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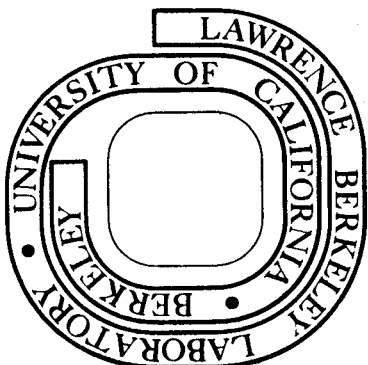
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THE STABILITY AND STRUCTURE OF HIGH MILLER INDEX PLATINUM CRYSTAL SURFACES
IN VACUUM AND IN THE PRESENCE OF ADSORBED CARBON AND OXYGEN

by

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Abstract

The surface structures of twenty-two high Miller Index crystal faces of platinum were studied in ultrahigh vacuum (uhv) when clean and in the presence of a monolayer of chemisorbed oxygen or carbon by low-energy electron diffraction (LEED). Besides the low Miller Index planes [the (001), (011), and (111)], only a few of the surfaces [the (112), (113), (133), (122) and (012)] were stable under all conditions of the experiments. The stable surfaces are characterized by a very high density of periodic steps of one atom in height or a complete lack of steps. The other platinum crystal faces restructure as the surface composition is changed. Some of the surface structures that are stable in uhv and in oxygen reconstruct in the presence of carbon while others are stable when clean and when carbon covered but restructure when covered with oxygen. In addition to the one atom high step-terrace configuration there are atomically clean surface structures with multiple height steps and structures in "hill and valley" configuration consisting of large facet planes detectable by LEED. The implications to heterogeneous catalysis of the observed stability and restructuring of the various crystal planes in changing reaction conditions are discussed.

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Introduction

Modern surface science has made good use of crystal planes of low Miller Index in studies of a wide variety of surface phenomena ranging from surface crystallography to chemisorption. The predominance and high symmetry of repetitive surface sites of only one type, the relative ease of preparation and ordering of the (111) and (001) crystal planes of face centered cubic solids also made them good candidates for theoretical scrutiny. Real surfaces, whether employed as polycrystalline foils, thin films or small, dispersed particles are heterogeneous in their atomic surface structures. There are several crystal planes present simultaneously; many sites co-exist on the same surface that are distinguishable by their number of nearest neighbors. There are steps of atomic height and there are kinks in the steps. There is great deal of evidence emerging from recent surface studies that the various structurally different surface sites have different chemical activities.^{1,2} Thus the complexity of surface structures is both responsible for and necessary to the rich surface chemistry attributable to so many practical catalytic systems.

High Miller Index surfaces have been studied less than low Miller Index crystal faces. The few studies that have been made using metal, semiconductor and oxide surfaces revealed that these surfaces are structurally heterogeneous.^{1,2,3,4,5,6,7,8} Many high Miller Index planes are characterized by atomic structures consisting of periodic steps of one atom height separated by terraces of several atoms wide. Both steps and terraces had low Miller Index orientations. Moreover, some of these stepped surfaces exhibited exceptional thermal stability up to the melting point and also structural stability when heated in either oxidizing or in

reducing ambients.

Clearly, there are a very large number of high Miller Index surfaces with step-terrace structures that can be concocted from say, the three low index (111), (001) and (011) crystal faces of face centered cubic solids. Those likely to have practical chemical importance, however, must exhibit thermal stability and stability in reaction environments. This stability is necessary to sustain their reactivity, mechanical strength or other surface properties. It is of importance, therefore, to determine the structure and stability of these "irregular" surfaces in a variety of experimental conditions.

This paper reports on a detailed study we undertook to determine the structure and stability of a large number of high Miller Index platinum surfaces. Twenty-two orientations were studied in various sections of the crystallographic zones by low-energy electron diffraction (LEED). LEED is an excellent technique for these investigations; the diffraction features are sensitive to both step height and terrace width. In addition, LEED readily detects faceting, allowing one to monitor structural changes as a function of time, temperature and ambient, when they do occur.

We have studied the high Miller Index surfaces of platinum in ultra-high vacuum, in the presence of oxygen, and in the presence of hydrocarbons that deposited a layer of carbon on the metal surface. Some of the crystal faces were stable in all three ambients, some of them in two or one, and some were unstable and faceted. Their structural behavior will be discussed in some detail and compared with theoretical predictions and with other experimental findings whenever available. Finally, the implications of structural instability in heterogeneous catalysis will be discussed as

it relates to particle size changes (dispersion) and chemical deactivation (poisoning).

Experimental

The Pt high Miller Index surfaces studied are shown in Fig. 1 on a stereographic projection. Both the Miller Index and a step-terrace notation⁵ are given for each surface. The step-terrace surface structure notation will be used throughout this paper as the macroscopic Miller Index cannot readily be employed to specify all the microscopic surface structure variations visible by LEED. The step-terrace notation describes the actual surface structure as composed of terraces of varying width separated by periodic steps of one or many atoms in height (see Fig. 2), while the Miller Index of the crystal plane only defines the macroscopic surface plane. The step-terrace notation describes the orientation, (hkl) , and mean width, m , of the terraces and orientation, $(h'k'l')$, and mean height, n , of the steps as $\text{Pt}(S)-[m(hkl) \times n(h'k'l')]$.⁵

There are three main types of structural features that appear on surfaces. First there are one atom high steps separated by terraces of width n (Fig. 2a). This is called the monatomic height step-terrace configuration and it is produced when the plane is stable with respect to surrounding planes. Second, there are multiple height steps separated by terraces with width that are multiples of n (Fig. 2b depicts $2m$).

The third structural types, the "hill and valley" configuration, consists of large (compared to the coherence length of the diffracted electrons, $\sim 100 \text{ \AA}$) facet planes which would form a surface resembling ridges of hills with valleys between them (Fig. 2c). The point where multiple height steps and multiple width terraces become facets is arbitrary. We have taken a surface to be faceted when the step

periodicity is no longer discernable from analysis of the diffraction beam splitting.⁵

Detailed description of the surface preparation has been given previously.² In brief, single crystal Pt rods were aligned by Laue back reflection X-ray diffraction, spark cut to the desired angle and metallurgically polished/ ^{with} the final step a 0.05 micron alumina powder. The 1 mm thick slices were mounted on Pt wires for heating and the crystal temperature was measured with a Pt--Pt-10% Rh thermocouple spot welded to the top of the crystal. The surfaces were cleaned by a combination of Ar ion sputtering and oxygen heat treatment combined with high temperature (>950°C) anneals.

The samples were clean of Ca, C and O by AES to the limit of detection, about 0.05 to 0.02 monolayers. There could be a very small amount of oxygen, ≤ 0.03 monolayer, on the surface which could be undetectable with the retarding potential Auger spectrometer used in this investigation.

The samples could be covered with a monolayer of carbon by heating to 800°C in 1×10^{-7} torr of hydrocarbon for a few minutes. Benzene was used for depositing carbon on the surface. Oxygen adsorption was carried out by heating the samples at 850°C in 5×10^{-6} torr of oxygen for 10 to 30 minutes. The ratio of the C-273 eV Auger peak to the Pt-240 eV peak was between 3.5 and 4 on a carbon covered surface; a graphitic monolayer corresponds to a ratio of ~4. The O-510 eV Auger peak was approximately the same height as the Pt-240 eV Auger peak on the oxygen covered surfaces.

Results

In Table I we list all of the crystal faces that were studied by the Miller Index and step-terrace notations. Their structural stability or

transformations into other crystal planes when heated in ultrahigh vacuum or in the presence of a monolayer of carbon or adsorbed oxygen are also indicated. The basic stereographic triangle may be divided into three regions for the discussion of the stability of the other high Miller Index surfaces. The regions are the surfaces vicinal to each of the low Miller Index poles at the corners of the stereographic triangle, (111), (001) and (011). The surfaces are listed by region and within each region they are arranged starting from the low Index plane ending with the surface on the edge of the region. Some region boundary planes have been repeated for clarity.

The Stable Crystal Faces of Platinum

The three low Miller Index surfaces, (001), (011) and (111) along with the crystal faces of (113), (112), (012), and (122)-(133) orientation are stable under all conditions studied as seen in Table I.

The clean (111) surface, hexagonal close packed and lowest free energy, gives LEED patterns corresponding to a (1x1) unreconstructed surface structure, a surface structure with a ring like diffraction feature when it is covered with carbon, and a high background (1x1) structure with oxygen adsorption. The ring diffraction pattern indicates the presence of rotationally disordered basal planes of graphite, while the high background intensity indicates surface disorder.

The clean (001) surface reconstructs to form a distorted hexagonal overlayer which results in a coincidence LEED pattern characteristic of a '(5x1)' structure; this surface structure is to be discussed in a subsequent paper.⁹ Coverage by graphitic carbon returns the surface to a (1x1) structure and produces ring like diffraction features as on the (111)

surface. The '(5x1)' surface structure remains stable upon exposure to oxygen.

The clean (011) surface also reconstructs to form a (1x2) surface structure.¹⁰ The surface structure returns to a (1x1) structure with carbon coverage. Many complex surface structures form upon varying exposure to oxygen.¹¹

The stable high Miller Index surfaces all produce a (1x1) surface structure when clean. These structures are shown in Fig. 3 and consist of a monatomic height step and a very narrow terrace. When these surfaces are covered with carbon, the ring like diffraction feature appears as on the low Miller Index surfaces. Oxygen adsorbs strongly in the steps on these surfaces, but does not seem to cause reconstruction as on the (011) surface, although this was not investigated thoroughly. When a surface vicinal to a low Miller Index plane facets, a large stable facet plane forms which is easily studied. The (012) surface was studied in this manner as one of the two facets on the (015) surface.

The (111) Vicinal Surfaces

A large number of surfaces have been studied in this region. The region includes from the (111) plane to the (122) and (112) planes on the boundary zone lines and all the planes within about 20° solid angle of the (111) plane.

Clean Surfaces

The surfaces in this region are stable in a monatomic height step configuration when clean. All the surfaces except one, Pt(S)-[3.5(111)x(100)], are stable at temperatures up to at least 1200°C; the few tested were stable to 1600°C. The Pt(S)-[3.5(111)x(100)] surface facets reversibly

near 900°C, when clean, from the monatomic height step configuration to a faceted surface with $[4(111) \times (100)]$ areas and $[3(111) \times (100)]$ areas. The average domain size of the facet planes can be determined by the width of the LEED beams from that plane, if the size of the plane is less than the coherence length of the electrons.¹² The broadening of the beams from the $[3(111) \times (100)]$ area gives a domain size of 25 Å by the simple formula: $Ma = \lambda / 2\theta$ where Ma is the domain size, λ is the electron wavelength and θ is the half width at half maximum of the LEED beam profile.¹³ The reversible rearrangement of terrace width and step height shows that the Pt atoms have high mobility and can obtain an equilibrium surface configuration under the conditions of our experiments. It also demonstrates that a high temperature structure can be quenched and studied by LEED at room temperature. Thus the step structure which is obtained by quenching rapidly from 1600°C (about 3 sec to reach 800°C below which appreciable diffusion does not occur) is the equilibrium structure at the high temperature. The steps probably have fewer thermally generated kinks at room temperature, but the step position should not change detectably.

The LEED patterns of several surfaces are shown in Figs. 3, 4 and 5. As seen all these diffraction patterns have the overall hexagonal symmetry of the (111) surface with the spot splitting inversely proportional to the step spacing and the splitting direction normal to the step direction. The ratio of the (10)-(00) distance (close-packed distance) to the doublet splitting agrees with the nominal value to within a 1/3 of a lattice spacing, i.e., for a $[6(111) \times (100)]$ surface the ratio is $5 - 2/3 \pm 1/3$. This is good agreement within the uncertainty introduced by cutting and polishing the crystal surface.

Graphite Covered Surfaces

A monolayer of graphitic carbon causes interesting surface structural rearrangements in this region. On samples between the Pt(S)-[9(111)x(100)] and Pt(S)-[3(111)x(100)], graphitic carbon causes facets of [3(111)x(100)] and Pt(S)-[9(111)x(100)] to form. The facets are small (as indicated by LEED beam broadening), about 35 Å. When the carbon is removed, either by burning in O₂ or by heating the sample to high temperature to dissolve the carbon into the bulk, the monatomic height step configuration returns. Surfaces with terraces wider than 9 atoms are unaffected by the presence of up to a monolayer of carbon. One edge of the unit cell, \vec{a} , in the basal plane of graphite is 8/9 of the close packed platinum distance, 2.77 Å, thus the graphitic layer apparently stabilizes the terrace width at which the Pt and graphite unit cells are in registry, i.e., Pt(S)-[9(111)x(100)].

Between the (111) and (011) orientations samples also facet with graphitic carbon on their surface. The facets appear to be the (111) plane and a combination of [3(111)x(111)] and [2(111)x(111)] planes. There is no clear facet specular reflection as for surfaces between the (111) and (001) orientations, but a fairly bright streak with more intensity corresponding to the diffraction beams from the [3(111)x(111)] and [2(111)x(111)] surfaces. The samples with (111)x(111) type surface structures have higher background and broader, less well defined beams when graphite covered (indicating surface disorder) as compared to samples with (111)x(100) type surfaces. It appears that the initial step orientation is quite important for the nucleation and growth of stable surface structures during faceting.

In this region between the zone lines, some of the samples are stable in monatomic height step-terrace configurations while others facet to the three lower Miller Index corners, (111), [3(111)x(100)] and [2-3(111)x(111)]. The Pt(S)-[7(111)x(210)] and Pt(S)-[13(111)x(310)] are stable with a monolayer of graphitic carbon on their surfaces. The [7(111)x(710)], ^{with} / 0.4 to 0.6 monolayers of carbon, facets to a [8.5(111)x(210)]-C ring and a [3(111)x(100)] structure, but when the surface is saturated, facets to the (111)-C ring, [3(111)x(100)] and [2-3(111)x(111)] planes. This is very similar to the behavior found by Ellis on UO₂ kinked surfaces.⁸ Upon heating and the loss of O₂, the UO₂ steps destabilized and faceted to the (111), (335) and (331) going through similar intermediate stages.

Oxygen Covered Surfaces

The surfaces in this region do not facet when exposed to 1×10^{-6} torr of O₂ at high (900°C) temperatures. However, sharp streaks appear in the diffraction pattern from the (111)x(100) type surface, in the 1/2 order position for the Pt(S)-[6(111)x(100)]⁵ and in the 1/3 order position for the Pt(S)-[3(111)x(100)] surface. The (111)x(111) samples form multiple height steps. The Pt(S)-[9(111)x(111)] becomes Pt(S)-[17(111)x2(111)]-0 when exposed to oxygen at high temperature.⁵

The (001) Vicinal Surfaces

Several surfaces have been studied in this region. The region includes surfaces from the (001) plane to the [2(100)x(111)] and [2(100)x(100)] planes on the boundary zone lines and all the planes within about 25° from the (001) plane.

Clean Surfaces

The surfaces in this region all possess a reconstructed (001)

terrace '(5x1)' surface structure as readily seen in Fig. 7. The reconstruction is probably a distorted hexagonal overlayer resembling a (5x1) coincidence pattern.⁹ Four rotationally distinct domains make up the diffraction pattern observed from the (001) surfaces (Fig. 7a). On the Pt(S)-[75(100)x25(210)] surface, two of the four domains are stabilized by the terrace structure (Fig. 7b). The two surfaces of the (100)x(111) step type, only one of the four possible domains is present (Fig. 7c and 7d). The (100)x(111) samples are stable in a monatomic height step configuration to above 1200°C, while (100)x(100) samples facet to (001)-(5x1) and [2(100)x(100)] planes. These facets formed upon annealing at 850°C, and were quite large compared with the facets which formed in the region near the (111) pole. The LEED beams from both facet planes were as sharp as the beams from any low Miller Index surface, thus the facet planes are large and well ordered.

Carbon Covered Surfaces

The Pt crystal planes in this region facet with a layer of carbon on their surfaces. The hill and valley structure that forms is composed of (001) and [2(100)x(111)] or [2(100)x(100)] planes. The ring like diffraction feature characteristic of graphitic carbon appears in the LEED pattern of each facet plane, and the reconstruction of the (001) disappears. The [2(100)x(111)] and [2(100)x(100)] both are stable with a monolayer of graphite on them. Lang¹⁴ observed similar faceting as was observed in this study.

Oxygen Covered Surfaces

The samples with (111)x(100) structures are very sensitive to oxygen. Less than 0.05 monolayer of oxygen causes the Pt(S)-[7(100)x(111)] to

facet to the (001) and [2(100)x(111)] planes. When the Auger 0-510 eV peak height to Pt-238 eV peak height ratio is less than 0.1, the sample still facets (noise in the Auger spectrum precludes accurately determining how much less than 0.1). One monolayer of oxygen gives an Auger 0-510 eV to Pt-238 eV peak height ratio of ~2. It is expected that oxygen stabilizes the [2(100)x(111)] stepped surface; this means that less than one O atom for every four Pt atoms along the step greatly influences the surface structures' stability. At higher coverages of oxygen a (2x1)-O pattern is present on [2(100)x(111)] facet plane, and a LEED pattern characteristic of the (5x1) reconstruction remains on the (001) facet plane. At oxygen coverages below ~0.2 monolayers, the (2x1) pattern fades and is not visible at coverages less than 0.05 monolayers. This behavior indicates most of the oxygen at coverages of less than 0.2 monolayer is on the [2(100)x(111)] facet plane and hence its surface free energy is affected more than that of the (001). The [2(100)x(111)] LEED beams are the same size as those from any well ordered low Miller Index surface at all coverages of oxygen investigated. Thus a very small amount of oxygen can cause large (>100 Å) new crystal faces to form by faceting.

The [5(100)x(100)] surface, which is faceted when clean, remains faceted after oxygen exposure. The facet domains are large, greater than 100 Å both clean and after oxygen exposure.

The (011) Vicinal Surfaces

Only two surfaces were studied in this region, one on each zone line. The region includes from the (011) plane to the (012) plane and to the (122)-(133) planes and all the planes within about 17° from the (011) plane.

The clean surfaces in this region are, as far as known, not stable in a monatomic height step configuration. The (110)x(111) type surfaces faceted to the (011) and [2-3(111)x(111)] planes. The (011) surface of Pt reconstructs to give a (1x2) pattern¹⁰ visible on the (011) facet in Fig. 8b, ([3(110)x(111)] nominal surface). The one surface studied of the (110)x(100) type, Pt(S)-[8(110)x2(100)], had an apparent double height step and a reconstructed terrace structure. The terraces were not reconstructed, however, to the (1x2) structure of the low Miller Index (011) plane. The surface structure, as seen in the LEED pattern of Fig. 8a, is a (1x2-2/3). Park and Houston¹⁵ have shown that fractional order structures can result from mixtures of integral order structures, in this case 1/3 of (1x2) and 2/3 of (1x3). Munroe and Merrill have observed distinct domains of (1x3) and (1x2) reconstruction on a (011) surface.¹⁶ This singular surface structure is thought to be the stable, equilibrium surface structure. The LEED pattern is identical after annealing 1 hour at 800°C or 1200°C. The Auger spectrum shows the absence of both carbon and oxygen; Ducros and Merrill¹¹ found that a short anneal at 1100°C removes oxygen from the (011), thus the longer 1200°C anneal employed in our study should remove any traces of oxygen.

Discussion

Many of the vicinal platinum surfaces are quite stable, under some conditions of this study. However, in only six small areas of the stereographic triangle are the platinum surfaces stable in all conditions of our studies (in uhv, with a carbon layer and with adsorbed oxygen). Besides the three low Miller Index surfaces, the (001), (011) and (111),

the highly stepped surfaces midway between the low index planes on the zone lines are also very stable. These planes are the $[3(111)x(100)]$ and $[2(111)x(100)]$ (Miller Indices (112) and (113) respectively) between the (111) and (001) planes, the $[2-3(111)x(111)]$ (Miller Indices (331)-(221)) between the (111) and (011); and the $[2(100)x(100)]$ surface (Miller Index (012)) between the (001) and (011) planes. These conclusions are readily apparent from inspection of Table II, which is a summary of the surface structures of the Pt crystal planes studied.

Some of the other surfaces are stable when clean and in oxygen but not in the presence of a carbon layer; examples are the kinked step surfaces vicinal to the (111). The (111) vicinal surfaces on the zone lines are stable when clean or when covered with carbon, but are unstable in oxygen. There is a trend of decreasing stability away from the low index planes with an abrupt restabilization under all conditions at half-way points on the zone lines. The varying effects of oxygen and carbon on step stability demonstrates the important influence of the local geometry of the step on the nucleation and growth of facet planes.

The data presented in Tables I and II is plotted on stereographic projections in Fig. 9. The area of predominance of each of the three types of surface structures are shown. Surfaces with the stable, monatomic height step structure are dominant on the clean samples and in the six stable regions. Monatomic height steps appear only occasionally on oxygen and carbon covered surfaces. Multiple height steps and multiple width terraces occur vicinal to the (111) in oxygen and between the (011) and (012) in all conditions of the experiment. The "hill and valley" configuration or faceted surfaces occur predominantly on the graphite covered samples. There is a small region of reversible faceting on the

clean [3.5(111)x(100)]. This data shows the remarkable stability of many of the highly stepped surfaces.

Effects of Surface Structure Stability and Instability in Heterogeneous Catalysis

There are two important findings that emerge from our LEED studies of high Miller Index surfaces. 1) There are a few surfaces that are stable under all conditions of our experiments, in uhv and in the presence of adsorbed carbon or oxygen (reducing and oxidizing environments). Some of these surfaces have high step and kink densities [(113), (112), (012), (133), (122)]. 2) Most crystal faces change their surface structures with changing ambients. The surface is restructured in an oxidizing environment and it changes structures again in the presence of hydrocarbons.

Both of these observations have implications to heterogeneous catalysis that is carried out on small metal particles which are dispersed on high surface area supports. 1) The stable surface structures must play important roles in catalytic studies.^{17,1,2} In hydrocarbon catalysis they are likely to be the dominant catalyst surface structures since they retain their stability even after removal of coke (surface carbon) by repeated heating in oxygen. It should be noted that many of these surfaces have high kink density and/or step density. Thus the chemical reactivity associated with these low coordination number surface sites would also be observable.

LEED studies indicate that when the melt of an fcc solid is cooled rapidly the crystallites that grow upon freezing have mostly (001) orientation.¹⁸ On the other hand when the melt is slowly cooled crystallites with (111) orientation surface structures grow on freezing. If the metal

catalyst particles that are produced upon reduction of the platinum salt by hydrogen follow the same trends as observed on crystal growth from the melt, rapid reduction will likely produce the (001) or some other non-minimum free energy surfaces. During thermal annealing of Ir field ion microscope tips, the (012), (113), (112) and (133) surfaces grew and ordered very rapidly compared with the low index planes, (111), (001) and (011).¹⁹ Thus the kinetics of growth of metal particles may cause the stable high Miller Index planes to become the dominant surface planes.

2) Changes of the surface structure of catalyst particles may alter markedly the rate and product distribution in many surface reactions and can lead to "poisoning" of catalytic activity.

The size of metal catalyst particle effects the rate of many catalytic reactions;¹⁷ presumably from a change in the surface structure of the particles with size. Changing support materials (for example, alumina to silica or graphite) while keeping the particle size constant also can cause the specific reaction rates of catalytic reactions to vary,²⁰ again presumably by a change in the stable surface structure. These conclusions are drawn from initial rate data; on many industrial catalysts as the rate decreases over long periods of time, the selectivity to the desired products also changes²¹ indicating a restructuring, or selective carbon deposition possibly with concomitant metal surface destabilization and rearrangement.

Oxygen adsorbed on a surface can effect the rates of reaction two ways, a simple site blockage by adsorption at steps or kinks as observed for the dehydrogenation of cyclohexane² or through a restructuring of the particle shape. Pareja, Amariglio and Amariglio²² found ethylene hydrogenation was promoted on Ni catalysts by traces of O₂. This could produce a small surface coverage of oxygen and cause rearrangement to sur-

face orientations which enhance hydrogenation. Somorjai²³ suggested that S poisoning of a catalyst results from the restructuring of the particle surface. It has been suggested^{24,25} the main effect of alloying metals on the catalytic reaction rate is through a geometrical effect. Selectivity might be increased by site blockage as suggested for Pt-Au and Ir-Au alloys by Hagen and Somorjai,²⁶ or the second component may cause the stabilization of certain planes which are more selective and/or active similar to the effect caused by O_2 .

High temperature oxidation-reduction cycles can disperse large metal particles ($\geq 100 \text{ \AA}$) into small particles ($\leq 20 \text{ \AA}$) on high surface area supports.^{27,28} The addition of small amounts of HCl or Cl_2 (~1%) to the gas speeds the dispersion. The effects of adsorbed Cl were not studied on single crystals, but are possibly greater than the effects caused by adsorbed oxygen because of chlorine's higher electronegativity. Heating Pt in oxygen at around 500°C causes the adsorption of O and the destabilization of most planes. It is well known that metals have much higher surface tensions than their oxides;¹² thus a larger semi-spherical particle of metal could be transformed to a flat platlet structure with only the oxygen stabilized low Miller Index planes exposed. A Pt-Al binary oxide surface monolayer may also form under certain conditions.^{27,29} The subsequent reduction cycle regenerates the semi-spherical particles of the metal, but in smaller size. This is demonstrated schematically in Fig. 10. This has been observed in a transmission electron microscope and by Ruckenstein and Malhotra²⁸ for Pt on an alumina film.

It should be noted that the onset of faceting and other structural rearrangements occurs at high temperatures and in the presence of near

monolayers of carbon or oxygen. At lower temperatures or at lower coverages the surface structure that is stable in one type of chemical environment (in oxygen or in hydrocarbons or in uhv) may be preserved in another chemical environment if the experiments are performed below the transformation temperature or pressure. Milder conditions of chemisorption or chemical reactions (lower temperature or coverage) in a changed atmosphere allows the stabilization of otherwise unstable surface structures for extended periods. Thus, it is entirely possible to carry out surface studies on platinum surfaces exhibiting metastable surface structures under appropriate experimental conditions. We have often been able to study hydrocarbon reactions on crystal surfaces that are stable only in ultrahigh vacuum employing $\sim 10^{-6}$ torr reactant pressures at 200°C.

The Stability of Pt Single Crystal Surfaces in Comparison with Other Studies of Surface Structure and Stability

The structure and stability of Pt single crystals as determined by LEED will now be compared to other studies. The surface structural stabilities found experimentally on Pt and other metals will be reviewed first, then the implications of these results to theories of surface structure will be discussed.

Lang¹⁴ used LEED to determine the stability and structure of four carbon covered single crystal surfaces, the Pt-(111), Pt-(001), Pt(S)-[6(111)x(111)] and Pt(S)-[5(100)x(111)]. His observations on the stability of surfaces are in general agreement with the results presented in this paper. The (111) surface was stable with a large amount of carbon on it. The exact coverage of carbon on their surfaces was not determined from the lack of an Auger spectrometer; however, it is at least as large,

if not larger as that used in this study. The (111) vicinal surface was found to facet to the $[2(111)x(100)]$, $[3(111)x(100)]$, $[3(111)x(111)]$ and (111) surfaces at high carbon coverages. The intermediate facet structure discussed previously (faceting to $[3(111)x(100)]$ and $[9(111)x(100)]$) was not directly observed by Lang,¹⁴ but at his lower carbon coverages streaking was observed in the proper locations. Lang observed the (001) surface to facet at high carbon coverages to the $[2(100)x(111)]$ and $[3(100)x(111)]$, but not uniformly across the single crystal. This faceting was not observed in this work or that of Morgan and Somorjai³⁰ and since it was not uniform across the surface studied by Lang, it may have been caused by the presence of other uncontrolled defects or impurities. The (001) vicinal surface faceted to the $[2(100)x(111)]$ as in this study, but Lang detected facets off the zone line which were not observed in this study on the $[7(100)x(111)]$ surface. The comparison of this work and the work of Lang demonstrate the sensitivity of the surface to the exact conditions of the experiment, surface contamination and the carbon coverage of the surface.

Schmidt and coworkers³¹ found the faceting predicted by this study when they annealed small Pt spheres ($\sim 200\mu$) in an oxidizing atmosphere. The spheres were annealed at 900°C in an atmosphere of oxygen (or NH_3+O_2) and the surface configuration observed by optical microscopy. Large facets of (111), (001) and (011) orientation were observed to grow in agreement with this work.

McLean and Mykura³² measured the surface energy of polycrystalline platinum samples that were annealed in vacuum or in air by a twin boundary groove technique. They did not detect faceting on any vacuum annealed

surfaces, but found extensive faceting after heating in 1 atm of air. Since they employed rather poor vacuum, the vacuum annealed samples were probably contaminated with carbon and/or calcium, thus discrepancies between this study and theirs in detecting faceting is not surprising. They found their oxygen annealed samples more extensively faceted particularly near the (111) plane and the facet planes exposed agree well with those found in this study and that of Schmidt's.³¹ The higher oxygen partial pressure used by Mclean and Mykura³² of 160 torr versus 10^{-6} torr used in our study could be responsible for the more extensive faceting than was found in this study. Similarly more carbon on the surface might destabilize the (111) vicinal kinked step surfaces and cause faceting similar to the behavior of the (111) vicinal straight stepped surfaces.

A comparison of the stability of Pt surfaces as studied by LEED can also be made with other group VIII and IA metals. Bellier and Somorjai³³ studying high Miller Index crystal surfaces of clean gold and after adsorption of oxygen found similar behavior to that of clean and oxidized high Miller Index surfaces of platinum vicinal to the (111) plane. The Au crystals with (001)x(011) type surface structures were stable when clean in contrast to Pt crystal planes with the same surface structures that faceted. Both Au and Pt (001) vicinal surfaces facet in oxygen at elevated temperature. The anisotropy of the surface energy of Au has been studied by Winterbottom and Gjostein³⁴ by the twin boundary groove method. All surfaces were found stable at 1030°C.

LEED studies have not as yet been carried out for most Ir high Miller Index surfaces. However, the relative surface free energies of the lower index faces were measured by field ion microscopy.¹⁹ It was found that

during the thermal annealing process the (012), (113), (112) and (133) iridium surfaces grew and ordered very rapidly compared with the other low index planes, (111), (001) and (011). This has implications in catalysis by small metal particles. If kinetics control the formation of the surface structure, the (012) etc. surfaces might be the dominant planes on a particle instead of the (111) or other lower free energy surfaces.

Low-energy electron diffraction has shown that Cu surfaces³ between the (001) and (011) planes are stable whereas Pt surfaces in this zone are not stable. A kinked step Ni surface vicinal to the (001) plane is stable;⁴ it is not known if the equivalent Pt surface is stable. These metals might be expected to have stable surfaces vicinal to the (001) whereas Pt is not since neither 3d metal reconstructs its (001) plane to lower the surface free energy. This extra lowering of the surface free energy may make clean Pt surfaces facet where Ni and Cu surfaces are stable. McLean³⁵ found that most Cu surfaces are stable and that the $[3(111)x(100)]$ and $[2(111)x(111)]$ planes are highly stable, analogous to what LEED data indicate for Pt in our study.

The relative stability of clean metal surfaces should be theoretically determinable by minimizing the product of the specific free energy of a surface structure and the area. Two types of theories have been used, statistical thermodynamic theories of the equilibrium structure³⁶⁻³⁸ and dynamic theories.^{39,40} The equilibrium theories predict that there are free energy differences between surface orientations. Pairwise additive potential models were shown by Herring³⁶ to produce special circumstances where the steps are non-interactive and the surface would

not facet or anneal. Other statistical thermodynamic models³⁷ have adjustable parameters for the surface energy and surface entropy, describe the surface free energy well close to the low index planes (with 10°), but not at larger angles where planes have a large density of steps. Dynamic models of surfaces show that ordered steps yield stable surface structures, but can easily facet. Schwoebel³⁹ has proposed a model for step motion (and surface stability) which depends on the probability of a step capturing or creating a diffusing atom. The key features are that the probabilities for capture and/or detachment of an atom depend on the direction of approach to the step. Weeks and Jackson⁴⁰ have extended this concept for calculations of crystal growth. These theories are useful, but again are dependent on unknown interaction potential terms. These various models are useful for qualitative descriptions only because of the lack of knowledge of the nature of interactions between steps.

As was shown experimentally, there are attractive interactions between steps that cause their segregation and faceting. Faceting terminates when surfaces are produced often with "two" atoms wide terraces, (112), (012) and (122) and in one case one atom wide, (133). This implies that up to 4th nearest neighbor interactions may be important in determining surface structural stability. (The 4th nearest neighbor in an fcc crystal is at a distance of two atomic diameters, i.e., diagonally across a face of the cubic unit cell.) Inelastic neutron scattering measurements of phonon dispersion curves indicate strong interaction to 4th nearest neighbors on Pt and most other fcc metals (about 10% of nearest neighbor force constant) with possible weak interactions at longer distances.⁴¹ The notion of longer range interactions is not contradicted by field ion

microscope data of Ayrault and Ehrlich⁴² and Tsong⁴³ or by calculations of interactions of adsorbates by Einstein and Schreiffer⁴⁴.

There are many areas of the crystallographic zones of platinum that remain unexplored in our studies and should be investigated. It is also not clear from the existing data if our conclusions concerning the structural stability of clean platinum surfaces can be applied to other face centered cubic metal surfaces. Changes in the platinum surface structure in the presence of adsorbates and the structural transformations as the chemisorbed layer changed from oxygen to carbon reflect the controlling influence of subtle differences in chemical bonding at the various surface sites. The surface structure with lowest free energy, that implies the strongest chemical bonds to the adsorbate, would likely form. Carbon an electron donor and oxygen an electron acceptor form different types of bonds and at different surface sites and induce the observed structural transformations. It would be interesting to learn if other electron donors (for example alkali metals) or electron acceptors (for example halogens) would also cause similar surface structural changes as we have observed in the presence of hydrocarbons and oxygen, respectively.

Acknowledgment

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Table I. Stability of high Miller Index platinum surfaces.

Nominal Surface Structure	Miller Index	Angle from Low Index Pole (°)	Angle from Zone Line (°)	Zone Line	Clean	C-Covered (C-273 eV/Pt-240 eV Auger Peak Ratio = 4)	0 Atmosphere (10 ⁻⁶ torr)
(111) Region							
(111)	(111)	0	0	[110]	Stable melt point	Stable	Stable 1500 ⁺
25(111)x(100)	(12,12,1)	2.2	0	[110]	Stable 1400 ⁺	N.D. ^a	N.D.
9(111)x(100)	(445)	6.2	0	[110]	Stable 1200 ⁺	Stable 1000 ⁺	Streaks-step disorder
6(111)x(100)	(557)	9.6	0	[110]	Stable 1600 ⁺	8.5(111)x(100)-C-ring+(211) 700 ⁺	Streaks-step disorder
3.5(111)x(100)	(55 $\bar{5}$)	17	0	[110]	Stable <900 ⁺ +(533) facet (211)+(533) above 900 ⁺	Facets (211)+(533) with C-ring above 300 ⁺	Stable <1000 ⁺ Facets (211)+(533) above 1000 ⁺
3(111)x(100)	(112)	19.5	0	[110]	Stable	Stable 1000 ⁺ C+	Stable
9(111)x(111)	(799)	6.5	0	[011]	Stable 1400 ⁺	25(111)x8(111)-C 700 ⁺	17(111)x2(111)-0 700 ⁺ C+
6(111)x(111)	(233)	10.0	0	[011]	Stable 1200 ⁺	Facets-(111)+(331),(221)	N.D.
5(111)x(111)	(655)	12.5	0	[011]	Stable 1200 ⁺	N.D.	N.D.
4(111)x(111)	(122)	15.8	0	[011]	Stable 1200 ⁺	Stable 1000 ⁺	Stable 1200 ⁺
3(111)x(111)	(133)	22.0	0	[011]	Stable 1200 ⁺	Stable 1000 ⁺	Stable 1200 ⁺
13(111)x(310)	(69,72,72)	4.2	20 (2 atoms)	[110]	Stable 1600 ⁺	Stable	Stable 1100 ⁺
6(111)x(14,1,0)	(33,34,47)	9.6	5 (8 atoms)	[110]	Stable 1200 ⁺	Saturated 15(111)x2(100)-C-ring 1600 ⁺	Stable 1100 ⁺
7(111)x(210)	(11,12,16)	9.8	13 (3 atoms)	[110]	Stable 1200 ⁺	0.4-0.6 layer C 8.5(111)x(?) -C-ring+(211) 700-900 ⁺ Saturated (111)-C-ring+(211)+(552) 700-900 ⁺	Stable 1100 ⁺
7(111)x(310)	(679)	10.0	20 (2 atoms)	[110]	Stable 1200 ⁺	N.D. -C-ring 900 ⁺	Stable 1100 ⁺
7(111)x(210)	(456)	10.0	33 (1 atom between kinks)	[110]	Stable 1200 ⁺	7(111)x(210)-C-ring 900 ⁺	Stable 1100 ⁺
(100) Region							
(100)	(001)	0	0	[110] [100]	Stable-reconstructed 1600 ⁺ C+	Stable-C-ring	Stable 1500 ⁺
7(100)x(111)	(1,1,15)	6.2	0	[110]	Stable 1100 ⁺	Facets (100)+(311)-C-ring both facets	Facets (001)+(113)
5(100)x(111)	(119)	8.9	0	[110]	Stable 1200 ⁺	Facets (100)+(311)-ordered C 700 ⁺ -1600 ⁺	Facets (001)+(113)
2(100)x(111)	(113)	29.5	0	[110]	Stable	N.D.	(1x2)-0
5(100)x(100)	(015)	11.3	0	[100]	(100)-(5x1)+(210)	Same as clean	Facets (100)-(5x1) and (210)
2(100)x(100)	(012)	26.6	0	[100]	Stable 1200 ⁺	Stable 1000 ⁺	Stable 1200 ⁺
(110) Region							
(110)	(011)	0	0	[011] [100]	Stable-reconstructed 1600 ⁺	N.D.	Stable-reconstructed
5(110)x(100)	(045)	6.3	0	[100]	Stable 1200 ⁺ C+ 8(110)x2(100)	N.D.	N.D.
2(110)x(100)	(012)	18.4	0	[100]	Stable 1200 ⁺	Stable 1000 ⁺	Stable 1200 ⁺
3(110)x(111)	(155)	8.0	0	[011]	Facets (110)+(331),(221)	Same as clean	Facets (110)+(331)-(221)
1(110)x(111)	(133)	13.3	0	[011]	Stable 1200 ⁺	Stable 1000 ⁺	Stable 1200 ⁺

^a No Data

Table II. The stable surface structures of high Miller Index platinum surfaces when clean or covered with a near monolayer of carbon or oxygen. (S-stable with one atom height steps, m-multiple height steps, f-facets)

Miller Index	Nominal One Atom Height Step Structure	Clean		Carbon Covered		Oxygen Covered
(111)	(111)	S		S		S
(12,12,13)	25(111)x(100)	S		No data		No data
(445)	9(111)x(100)	S		S	m	Disorder
(557)	6(111)x(100)	S		15(111)x3(211)	m	Disorder
(559)	3.5(111)x(100)	S below 900°C	f	(111)+(112)	f	(111)+(112)
(112)	3(111)x(100)	S		S		S
(113)	2(111)x(100)	S		S		S
(799)	9(111)x(111)	S	m	25(111)x3(111)	m	17(111)x2(111)
(233)	6(111)x(111)	S	f	(111)+(122),(133)	f	No data
(355)	5(111)x(111)	S		No data	f	(111)+(011)*
(122)	4(111)x(111)	S		S		S
(133)	3(111)x(111)	S		S		S
(69,71,72)	13(111)x(310)	S		S		S
(456)	7(111)x(210)	S		S - ?		S
(679)	7(111)x(310)	S		No data		S
(11,12,16)	7(111)x(710)	S	f	(111)+(112)+(122),(133)	f	S
(33,34,47)	6(111)x(14,1,0)	S	f	15(111)x2(100)+(122),(133)	f	
(001)	(001)	(5x1)		(1x1)+ring		(5x1)
(1,1,13)	7(100)x(111)	S	f	(001)-(5x1)+(113)	f	(001)-(5x1)+(113)
(119)	5(100)x(111)	S	f	(001)-(5x1)+(113)	f	(001)-(5x1)+(113)
(015)	5(100)x(100)	f (001)-(5x1)+(012)	f	(001)-(5x1)+(012)	f	(001)-(5x1)+(012)
(012)	2(100)x(100)	S		S		S
(011)	(011)	(1x2)		S		S
(045)	5(110)x(100)	m 8(110)x2(100)		No data		No data
(155)	3(110)x(111)	f (011)+(122),(133)	f	(011)+(122),(133)	f	(011)+(122),(133)

* Ca + O covered

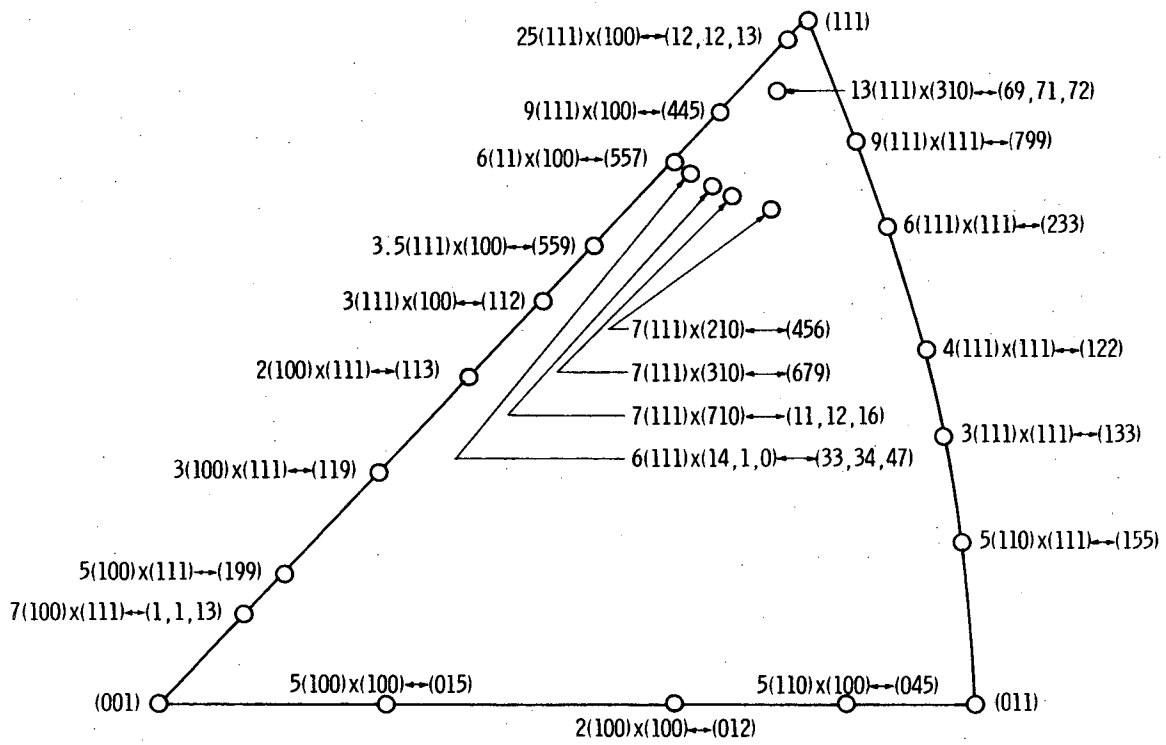
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-25b-

Figure Captions

1. Stereographic projection showing the crystallographic orientation of the Pt single crystal faces studied.
2. Three structural types of surface topology. a) Monatomic height steps where the surface structure is noted as $[5(hkl) \times 1(h'k'l')]$; b) Multiple height step surface, $[8(hkl) \times 2(h''k''l'')]$, in this case; and c) Hill and valley structure where n, m are large. Values of $m \leq 50$ can sometimes be resolved into multiple height steps.
3. Photographs of the LEED patterns from the clean surface of the (a) Pt(S)- $[6(111) \times (100)]$; (b) Pt(S)- $[7(111) \times (310)]$; (c) Pt(S)- $[9(111) \times (100)]$ and (d) Pt(S)- $[3.5(111) \times (100)]$ stepped surfaces.
4. Photographs of the LEED patterns from the clean surface of the (a) Pt(S)- $[7(111) \times (111)]$; (b) Pt(S)- $[7(111) \times (210)]$ and (c) Pt(S)- $[13(111) \times (310)]$ stepped surfaces.
5. Photographs of the LEED patterns from the clean surface of the (a) Pt-(111); (b) Pt(S)- $[9(111) \times (111)]$ and (c) Pt(S)- $[6(111) \times (111)]$ surfaces.
6. Photographs of the LEED patterns from the clean surface of the (a) Pt-(001); (b) Pt(S)- $[75(100) \times 25(210)]$; (c) Pt(S)- $[5(100) \times (111)]$ and (d) Pt(S)- $[7(100) \times (111)]$ surfaces.
7. Photographs of the LEED patterns from the clean surface of the (a) Pt(S)- $[8(110) \times (100)]$ and (b) Pt(S)- $[3(110) \times (111)]$ -facet and stepped surfaces.
8. Stereographic projection unit triangles indicating regions of stability in monatomic height steps, regions where reversible faceting occurs, regions where multiple height steps are stable, and regions where

- steps are unstable and a hill and valley structure forms for (a) the clean Pt surfaces (b) Pt surfaces heated in an oxygen ambient and (c) Pt surfaces covered with a monolayer of graphitic carbon.
9. Schematic diagram of possible mechanism for dispersion of a metal by oxidation-reduction cycles. The observed faceting in oxygen could cause the flattening of the metal particles. Subsequent reduction would break the oxide layer up into smaller particles.



XBL 7612-10983

Fig. 1

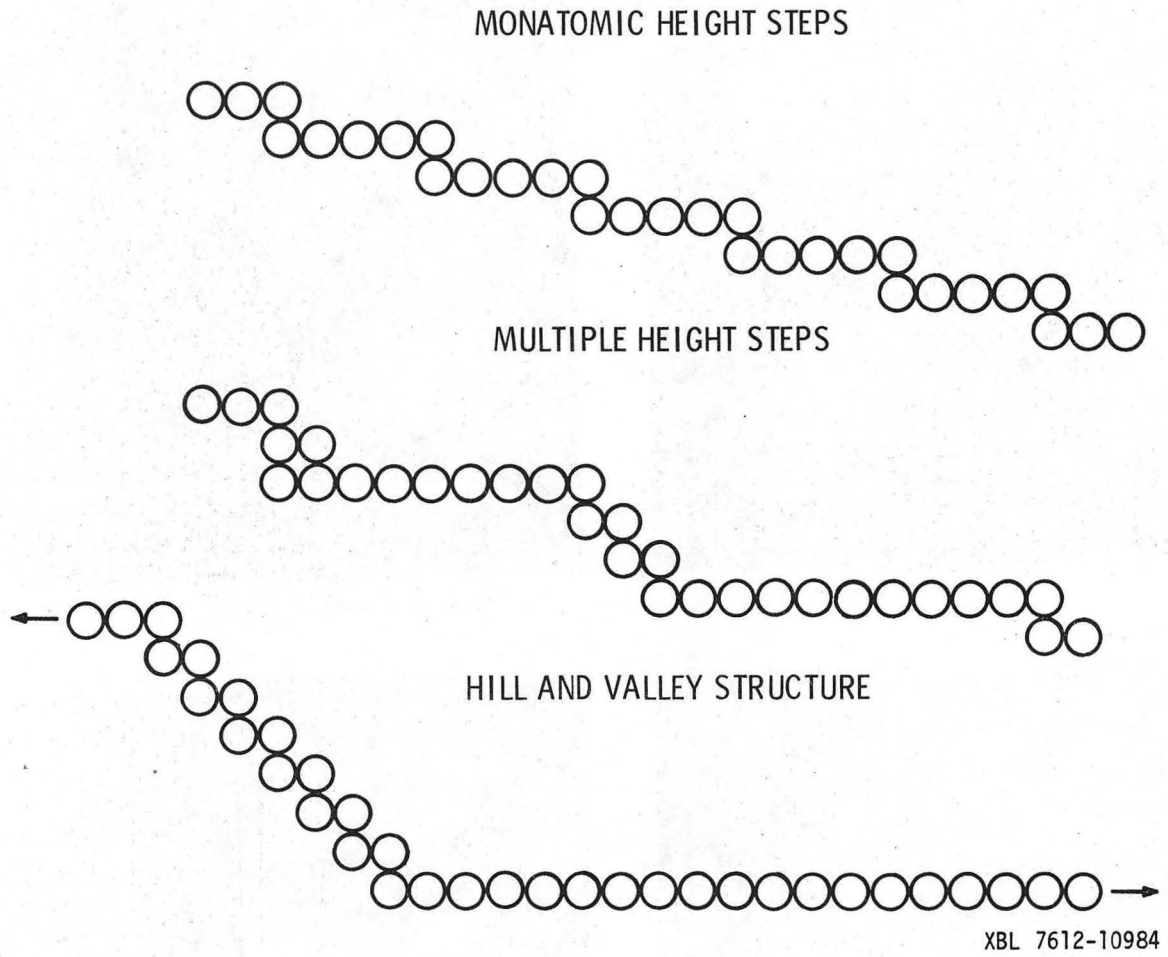
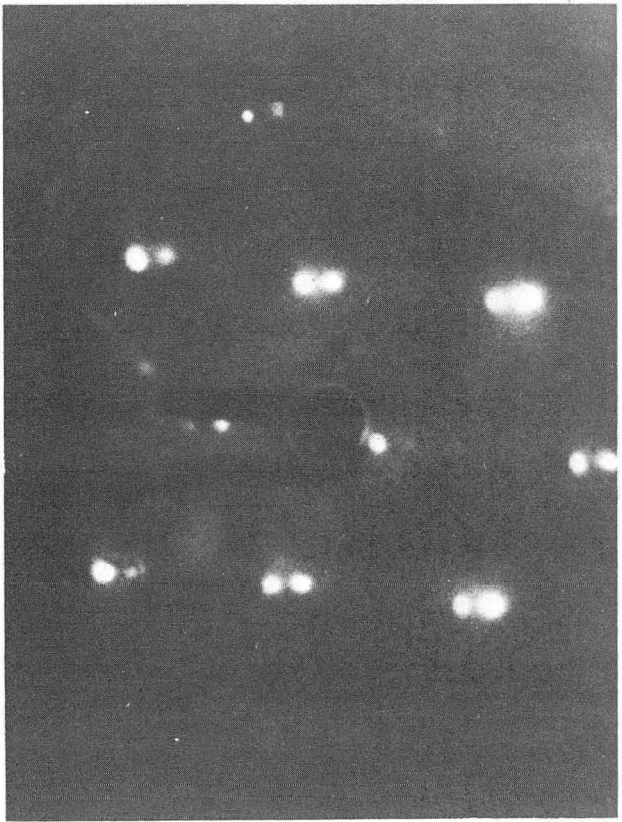
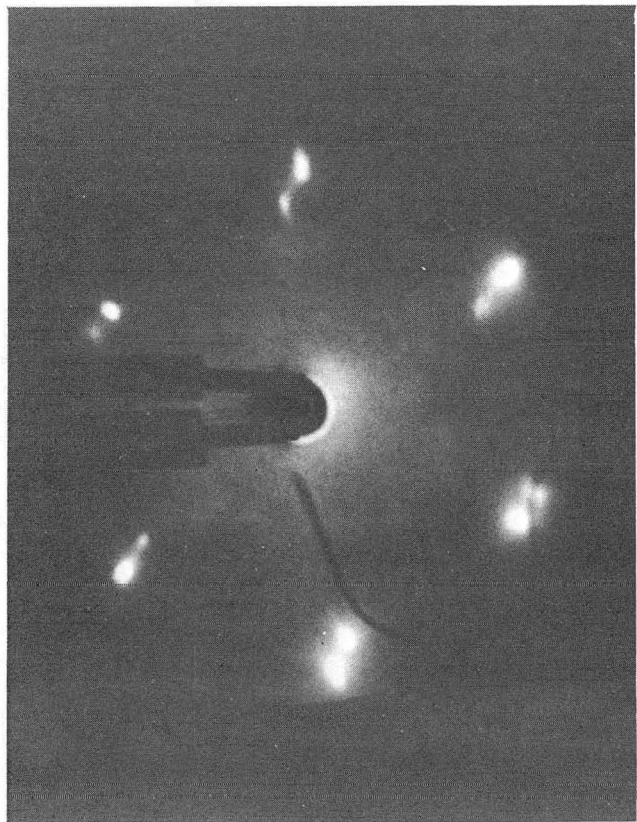
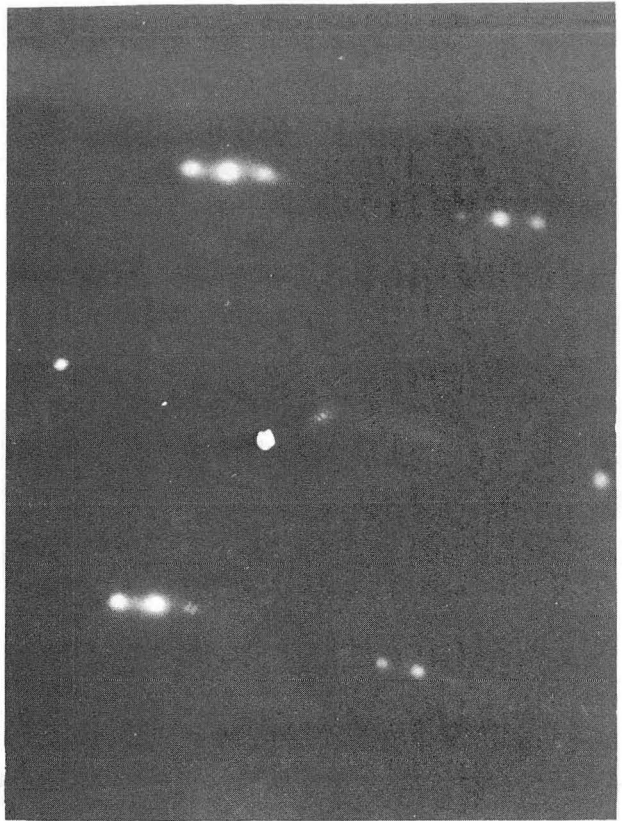
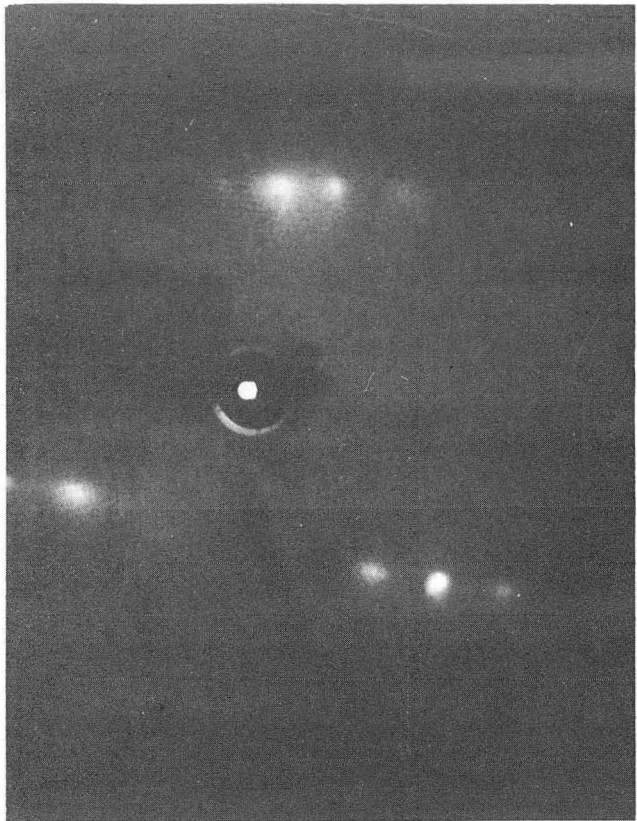
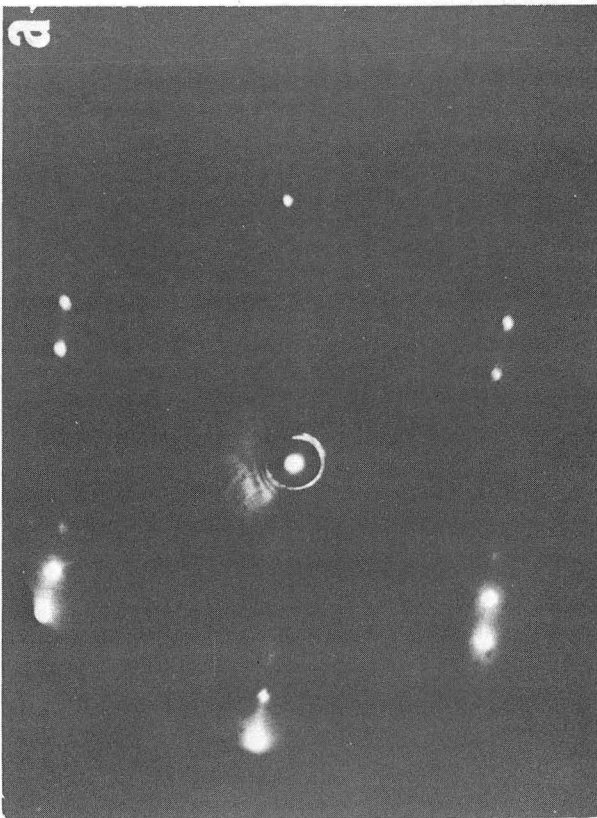
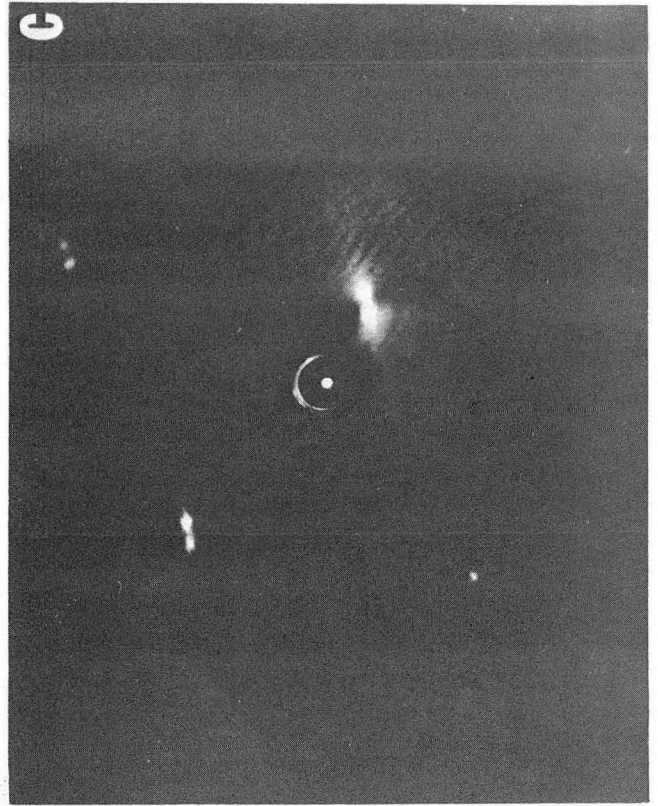


Fig. 2



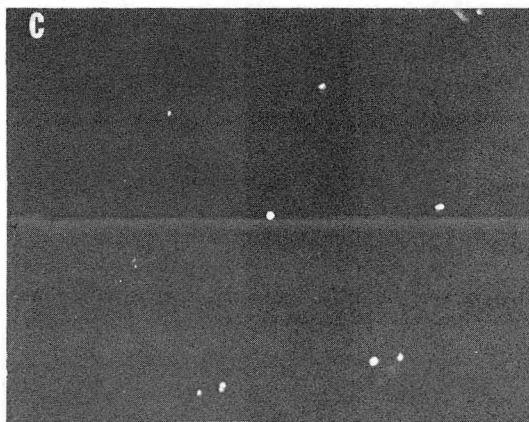
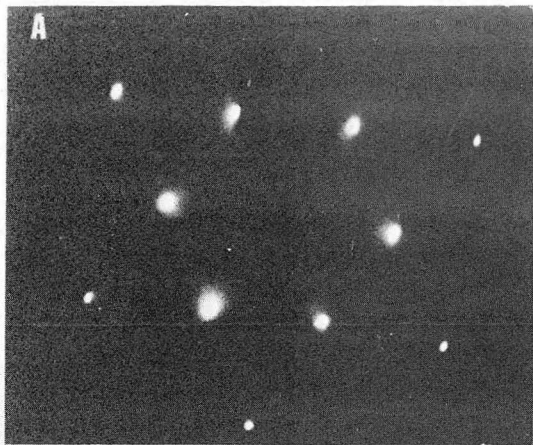
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Fig. 3



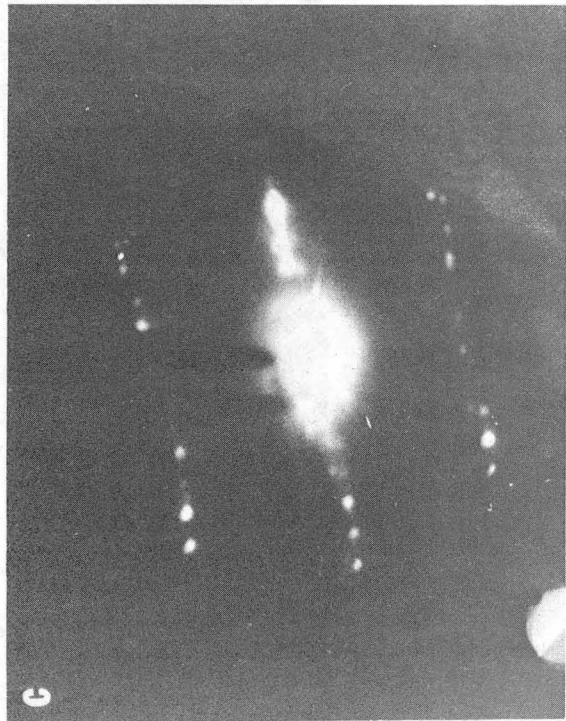
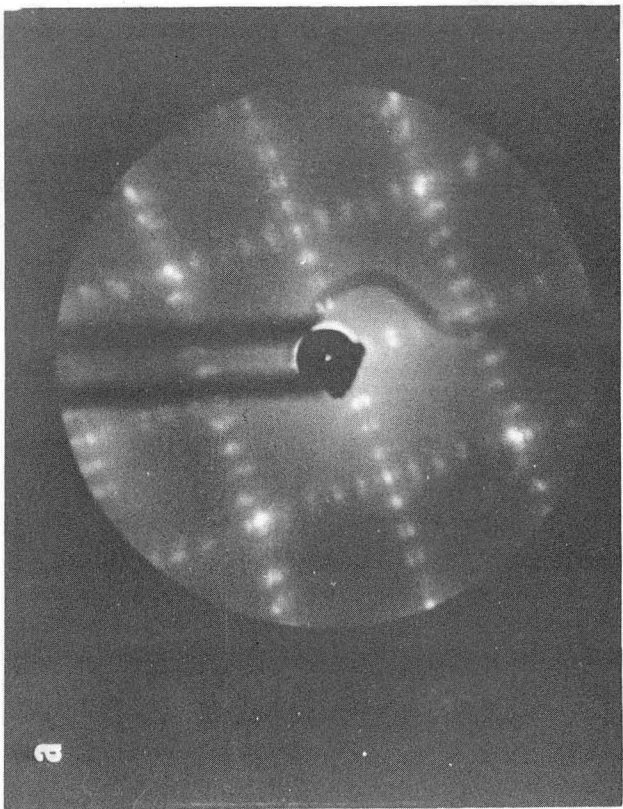
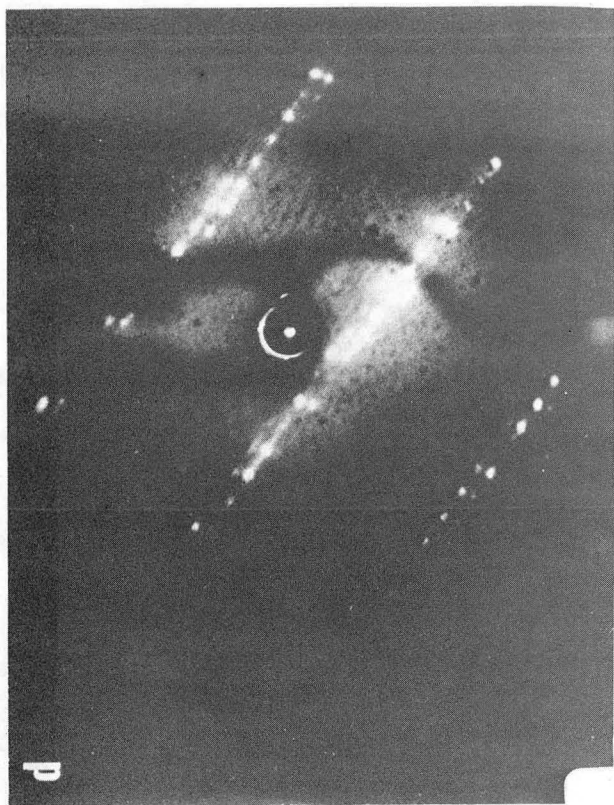
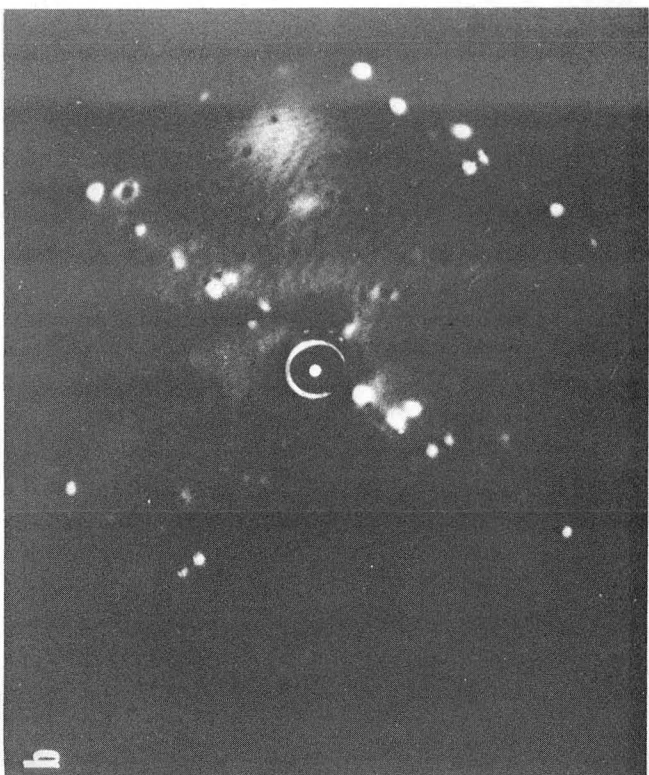
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Fig. 4



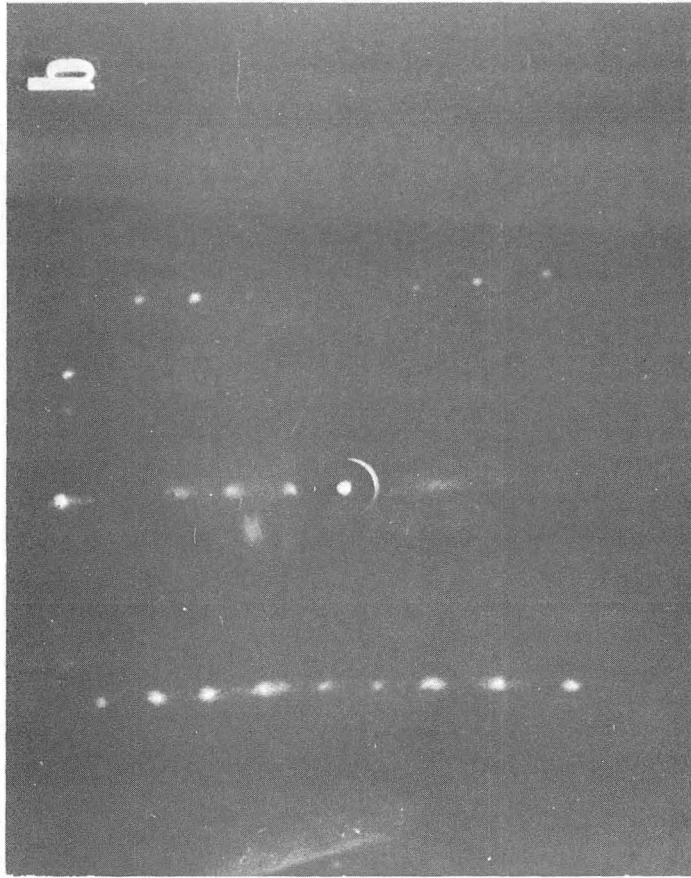
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Fig. 5



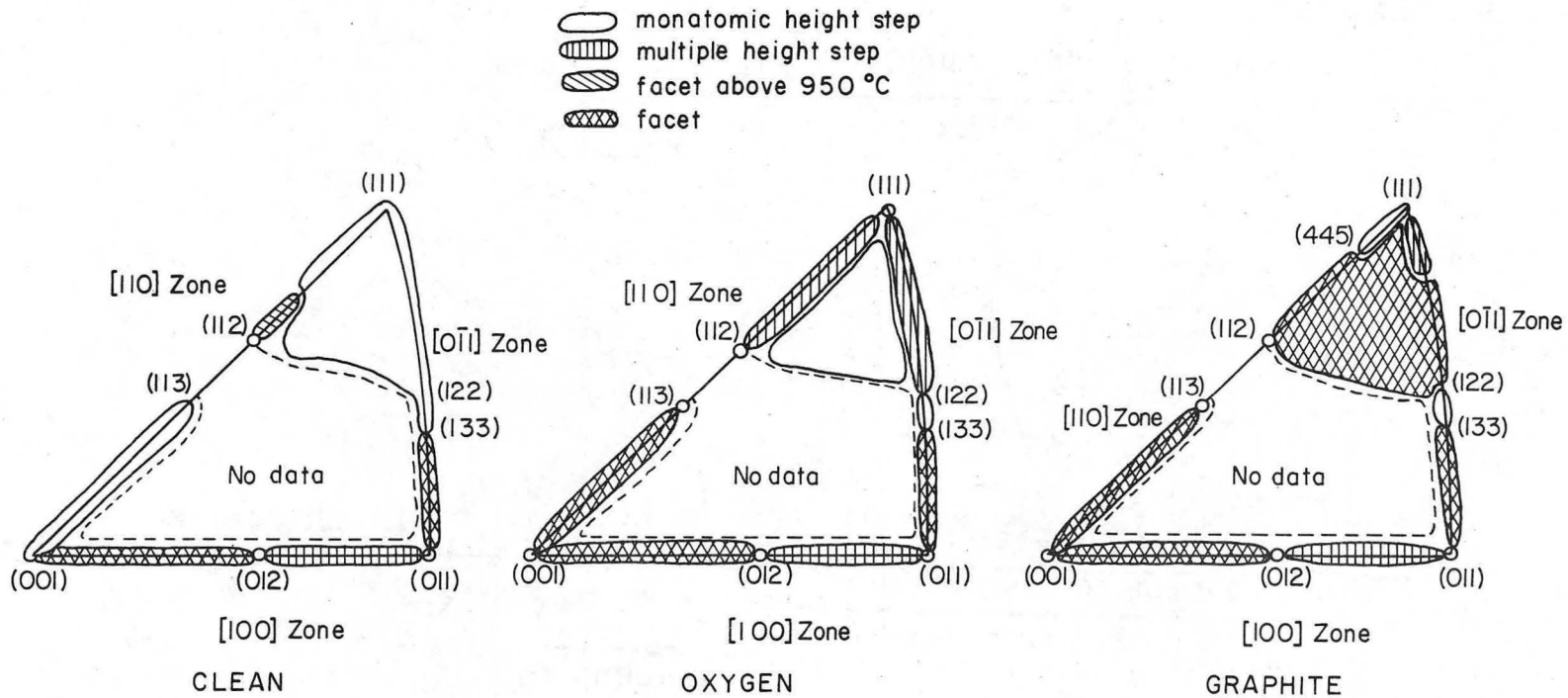
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Fig. 6



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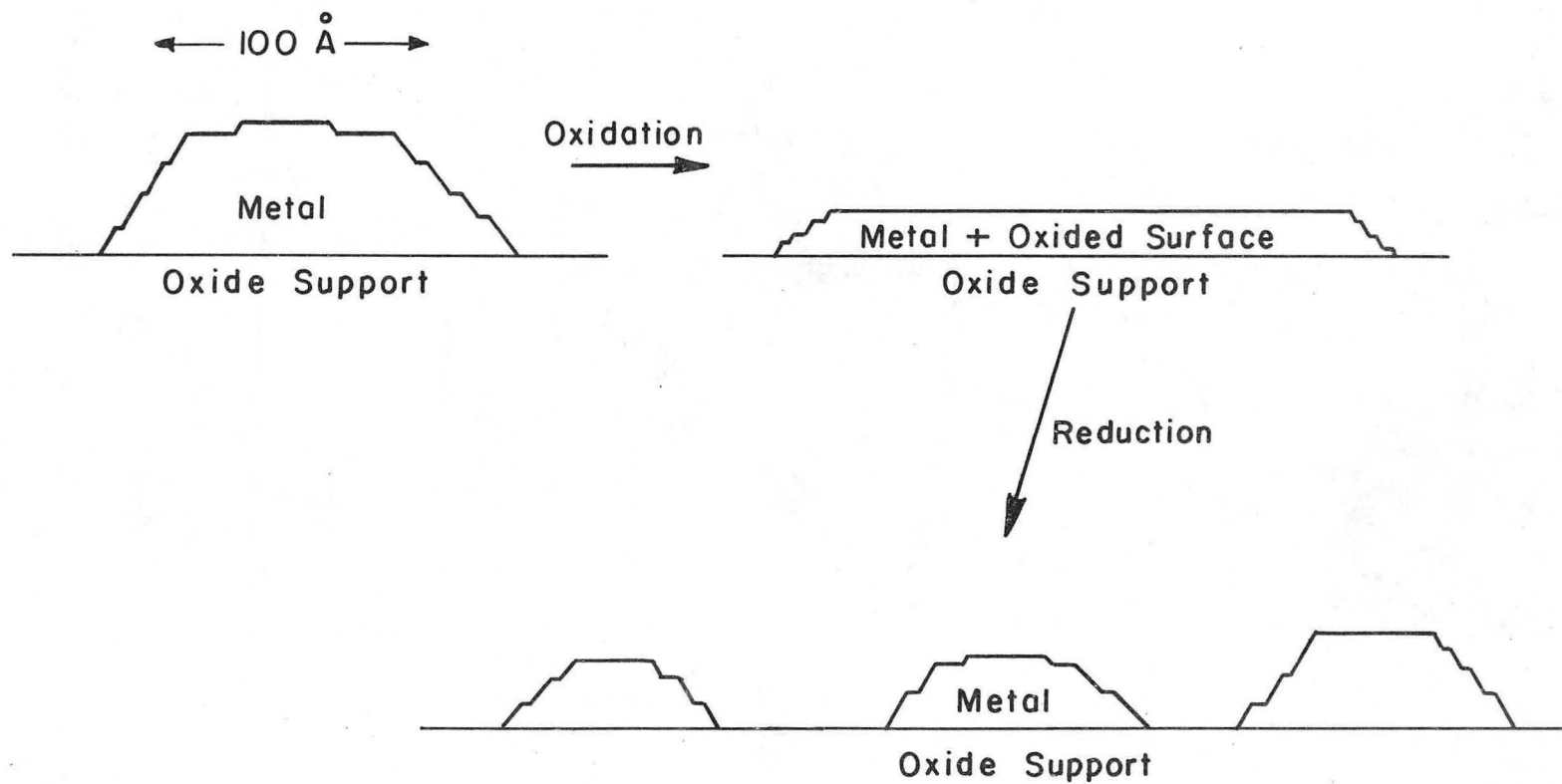
Fig. 7



XBL 763- 6633

Fig. 8

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XBL 7 63- 6 634A

Fig. 9

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