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LOW ENERGY ELECTRON DIFFRACTION STUDIES OF GAS ADSORPTION ON THE PLATINUM (100) SINGLE CRYSTAL SURFACE

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Low Energy Electron Diffraction Studies of Gas Adsorption on the Platinum (100) Single Crystal Surface

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ABSTRACT

The chemisorption of various gases (H_2, N_2, N_2O, O_2, CO, CO_2, CH_4, C_2H_6, C_2H_2 and C_2H_4) on the Pt(100) single crystal surface has been studied, using low energy electron diffraction (LEED), mass spectrometry, flash desorption and work function measurements, at gas pressures $\leqslant 1 \times 10^{-7}$ torr and at temperatures between 25°C-700°C. The Pt(100) substrate was characterized by a (5 x 1) surface structure. Those gases which chemisorbed on the platinum surface (CO, H_2, C_2H_2 and C_2H_4) formed ordered surface structures. Also, a further surface structure was formed by the co-adsorption of H_2 and CO. A strong affinity was found between carbon, or carbon-containing molecules, and the platinum surface. Carbon monoxide adsorbed in three bonding states on the (100) surface. The adsorption results differed somewhat from those observed in adsorption experiments performed at higher gas pressures.

INTRODUCTION

The mechanism of heterogeneous catalytic processes has always been one of the more important subjects for exploration in chemical kinetics. Platinum is an excellent catalyst for many chemical reactions involving gaseous reactants and thus has been widely investigated. The recent advent of low energy electron diffraction (LEED) techniques has permitted such studies to be made on an atomic scale under well-defined experimental conditions.[1]

LEED studies of single crystal surfaces have indicated that a) the low index faces of several solids undergo atomic rearrangements, as a function of temperature, in the absence[2] or presence[3] of adsorbed gas molecules and b) chemisorbed gases may form ordered surface structures which depend upon the orientation of the crystal substrate and upon the nature and concentration of the adsorbed gas species.[4]

It is reasonable to suppose that surface rearrangements or the formation of ordered surface structures play an important role in heterogeneous catalysis. In order to define this role more precisely, LEED studies of surface reactions may be subdivided into 1) investigations of the structural properties of the clean catalyst surface, 2) studies of the surface structures formed upon the adsorption, either individually or together, of the gaseous reactants and finally 3) studies of how these factors influence the kinetics and nature of the chemical surface reaction itself. The structural properties of low index platinum surfaces have already been described.[5] In this paper, these findings are further clarified and the adsorption of various gases (CO, C_2H_2, C_2H_4, C_2H_6, CH_4,

O_2, N_2, N_2O and CO_2) on the (100) face of platinum single crystals is discussed. This investigation is a necessary precursor to a more definitive study of platinum catalysis.

The (100) face was chosen for two reasons. First, this face exhibits stable fractional order diffraction features which could result from the rearrangement of platinum surface atoms into a new ordered surface structure. The effect of these surface rearrangements on gas adsorption and on chemical surface reactions could thus be explored. Also, the (100) face does not seem to facet at any temperature below the melting point of platinum, and hence its diffraction properties are easily reproducible with each platinum crystal used. Mass spectrometric, work function and flash-desorption techniques were combined with LEED observations in order to follow gas adsorption. Careful attention was paid to any change in adsorption characteristics due to the presence of a substrate surface structure, and to the behavior of the extra substrate diffraction spots on exposure to a gas.

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[6] has shown 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.

The present experiments indicate that those gases which chemisorbed on the platinum surface formed ordered surface structures. Furthermore, the order of gas adsorption on the (100) face of platinum was different

at the low working pressures used than that obtained at higher pressures on polycrystalline samples. CO, C_2H_2 and C_2H_4 were readily adsorbed at room temperature, H_2 at higher working pressures and the remainder of the gases, including O_2, did not appear to chemisorb. Also the chemisorption and formation of ordered surface structures were affected by the presence of carbon on the platinum surface.

EXPERIMENTAL PROCEDURE

The post-acceleration type LEED apparatus, the preparation and mounting (platinum holders) of the platinum specimen have been described previously.[5] A diagram of the diffraction chamber is shown in Figure 1. 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 crystal sample (2 mm. thick, 6 mm. diameter disk) was heated by d.c. current and its temperature measured by a Pt/Pt-10% Rh thermocouple, which was spot welded to the back surface of the crystal.

Matheson research-grade gases were admitted to the chamber via a Granville-Phillips leak valve and a fine capillary so that they were incident directly on the crystal surface. By rotation of the crystal through 90°, those gases desorbing from the surface could be analyzed directly in the mass spectrometer.* Background pressures were $\sim 4 \times 10^{-10}$ torr and consisted mainly of H_2, H_2O and CO. The flow rates were maintained deliberately small in order to minimize the backstreaming of previously-

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* Quadrupole Mass Spectrometer EAI Model 2000 was used in these experiments.

pumped gases from the VacIon pump. The pressure, recorded on the ionization gauge, was always less than 1×10^{-7}torr during the adsorption studies. Mainly CO and argon were liberated from the ion-pump, the amount depending on the quantity and on the particular gas being pumped. Figure 2 shows a representative mass spectrum obtained with 9×10^{-9}torr C_2H_2 in the diffraction chamber; M/e = 26 was the parent ion peak while 24 and 25 were peaks due to ion fragments. Sufficient gas purity could be maintained only at these low overall pressures and hence the exposure times were 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, c) monitoring work function changes during adsorption with a variation of the retarding potential difference method[7] using the LEED electron gun itself and d) 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.

RESULTS AND DISCUSSION

1) The Structure of the Pt(100) Substrate

The crystal structure of platinum is face-centered cubic with a bulk lattice parameter of 3.923Å. From the bulk structure, a square unit mesh of side 2.77Å is predicted for the (100) face and such a (1 x 1) diffraction pattern was initially visible. However, when the crystal was heated above 1000°C, a new diffraction pattern slowly appeared, Figure 3. This was

characterized by narrow, circular segments which eventually coalesced into rings. Continued heating caused the intensities of the integral order diffraction spots to decrease while the intensities of the rings increased. The rings were concentric about the (0,0) reflection of the (100) substrate. The first three ring-like reflections appeared at positions of 0.75d, 0.43d and 0.41d, where d is the nearest neighbor distance in the (100) plane (2.77Å). The rings were removed by heating the crystal at 900°C in 1×10^{-5} O_2 for 30 minutes, but were unaffected by high-temperature heating in hydrogen. After the crystal had been heated a few times at high temperatures, first in vacua and then in oxygen, the ring-like diffraction pattern could not be regenerated. This suggested that the rings were associated with carbon which had diffused from the bulk crystal to the surface. Furthermore, if carbon was deliberately deposited onto the surface by the cracking of adsorbed hydrocarbons, the ring-like diffraction pattern returned. Also, studies of the Pt(100) surface by Auger spectroscopy[8] indicated the appearance of surface carbon when the ring-like diffraction patterns were formed.

The diffraction pattern, obtained after the surface has been cleaned by heating in oxygen, is shown in Figure 4. The pattern displayed 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. The extra spots were most intense at an incident electron beam voltage E = 45V and only faintly visible for E > 225V. There were no diffraction spots in between the rows emanating from the (0,0) reflection. The pattern suggested the existence of a surface structure with a unit

mesh of dimensions five times that on the substrate along one principal axis and the same as that of the substrate along the other. There could be surface domains in which the longer periodicity was along the x-axis while in other domains it was along the y-axis.

Thus the pattern shown in Figure 4 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. Using the nomenclature of Wood,[9] such a surface structure would be designated Pt(100)-(5 x 1). Using the matrix notation,[10] the (5 x 1) surface structure could be generated in real space by two sets of unit mesh vectors, $\vec{i}$ and $\vec{j}$, whose components are given by the rows of the transformation matrices, $A = \begin{vmatrix} 5 & 0 \\ 0 & 1 \end{vmatrix}$ and $B = \begin{vmatrix} 1 & 0 \\ 0 & 5 \end{vmatrix}$. These unit mesh vectors are defined relative to the substrate unit mesh.* The splitting of the fractional order diffraction spots might result from the presence of antiphase domains.[11]

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* Using the matrix notation, the (100) substrate can be generated by the same set of unit mesh vectors, $\vec{i}$ and $\vec{j}$, whose components are given by the matrix $\begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix}$. The diffraction pattern showing 1/5-order spots can easily be generated from the components of the reciprocal unit mesh vectors, $A^{-1} = \begin{vmatrix} 1/5 & 0 \\ 0 & 1 \end{vmatrix}$ and $B^{-1} = \begin{vmatrix} 1 & 0 \\ 0 & 1/5 \end{vmatrix}$. In general if $A = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}$,

then $A^{-1} = \frac{1}{|A|} \begin{vmatrix} a_{22} & -a_{21} \\ -a_{12} & a_{11} \end{vmatrix}$

If the crystal was heated at elevated temperatures, the (5 x 1) surface structure slowly disappeared as the ring-like diffraction pattern formed. However, if the surface carbon had been completely removed, the (5 x 1) structure appeared stable at all temperatures (<1400°C) employed in these experiments. Thus the Pt(100)-(1 x 1) diffraction pattern, formed in previous studies[5] by annealing out the (5 x 1) surface structure above 500°C, was probably stabilized by trace amounts of surface carbon. Also, the (5 x 1) structure gradually disappeared at room temperature which was due to the adsorption of residual carbon monoxide, as will be discussed later.

Thus, it appeared that the stable structure of the (100) face of platinum is the Pt(100)-(5 x 1) structure, and that both the (1 x 1) and the ring-like diffraction patterns were stabilized by or were due to impurities (such as carbon, carbon monoxide, etc.).

The (5 x 1) surface structure has also been observed[12,13] on the (100) face of gold, which directly follows platinum in the periodic table. Gold also has a face-centered cubic bulk structure and many physical-chemical properties similar to those of platinum. The appearance of this surface structure on gold has been interpreted[12] as indicating the presence of an hexagonal arrangement of scattering centers superimposed on the underlying square (100) gold substrate, Figure 5. The interatomic spacing of the surface layer is the same as that of the substrate along one principal axis but is 5/6 that of the substrate along the other. Thus the surface and substrate atoms are coincident every 5th substrate atom and this could generate an apparent five-fold surface periodicity.

Fedak and Gjostein[12] claim that the hexagonal layer on gold is comprised of impurity atoms but Palmberg and Rhodin,[13] who epitaxially deposited a few layers of Au on KCl and MgO substrates, believe that Au atoms alone comprise this layer. Auger spectroscopy studies on Au[14] and Pt[8] have indicated the absence of surface impurities associated with the (5 x 1) surface structure. 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 six rows of the surface layer to fit onto five rows of the substrate.

2) Adsorption of Carbon Monoxide

The adsorption of carbon monoxide on supported platinum has been studied by Eischens and Pliskin[15] using infrared spectroscopy. Their results showed that carbon monoxide was adsorbed in both, the bridged and unbridged configurations:

A work function increase of 0.68V and a heat of desorption of 32 kcal/mole were obtained from field emission studies.[16] The carbon monoxide was found to desorb between 150°C and 220°C. Work function increases of 0.23V[17] and 0.68V[18] were measured for adsorption of carbon monoxide on evaporated Pt films, but Heyne and Tompkins[19] found no change in the work function.

When carbon monoxide was introduced into the diffraction chamber and impinged on the platinum surface displaying the (5 x 1) structure, the 1/5 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 x 1) structure to the presence of trace amounts of carbon monoxide accounted for 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 x 1) structure readily reappeared.

The intensities of the integral order diffraction spots increased during the initial stages of CO adsorption as the extra 1/5 order spots disappeared. Continued adsorption of CO then caused a gradual decrease in the intensities of the remaining (1 x 1) diffraction spots until new diffraction features appeared. The flash desorption curve, Figure 6, 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 adsorbed carbon monoxide in 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 produced a (1 x 1) diffraction pattern. Figure 7 illustrates the diffraction pattern obtained after the adsorption of carbon monoxide had reached saturation at room temperature. (This pattern has also been reported by Tucker[20].) The extra spots were visible only for $E < 150V$ and reached their maximum intensity at $E = 15V$ and 90V.

The intensities of the extra spots were weaker than those of the substrate diffraction spots and only those around the (00) reflection could be easily distinguished. A (4 x 2) unit mesh which could lead to the observed pattern is shown in Figure 8. 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 transformation matrices giving the components of the new unit mesh in real space, referred to the substrate mesh, are $A = \begin{vmatrix} 1 & -2 \\ -2 & 0 \end{vmatrix}$ and $B = \begin{vmatrix} 2 & -1 \\ 0 & 2 \end{vmatrix}$. The carbon monoxide coverage necessary to produce this surface structure is approximately 3/4 of a monolayer.

The Pt(100)-(4 x 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 on the diffraction pattern due to the electron beam impinging on the carbon monoxide surface is shown schematically in Figure 9. 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 x 1) surface structure reappeared. There was no evidence of CO disproportionation on the surface; the intensities of the diffraction spots of the (5 x 1) pattern remained unaltered after CO had been adsorbed and desorbed several times. When the crystal was heated to between

200°C-600°C in carbon monoxide, the gas adsorbed only in the β-form and the 1/5 order spots disappeared, the rate of disappearance being faster the lower the temperature. Also, when carbon monoxide was adsorbed at room temperature on a surface displaying the diffraction pattern shown in Figure 3, the rings did not disappear. Also, the Pt(100)-(4 x 2)-CO structure did not fully develop, presumably because some of the surface sites were occupied by carbon.

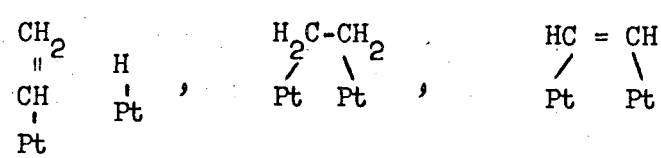
In summary, as carbon monoxide was adsorbed on the platinum surface, the (5 x 1) surface structure first disappeared leaving a (1 x 1) diffraction pattern. This was followed by the formation of ill-defined extra diffraction spots [Figure 9(d)] and finally, with increasing exposure time, the Pt(100)-(4 x 2)-CO pattern [Figure 7] developed. It was interesting to record a work function decrease of 0.45 ± 0.02V when carbon monoxide had adsorbed to saturation, indicating the presence of an electron donating adsorbate.

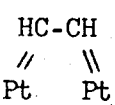
3) Adsorption of Hydrocarbons

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 x 1) surface at room temperature. A work function decrease of 0.76 ± 0.02V was recorded, indicating a donation of electrons to the substrate. The 1/5 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 x 2) surface structure, Figure 10, which could also be indexed by the transformation matrix $\begin{vmatrix} 1 & 1 \\ 1 & -1 \end{vmatrix}$. The pattern contained, in addition to the (1 x 1) spots, extra spots of half-integral indices at the center of each platinum reciprocal unit mesh. The structure was visible only at beam voltages below 200V and the extra spots were most intense at E = 16, 42, 96 and 155V. These spots were less intense and more diffuse than the (1 x 1) diffraction spots. The unit mesh of the surface structure may be taken to be a centered square of side 2a. Possible atomic arrangements leading to the c(2 x 2) structure are depicted in Figure 11, where the shaded circles represent the adsorbed ethylene. Various structures can be postulated for adsorbed ethylene, such as those involving σ-bonding between platinum and carbon;



and  . The ethylene molecule could also Π-bond directly to the substrate; only alternate Pt atoms would participate in the bonding due to steric factors. Any of these atomic configurations could lead to the formation of a c(2 x 2) diffraction pattern and thus the available LEED data does not distinguish between them.

When the crystal was heated at 150°C, the extra spots became streaked and gradually the c(2 x 2) surface structure disappeared. Also, the (5 x 1)

surface structure was simultaneously 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 a few times, the ring-like diffraction pattern (Figure 1) was formed. With this carbon on the surface, the Pt(100)-c(2 x 2)-C_2H_4 structure was not formed and less ethylene was adsorbed, as shown by work function measurements. Also, it became more and more difficult to regenerate the (5 x 1) surface structure. After the crystal had been heated in ethylene, the pattern background increased and all diffraction spots became very faint. The carbon was removed from the surface by high temperature treatment in oxygen. Sometimes the ring-like diffraction pattern was obtained after the surface had been ion-bombarded. Flash desorption studies, after ion bombardment, showed that mainly CO was desorbed from the surface. Thus, in this case, presumably CO was the source of the surface carbon.

The Pt(100)-c(2 x 2)-C_2H_4 structure was not removed by hydrogen at room temperature. Also, 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. Thus, there was no evidence for ethylene hydrogenation under the experimental conditions employed in these studies.

Acetylene is expected to adsorb more strongly than ethylene due to the greater reactivity of the triple bond. This was found to be the case in this study. Acetylene was adsorbed at room temperature, causing a work function decrease of 1.02 ± 0.02V ; acetylene could also be 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 x 1) surface structure vanished extremely rapidly upon introduction of acetylene into the diffraction chamber, at an even faster rate than with carbon monoxide. Also, a clearer diffraction pattern of the c(2 x 2) surface structure was formed, which could be removed by heating the platinum crystal at 150°C for about one hour.

The plots of intensity of the specular reflection I_{oo} as a function of beam voltage, for the Pt(100)-(4 x 2)-CO and Pt(100)-c(2 x 2)-C_2H_2 surface structures, are shown in Figure 12 along with the curves for the Pt(100)-(5 x 1) surface. The arrows mark the positions of the expected Bragg maxima, calculated using the spacing between (100) planes; no inner potential corrections have been made. For platinum surfaces, the shape of the I_{oo} plot depends critically upon the angle of incidence of the electron beam. Generally, when the (5 x 1) surface structure was removed, the maxima in the I_{oo} plot were better defined but their positions remained unaltered.

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 chemisorb on the (100) face of platinum. These gases did not remove or interact in any way with the (5 x 1) surface structure and showed no cracking on the platinum surface.

4) Adsorption of Oxygen

Surprisingly, oxygen did not seem to chemisorb on the (5 x 1) platinum surface at room temperature. Adsorption was tried at elevated temperatures a) to prevent the adsorption of residual carbon monoxide on the surface,

b) most platinum catalytic reactions are performed at these temperatures and c) sufficient thermal energy should increase the dissociation rate of diatomic gases and this may facilitate their adsorption. Again, apparently no chemisorption of oxygen occurred; there was no change in the work function or in the intensities of the diffraction spots, no new surface structures were formed and no M/e = 32 desorption peak was observed in the mass spectrometer during flashing the crystal to high temperatures. Also there was no indication of the previously reported[21] Pt(100)-c(2 x 2)-O_2 surface structure. In this previous work, the stable diffraction pattern of the substrate was (1 x 1) indicating the existence of trace amounts of carbon on the surface. Also, it was noted that there appeared to be a competition between the formation of the (5 x 1) and c(2 x 2) surface structures. In the present work, the substrate was arranged in a stable (5 x 1) configuration and oxygen did not appear to chemisorb on this surface. An attempt was made to remove the (5 x 1) surface structure and hence facilitate the chemisorption of oxygen, by introducing an equi-mixture of CO and O_2 into the diffraction chamber at various crystal temperatures. However CO alone was chemisorbed and the Pt(100)-(4 x 2)-CO surface structure formed at room temperature.

This lack of any experimental evidence for chemisorption of oxygen is an apparent contradiction to the strong oxygen chemisorption on platinum found[6] in conventional adsorption and catalysis studies. Hence it may be concluded that either 1) higher oxygen pressures are required for chemisorption to occur, 2) oxygen chemisorbs only on contaminated platinum surfaces or 3) oxygen chemisorbs on platinum surfaces other than the (100). Further studies are in progress to resolve this question.

5) Adsorption of Hydrogen

Hydrogen, at temperatures up to 1000°C and at gas pressures in the range 10^{-9} to 10^{-7}torr did not appear to chemisorb on the (100) face of platinum. However, if the hydrogen pressure was greater than 2×10^{-5}torr and the crystal heated to between 500°C-1000°C, so that the carbon monoxide from the ambient did not adsorb on the surface, the (5 x 1) surface structure was removed and a (2 x 2) structure formed, (Figure 13). The transformation matrix for this structure is $\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$. The fractional order diffraction spots were visible at $E < 300V$ and were most intense at $E = 37V$, 88V and 150V. They were as well-defined but less intense than the (1 x 1) diffraction spots. The I_{oo} plot, Figure 14, was similiar to those obtained after the adsorption of CO or the unsaturated hydrocarbons. A possible atomic arrangement leading to the (2 x 2) structure is shown in Figure 15(a), where the shaded circles represent the adsorbed hydrogen. However, since the scattering cross-section of adsorbed H_2 for low energy electrons is expected to be smaller than that of platinum, models involving the reconstruction of the platinum surface in the presence of the adsorbed hydrogen could be proposed for the observed (2 x 2) structure. One such model is shown in Figure 15(b). The diffraction pattern arises from the rearranged arrays of platinum atoms alone.

The (2 x 2) structure was very stable and it was necessary to heat crystal at 1200°C in vacuo, for a few minutes, to remove this structure and to regenerate the (5 x 1) structure. However, heating the crystal to only 500°C in 2×10^{-8}torr of oxygen was sufficient to remove the (2 x 2) surface structure. Since a relatively high pressure of H_2 was necessary

to form this structure, trace amounts of other substances could have also been adsorbed on the surface. Indeed, occasionally faint rings were also visible along with the (2 x 2) diffraction pattern arising presumably from the cracking of ambient hydrocarbons at the elevated crystal temperatures. However, if trace amounts of carbon were present initially on the surface, no chemisorption of hydrogen occurred and it became impossible to generate the (2 x 2) diffraction pattern. Finally, when CO was adsorbed on the Pt(100)-(2 x 2)-H_2 surface structure at room temperature, a c(2 x 2) diffraction pattern was produced. The fractional order spots were faint but as sharp as the (1 x 1) diffraction spots. The (2 x 2) pattern returned after all of the CO had been desorbed from the surface.

6) Adsorption of Carbon Dioxide, Nitrous Oxide and Nitrogen

There was no evidence of the chemisorption of carbon dioxide, nitrogen or nitrous oxide on the (100) face of platinum at pressures up to 1×10^{-7} torr and temperatures up to 700°C; there was no removal of the (5 x 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.

SUMMARY

The adsorption of several gases (CO, O_2, H_2, C_2H_2, C_2H_4, CH_4, C_2H_6, N_2, CO_2 and N_2O) on the (100) face of platinum single crystals has been studied using low energy electron diffraction and other complimentary techniques (mass spectrometry, work function and flash desorption

measurements). The (100) face of platinum appeared to be characterized by a (5 x 1) surface structure [Pt(100)-5 x 1]. The (1 x 1) structure, which is characteristic of the bulk unit cell, was stabilized by carbon and carbon-containing molecules (CO, C_2H_2, C_2H_4). A list of surface structures which were detected on the Pt(100) single crystal surface is given in Table I.

The platinum surface seemed to have a strong affinity for carbon; those unsaturated gas molecules containing carbon were readily chemisorbed at room temperature. The (5 x 1) diffraction pattern disappeared rapidly upon the adsorption of CO, C_2H_2 and C_2H_4. This behavior is very difficult to rationalize in terms of the proposed[12] model of an hexagonal surface layer. Carbon monoxide adsorbed in three bonding states; the low coverage form was removed at 600°C and the higher coverage forms at 130°C and 170°C. The carbon monoxide molecules desorbed without disproportionation and the (5 x 1) pattern returned immediately. However, some cracking of the adsorbed hydrocarbon molecules occurred and the (5 x 1) structure was not so readily regenerated. A ring-like diffraction pattern, which appeared at elevated temperatures, seemed to be associated with the presence of surface carbon. Hydrogen was chemisorbed only at elevated temperatures (> 500°C) and this was associated with the formation of a very stable surface structure. The other gases (O_2, CH_4, C_2H_6, CO_2, N_2 and N_2O) did not seem to chemisorb on the platinum (100) surface. Apparent order of adsorption at the low gas pressures used was $C_2H_2 > CO > C_2H_4 > H_2 > O_2 \sim CO_2$, N_2, CH_4, N_2O. The co-adsorption of the H_2 and CO produced a surface structure different from those formed by the chemisorption of CO or H_2 alone.

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TABLE I.

Structures on the (100) Platinum Surface

Under Different Experimental Conditions

Structure	Temperature Range of Stability
Pt(100) - (5 x 1)	All temperatures studied (< 1400°C)
Pt(100) - (4 x 2) - CO	< 130°C
Pt(100) - (1 x 1) - CO	300° - 500°C
Pt(100) - c(2 x 2) - C_2H_4	< 150°C
Pt(100) - c(2 x 2) - C_2H_2	< 150°C
Pt(100) - (2 x 2) - H_2	< 1200°C
Pt(100) - c(2 x 2) - (H_2 + CO)	< 600°C
Pt(100) - ring - C	All temperatures studied (< 1400°C)

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FIGURE CAPTIONS

Figure 1. The diffraction chamber.

Figure 2. Mass spectrum with 9×10^{-9} torr acetylene flowing through the diffraction chamber.

Figure 3. Pt(100) - ring-like diffraction pattern at beam voltage E = 72V.

Figure 4. Pt(100) -(5 x 1) diffraction pattern at E = 124V.

Figure 5. Possible interpretation of (5 x 1) surface structure showing an hexagonal surface layer superimposed on square substrate layer.

Figure 6. Carbon monoxide flash desorption spectrum.

Figure 7. Pt(100) -(4 x 2)- CO diffraction pattern at E = 95V.

Figure 8. Possible interpretation of Pt(100) -(4 x 2)- CO surface structure.

Figure 9. Gradual change in diffraction pattern due to electron beam desorption of some adsorbed carbon monoxide.

Figure 10. Pt(100) - c(2 x 2) - C_2H_4 diffraction pattern at E = 94V.

Figure 11. Possible interpretations of the c(2 x 2) surface structure.

Figure 12. Intensity distributions of the 00 beam for Pt(100) surface structures (a) at angle of incidence $\theta = 6°$ (b) at $\theta = 4°$.

Figure 13. Pt(100) - (2 x 2)- H_2 diffraction pattern at E = 106V.

Figure 14. Intensity distribution of the 00 beam from a Pt(100) - (2 x 2)-H_2 surface at $\theta = 5°$.

Figure 15. Possible interpretations of the (2 x 2) surface structure.

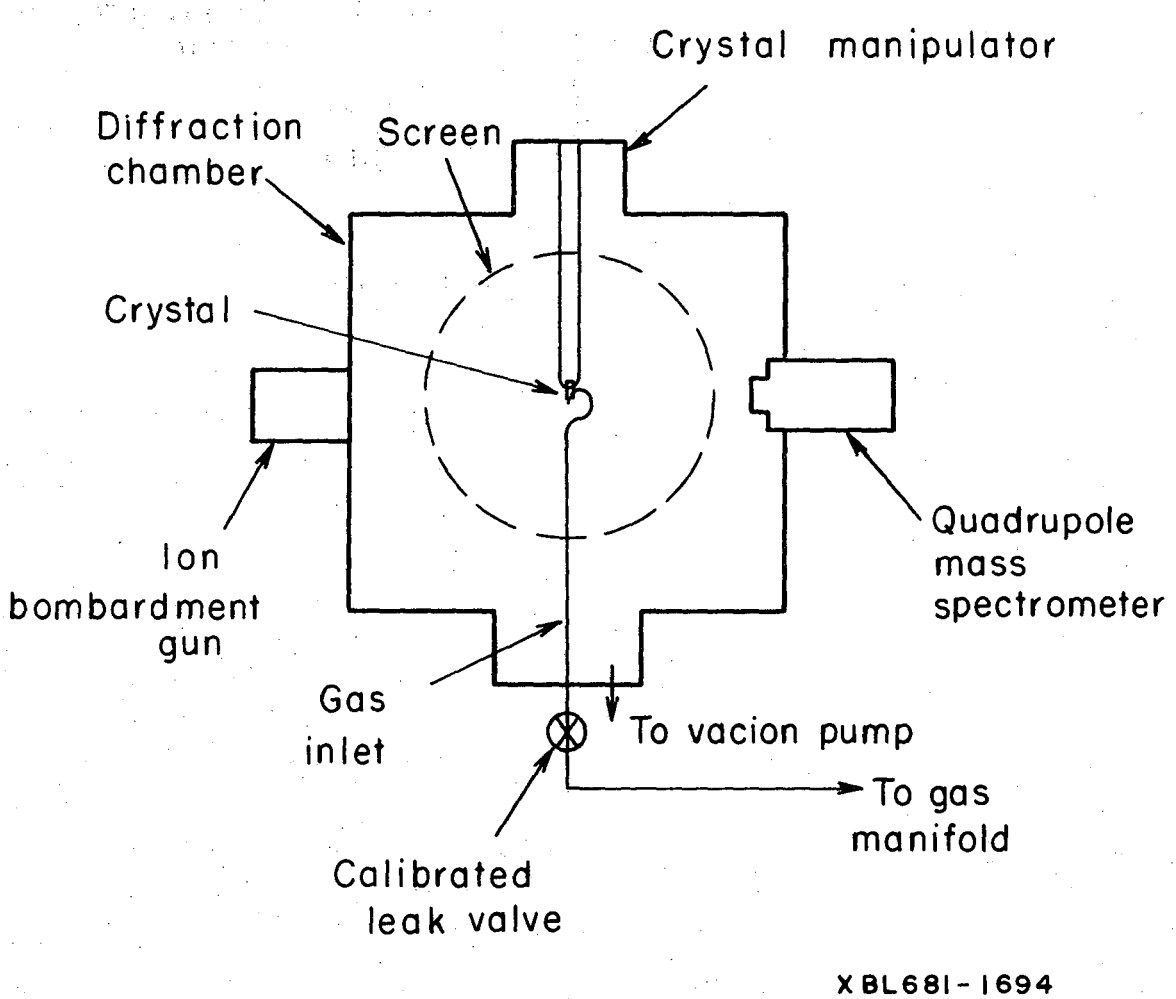

Crystal manipulator
Diffraction chamber
Screen
Crystal
Ion bombardment gun
Quadrupole mass spectrometer
Gas inlet
To vacion pump
To gas manifold
Calibrated leak valve
XBL681-1694

Fig. 1

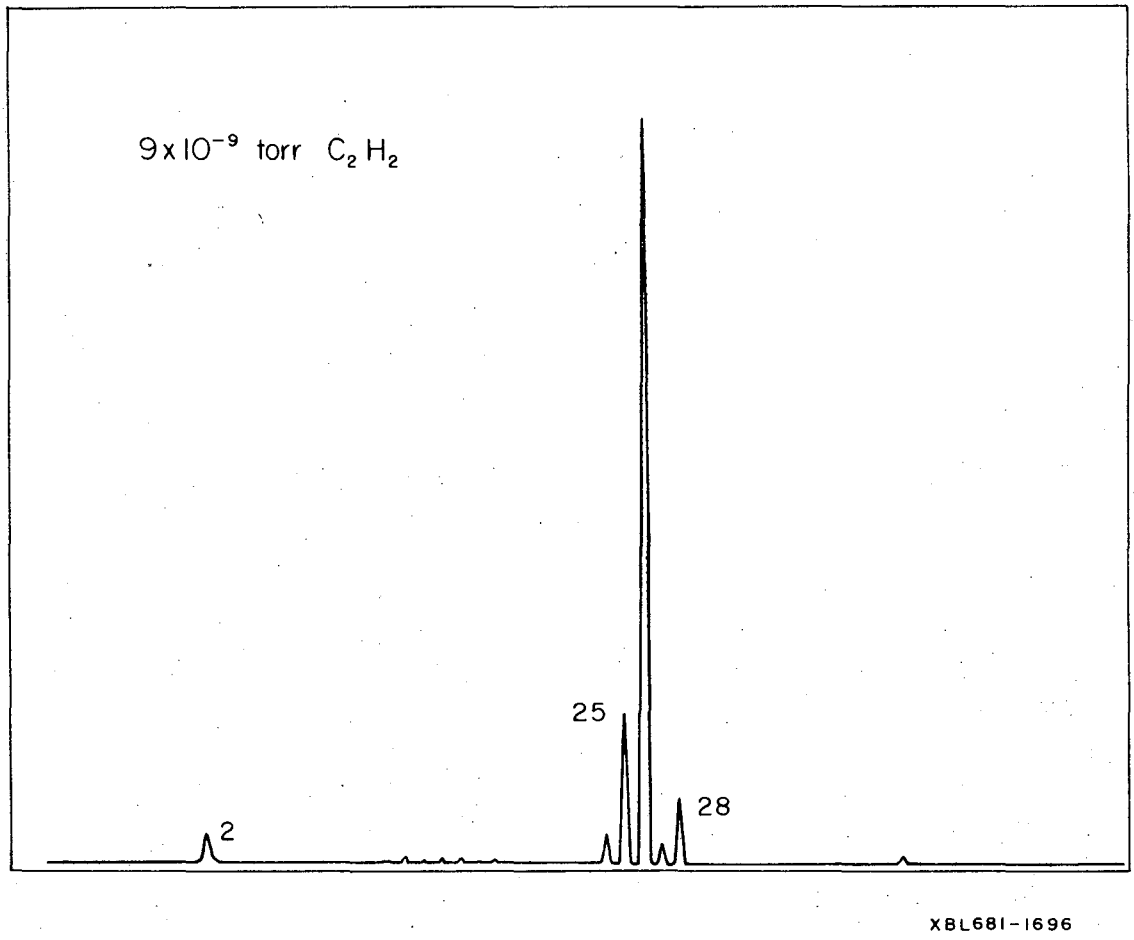
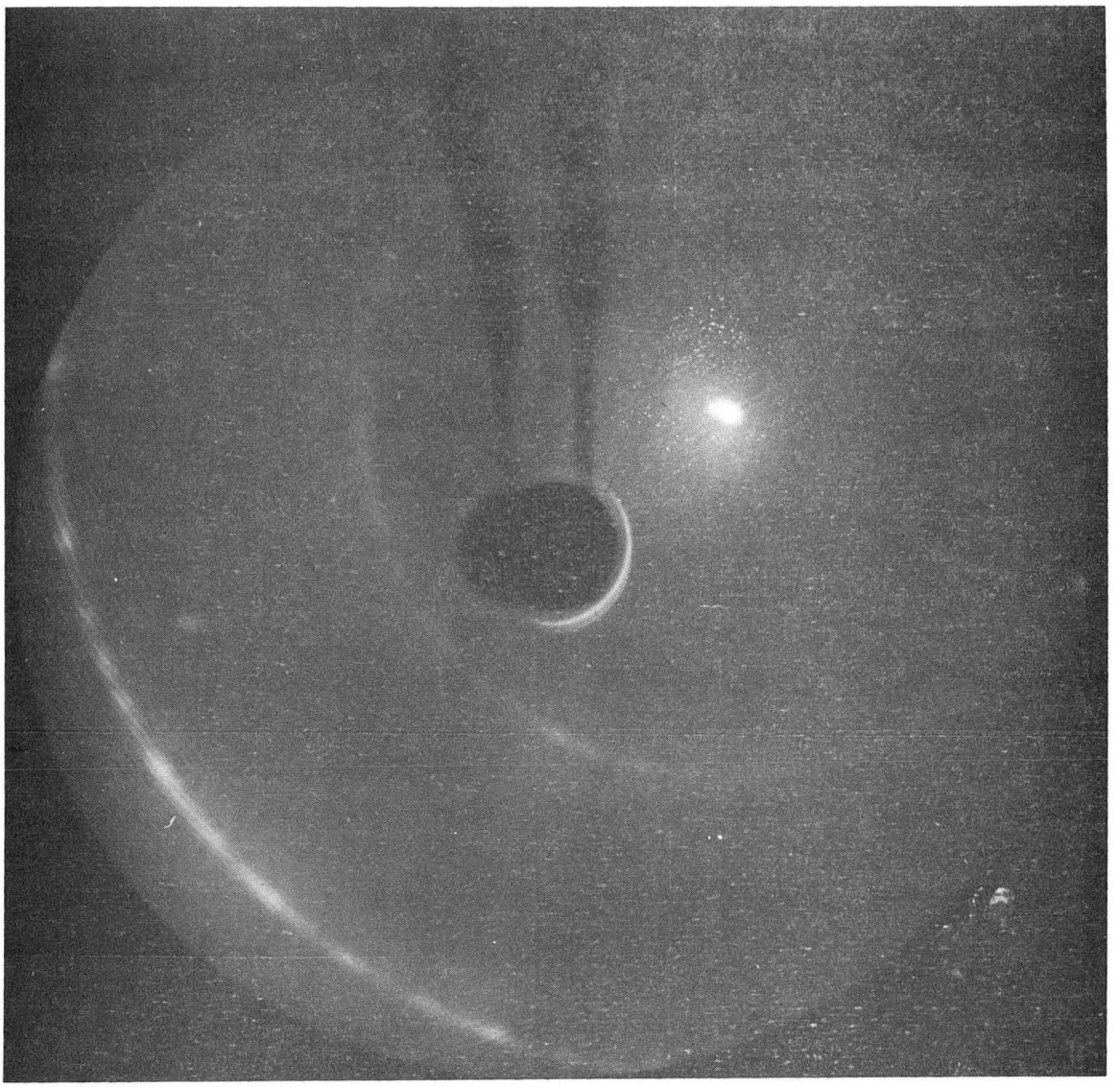
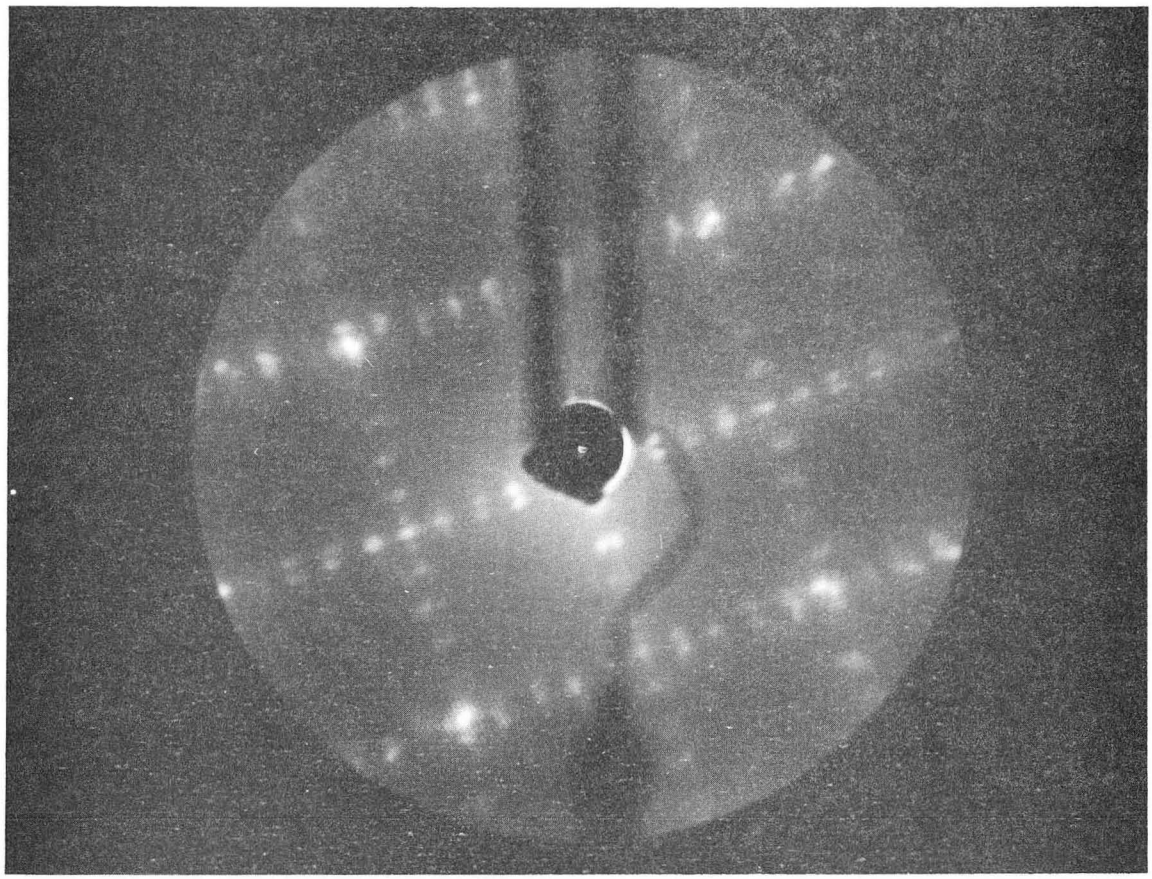


Fig. 2



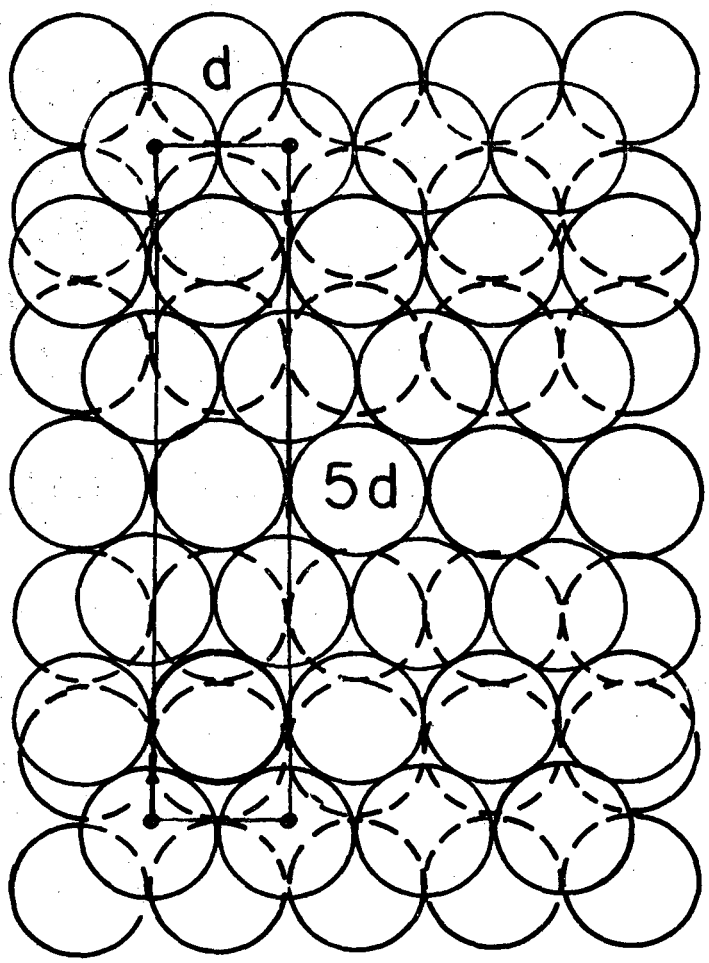
XBB 687-4546

Fig. 3



XBB 684-1737

Fig. 4



Reconstructed layer

XBL684-2424

Fig. 5

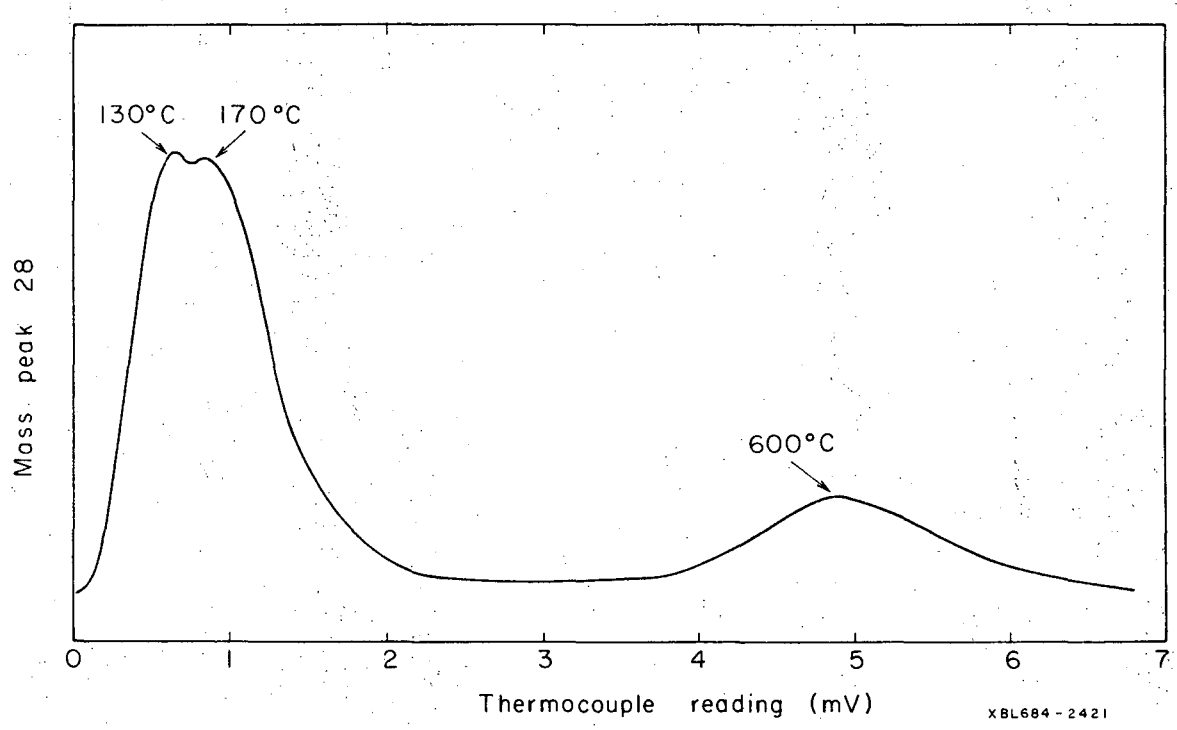
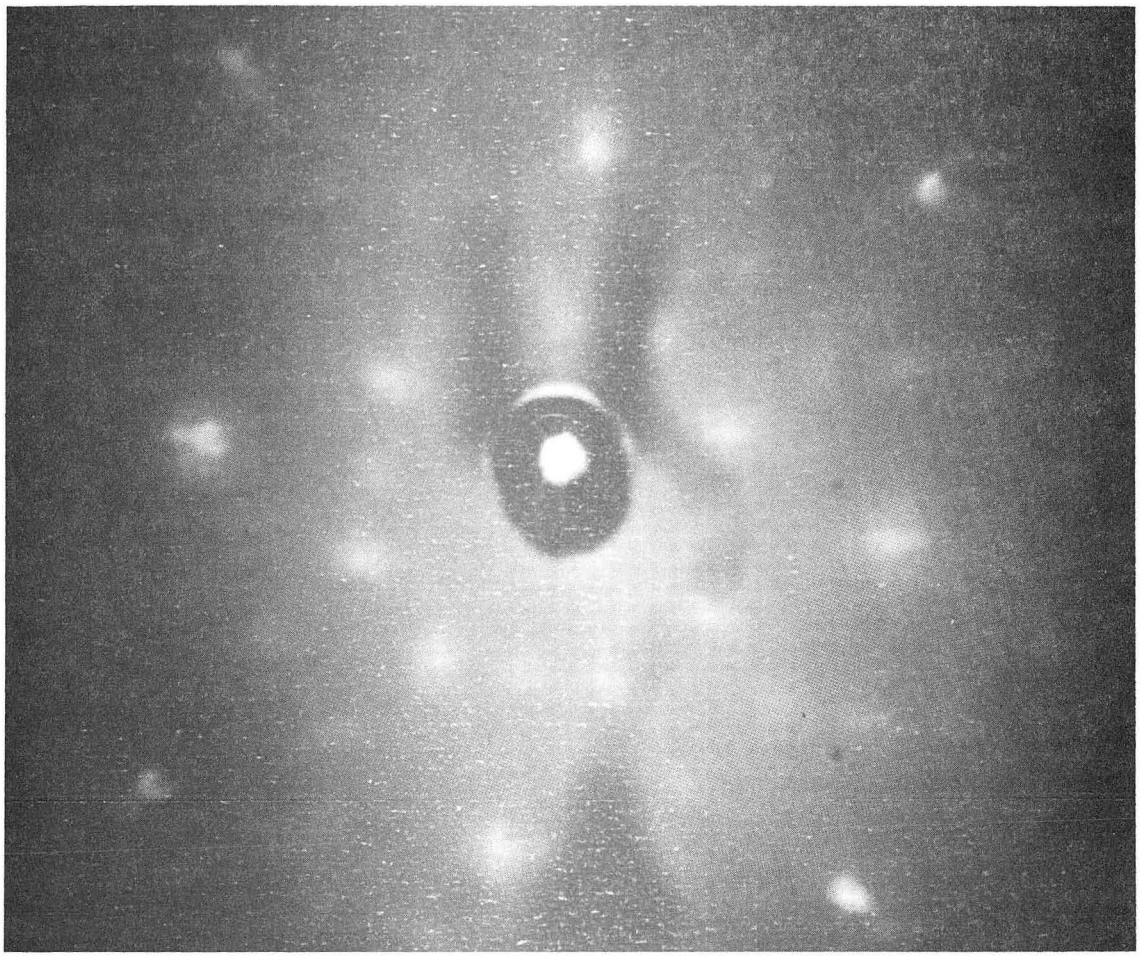
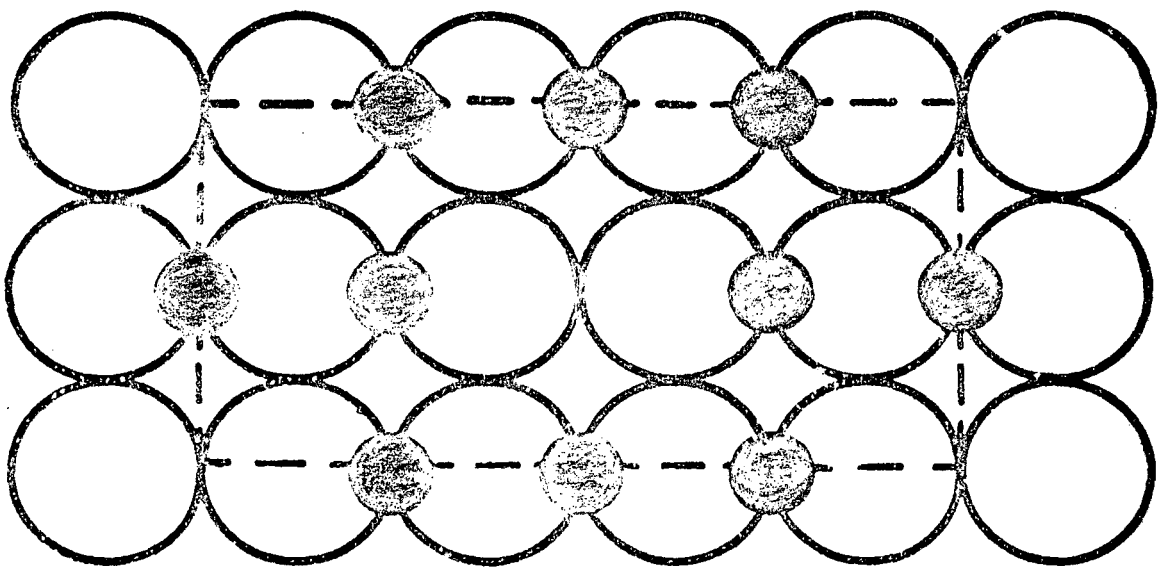

130°C
170°C
600°C
Mass peak 28
0
1
2
3
4
5
6
7
Thermocouple reading (mV)
XBL684-2421

Fig. 6



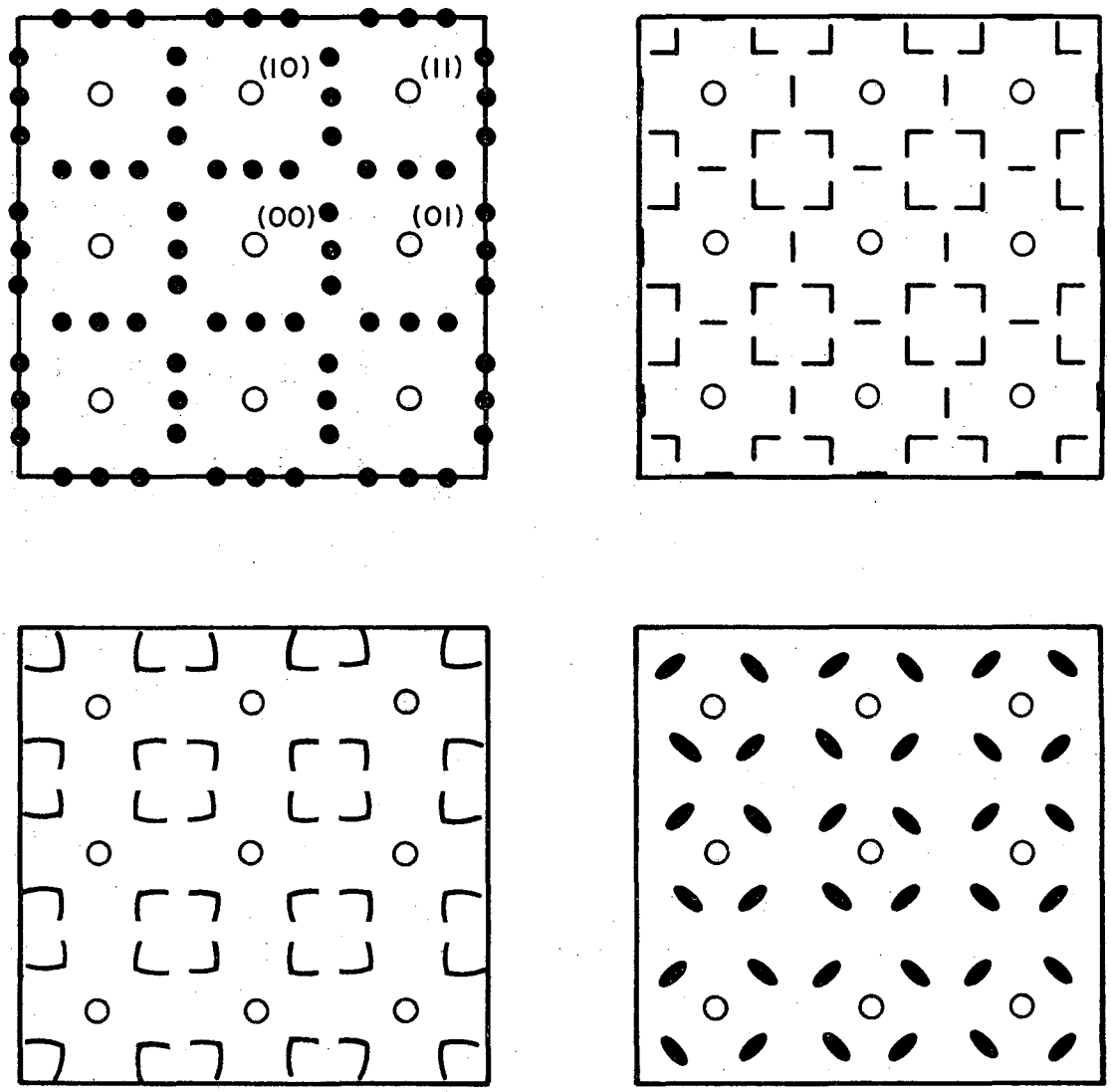
XBB 685-2996

Fig. 7



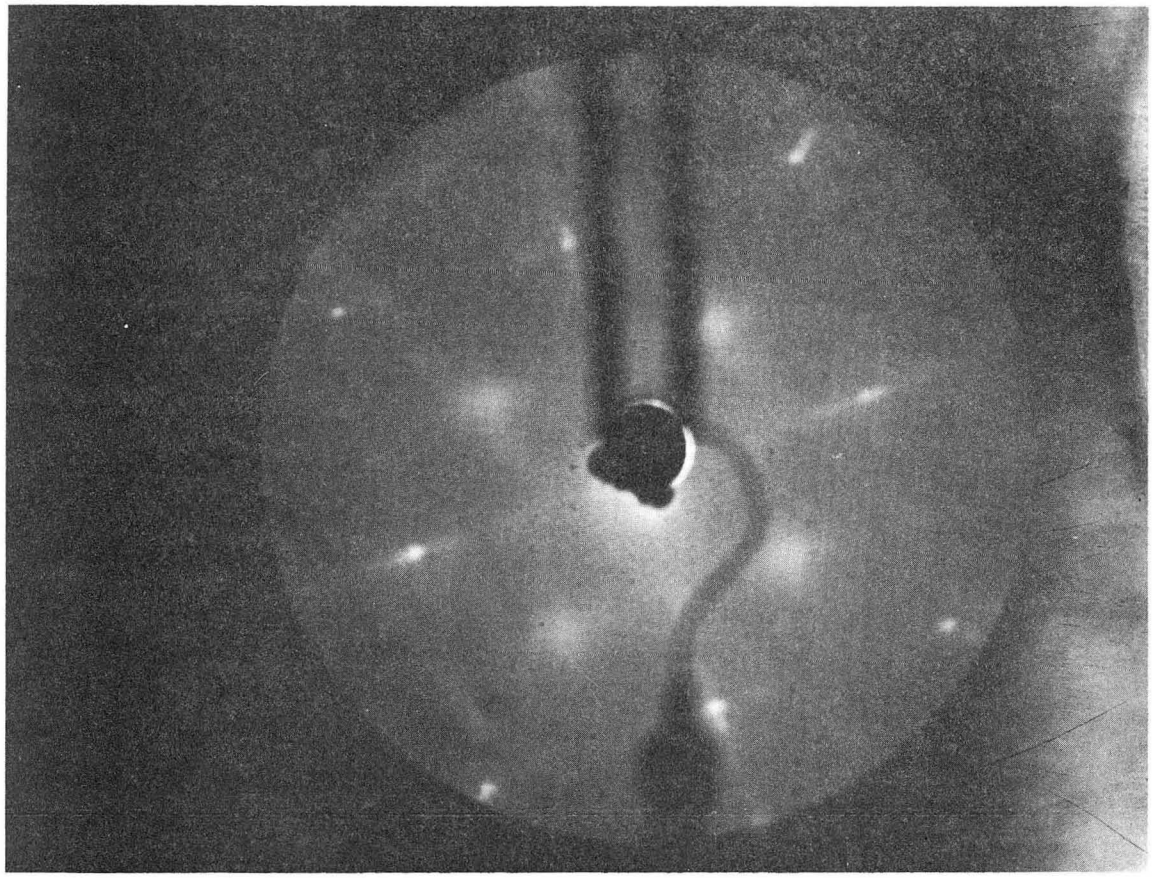
XBL684-2425

Fig. 8



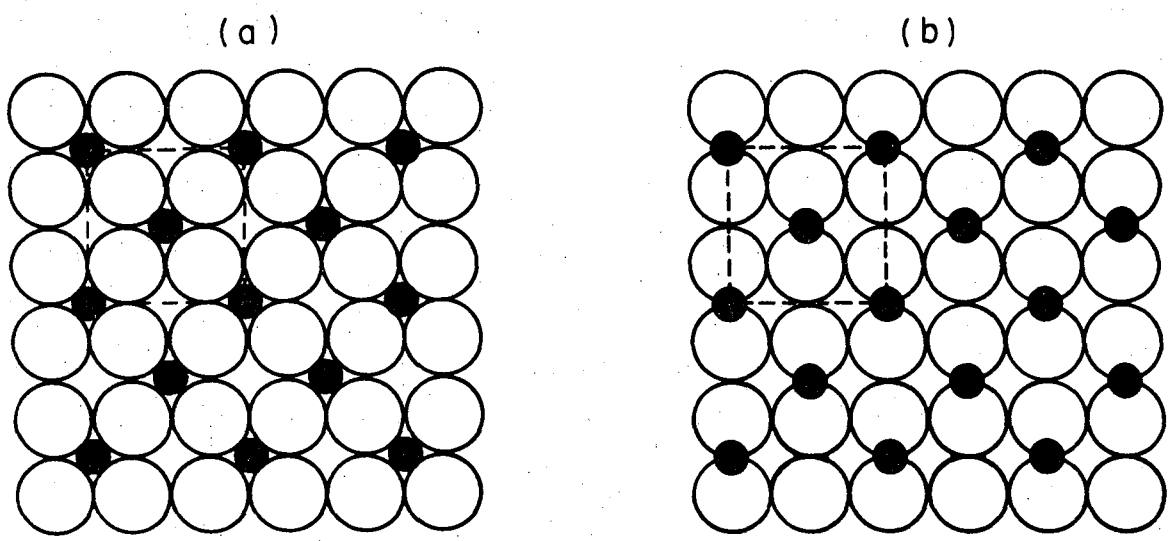
XBL681-1692

Fig. 9



XBB 684-1736

Fig. 10



XBL 684-2422-A

Fig. 11

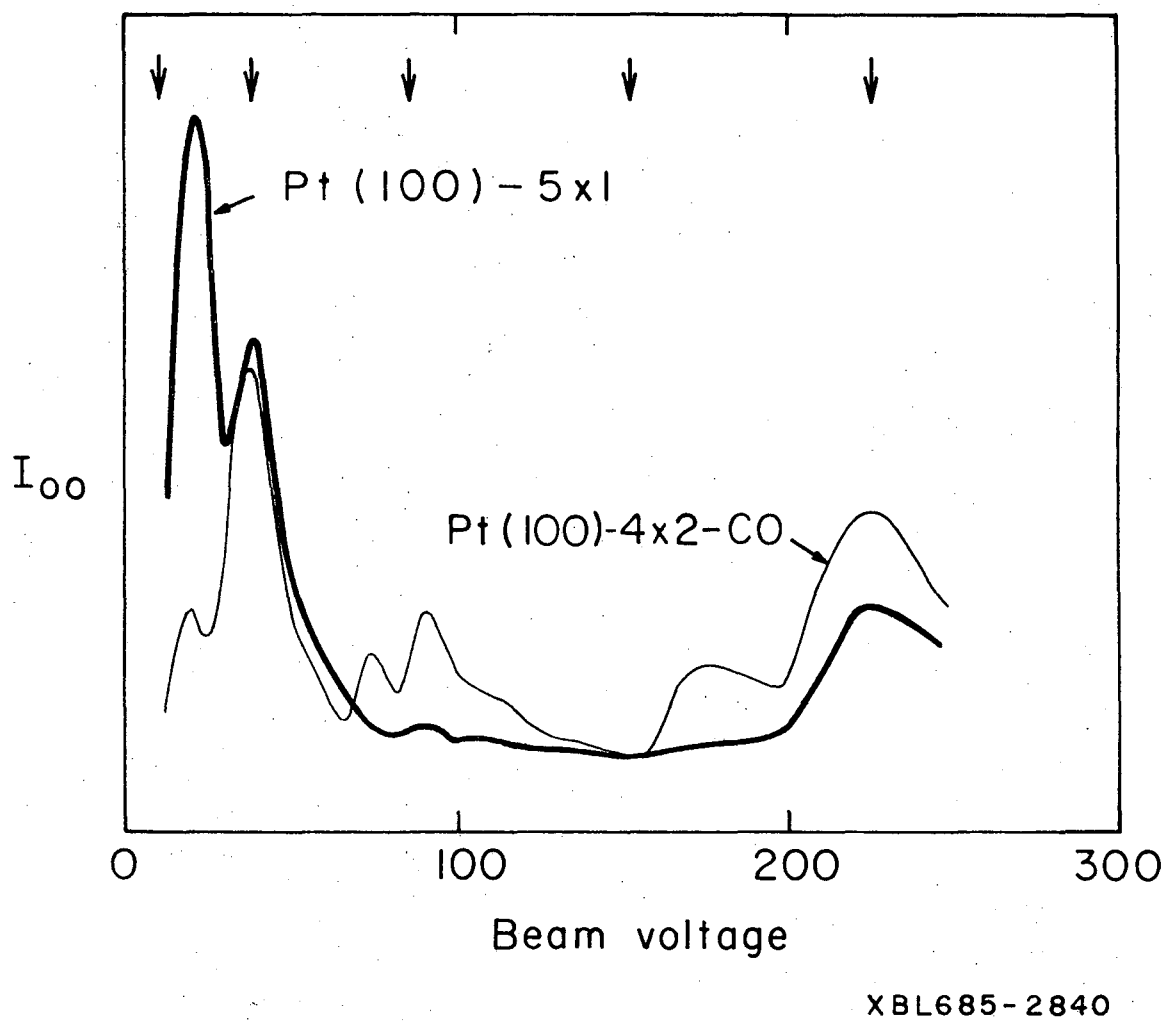
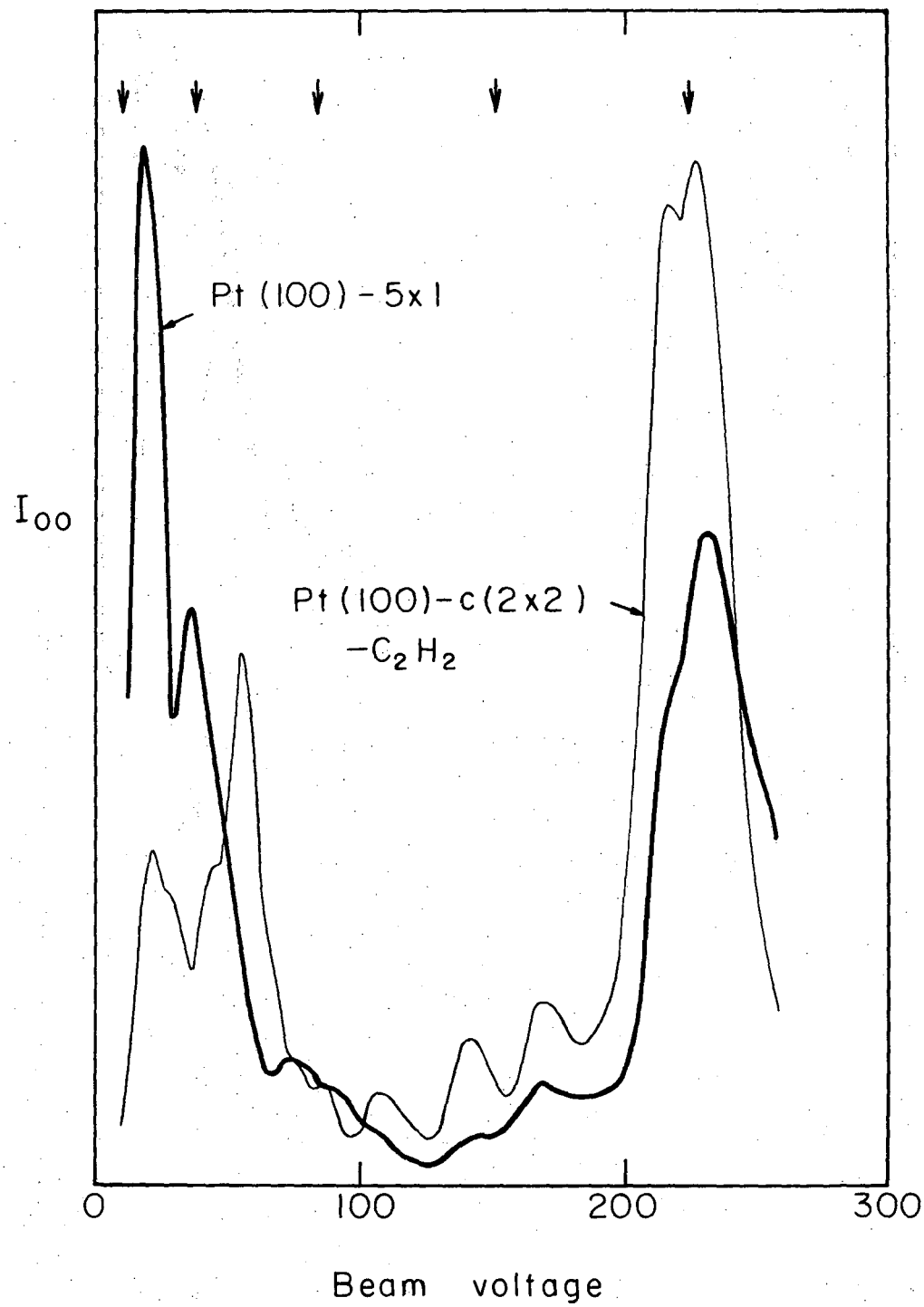
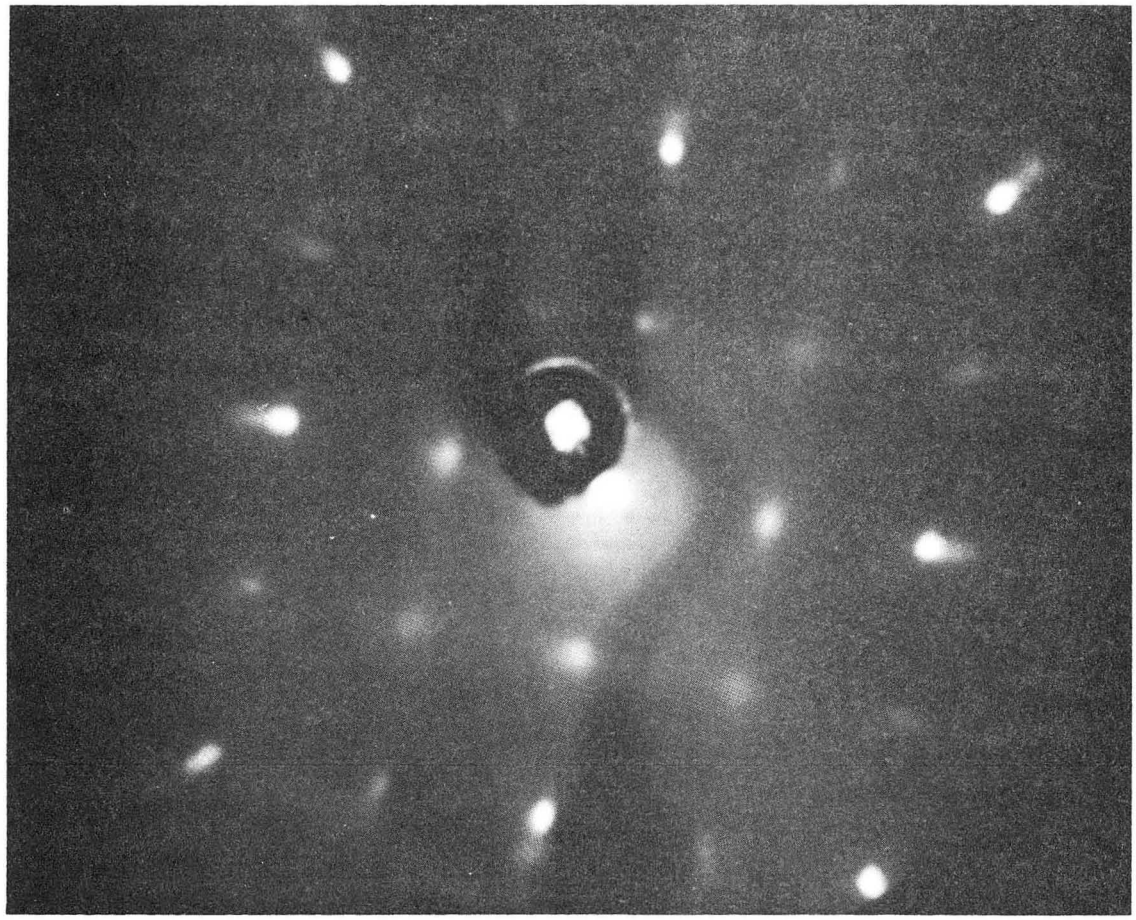

Pt (100) – 5x1
Pt (100)-4x2-CO
I_{00}
0
100
200
300
Beam voltage
XBL685-2840

Fig. 12a



XBL685-2841

Fig. 12b



XBB 686-3518

Fig. 13

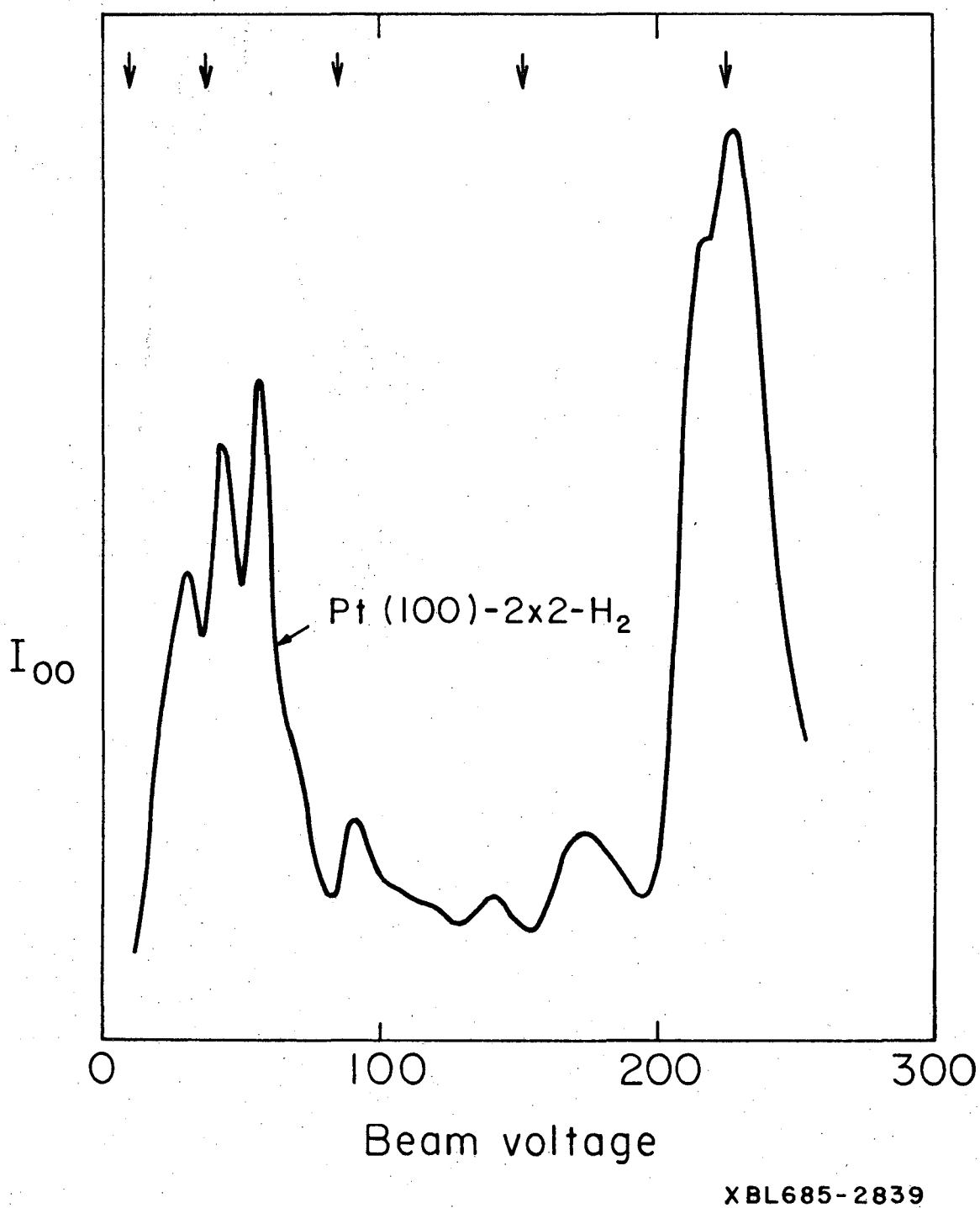
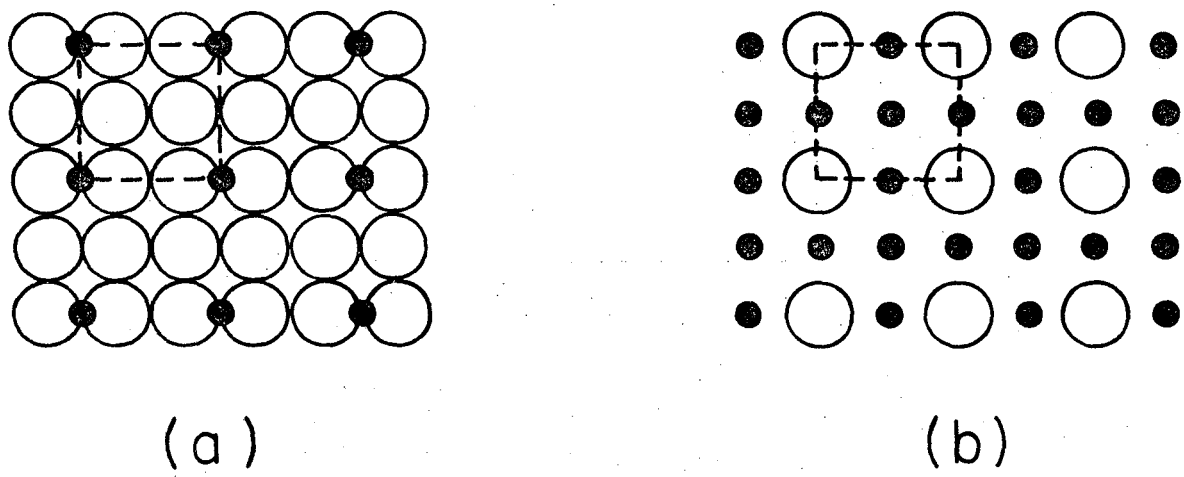


Fig. 14



XBL686-2899

Fig. 15

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