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ADSORPTION STUDIES ON PLATINUM SINGLE CRYSTAL SURFACES

A. E. Morgan and G. A. Somorjai

June 1968

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A. E. Morgan and G. A. Somorjai

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The adsorption of various gases on the (100) face of a platinum single crystal has been studied using low energy electron diffraction (LEED). This study was designed as a necessary precursor to a more detailed investigation of reactions and catalysis on platinum surfaces.

The sample (1 mm thick, 6 mm in diameter) was cut from a single crystal rod of 99.999% pure platinum and orientated to within 1° of the (100) face using back-reflection Laue photographs. The crystal was then polished and finally etched in diluted aqua regia (50%) at 100°C. The sample was spot-welded to a holder (two strips of high purity platinum) and this was subsequently attached to the crystal manipulator. The crystal was heated by d.c. current and its temperature measured by a platinum/platinum-10% rhodium thermocouple, which was spot-welded to the back surface of the crystal. Ion bombardment, using high purity argon, was used to remove any surface damage introduced in sample preparation and mounting. Usual conditions for ion bombardment were 2×10^{-5} torr argon, 290 eV accelerating potential for 30 minutes.

The low energy electron diffraction apparatus used in these experiments was of the post-acceleration type.[1] The electrostatically focused electrons (0-500 V) were back reflected from the crystal surface and, after separation of the inelastically scattered fraction by a retarding potential, the elastic electrons were accelerated and impinged on a fluorescent screen. After bakeout and degassing, the pressure in the

diffraction chamber was around 4×10^{-10} torr.

The Pt(100) Substrate

The diffraction properties of the Pt(100) surface have been previously investigated[2] and will be summarized here. Figure 1 shows the diffraction pattern at an incident electron beam voltage E =165V. . The crystal structure of platinum is face-centered cubic with a lattice parameter of 3.92Å at 25°C. From the bulk structure, a square unit mesh of side 2.77Å is predicted for the (100) face. The distances between the diffraction spots corresponded to such a unit mesh within the accuracy of the measurements and Figure 1 could thus be labelled a (1x1) diffraction pattern using the terminology of two-dimensional crystallography.[3] However, if the crystal was ion-bombarded and then annealed above 200°C, extra diffraction spots were visible. Figure 2 shows a characteristic diffraction pattern at E = 164 V displaying fractional order diffraction spots along the x- and y-axes. The intensities of these extra spots were sometimes greater along one axis than along the other. There were no diffraction spots in between the rows emanating from the (00) reflection. The pattern suggested the existence of a surface structure with a unit mesh of dimensions five times that of the substrate along one principal axis and the same as that of the substrate along the other. Using the nomenclature of Wood,[3] such a surface structure would be designated Pt(100) - (5x1). There could be surface domains in which the longer periodicity was along the x-axis while in other domains it was long the y-axis. Thus the pattern shown in Figure 2 could result from the superposition of two structures rotated 90° to one another. As long as the size of the surface domains was much smaller than the size of

the electron beam, many domains would contribute to the observed pattern. The activation energy for the formation of the (5×1) surface structure was determined by measuring the rate of increase in the intensities of the extra diffraction spots at various temperatures, and found to be 38 kcal/mole.[2] Continued heating of the crystal caused the surface structure to disappear and the (1×1) diffraction pattern to return. The (5×1) surface structure could be regenerated by ion bombardment and subsequent annealing. Also the structure gradually disappeared at room temperature which was due to the adsorption of residual carbon monoxide, as will be discussed later.

The (5×1) surface structure has also been observed[4,5] on the (100) face of gold, which also has a face-centered cubic bulk structure. This has been interpreted[4] as indicating the presence of an hexagonal arrangement of scattering centers superimposed on the underlying gold atoms, Figure 3. The spacing along, say, the x-axis, between atoms in the surface layer is 5/6th the x-axis spacing of the substrate atoms but is identical along the y-axis. Thus the hexagonal surface and square unit mesh substrate lattices are coincident at every fifth substrate atom and this could generate an apparent five-fold surface periodicity.

Fedak and Gjostein claim that the hexagonal layer on gold is comprised of impurity atoms but Palmberg and Rhodin, who epitaxially deposited a few layers of Au on KCl and MgO substrates, believe that Au atoms alone comprise this layer. If the hexagonal layer is essentially the (111) face of gold or platinum, a compression of this layer by approximately 5% in the 1/5 order direction is necessary to allow 6 rows of the surface layer to fit onto 5 rows of the substrate.

Ring-like diffraction patterns,[2] (Figure 4), were obtained by heating the platinum crystal above 800°C, without prior ion-bombardment being necessary. The rings could be removed by ion bombardment. Their properties have not been investigated in these experiments and gas adsorption has been studied at temperatures below 800°C, to prevent ring formation. Thus results will be referred to gas adsorption on either the Pt(100)-(1×1) or Pt(100)-(5×1) surfaces.

Adsorption of Gases

Figure 5 is a schematic of the diffraction chamber. The quadrupole mass spectrometer was used to monitor the purity of the gas flowing through the chamber. Also, by rotation of the crystal through 90°, those gases desorbing from the surface could be analyzed directly in the mass spectrometer. The gas was introduced into the chamber via a Granville-Phillips leak valve and a fine capillary so it was incident directly on the crystal surface. Figure 6(a) shows a typical mass spectrum at a pressure of 4×10^{-10} torr; carbon monoxide, water, hydrogen and carbon dioxide were the major constituents of the ambient. In order to minimize the back-streaming of previously pumped gases from the Vacion pump, the flow rates into the diffraction chamber were maintained deliberately small. The pressure, recorded on the ionization gauge, was always below 1×10^{-7} torr during the adsorption experiments. The major gases liberated from the Vacion pump were CO and Ar. Figure 6(b) shows a representative mass spectrum, obtained with acetylene flowing through the chamber at 9×10^{-9} torr. Only at these low pressures could sufficient gas purity be maintained and hence the flow times were necessarily of the order of minutes.

The methods used to follow gas adsorption included a) studying the formation of new surface structures during adsorption, b) measuring the change in intensity of a given diffraction spot with time during adsorption, and (c) flash desorption; the crystal was heated from room temperature to 800°C in a few seconds and a plot made of the height of a given mass spectral peak as a function of temperature.

The majority of previous work of gas adsorption on platinum has been performed under significantly different experimental conditions; the residual vacua were poor ($> 10^{-5}$ torr), the substrates were polycrystalline, the gas introduced into the system was of unknown purity and its pressure usually greater than 10^{-2} torr. However, previous work has shown[6] that the order of gas adsorption on platinum is $O_2 > C_2H_2 > C_2H_4 > CO > H_2 > CO_2 \sim N_2$. The last two gases were found not to adsorb.

Carbon Monoxide

The adsorption of carbon monoxide on supported platinum has been studied by Eischens and Pliskin[7] using infrared spectroscopy. Their results showed that carbon monoxide was adsorbed in both the bridged and unbridged configurations:

An integral heat of adsorption of 30 kcal/mole has been reported.[6]

When carbon monoxide was introduced into the diffraction chamber and impinged on the platinum surface displaying the (5×1) structure, the 1/5th order diffraction spots rapidly disappeared. For instance, at

a carbon monoxide pressure of 8×10^{-9} torr, the extra spots vanished completely within two minutes. This extreme sensitivity of the (5×1) structure to the presence of trace amounts of carbon monoxide explained the slow, apparent disappearance of this surface structure as the crystal remained in the diffraction chamber in ultra-high vacuum at room temperature. When all the carbon monoxide was desorbed by heating the crystal above 600°C, the (5×1) surface structure readily reappeared.

The intensities of the diffraction spots due to the (1×1) substrate increased during the initial stages of CO adsorption as the extra 1/5th order spots disappeared. Continued adsorption of CO then caused a gradual decrease in the intensities of the remaining diffraction spots until new diffraction features appeared. The flash desorption curve, Figure 7, indicated the existence of three discrete adsorption states, the low coverage but strongly bound β-form and the higher coverage weakly held α_1 and α_2 forms. The total concentration of the α forms ($\alpha_1 + \alpha_2$) was about 20 times that of the β form. The desorption temperatures were approximately 130°C (α_1), 170°C (α_2) and 600°C (β) for the different CO surface species. Adsorption of carbon monoxide in the strongly-held β form caused a decrease in the intensities of the (1×1) diffraction spots but gave rise to no new diffraction features. Figure 8 illustrates the new diffraction pattern obtained after the adsorption of carbon monoxide had reached saturation. [This pattern has also been reported by Tucker.[8]] The intensities of the extra spots were much weaker than those of the substrate diffraction spots. A (4×2) unit mesh which could lead to the observed pattern is shown in Figure 9. The open circles represent the platinum substrate atoms and the shaded circles represent the CO molecules.

It would be necessary to have other domains of the same structure rotated by 90° to generate the complete pattern. The carbon monoxide coverage necessary to produce this surface structure is approximately 3/4 of a monolayer.

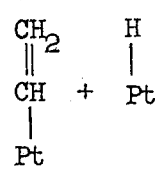
The Pt(100) - (4×2) CO structure could be converted to the pattern characteristic of α_2-CO by heating the crystal to 140°C or by allowing the electron beam to strike a certain area of the surface for a few minutes. The change in the diffraction pattern due to the electron beam impinging on the carbon monoxide covered surface is shown schematically in Figure 10. The extra diffraction spots first became streaky, then those along the x- and y-axes disappeared and finally, only very faint and ill-defined extra spots remained. Calculations indicate that surface heating by the incident electrons should be negligible (< 0.1°C). Thus, the desorption of the weakly adsorbed (α_1) carbon monoxide was caused by the interaction between the impinging electrons and the adsorbed CO molecules. When the crystal was heated above 600°C, so that all the carbon monoxide desorbed, the (5×1) surface structure reappeared. Also, when the crystal was heated to between 200°-600°C in carbon monoxide, the gas adsorbed only in the β-form and the 1/5th order diffraction spots disappeared, the rate of disappearance being faster the lower the temperature.

In summary, as carbon monoxide was adsorbed on the platinum surface, the (5×1) surface structure first disappeared producing a (1×1) diffraction pattern. This was followed by the formation of ill-defined extra diffraction spots [Fig. 10(d)] and finally, with increasing exposure time, the Pt(100)-(4×2) CO pattern [Fig. 8] developed.

Hydrocarbons

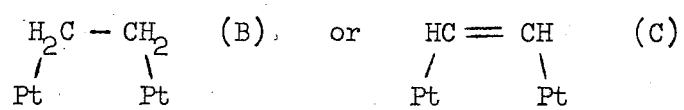
The mass spectrum of ethylene contains relatively large peaks at m/e = 26 and 27 in addition to the one at m/e = 28 due to ion fragmentation. Hence, the adsorption of ethylene was followed by monitoring those peaks in order to differentiate it from the carbon monoxide present in the ambient.

Ethylene was adsorbed on the Pt(100)-(5×1) surface at room temperature. The 1/5th order diffraction spots again disappeared but 2-3 times slower than during the adsorption of CO at the same flow rate. After the disappearance of the n/5 diffraction spots, continued ethylene adsorption resulted in the formation of a c(2×2) surface structure, Figure 11. The pattern contained, in addition to the normal substrate spots, extra spots of half-integral indices at the center of each platinum reciprocal unit mesh. The extra spots were less intense and more diffuse than the (1×1) diffraction spots. The c(2×2) surface structure was formed, by ethylene adsorption, from either the (1×1) or (5×1) diffraction pattern. The unit mesh of the surface structure may be taken to be a centered square of side 2a. Possible atomic configurations, leading to the c(2×2) structure are depicted in Figure 12, (a) and (b), where the shaded circles represent the adsorbed ethylene. Adsorption of ethylene[6] may be dissociative



(A)

or associative,



Assuming normal bond lengths and angles, the ideal Pt-Pt distance for structure (B) can be calculated to be 2.73Å, a value close to the distance between (n,0) rows on the platinum (100) surface, and 3.43Å for structure (C). However, any of the above atomic configurations could lead to the formation of a c(2×2) diffraction pattern and thus the LEED data cannot distinguish between them.

When the crystal was heated at 150°C, the extra spots became streaked and gradually the surface structure disappeared. Also the (5×1) surface structure was regenerated. The flash desorption spectrum showed an ethylene peak around 80°C and also hydrogen peaks at 200°C and 320°C. After ethylene had been adsorbed and then desorbed from the surface several times, the diffraction spots became very faint, the pattern background increased and it became difficult to regenerate the (5×1) surface structure. The effect was even more dramatic when heating the crystal in ethylene at higher temperatures. The surface impurity was removed by heating the crystal in oxygen or by a lengthy (4 hrs) ion bombardment. These observations suggested that the surface impurity deposit was carbon formed by the cracking of adsorbed ethylene. It should be noted that the strength of the Pt-C bond (65.6 kcal/mole) is comparable to that of the C-C bond (66.2 kcal/mole). The ring-like

diffraction patterns (Figure 4) were formed after repeated adsorption and subsequent desorption of ethylene. This suggested that they too resulted from the presence of carbon on the surface.

An equi-mixture of hydrogen and ethylene introduced at various crystal temperatures, showed the same adsorption characteristics as ethylene alone and there was no mass-spectrometric indication of ethane formation.

Acetylene is expected to adsorb more strongly than ethylene due to the greater reactivity of the triple C-C bond. This was found to be the case in this study. Acetylene was adsorbed at room temperature and desorbed at 140°C. The flash desorption spectrum also contained H_2 peaks at 200°C and 340°C. Although acetylene showed the same adsorption characteristics as ethylene, all features of the adsorption were more pronounced. For example, the (5×1) surface structure vanished extremely rapidly upon the introduction of acetylene into the diffraction chamber, at an even faster rate than with carbon monoxide. A clearer diffraction pattern of the c(2×2) surface structure was formed, which could be removed by heating the platinum crystal at 150°C for about one hour. It has been widely assumed[6] that acetylene is adsorbed as structure (C) and that, whereas olefins are adsorbed with least strain along the shorter interatomic distances [Fig. 12(a)], acetylene adsorbs along interatomic spacings greater by $\sqrt{2}$ [Fig. 12(b)]. Thus it is predicted that, since none of the longer spacings are available in the (111) plane of face-centered cubic metals, acetylene will not adsorb strongly on this face. Future experiments will test this hypothesis.

Methane and ethane, at temperatures up to 700°C and at gas pressures

in the range of 10^{-9} to 10^{-7} torr did not seem to adsorb on the (100) face of platinum. These gases did not remove or interact in any way with the (5×1) surface structure and showed no cracking on the platinum surface.

Oxygen

Oxygen did not seem to adsorb on platinum at room temperature. If the crystal was heated at 300°C in oxygen, the (5×1) surface structure was not removed and there was no detectable adsorption of oxygen. However, when the crystal was flashed to 800°C in vacuo, a small, broad desorption peak was recorded in the mass spectrometer between 400° and 750°C at m/e = 32, and a c(2×2) surface structure was formed, Figure 13. The extra spots were as sharp and as intense as the substrate diffraction features, in direct contrast to the surface structures formed by adsorbed CO, C_2H_4 or C_2H_2 which showed faint, diffuse fractional order spots. The c(2×2) pattern disappeared when the crystal was heated between 200°C-400°C in oxygen. However, this removal was reversible since the structure returned immediately after flashing the crystal to 800°C. The c(2×2) structure could be permanently removed by heating in vacuo at 800°C for about 30 minutes, by ion bombardment or by heating in 2×10^{-7} torr hydrogen at 600°C for about half an hour. This latter treatment removed the c(2×2) structure but had no effect on the (5×1) surface structure. By heating the crystal in oxygen, the (5×1) surface structure was formed rapidly on a surface which had not been ion bombarded or from which this surface structure had been annealed out. The rate of formation of the (5×1) structure in oxygen was greatest at the higher temperatures. However, there appeared to be a competition between the

formation of the (5×1) and c(2×2) surface structures. By heating the crystal at 300°C in oxygen, only the (5×1) structure was formed. However, if the experiment was performed at 600°C, the c(2×2) structure predominated. The c(2×2) structure appeared to be present on certain regions of the surface while the (5×1) was visible on the remainder. In this respect, Figure 13 is misleading since both types of surface regions contributed to the diffraction pattern. Also, the c(2×2) pattern developed more easily from the (1×1) pattern than from the (5×1) pattern.

It has been reported[9] that a particular feature of oxidation catalysis is the rearrangement of metal surfaces during the reaction, sometimes as low as 250°C. Hence, another model, involving the reconstruction of the platinum surface in the presence of adsorbed oxygen, could lead to a c(2×2) structure and this is shown in Figure 12(c). The surface layer consists of alternate diagonal rows of platinum and oxygen atoms and the diffraction pattern arises from the array of platinum atoms alone. This model of oxygen adsorption could be tested by structure analysis using the relative intensities of the different diffraction spots. It is hoped that such a treatment will be carried out in the near future.

When carbon monoxide was preadsorbed on the surface and then, the crystal heated above 200°C in oxygen, the (5×1) and c(2×2) structures were formed but at a slower rate than that with a clean surface. Alternatively, if these structures were first formed by heating in oxygen, then carbon monoxide appeared to adsorb only on the (5×1) surface regions; the (5×1) structure disappeared but the c(2×2) pattern remained visible.

Finally, the crystal was heated at 300°C and an equimixture of carbon monoxide and oxygen was introduced into the diffraction chamber at 1×10^{-8} torr. After 30 minutes a faint c(2×2) structure had formed. [Under identical conditions, but with O_2 alone, the (5×1) was the surface structure formed.] At 500°C, a clearer c(2×2) pattern was produced, but in a few surface regions the (5×1) structure was also detectable.

Carbon Dioxide, Nitrogen and Hydrogen

There was no evidence of the adsorption of carbon dioxide, nitrogen or hydrogen on the (100) face of platinum at pressures up to 1×10^{-7} torr and temperatures up to 700°C; there was no removal or formation of the (5×1) surface structure, no change in the diffraction pattern and no desorption peaks were observed in the mass spectrometer during flashing the sample to high temperatures.

Furthermore, an equimixture of hydrogen and oxygen was introduced into the chamber at 1×10^{-7} torr pressure and at various crystal temperatures. The adsorption characteristics were the same as those observed for oxygen alone, and there was no indication of water formation. Present investigations include the effect of increasing the pressure of the hydrogen used in the adsorption experiments. Further studies will encompass the properties of the ring-like diffraction patterns and their effect on gas adsorption.

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FIGURE CAPTIONS

Fig. 1 Pt(100)- 1x1 diffraction pattern at beam voltage E = 165V.

Fig. 2 Pt(100)- 5x1 diffraction pattern at E = 124V.

Fig. 3 Possible interpretation of (5x1) surface structure showing a hexagonal surface layer superimposed on square substrate layer.

Fig. 4 Pt(100) - ring-like diffraction pattern at E = 90V.

Fig. 5 The diffraction chamber

Fig. 6 a) Mass spectrum at ambient pressure = 4×10^{-10} torr

b) Mass spectrum with 9×10^{-9} torr acetylene flowing through diffraction chamber.

Fig. 7 Carbon monoxide flash desorption spectrum.

Fig. 8 Pt(100)- (4x2)-CO diffraction pattern at E = 95V.

Fig. 9 Possible interpretation of Pt(100)-(4x2) CO surface structure.

Fig. 10 Gradual change in diffraction pattern due to electron beam desorption of some adsorbed carbon monoxide.

Fig. 11 Pt(100) - c(2x2)- C_2H_4 diffraction pattern at E = 94V.

Fig. 12 Possible interpretations of c(2x2) surface structure.

Fig. 13 Pt(100) - 5x1 and c(2x2)-O_2 diffraction pattern at E = 90V.

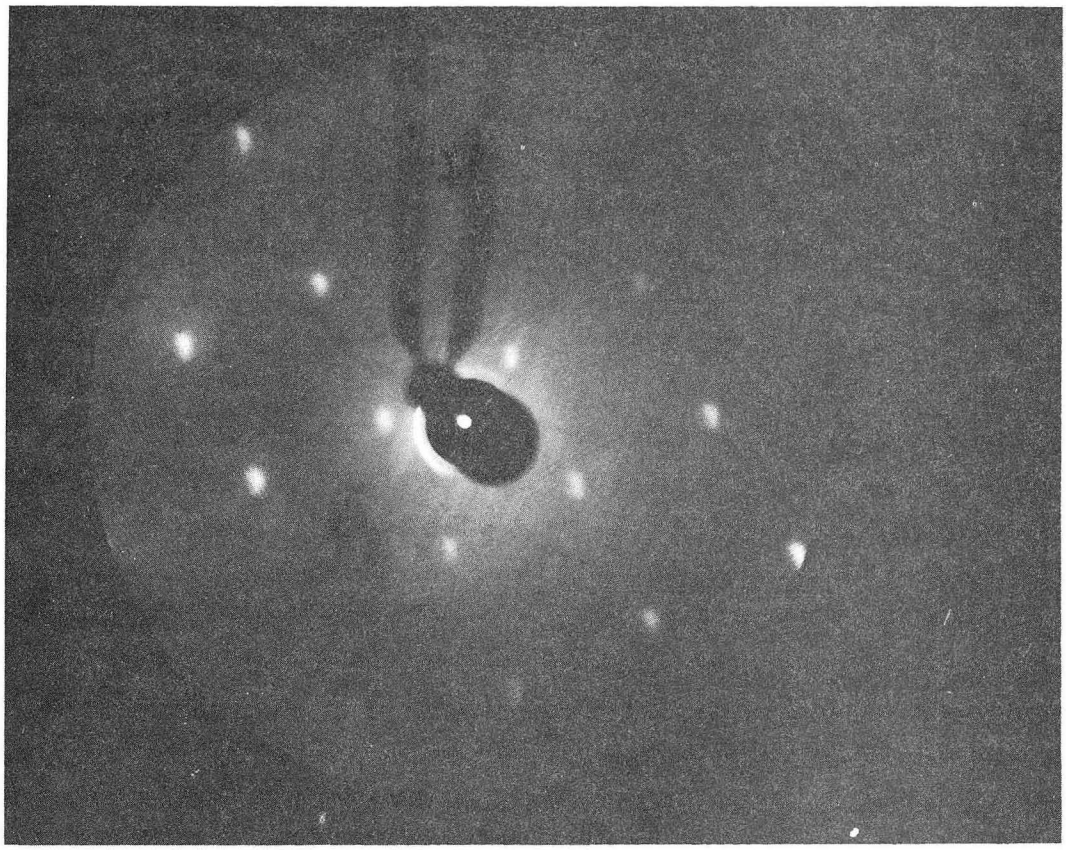

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Fig. 1

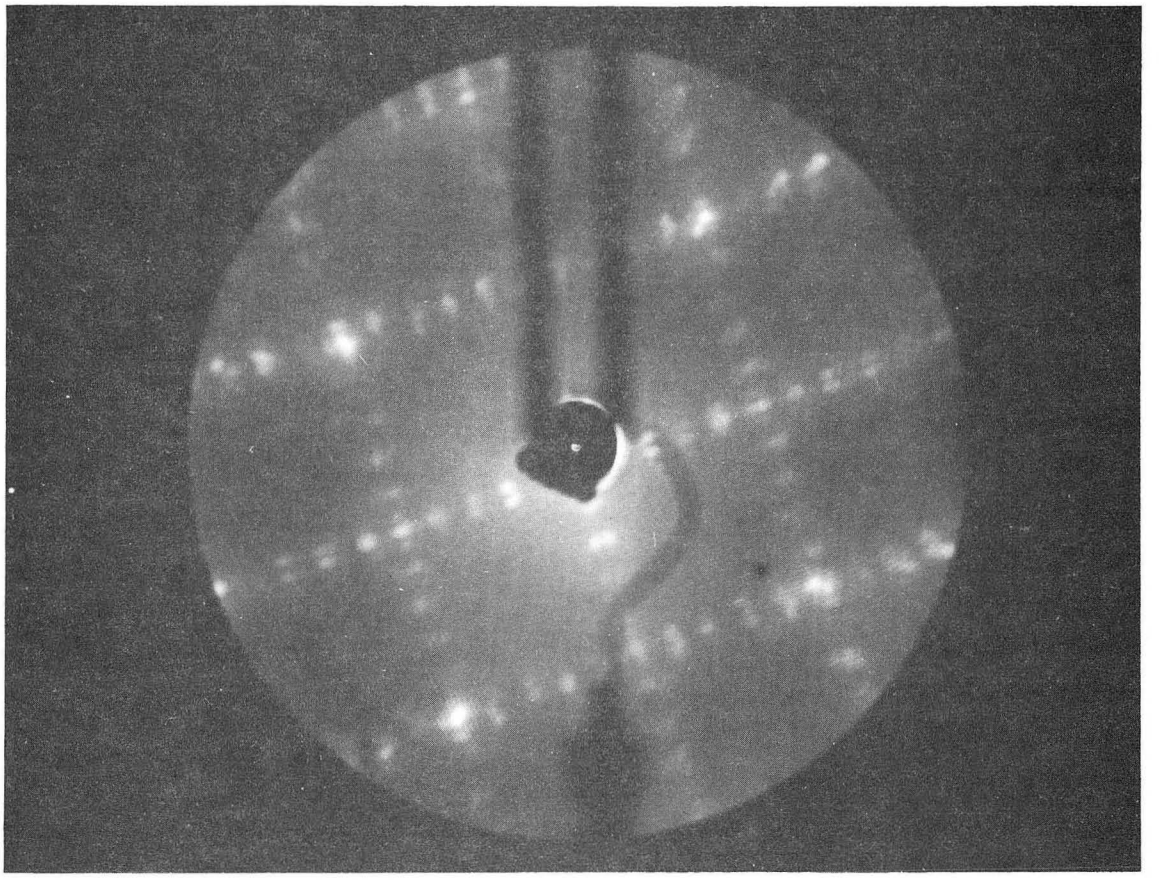

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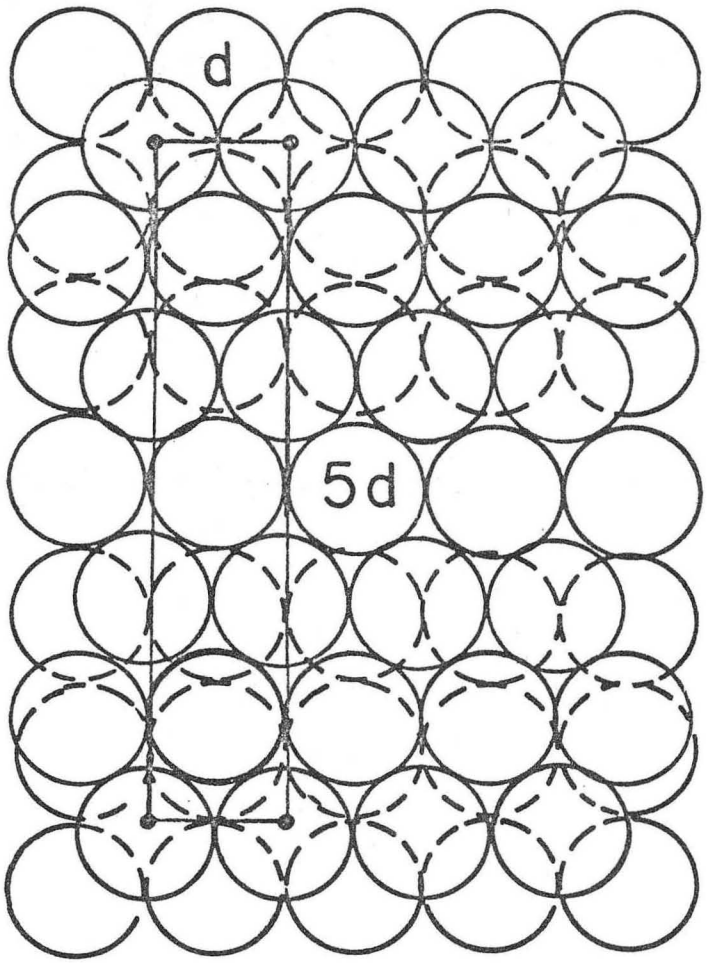
Fig. 2



Reconstructed layer

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Fig. 3

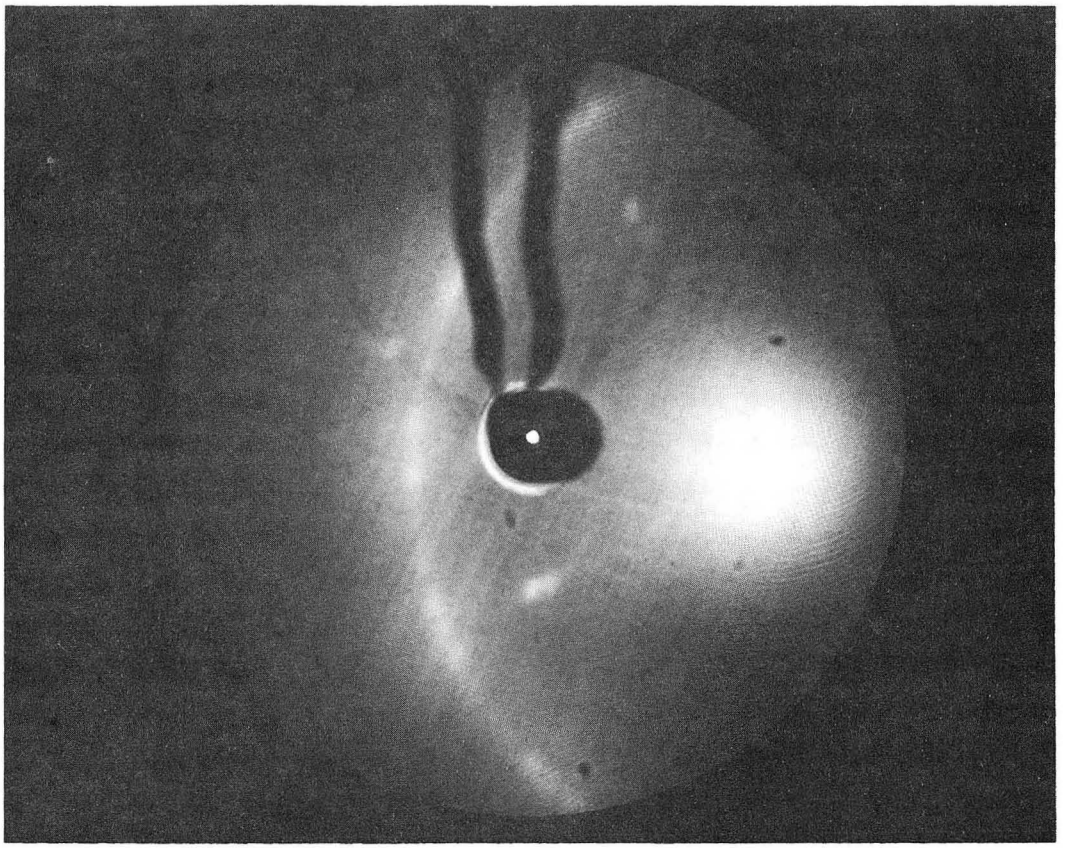

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Fig. 4

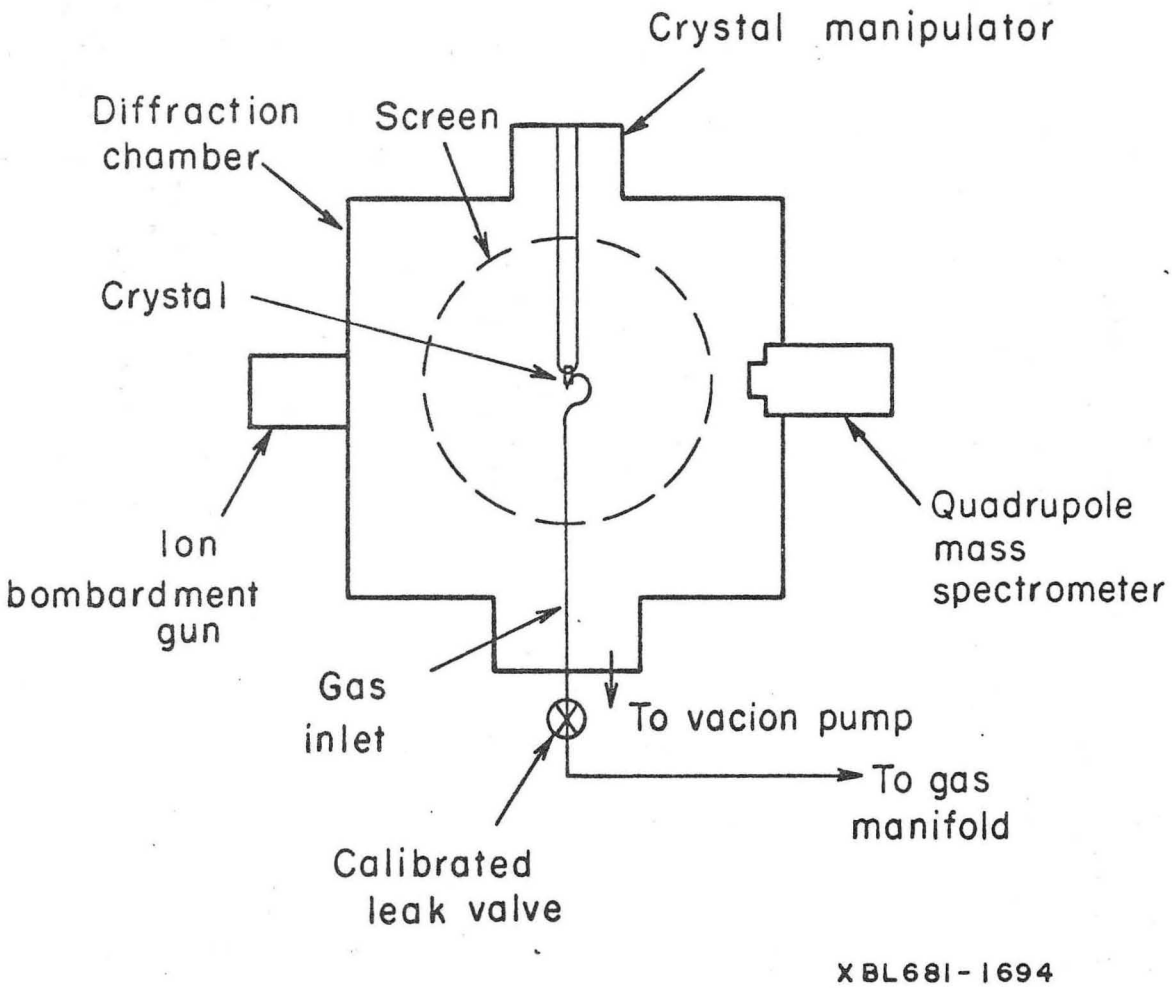
Crystal manipulator
Diffraction chamber
Screen
Crystal
Ion bombardment gun
Quadrupole mass spectrometer
Gas inlet
To vacion pump
To gas manifold
Calibrated leak valve
XBL681-1694

Fig. 5

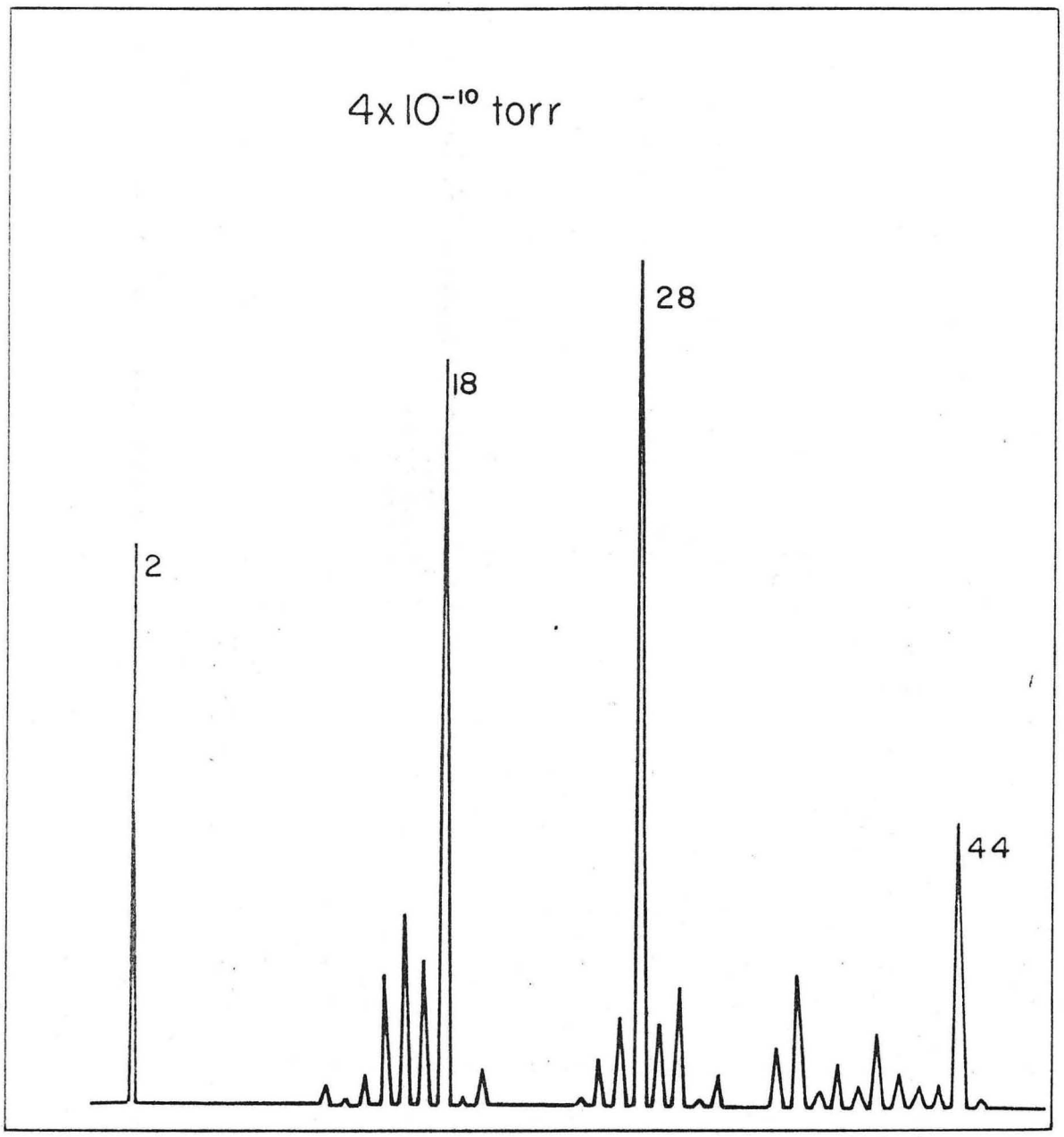

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Fig. 6a

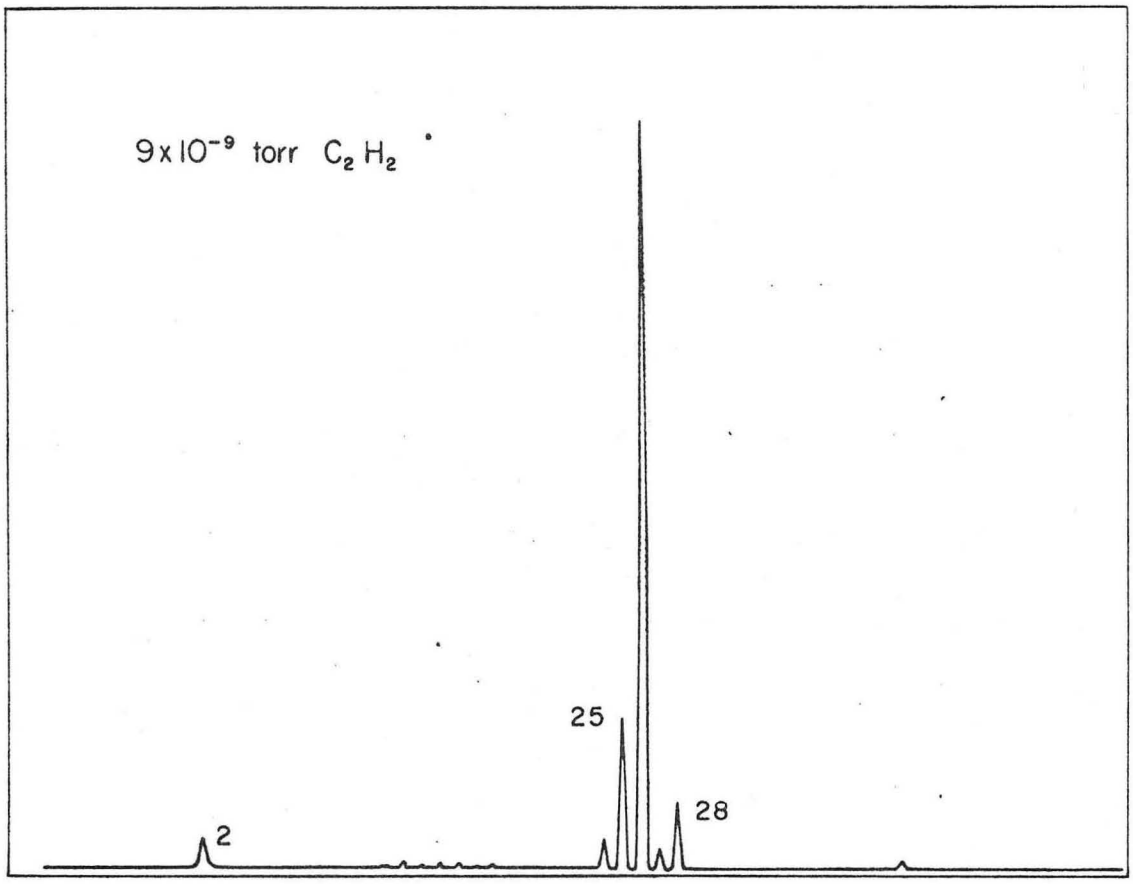

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Fig. 6b

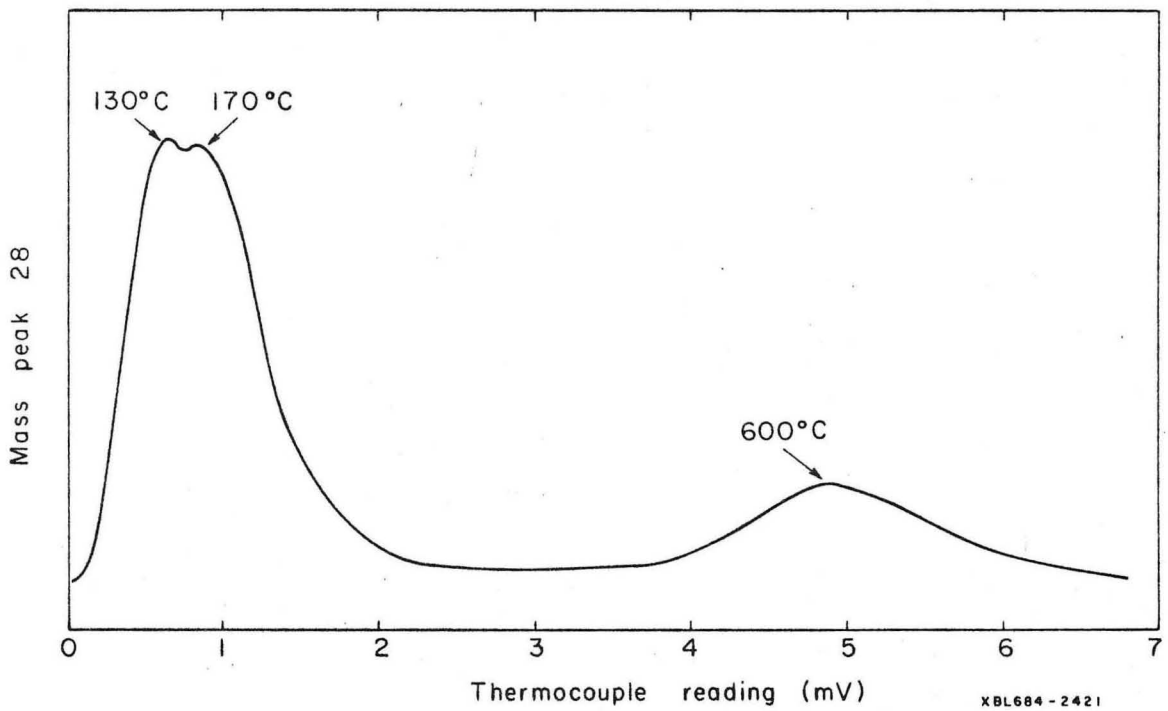
130°C
170°C
600°C
Mass peak 28
0
1
2
3
4
5
6
7
Thermocouple reading (mV)
XBL684-2421

Fig. 7

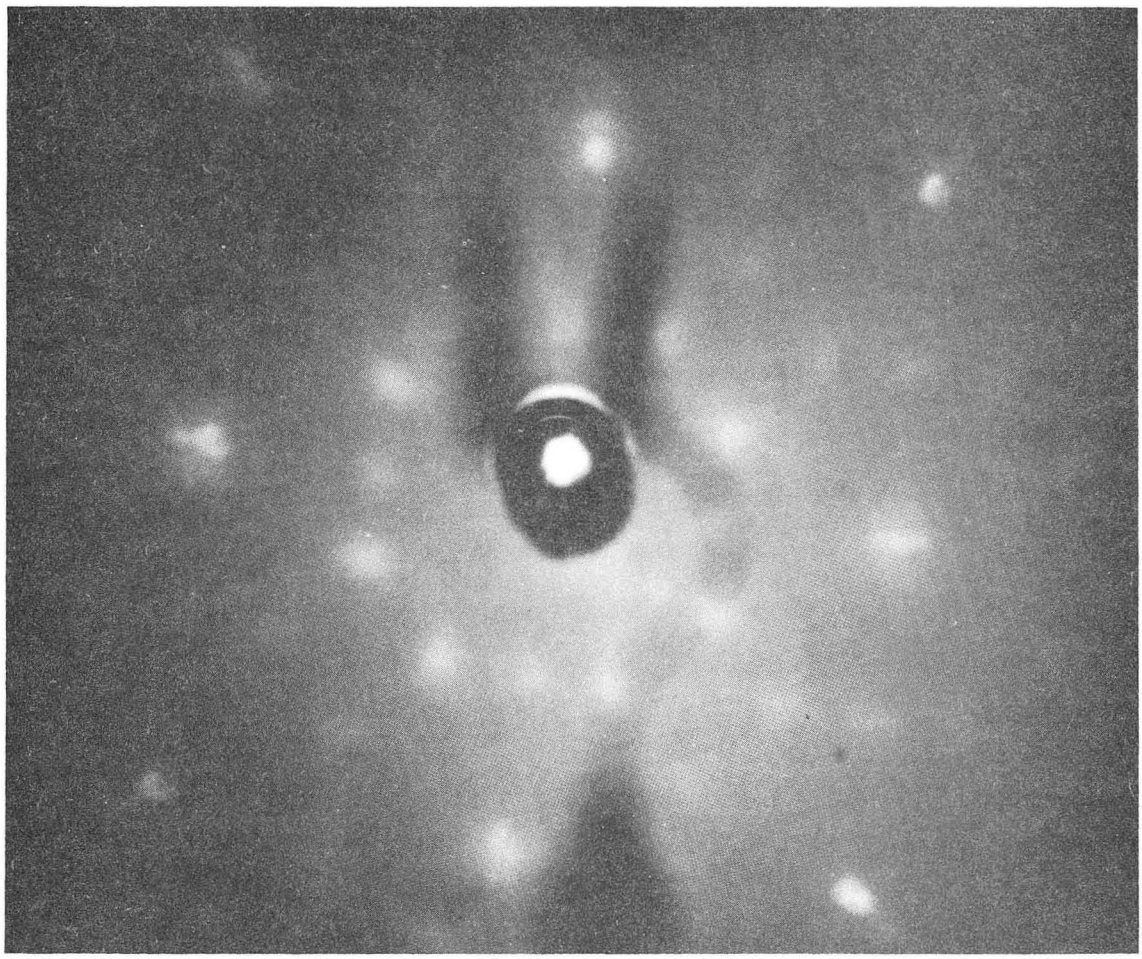

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Fig. 8

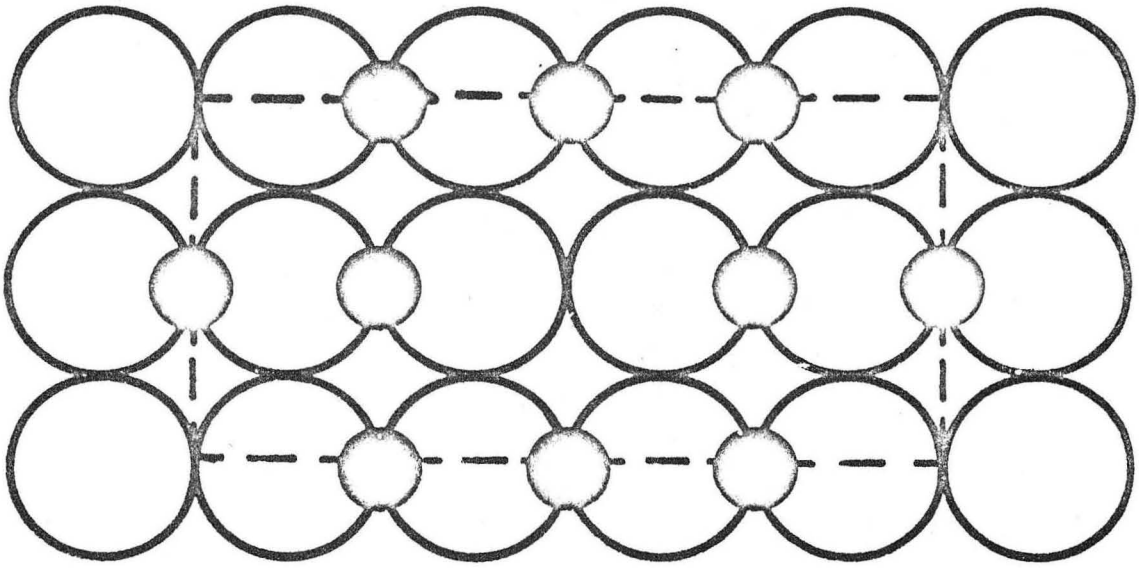

Fig. 9

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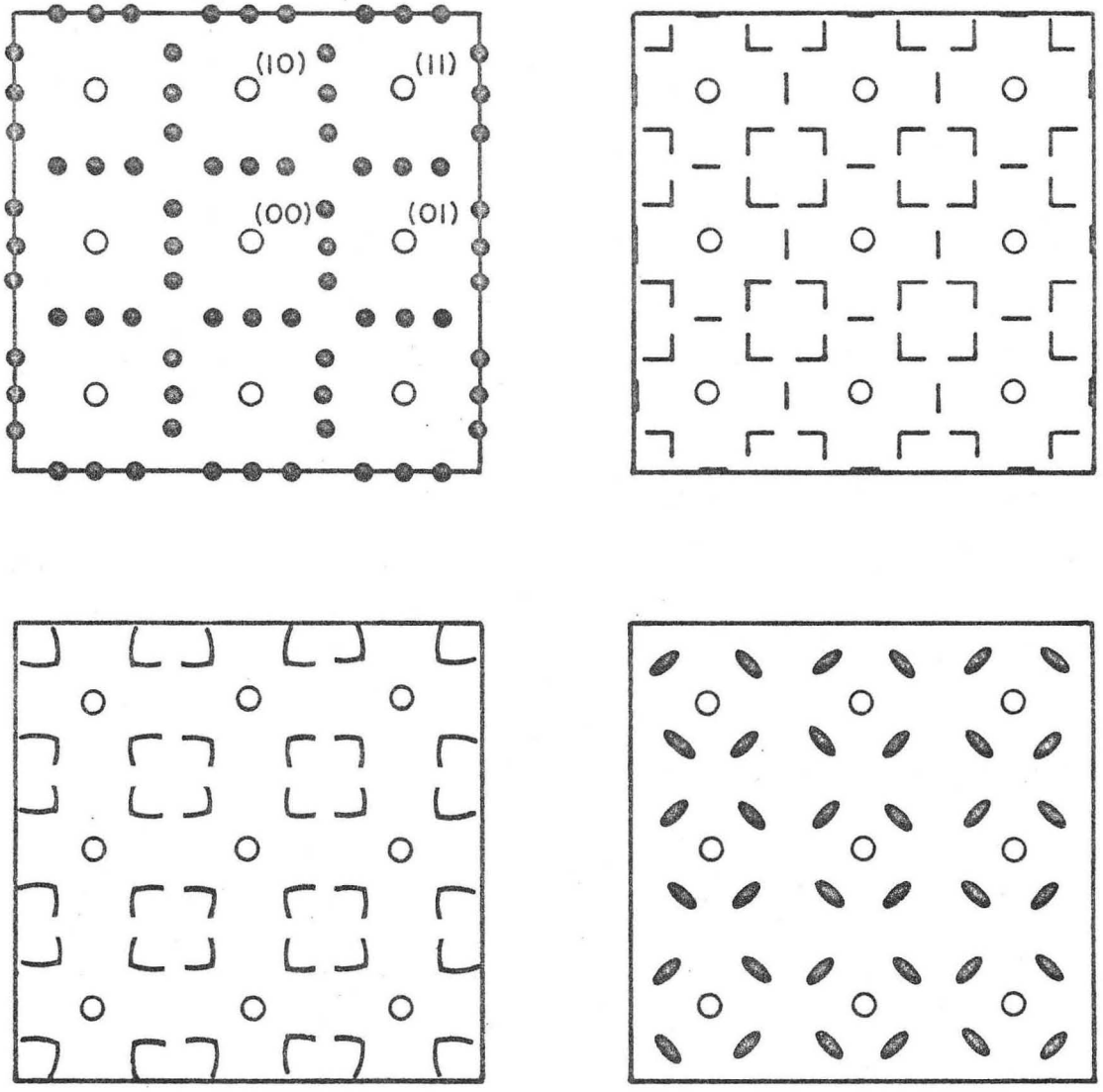

Fig. 10

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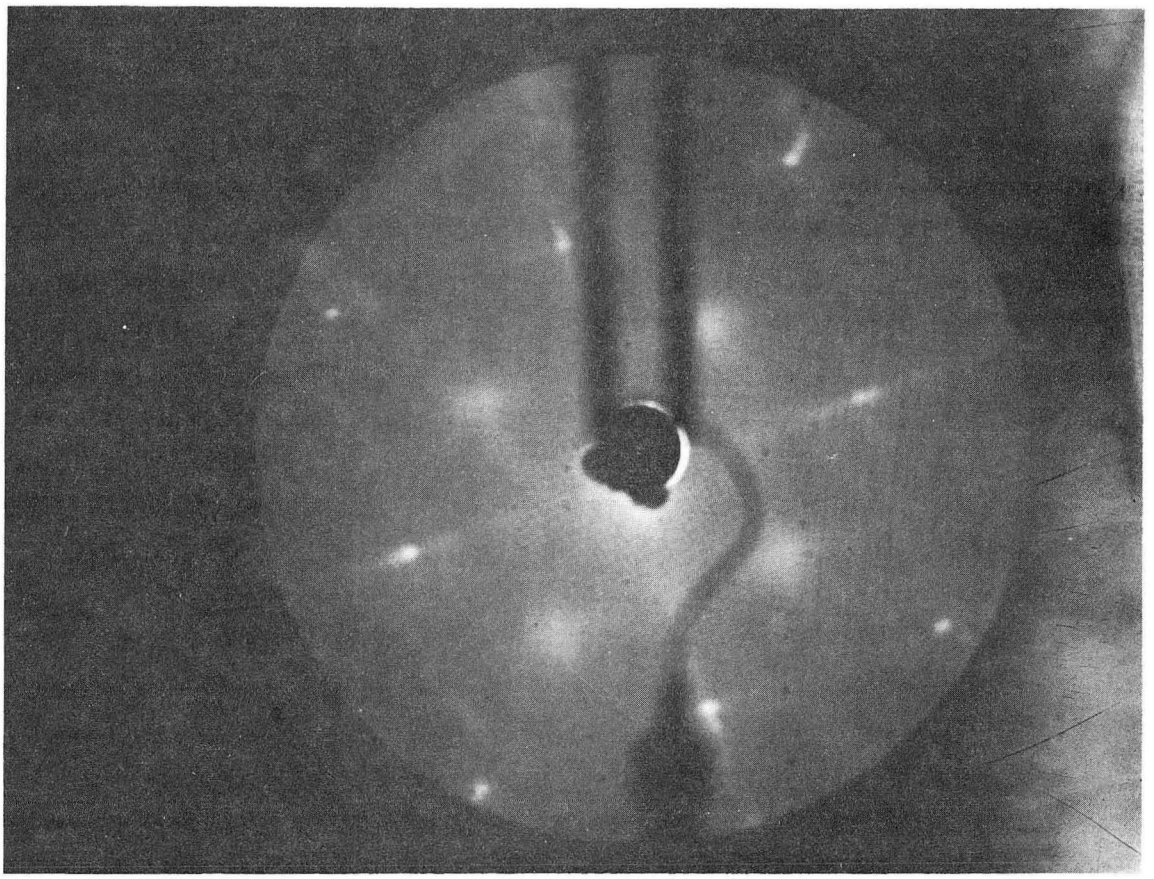

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Fig. 11

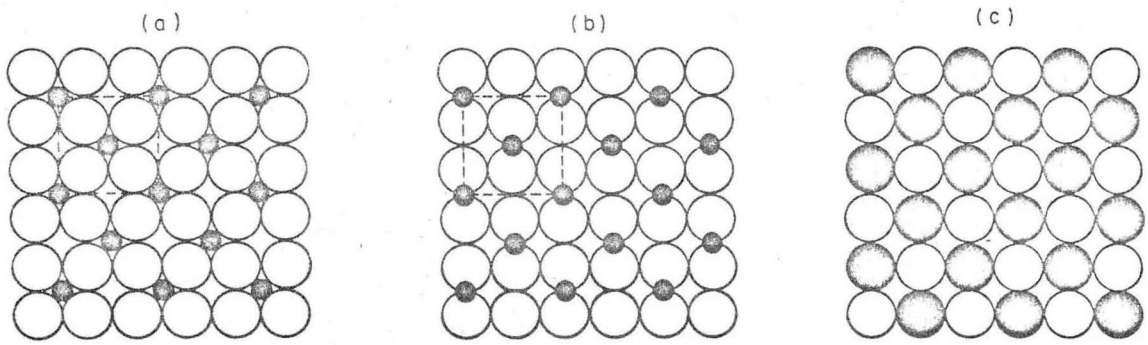

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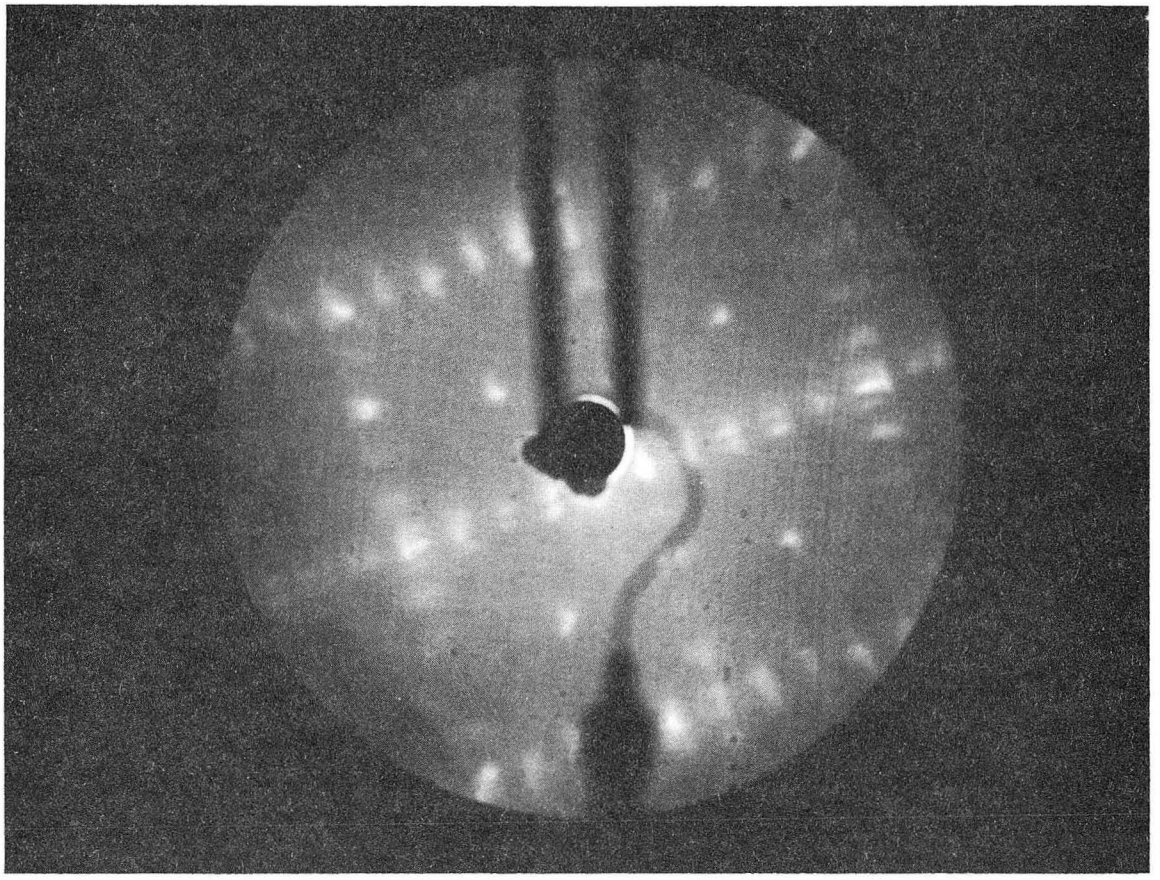
Fig. 12



XBB 685-3211

Fig. 13

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