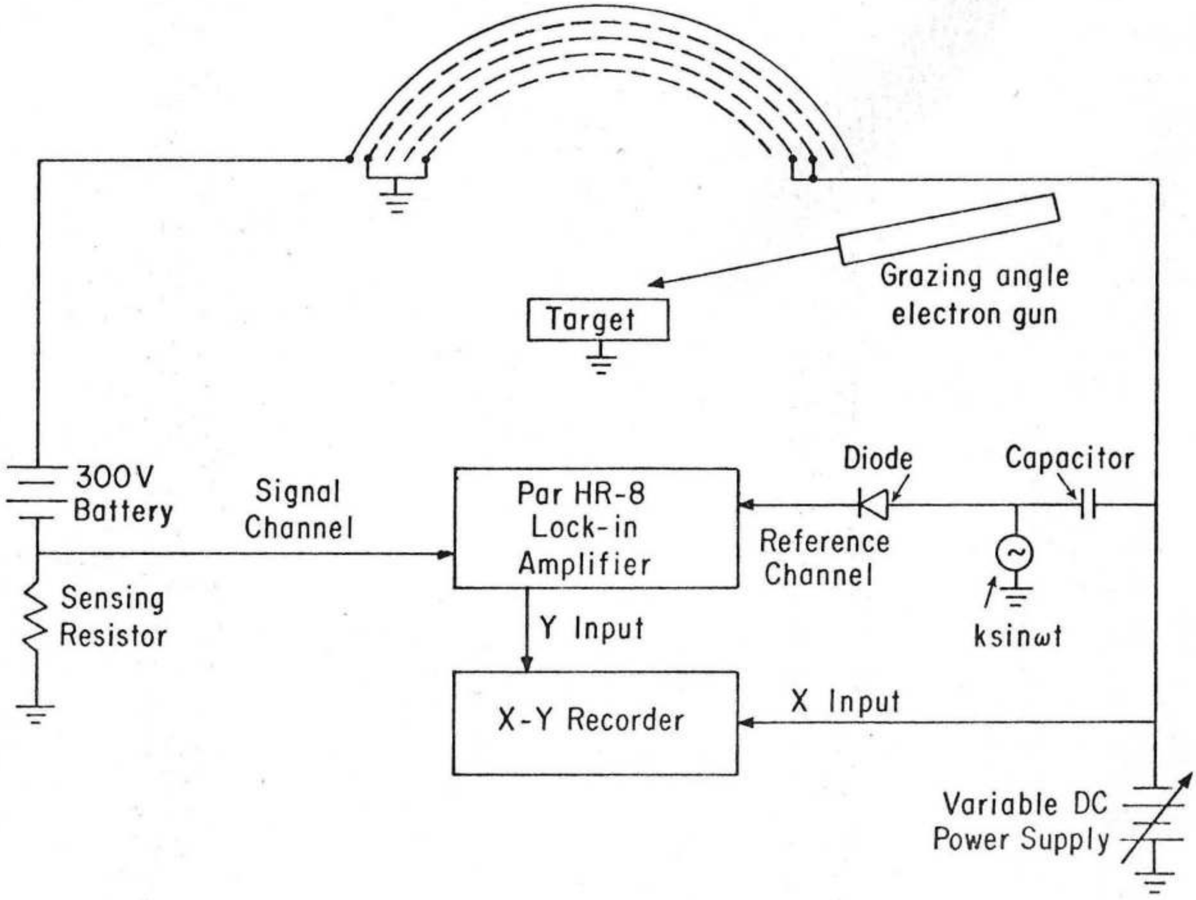
XBL 703-556

Fig. 1.



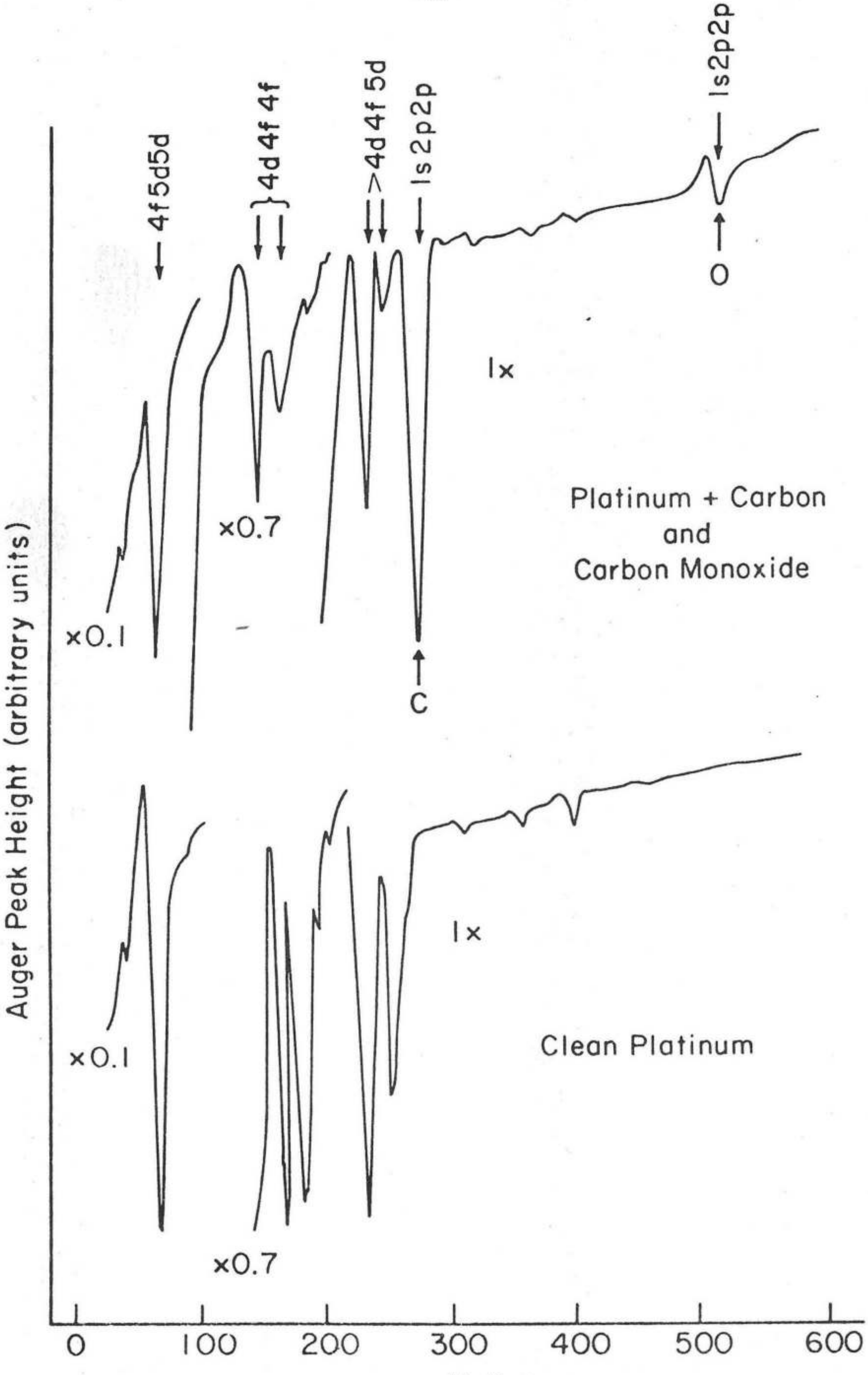
XBB 7012-5685

Fig. 2



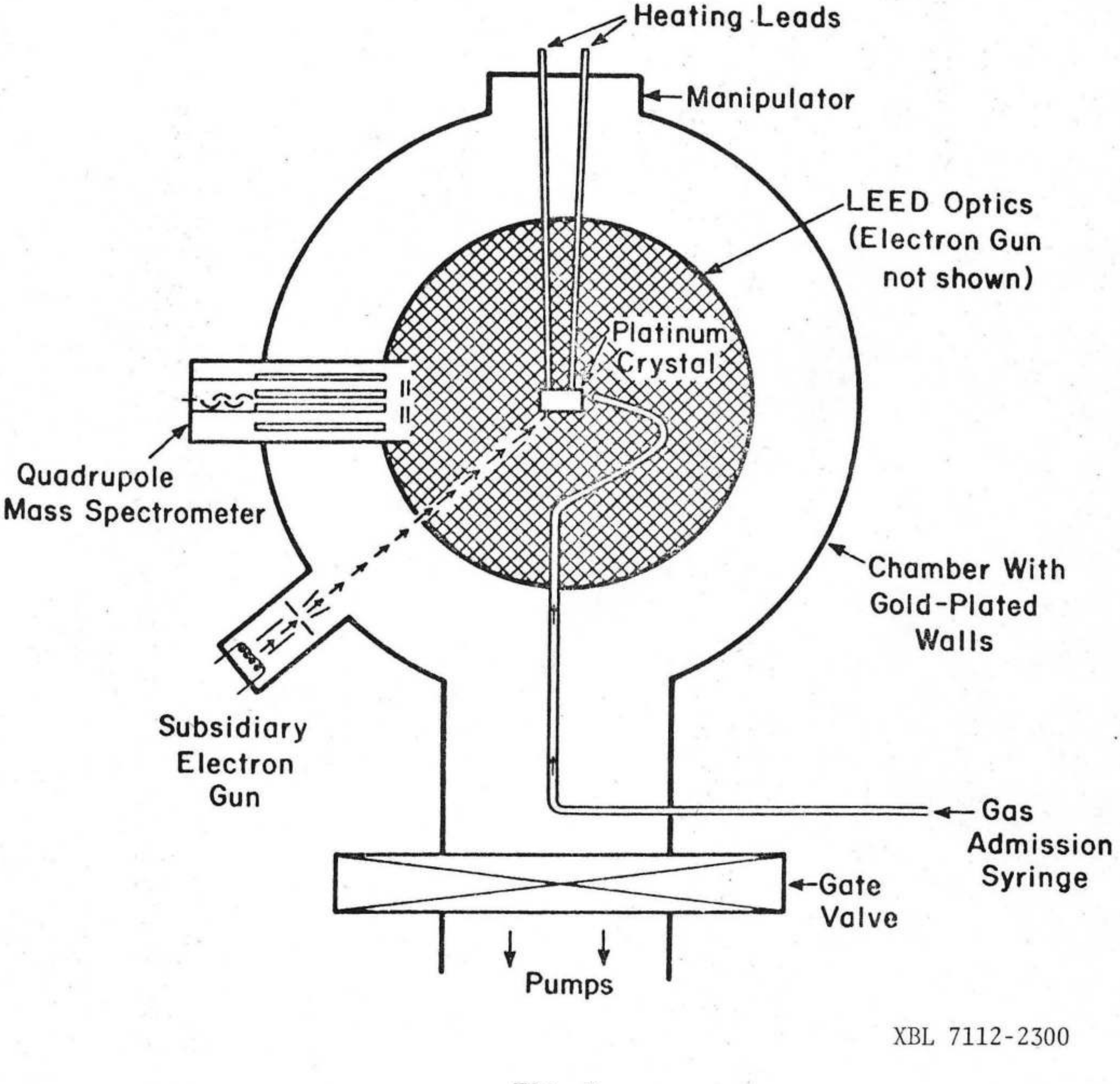
XBL 708-1722

Fig. 3.



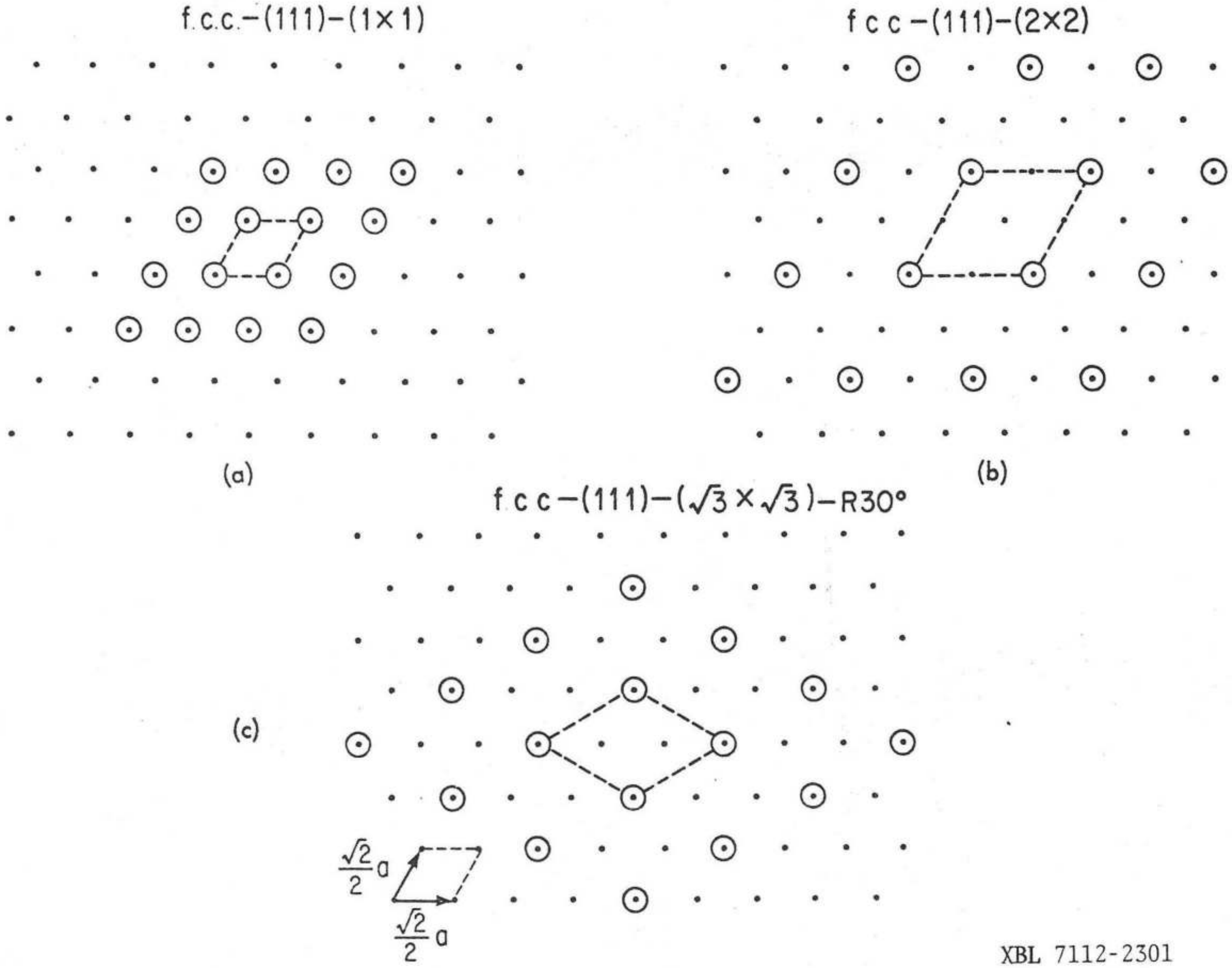
XBL 7112-2299

Fig. 4.



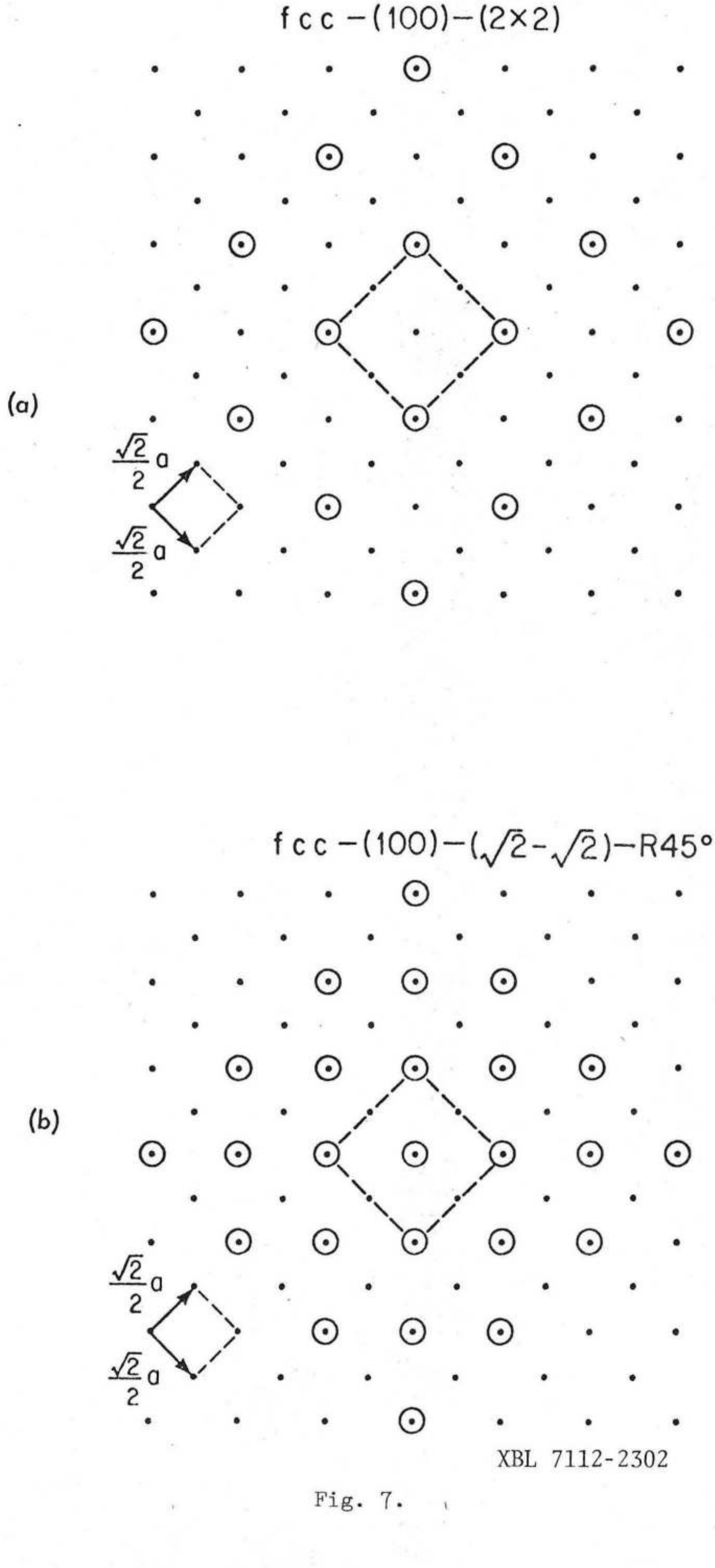
XBL 7112-2300

Fig. 5.



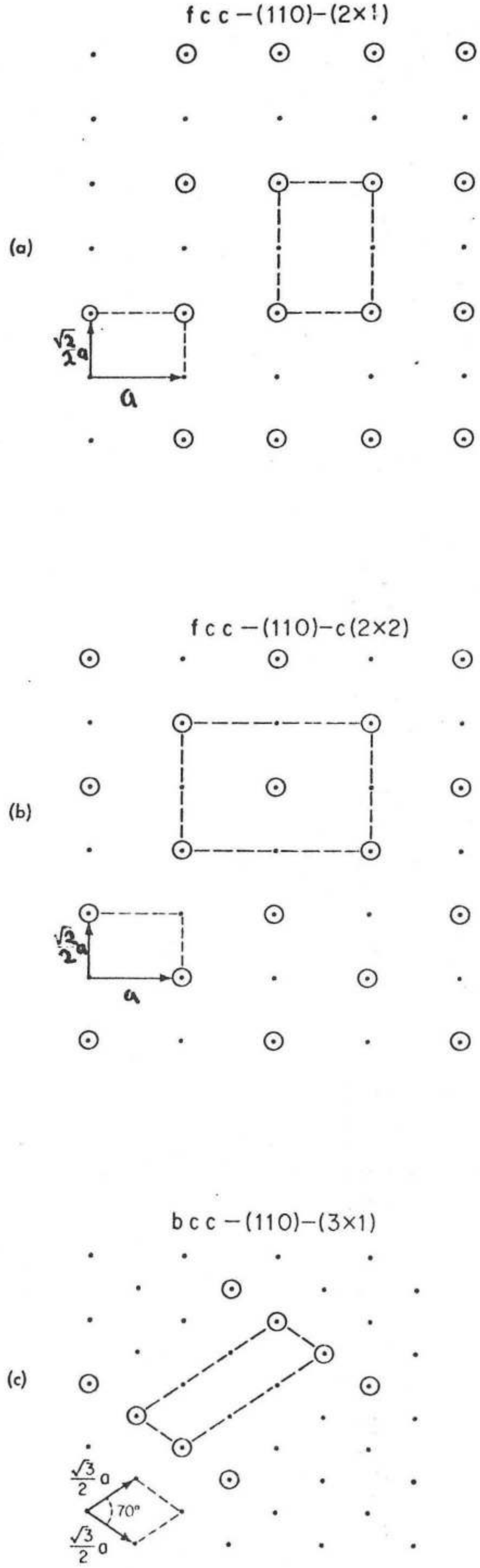
XBL 7112-2301

Fig. 6.



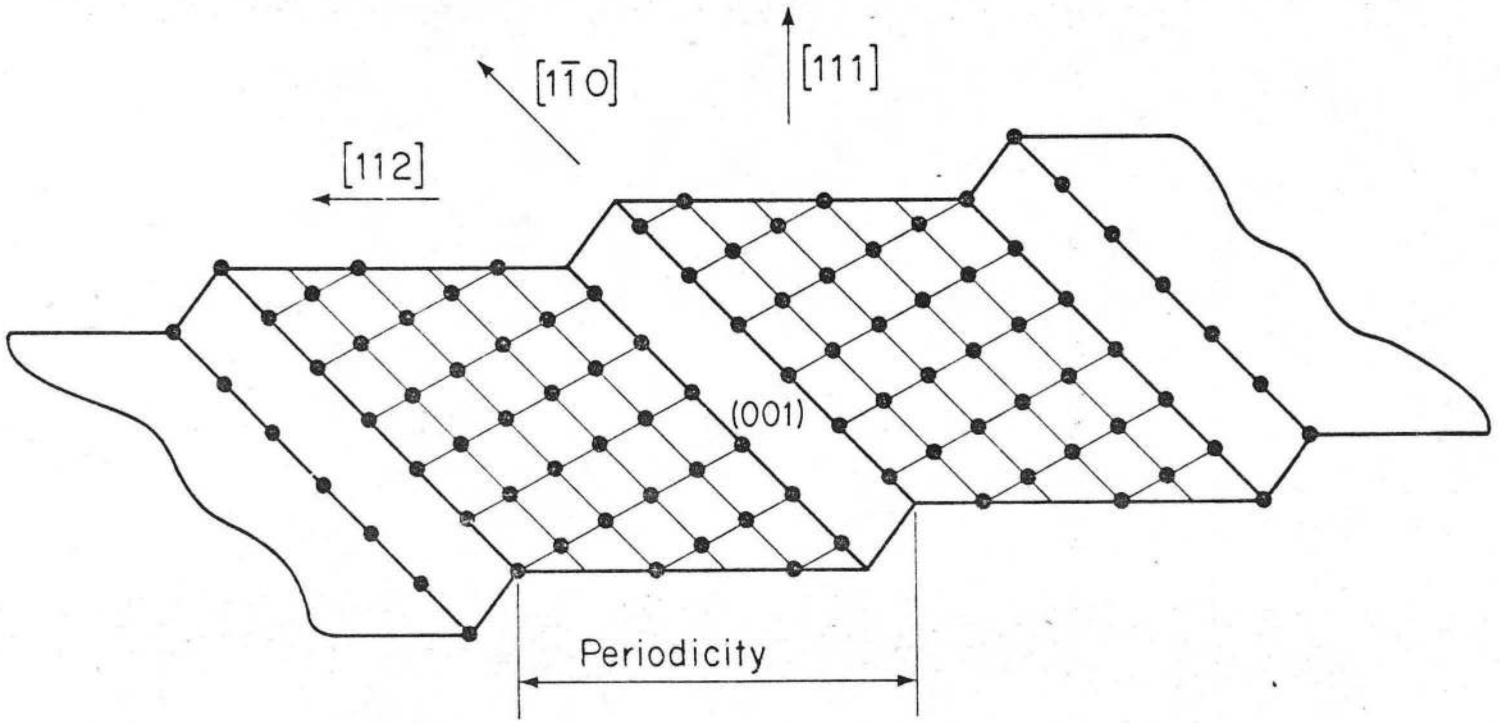
XBL 7112-2302

Fig. 7.



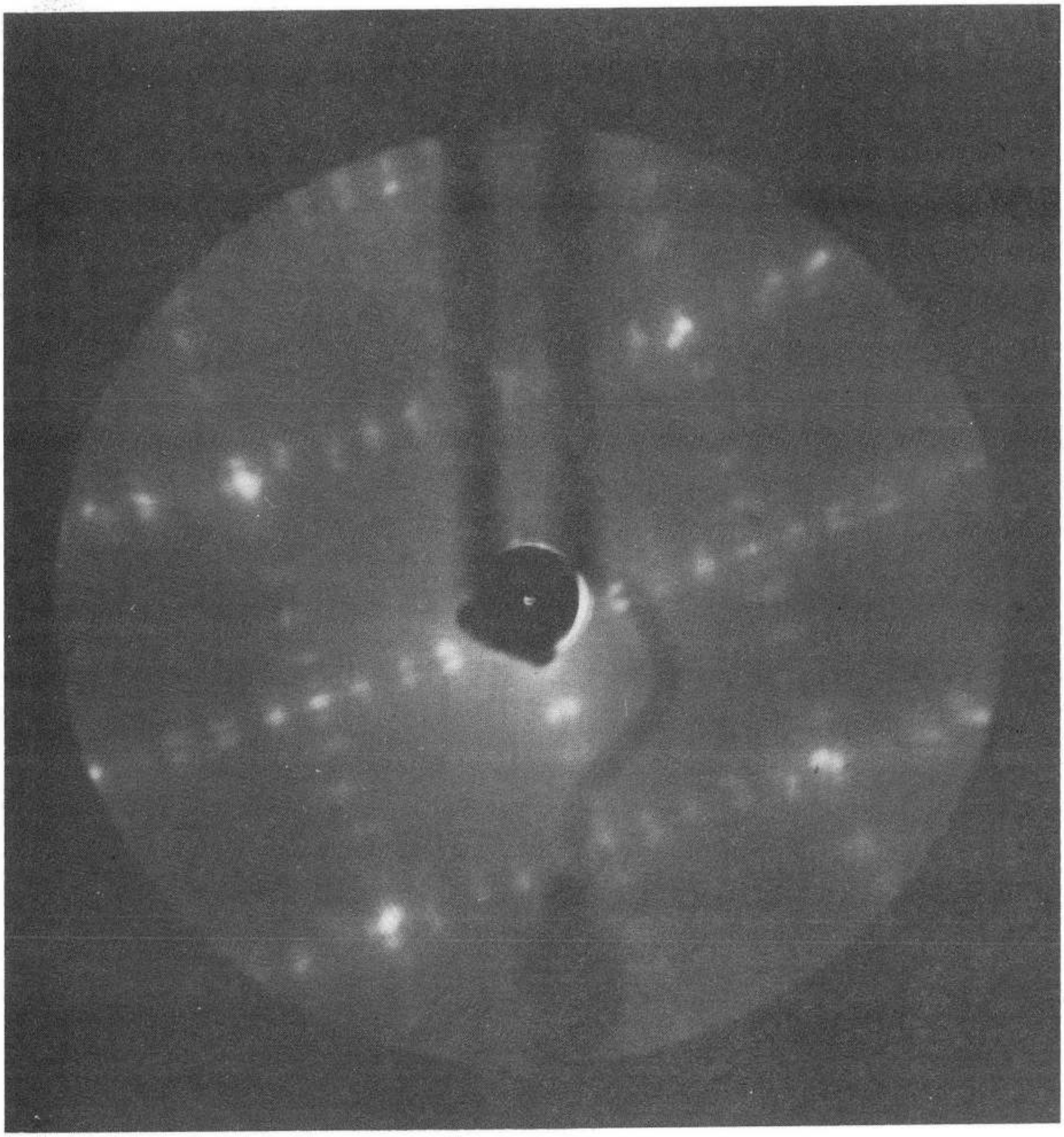
XBL 7112-2303

Fig. 8.



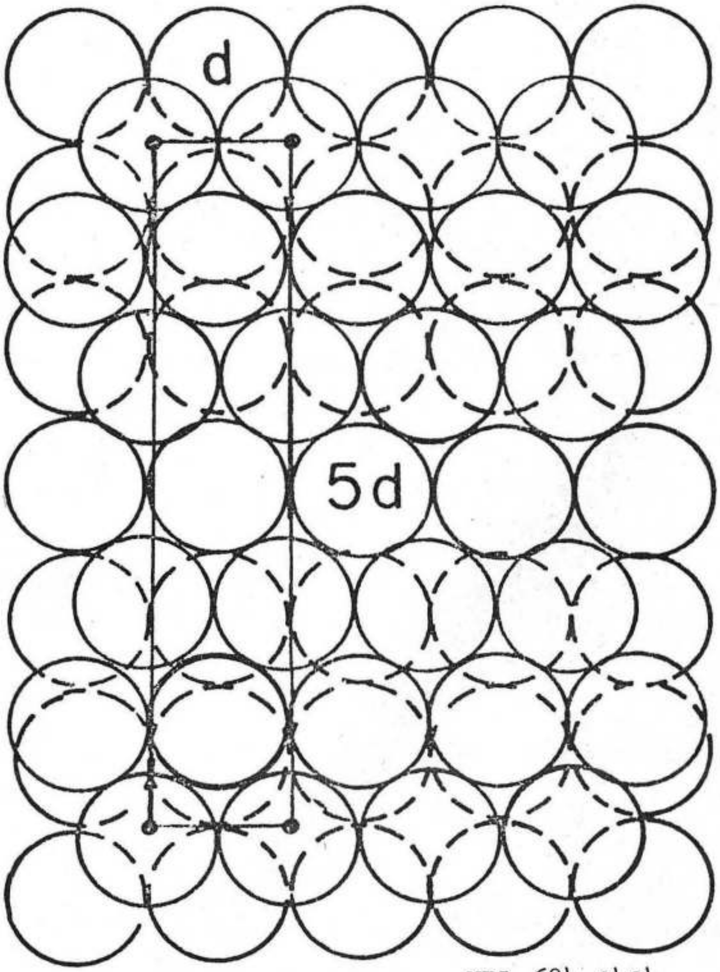
XBL 716-6801

Fig. 9.



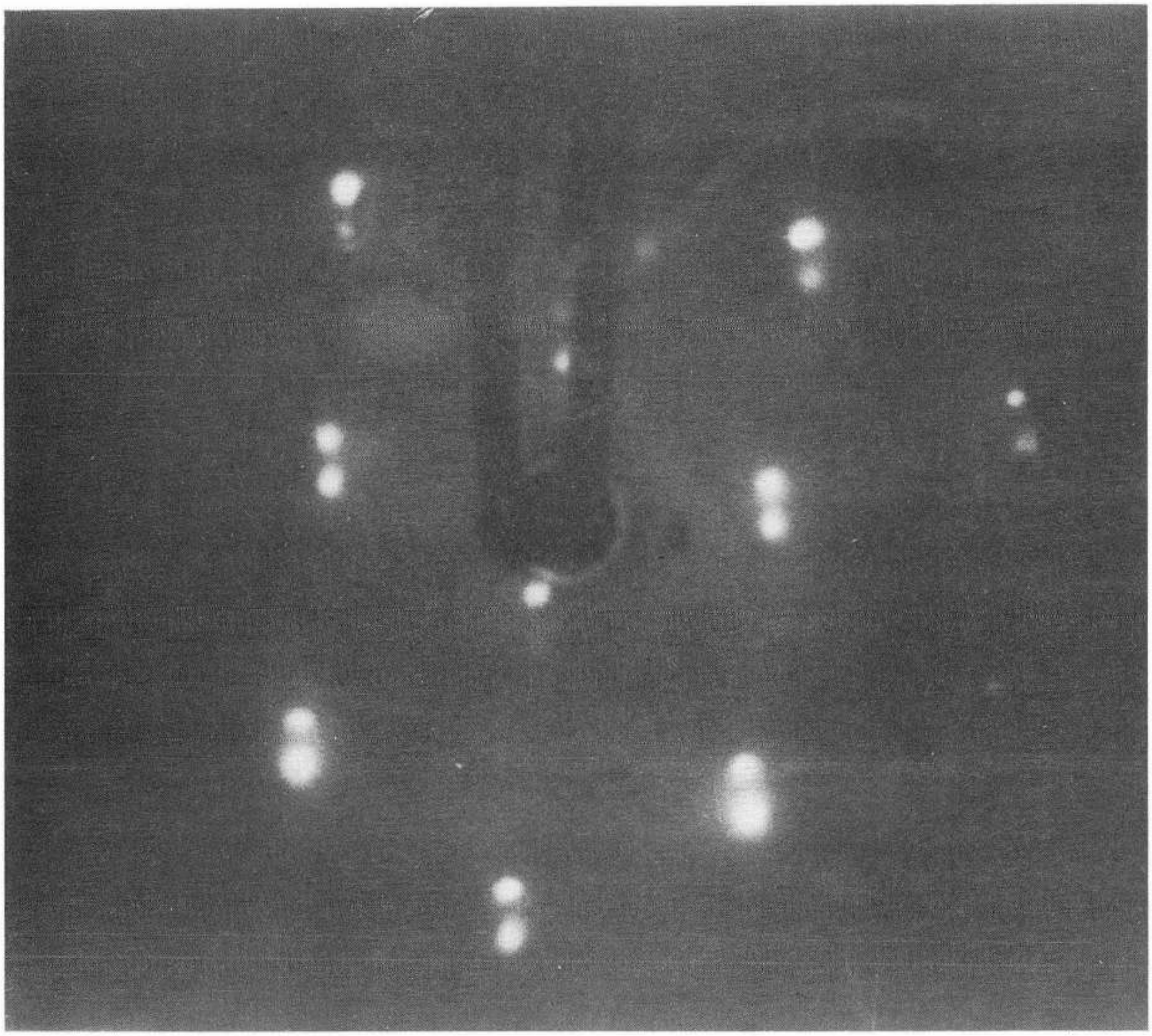
XBB 684-1737

Fig. 10a



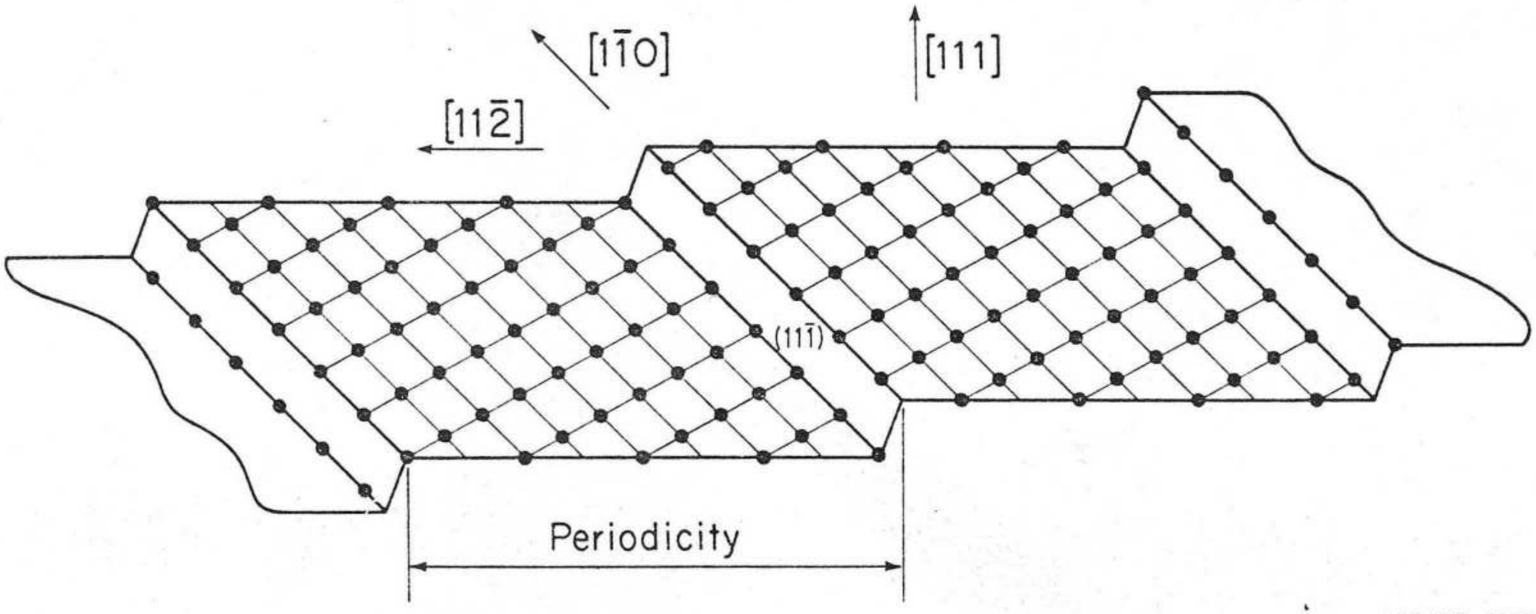
XBL 684-2424

Fig. 10b



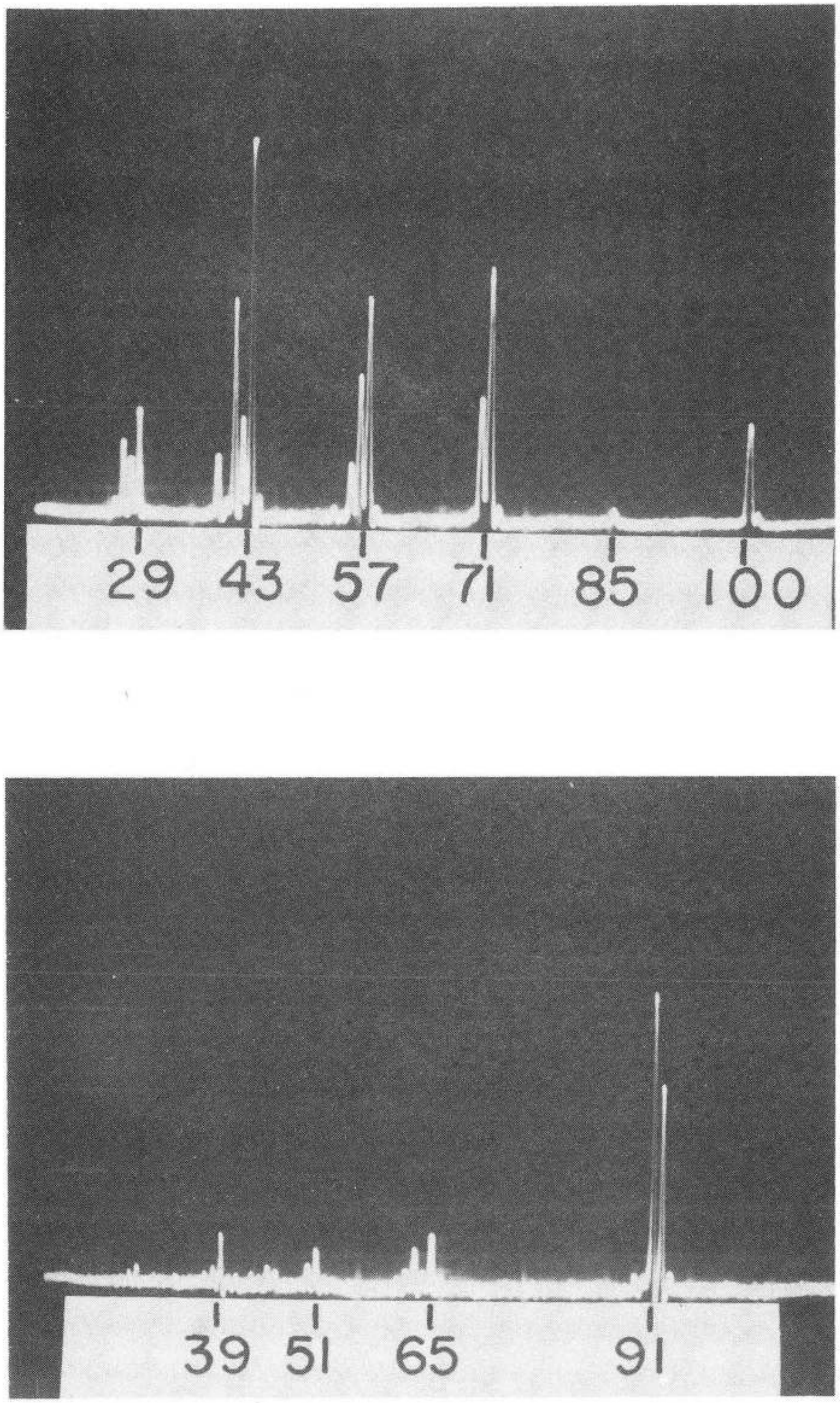
XBB 7110-4951

Fig. 11a



XBL 716-6802

Fig. 11b



XBB 7110-5215

Fig. 12

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720