

# Lawrence Berkeley National Laboratory

## Recent Work

### **Title**

THE APPLICATION OF LOW ENERGY ELECTRON DIFFRACTION IN CONTACT CATALYTIC REACTIONS

### **Permalink**

<https://escholarship.org/uc/item/395726dp>

### **Author**

Somorjai, G.A.

### **Publication Date**

1975-05-01

To be published as a Chapter in  
'Enciclopedia della Scienza e della  
Technica,' 1976 edition, ~~Mondadori~~  
Publishing Company *Mondadori*

LBL-3920

c. |

THE APPLICATION OF LOW ENERGY ELECTRON  
DIFFRACTION IN CONTACT CATALYTIC REACTIONS

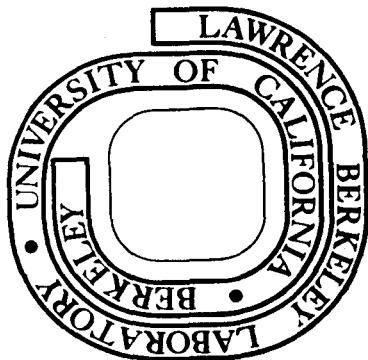
G. A. Somorjai

May 1975

Prepared for the U. S. Energy Research and  
Development Administration under Contract W-7405-ENG-48

**For Reference**

Not to be taken from this room



LBL-3920

c. |

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.



On platinum the complex dehydrocyclization reaction can occur at sufficiently high rates to produce aromatic molecules in large quantities. This is one reason for the widespread use of platinum as a "reforming" catalyst in the petroleum industry. The aromatic molecules have high "octane numbers" while the straight chain aliphatic molecules such as n-heptane have octane numbers near zero.

What does the atomic structure of the metal surface where catalysis takes place look like? Where are the surface sites where the selective breaking of the H-H, C-H, and C-C bonds occur? How does the complex rearrangement that accompanies dehydrocyclization take place on a metal surface? Answers to these fundamental problems that are being probed are emerging from studies of catalytic reactions carried out on single crystal surfaces.

A scheme of a metal surface is displayed in Figure 1. We can distinguish various surface sites where atoms have different number of nearest neighbors. There are atoms in steps, there are kinks in the steps. Atoms are present in large numbers in the well-ordered terraces where they are surrounded by the largest number of nearest neighbors. There are atoms diffusing along the terrace called adatoms, which have the smallest number of nearest neighbors. There are atomic vacancies in the terrace. There are experimental evidences for the presence of all of these different surface sites that come mostly from low-energy electron diffraction (LEED) and field ion microscopy studies. These techniques will not be discussed here but they are described in detail in other publications.<sup>1,2</sup>

Using single crystal surfaces, the atomic surface structures can be prepared in such a way that a large concentration of the desired atomic steps or kinks are present. This is carried out by cutting the high purity perfect single crystals at certain angles to obtain surfaces with large Miller Index.<sup>3</sup> Surfaces where 20 - 30% of all atoms are located in steps have been prepared. Conversely, surfaces with very low density of irregularities (steps, kinks) have also been prepared by cutting single crystals along surfaces of low Miller Index.

By studying the catalytic activity of these crystal surfaces that were prepared with well-defined atomic surface structure, the relationship between the atomic structure and the reactivity can be explored.

Let us restrict our discussion to platinum that will serve as a model to introduce the atomic structure of the various types of surfaces that are important in catalysis and to describe the fundamental steps of important catalytic reactions.

#### The Atomic Surface Structure of Platinum

The figure below shows the diffraction pattern obtained from the clean (111) crystal face of platinum by low-energy electron diffraction at four different electron energies. The symmetry of the pattern and the distance between diffraction spots yields the size of the surface unit cell and its orientation. Figure 3 shows the intensity of one of the diffraction beams as it varies with electron energy. These intensities can be monitored for all of the diffracted beams and displayed similarly as in Figure 3. The I vs eV curves can also be computed using a scattering model in which the only adjustable parameters are the positions of the surface atoms. These calculations have been carried out for the

Pt(111) surfaces<sup>4</sup> and the results that give the best agreement between calculated and experimentally determined intensities are also displayed in Figure 3. The best agreement is reached if the surface platinum atoms are placed in equilibrium positions that are predicted from the bulk X-ray unit cell. Similar surface crystallography calculations for other metal surfaces show the atoms in the first layer are often nearer to the second layer than predicted by the projection of the X-ray unit cell.<sup>5</sup> Such restructuring in the surface is the consequence of the anisotropic environment about surface atoms and their lower coordination number when compared with atoms in the bulk. Sometimes the surface atoms occupy entirely new sites in the surface that leads to the appearance of a very different surface unit cell that cannot be predicted from the X-ray unit cell. This happens in the clean (100) face of platinum where the surface atoms are located in a close packed hexagonal arrangement instead of the expected square unit cell that is the result of atoms moving slightly out of place to new equilibrium positions.<sup>5</sup> The diffraction pattern and the scheme of the (100) surface structure is shown in Figure 4.

High Miller Index surfaces are obtained by cutting the crystal at some small angle with respect to a low Miller Index surface.<sup>6</sup> For example, a surface that is cut at  $9.5^\circ$  away from the (111) face in the direction of the (100) face has a Miller Index of (775). The LEED pattern that is obtained from this surface and the schematic diagram of its surface structure are shown in Figure 5. At certain electron energies the diffraction beams split into doublets or triplets indicating the appearance of a new periodicity on the surface. Otherwise the diffraction pattern is similar to that for a (111) crystal face. Analysis

of the pattern indicates that the (775) face is a stepped surface; it has a periodic step structure with steps of one atom height. These steps are separated by terraces of (111) orientation which are, on the average, 6 atoms wide. By cutting the crystal at a steeper angle ( $14^\circ$ ) with respect to the (111) face, a surface with a higher concentration of steps and shorter terraces results. (Figure 6a) The (976) Miller Index face is cut at  $9.5^\circ$  from the (111) crystal face and rotated  $20^\circ$  in the direction of the (310) face. This crystal face is characterized by steps of high Miller Index. The second step must have a large concentration of kinks as shown by its surface structure in Figure 6b. Since the Miller Index does not reveal the real atomic surface structure, a new nomenclature has been devised. The (775) orientation is called the Pt (S)-[6(111) x (100)] surface. Thus, this stepped (S) surface has six atom wide terraces of (111) orientation separated by steps of one atom in height and of (100) orientation. The various surface structures are identified by this nomenclature in Figures 5 and 6.

By cutting the platinum crystal in different directions, a very large number of stepped surfaces can be created. Their study revealed that most of them that are composed of steps and terraces of (111) and (100) orientation are remarkably stable and remain ordered under heat treatment to above  $1000^\circ\text{C}$ .<sup>3,6</sup> Thus these surfaces must play important roles in most catalytic surface reactions since these are commonly carried out in the temperature ranges of  $150 - 400^\circ\text{C}$ .

#### The Structure of Adsorbates on Platinum Surfaces

Adsorption of hydrocarbons on the Pt(111) or (100) crystal face often results in the formation of ordered surface structures of the



adsorbates. Figure 7a shows the ordered surface structure of acetylene. It has a surface unit cell that is twice as large as the platinum unit cell and parallel to it. This is called a (2 x 2) surface structure. Benzene yields a more complex diffraction pattern that is shown in Figure 7b. Studies of a large group of hydrocarbons<sup>7,8</sup> indicate that these molecules remain largely intact on the (111) and (100) crystal faces. They do not decompose unless heated to about 200°C so that their surface crystallography can readily be studied. On heating to higher temperatures ( ~ 600 - 800°C) a diffraction pattern is observed (Figure 8) that can be identified as due to ordered domains of graphite that show rotational randomness that gives rise to the ring-like diffraction features.

Organic adsorbates behave in an entirely different manner when adsorbed on stepped surfaces. The adsorbate layer remains disordered and hydrogen evolution indicates rapid decomposition of the molecules.<sup>6</sup> Under certain experimental conditions and depending on the stepped platinum surface structure, the disordered carbonaceous layer becomes ordered. One of these ordered structures is shown in Figure 9. This carbonaceous deposit, ordered or disordered, plays important roles in many catalytic surface reactions.

#### Catalytic Reactions on the Various Platinum Crystal Surfaces

Recent studies indicate that complex chemical surface reactions of low reaction probabilities can readily be studied on one face of a crystal of surface area of about 1 cm<sup>2</sup>.<sup>9</sup> At low pressures (10<sup>-6</sup> - 10<sup>-4</sup> Torr) the reactant and product distributions are monitored by mass spectrometry;<sup>10</sup> while at high pressures (atmospheres), by gas chromatography.<sup>11</sup> Catalytic

reactions ranging from the exchange of  $H_2 + D_2$  to form HD to the dehydrogenation of cyclohexane and the rearrangements of n-heptane have been studied in this way. It was found that the reaction probability of forming HD at low pressure on stepped surfaces was of the order of  $10^{-1}$  while as low as  $10^{-4}$  on the (111) crystal face and hardly detectable.<sup>12</sup> It is clear that atomic steps play a controlling role in breaking the H-H bond that is the prerequisite to forming HD. Similarly, atomic steps are necessary to break C-H bonds efficiently that take place during the conversion of cyclohexane ( $C_6H_{12}$ ) to benzene ( $C_6H_6$ ). On platinum crystal surfaces that have large concentrations of kinks, hydrogenolysis reactions that are the result of C-C bond breaking processes also occur efficiently. In studies of hydrocarbon reactions on platinum crystal surfaces where several reaction paths are possible, microstructures on the surfaces have been identified where C-C bond breaking also occurs in addition to C-H and H-H bond breaking processes.<sup>13</sup> At other microstructures only C-H and H-H bond breaking processes predominate. It appears that surface irregularities or various surface sites with different coordination numbers have different and distinct chemical activity. Curiously gold, a neighbor of platinum, does not show such a structure sensitive reactivity as platinum does.<sup>14</sup> It appears that transition metals with unfilled d-orbitals (and high electron density of states) are the group that exhibit multifunctional reactivity behavior that is controlled by detailed atomic structure of the heterogeneous surface.<sup>15</sup> By preparing transition metal surfaces with controlled concentration and configurations of atomic steps and kinks, the reaction rate as well as the reaction specificity may also be controlled.

n-Heptane may react along several reaction paths on platinum surfaces as shown above, and these various reactions have been studied as a function of the atomic surface structure of platinum. Rates of hydrogenolysis and isomerization reactions have not varied markedly (less than a factor of 10) from crystal face to crystal face, but the product distributions were a strong function of the atomic structures. The rate of formation of toluene, on the other hand, may vary by a factor of 100 from crystal face to crystal face. It was found that shortly after the beginning of the reaction the surface became covered with an overlayer of carbonaceous deposit that was either disordered or ordered depending on the conditions of the experiment and on the platinum surface structure. The high initial rates were reduced somewhat as the carbonaceous residue formed but the surface was not poisoned by the formation of this deposit. Whether the reaction was carried out either at low or at high pressure, the catalyst surface was always largely covered by the carbonaceous overlayer. The model of the platinum surface that yields steady state rates and product distributions during the catalysis of hydrocarbon reactions is shown below. (Figure 10) Islands of platinum atoms perform the various C-C, C-H, and H-H bond breaking functions and perhaps some of the molecular rearrangements. Then the specie breaks away from the metal atoms, diffuse onto the terrace where further rearrangements may occur, followed by desorption of the product molecule.

Other important catalytic reactions such as the nitrogen fixation that requires  $N\equiv N$  bond breaking or the reaction of CO with  $H_2$  that necessitates C=O and H-H bond breaking are being studied. Similar studies on other metal surfaces will certainly lead to a molecular level

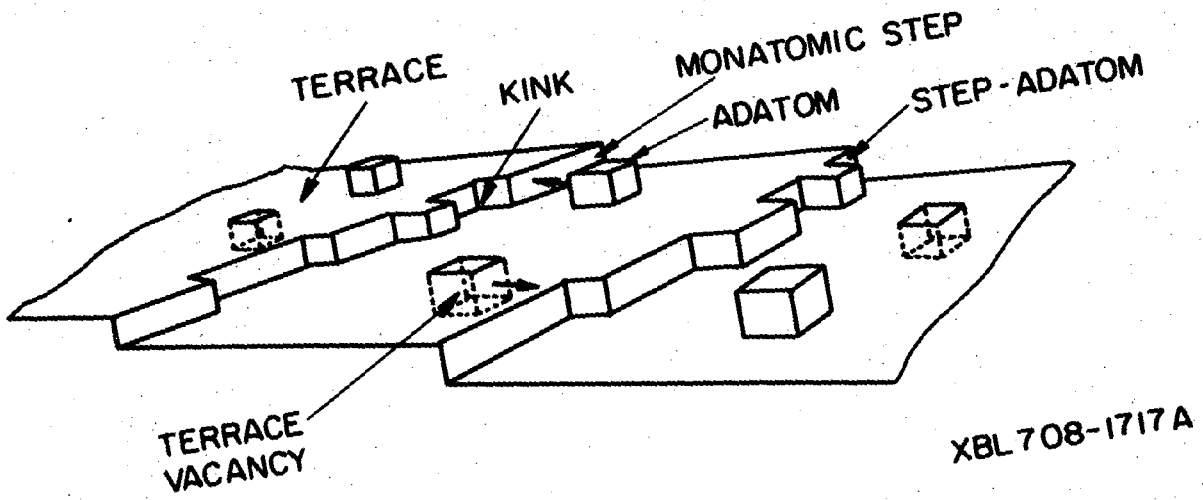
understanding of the elementary steps of heterogeneous catalysis, adsorption, surface diffusion, bond breaking rearrangement and desorption. The understanding of catalytic surface reactions on the atomic scale, uncovering the relationship between atomic structure and reactivity, is the foundation of catalysis science that attempts to develop more selective, more poison resistant, and more efficient catalysts.

REFERENCES

1. G. A. Somorjai. Principles of Surface Chemistry. (Prentice-Hall, 1972).
2. E. W. Muller and T. T. Tsong. Field Ion Microscopy. (American Elsevier Co. Inc, 1969).
3. B. Lang, R. W. Joyner and G. A. Somorjai, *Surface Sci.*, 30, 440 (1972).
4. L. L. Kesmodel and G. A. Somorjai, *Phys. Rev. B.*, 11, 630 (1975).
5. L. L. Kesmodel and G. A. Somorjai, *MTP International Review of Science* (To be published 1975).
6. K. Baron, D. Blakely and G. A. Somorjai, *Surface Sci.*, 41, 45 (1974).
7. J. Gland and G. A. Somorjai, *Surface Sci.*, 38, 157 (1973).
8. J. Gland and G. A. Somorjai, *Surface Sci.*, 41, 387 (1974).
9. G. A. Somorjai, *Catalysis Rev.*, 7, 87 (1972).
10. B. Lang, R. W. Joyner and G. A. Somorjai, *J. of Catalysis*, 27, 405 (1972).
11. D. R. Kahn, E. E. Petersen and G. A. Somorjai, *J. of Catalysis*, 34, 294 (1974).
12. S. L. Bernasek, and G. A. Somorjai, *J. Chem. Phys.*, 62, 3149 (1975).
13. G. A. Somorjai, *Proc. of the Battelle Cong. on Heterogeneous Catalysis* (To be published 1975).
14. M. A. Chesters and G. A. Somorjai, *Surface Sci.* (To be published 1975).
15. L. L. Kesmodel and L. M. Falicov, *Solid State Comm.* (To be published 1975).

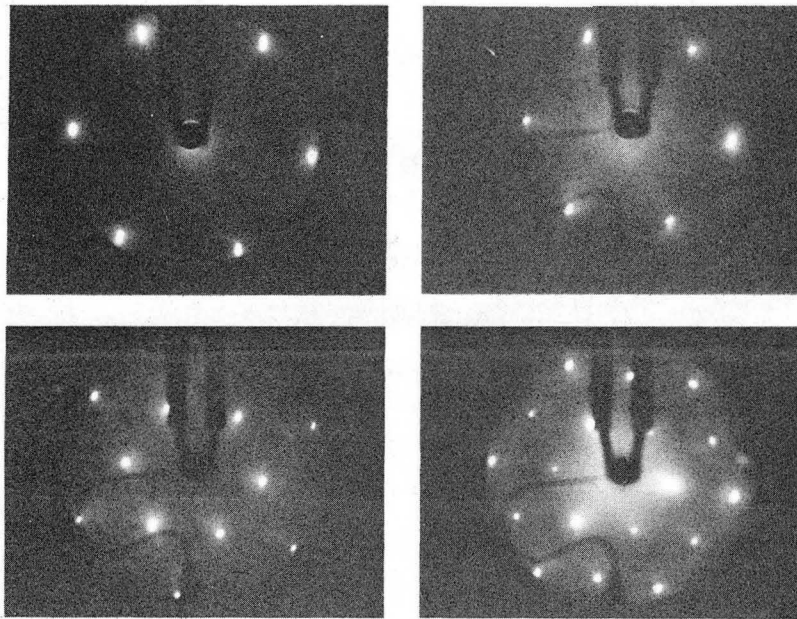
## FIGURE CAPTIONS

- 1) Model of the heterogeneous surface depicting the different surface sites: terrace, kink, step, vacancy, step-adatom, and adatom.
- 2) Diffraction pattern of the (111) face of platinum single crystal at four different incident electron beam energies: (a) 51 volts; (b) 63.5 volts; (c) 160 volts; (d) 181 volts.
- 3) I vs eV curve of Pt(111) and scheme of the (111) crystal face.
- 4) Pt(100) and scheme of the (100) crystal face.
- 5) Diffraction pattern and schematic representation of the Pt(S)-[6(111)x(100)] stepped surface.
- 6a) Diffraction pattern and schematic representation of the Pt(S)-[4(111)x(100)] stepped surface.
- 6b) Diffraction pattern and schematic representation of the Pt(S)-[7(111)x(100)] stepped surface.
- 7a) The diffraction pattern resulting from acetylene adsorption on the Pt(111) surface at 20°C showing also the first order Pt diffraction features.
- 7b) Diffraction pattern due to adsorbed benzene on the Pt(111) surface.
- 8) Segmented ring pattern due to graphite carbon on the Pt(111) surface.
- 9) Diffraction pattern due to ordered carbonaceous overlayer on the stepped platinum surface.
- 10) Scheme of the catalytic platinum surface structure with a deposit of carbonaceous overlayer and islands of platinum clusters due to atoms in steps and kinks.



XBL 708-1717 A

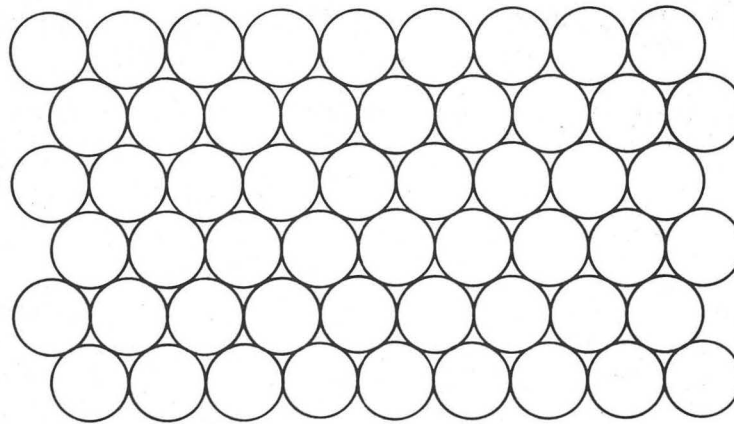
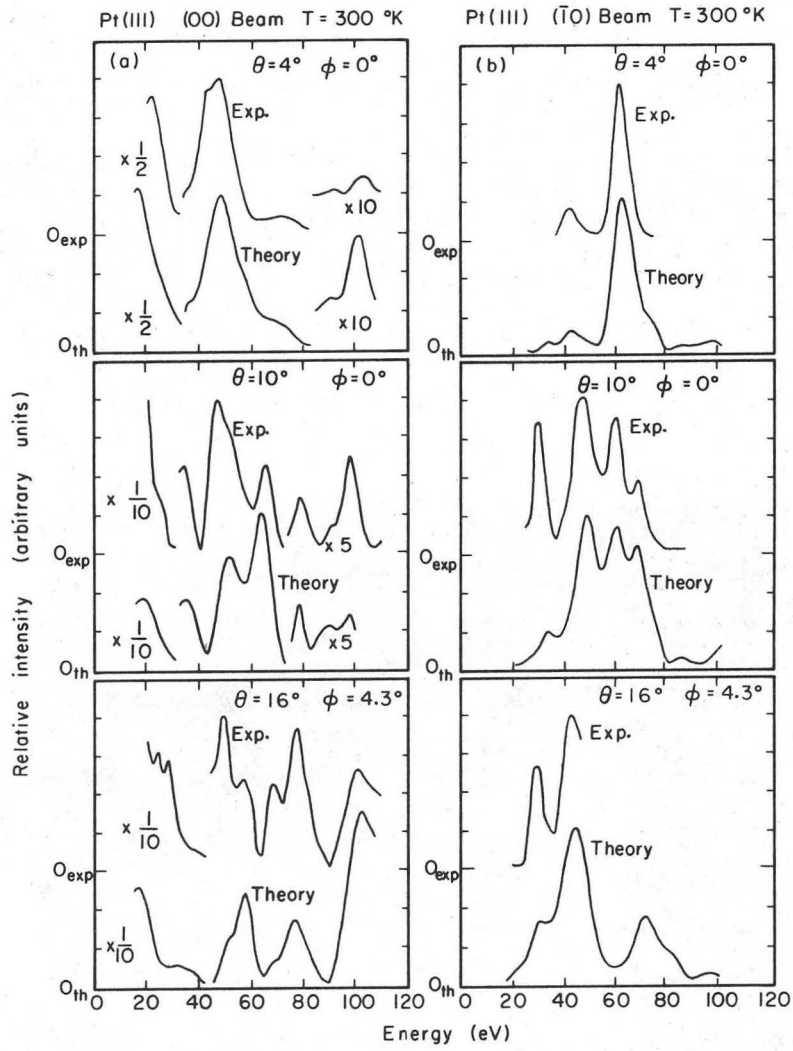
Fig. 1.



XBB 7012-5685

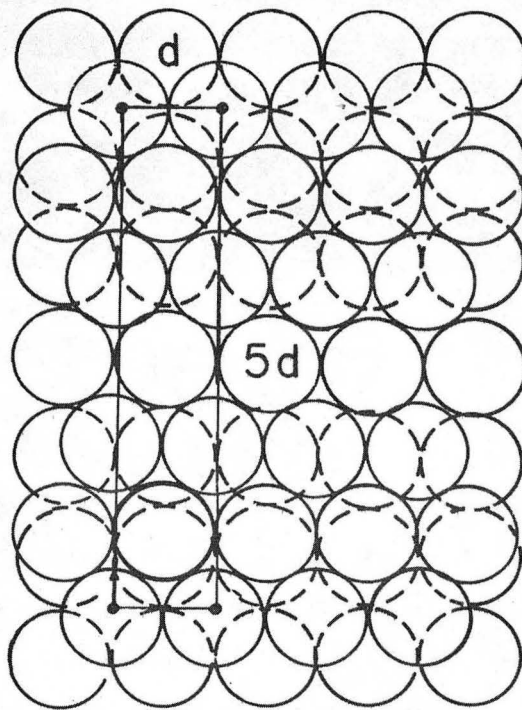
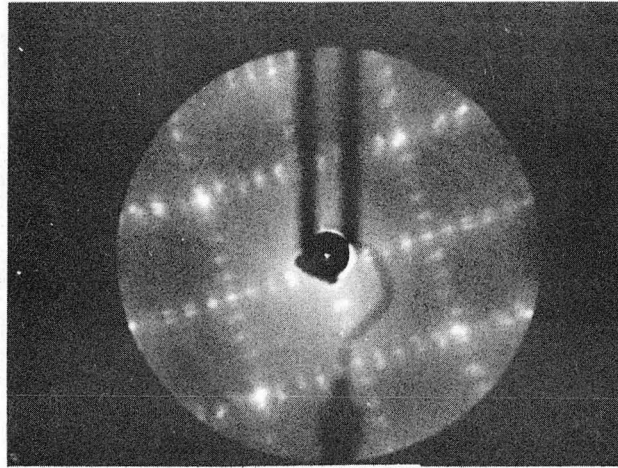
Fig. 2.





XBL 755-6271

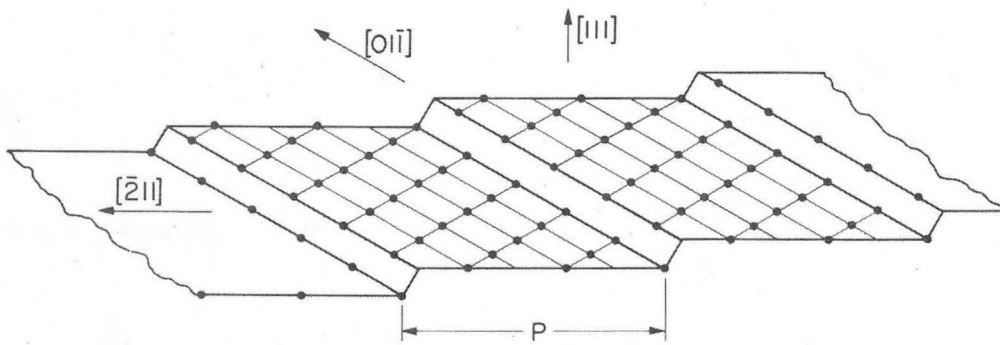
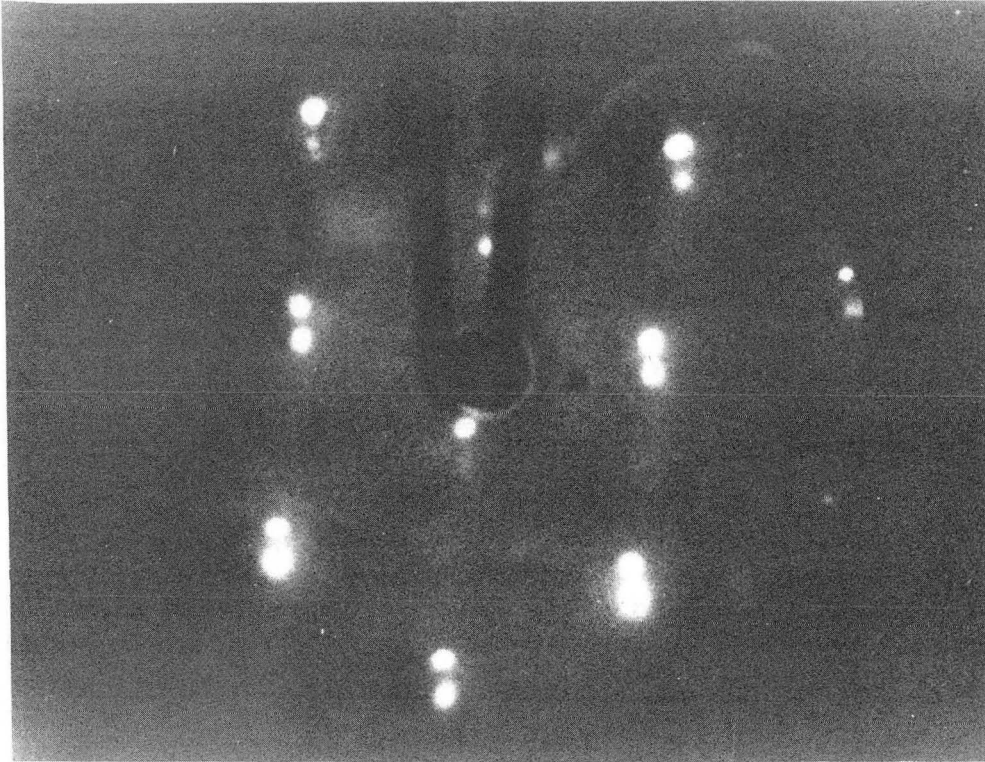
Fig. 3.



Reconstructed layer

XBB 755-3761

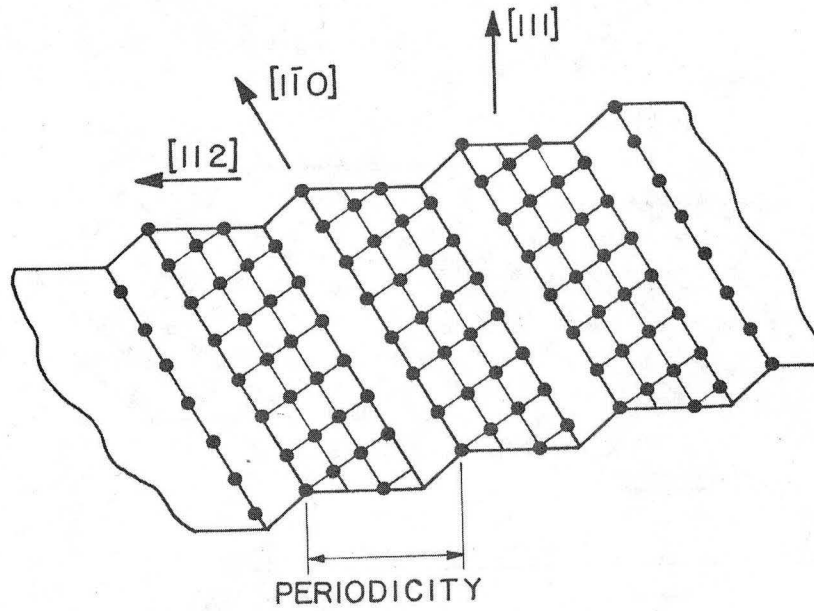
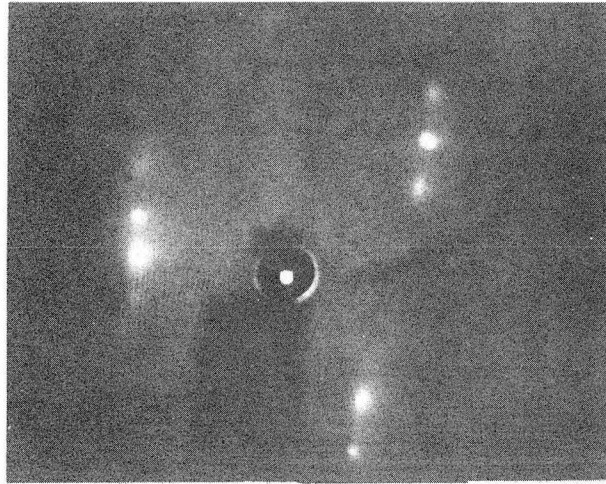
Fig. 4.



XBB 733-2083

Fig. 5.

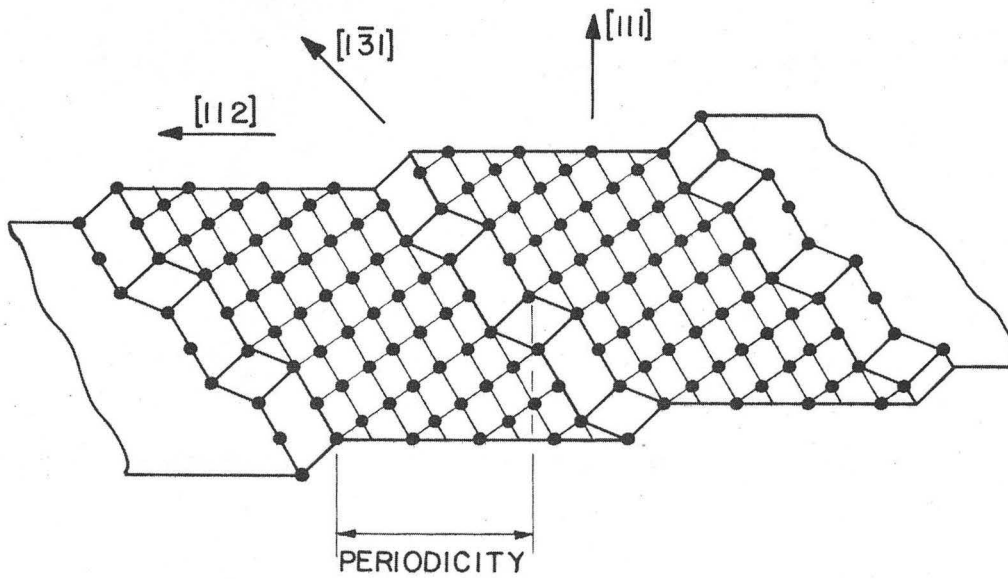
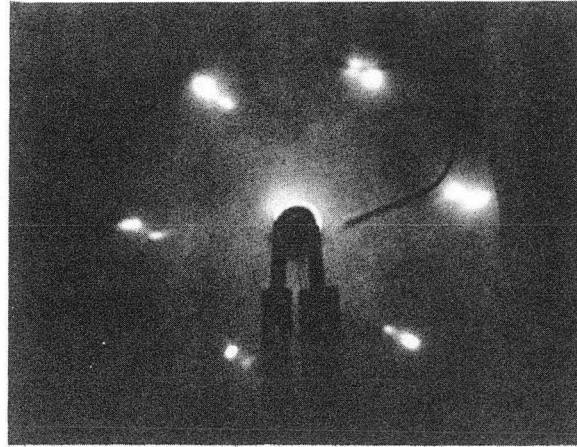
$P_f(S) - [4(111)X(100)]$



XBB 733-2190

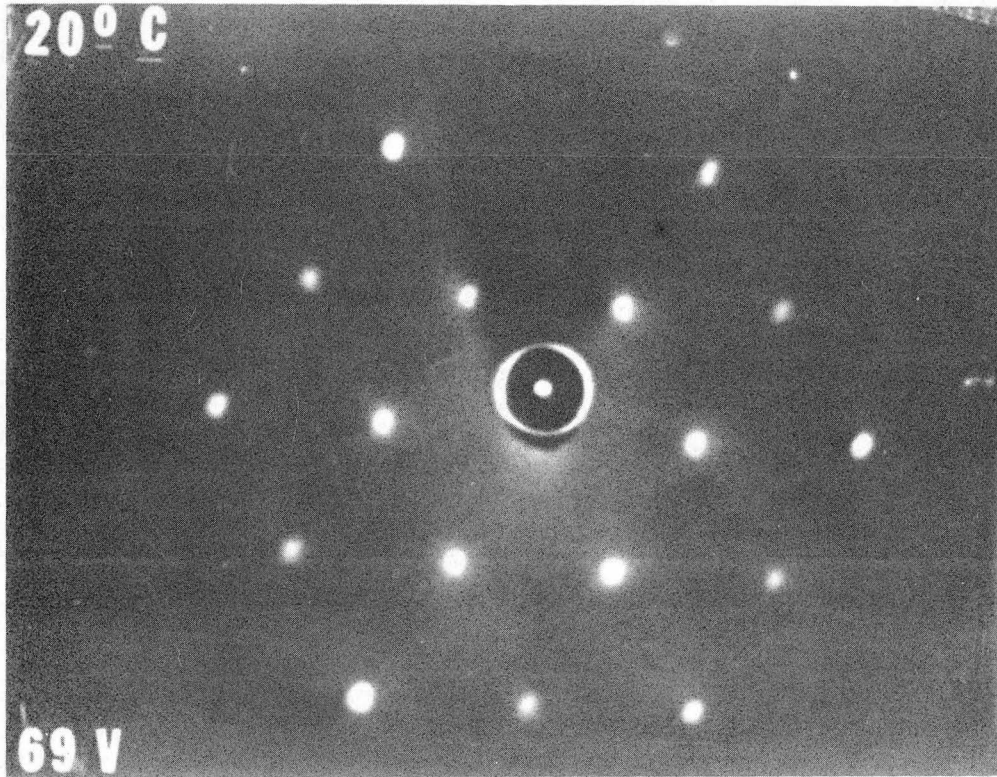
Fig. 6a.

$P+(S)-[7(111)X(310)]$



XBB 733-2189

Fig. 6b.



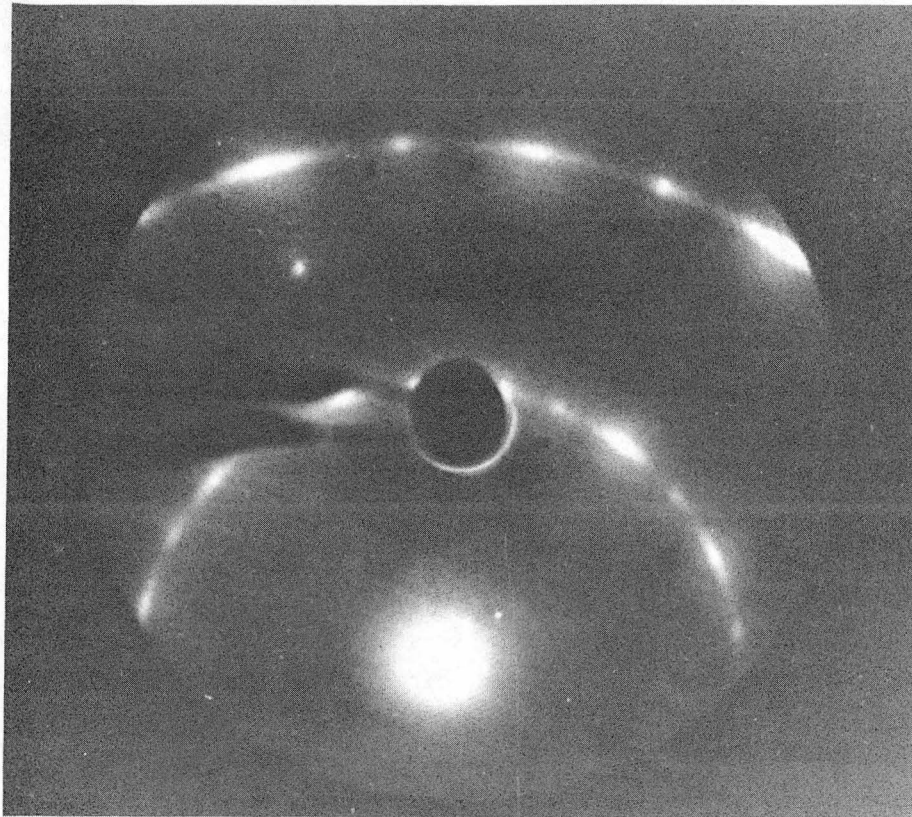
XBB 737-4295

Fig. 7a.



XBB 732-664

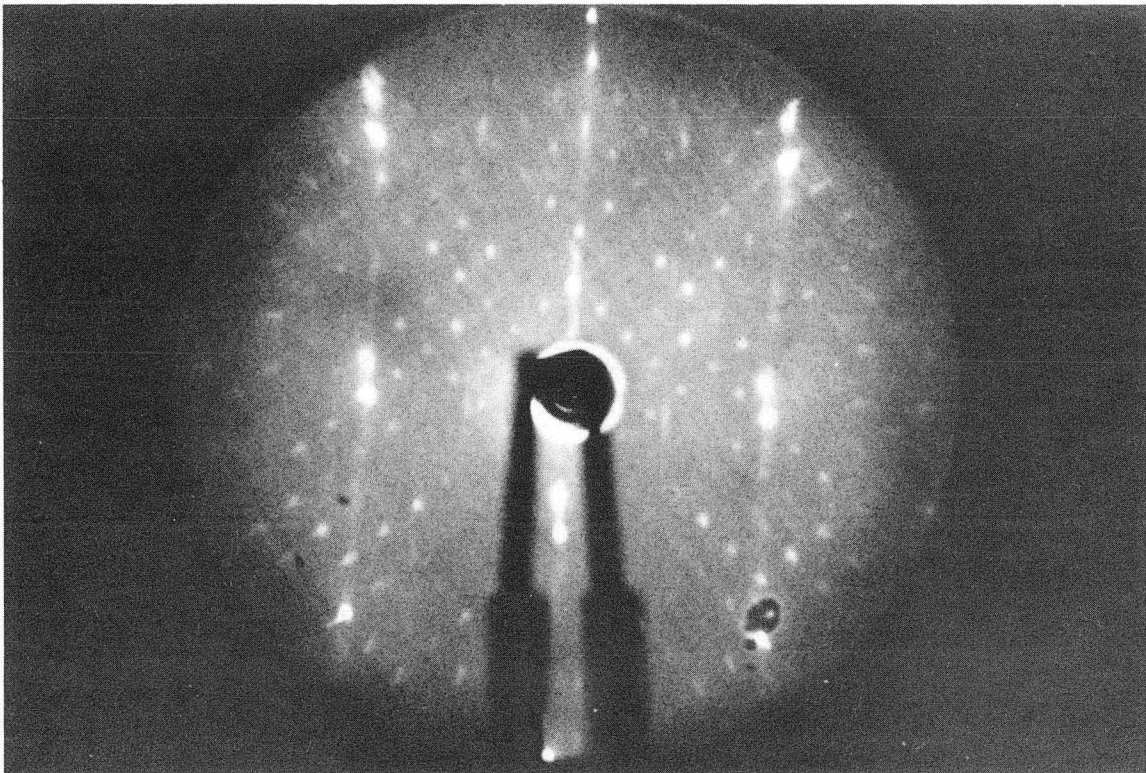
Fig. 7b.



IM 2373

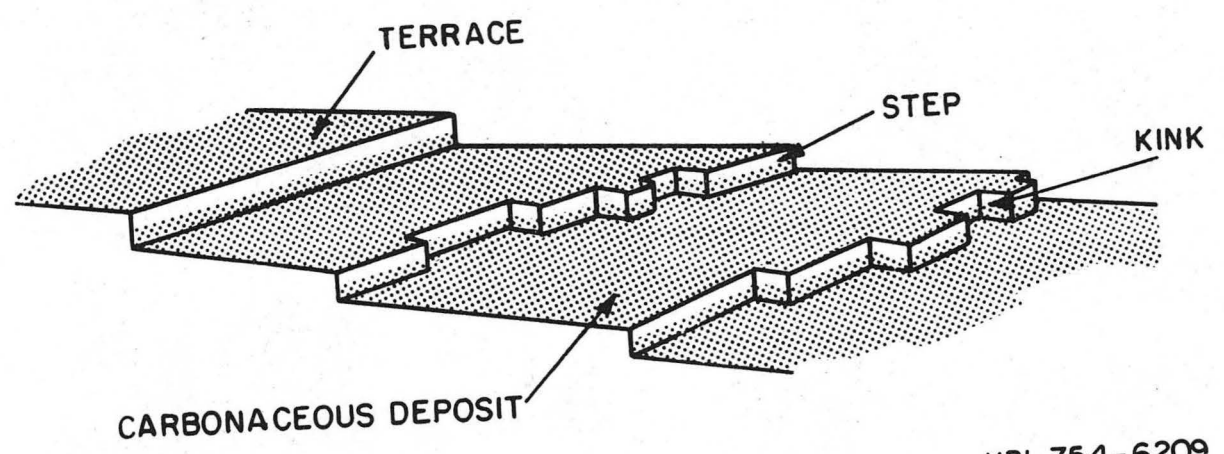
Fig. 8.





XBB 718-3666

Fig. 9.



XBL 754-6209

Fig. 10.

**LEGAL NOTICE**

*This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.*

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