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H. B. Lyon, and G. A. Somorjai

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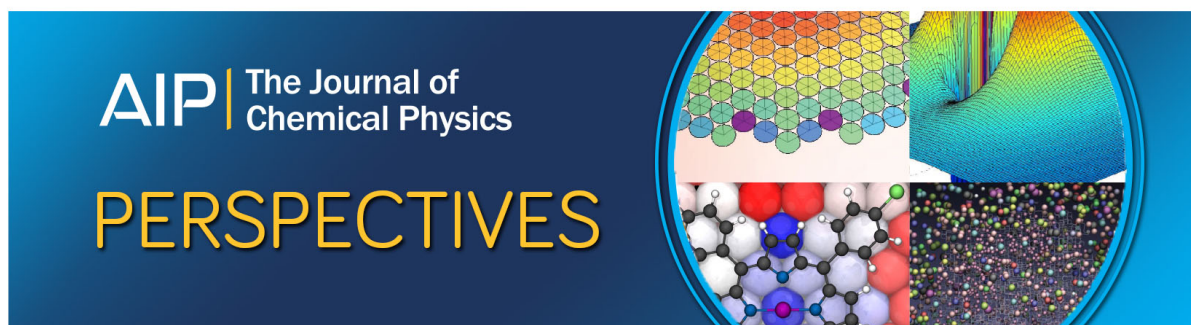
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present when the pertinent group interacts weakly with the iron and disappears due to the shift in the energy of the d_{z^2} orbital in the configuration where there is stronger interaction.

A general feature of this work has been the realization that the study of hemoprotein crystals in polarized light is a most informative one; the spectra are not complicated by porphyrin-porphyrin interactions and the oriented gas model appears to hold well—apparently

better than in any other known molecular crystal spectrum.

ACKNOWLEDGMENTS

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Low-Energy Electron-Diffraction Study of the Clean (100), (111), and (110) Faces of Platinum

H. B. LYON AND G. A. SOMORJAI

Department of Chemistry and Inorganic Materials Research, Division of the Lawrence Radiation Laboratory, University of California, Berkeley, California

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The structures of the (111), (100), and (110) crystal faces of platinum were studied as a function of temperature in the range 300°–1769°C (melting point). The (111) and (100) substrates are stable while the (110) face shows faceting above 600°C. Several surface structures were found to exist on the stable platinum substrates. These have well-defined temperature ranges of stability. There are two types of surface structures, ordered and disordered. Both types appear to be the property of the clean platinum substrates. The ordered structures appear during annealing, after ion bombardment at lower temperatures (<900°C). They exhibit long-range order and their stability ranges overlap on a given substrate. These structures are believed to be due to ordered arrays of vacancies in the substrate plane which, under proper conditions, show remarkable stability. A high, nonequilibrium concentration of defects at the surface may be necessary to induce their formation.

The disordered surface structures appear at high temperatures, above the stability range of most of the ordered structures. They are characterized by ringlike diffraction features which develop gradually as a function of increased heating time or temperature. The formation of these structures is irreversible and they can only be removed by ion bombardment. Near the melting point, the ring patterns remain the only diffraction features of the presumably greatly disordered surfaces.

The ratio of lattice parameters assigned to the diffraction rings on each substrate indicate that they can be due to domains of (111) surface structures. These hexagonal structures appear on all of the platinum surfaces, are freely rotated in the substrate plane, and show an ~11% contraction with respect to the interplanar spacing in the ordered (111) face. The disordered close-packed-hexagonal structure seems to be the stable high-temperature surface phase of platinum.

INTRODUCTION

ONE of the striking results of low-energy electron-diffraction studies on "clean" solid surfaces (defined later) is the discovery that the substrate atoms may reside in surface structures of different kind.¹ The presence of these surface structures is indicated by the appearance of extra diffraction features which are superimposed on the diffraction pattern of the substrate unit mesh predicted by the bulk unit cell. One can assign lattice parameters to these surface structures which, in general, were found to be integral

multiples of the lattice parameters which characterize the substrate. Studies on "clean" germanium, silicone, and gallium arsenide surfaces have revealed the presence of several surface structures with unit cells in the range of twice (2×2) or as large as eight times (8×8) the unit-cell dimensions of the substrate.^{2,3} The exact arrangement of atoms which produce these structures is still in question. Their appearance, however, indicates (a) long-range order on the surface, and (b) that transformation (reversible or irreversible) from one type of surface structure to another can readily occur. Thus, these structures which may be

¹ R. E. Schlier and H. E. Farnsworth, *Semiconductor Surface Physics* (University of Pennsylvania Press, Philadelphia, Pa., 1956).

² J. J. Lander, *Progr. Solid State Chem.* **2**, 26 (1965).

³ A. U. MacRae, *Surface Sci.* **4**, 247 (1966).

TABLE I. Major impurities in the platinum sample used in the LEED study.

Impurity	Wt (ppm)
Fe	30
Cr	25
Rh	15
Ag	<30
Au	<10
Ir	7
Pb	<6
Si	4
Pd	2

called surface phases have a temperature range of stability, and phase transformations at the surface can take place without any apparent effect on the bulk structure.

There are several reasons for the existence of surface structures which are indicated by recent experiments.² The activation energy for surface diffusion is appreciably smaller than either the activation energy for bulk diffusion or the heat of sublimation in monatomic solids.^{4,5} The surface atoms are shielded by large potential-energy barriers from rapid exchange with the bulk or vacuum. The phonon spectrum of surface atoms is different from that of the bulk atoms as shown by surface Debye temperature measurements.^{6,7} There is also some experimental evidence that, in addition to the change in the mean-square displacement of atom at the surface, there is a net expansion or contraction with respect to the bulk lattice spacing.^{8,9}

The "clean" surfaces of metal single crystals have been studied to a lesser extent than semiconductor surfaces. Different crystal faces of nickel have been investigated extensively^{10,11} but no surface structures were reported which could be attributed to the substrate. This may be the reason why further studies on metal surfaces have not been aimed at investigating the substrate properties but rather the structure of adsorbed gases or condensable impurities. It has even been proposed¹² that surface structures which are the property of the clean substrate cannot occur on metal

surfaces. Thus, their presence is likely only on semiconductor surfaces.

Farnsworth,¹³ however, has reported the presence of fractional order diffraction features on the clean copper (100) surface as early as 1957. Boggio and Farnsworth¹⁴ have reported on a Ta(110)5 surface structure's being quite reproducible and serving as a convenient reference for the study of surface oxidation. We have found surface structures to be present on the (100) platinum substrate¹⁵ and on the (100) surfaces of other face-centered-cubic crystals.^{16,17} It is the purpose of this paper to report on the surface properties of the "clean" (100), (111), and (110) faces of platinum single crystals.

Platinum is particularly suitable for studies of the "clean surface" since it can be prepared in high purity, does not form stable carbides,¹⁸ and has a slow oxidation rate even at elevated temperatures.¹⁹ It is also inert in many chemical reactions, which can therefore serve to eliminate the more reactive impurities from the crystal. In addition, platinum is an excellent catalyst in many oxidation or dehydrogenation reactions. It is well known²⁰ that the catalytic activity is a strong function of the method of surface preparation and the temperature at which the reaction is carried out. Therefore, understanding of the surface properties of "clean" platinum is a prerequisite for definitive studies of catalytic surface reactions.

The platinum single-crystal surfaces were studied in ultrahigh vacuum as a function of temperature. Several surface structures were found to exist on the (100) and (111) crystal faces. The low-temperature surface structures ($T < 750^\circ\text{C}$) are ordered and characterized by lattice parameters which are integral multiples of that of the substrate lattice parameter, similar to those found on the monatomic semiconductor surfaces. They are stable only in well-defined temperature ranges. Transition from one type of ordered surface structure to another can be reversible or irreversible. If their temperature range of stability overlaps they may coexist on the same crystal surface.

At elevated temperatures ($T > 750^\circ\text{C}$) the ordered surface structures seem to be unstable. A new disordered phase appears on all faces of platinum which were studied, which is characterized by ringlike diffraction patterns. The formation of the ring pattern

⁴ N. A. Gjostein, *Metal Surfaces* (American Society for Metals, Cleveland, Ohio, 1963), Chap. 4.

⁵ W. Jost, *Diffusion* (Academic Press Inc., New York, 1952).

⁶ B. C. Clark, R. Herman, and R. F. Wallis, *Phys. Rev.* **139**, A860 (1965).

⁷ H. B. Lyon and G. A. Somorjai, *J. Chem. Phys.* **44**, 3707 (1966).

⁸ A. U. MacRae and L. H. Germer, *Ann. N.Y. Acad. Sci.* **101**, 627 (1963).

⁹ L. G. Feinstein and D. P. Shoemaker, *Surface Sci.* **3**, 294 (1965).

¹⁰ H. E. Farnsworth and H. H. Madden, Jr., *J. Appl. Phys.* **32**, 1933 (1961).

¹¹ A. U. MacRae, *Science* **139**, 379 (1963).

¹² D. G. Fedak and N. A. Gjostein, *Phys. Rev. Letters* **16**, 171 (1966).

¹³ R. E. Schlier and H. E. Farnsworth, *Advan. Catalysis* **9**, 434 (1957).

¹⁴ J. E. Boggio and H. E. Farnsworth, *Surface Sci.* **3**, 62 (1965).

¹⁵ S. Hagstrom, H. B. Lyon, and G. A. Somorjai, *Phys. Rev. Letters* **15**, 491 (1965).

¹⁶ G. A. Somorjai, A. Chutjian, and A. M. Mattera, *Bull. Am. Phys. Soc.* **11**, 727 (1966).

¹⁷ A. M. Mattera, R. M. Goodman, and G. A. Somorjai, "LEED Study of the (100) Face of Silver, Gold, and Palladium," *Surface Sci.* (to be published).

¹⁸ M. R. Nadler and C. P. Kemper, *J. Phys. Chem.* **64**, 1468 (1960).

¹⁹ J. C. Chaston, *Platinum Metals Rev.* **8**, 54 (1964).

²⁰ J. A. Becker, *Advan. Catalysis* **7**, 136 (1955).

represents an irreversible phase transformation. The disordered surface structure is stable indefinitely and can only be removed by ion bombardment. As the melting temperature is approached (1769°C) the diffraction features of the substrate diminish while the intensities of the ring patterns increase. Thus, more surface atoms transfer into the disordered phase.

The conditions which were necessary to produce each surface structure are discussed in this paper along with the properties of these structures. The surface structures reported could always be reproduced on all of the platinum samples which were studied. In order to prove that a given surface structure is the property of the clean platinum substrate the low-energy electron-diffraction studies were implemented by other investigations. These included heat treatments in reactive ambients to cause selective chemical reactions which could be used to remove impurities from the samples, the use of a mass spectrometer to monitor the ambient composition and detect the presence of volatile impurities, and chemical analysis of the samples.

DEFINITION AND PREPARATION OF THE CLEAN PLATINUM SURFACE

The definition of what is a "clean" surface should reflect the experimental conditions which determine the limit of detection of impurities. Low-energy electron-diffraction studies of semiconductor² and metal¹⁵ surfaces revealed the presence of open surface structures which occupy less than 5% of the total number of surface sites [total surface concentration on the Pt(100) substrate is 1.29×10^{15} atoms/cm²].

The detection limit is a function of several experimental parameters, such as the electron optics characteristics (current density, energy distribution of impinging electrons, size of the electron beam, collector efficiency, ...) and the properties of the studied single-crystal surface (atomic density, electron density, extent of damage introduced by surface preparation). The presence of adsorbed species which are randomly distributed and therefore do not give extra two-dimensional diffraction features can also be detected on the solid surface in some cases. For example, May²¹ has reported that the variation of the intensity of the specularly reflected electron-beam (00 reflection) could be used to monitor the adsorption of amorphous layers of oxygen on tungsten. It should be noted, however, that there are several adsorbed species the presence of which do not affect the intensity of the elastically reflected electron beam. For example, N₂ on the (111) face of platinum.

The use of a mass spectrometer can greatly aid the detection of surface contaminants. The detection

sensitivity of 10^{-12} torr partial pressure of the instrument which is used in this study allows one to monitor changes in the mass spectrum which are caused by less than 1% of the monolayer provided that the desorption takes place in short times (about 1 min). We have used a quadrupole mass spectrometer which was attached to the diffraction chamber throughout these measurements.

We can therefore define the clean solid surface in low-energy electron-diffraction studies as one in which the concentration of ordered impurities is below the detection limit of our present techniques (less than 10^{12} cm⁻² impurities). There should also be no change in the mass-spectrometer trace which is due to the sample surface when it is heated to elevated temperatures at which layers of substrate atoms may be removed by vaporization.

Platinum single crystals of the highest purity (99.9999%) were used in the experiments. Table I lists the impurities and typical values of their concentrations in the samples. The samples (0.5–2 mm thick and 6 mm in diameter) were cut (diamond saw or spark cutter) after orienting the particular face by x ray within 1 deg. The crystals were then polished ($\frac{1}{4}$ - μ diamond paste) and etched by dilute aqua regia (50% H₂O by volume) at 100°C. This treatment produced smooth surfaces relatively free from etch pits. On one sample large etch pits were allowed, but their presence had no noticeable effect on the diffraction features. Chemical etching removes most of the surface damage introduced by the mechanical treatments.

The sample was then spotwelded to a holder which was subsequently mounted on the crystal manipulator. In every case the holder was attached to the thin side of the disk-shaped sample. Either uniform resistance heating (dc) or temperature gradient along the sample surface could be produced using holders of different thickness with respect to that of the crystal. It was found that surface structures could be produced more easily in the presence of a temperature gradient along the surface. In order to avoid contamination of the platinum surface from the holder material, the holder was also fabricated from high-purity platinum. No difference, however, has resulted in the observed diffraction features when using tantalum holders instead of platinum.

The temperature gradient along the crystal surface was monitored by several Pt/Pt-10% Rh thermocouples which were spotwelded onto the sample surface. After the temperature gradient has been established the temperature was monitored by one thermocouple which was mounted on the back side of the sample. In experiments which were performed to prove that the observed surface structures are the property of the clean surface, the thermocouple was eliminated after a calibration of heater current versus surface temperature was determined. The diffraction

²¹ J. W. May and L. H. Germer, J. Chem. Phys. **44**, 2895 (1966).

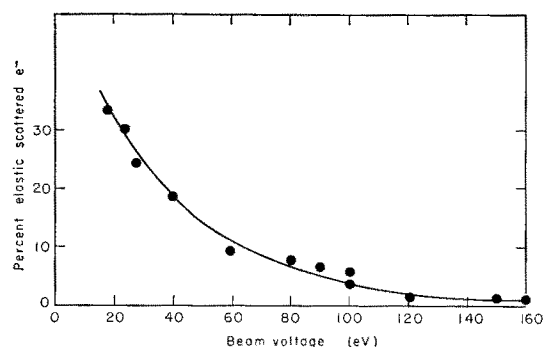


Fig. 1. The fraction of elastically reflected electrons from the (111) face of platinum as a function of electron energy.

features were not affected by the presence of the thermocouple.

Ion bombardment using high-purity xenon or argon was employed in order to (a) remove the surface damage which was caused by the mechanical surface treatments or (b) remove the disordered surface structure which formed irreversibly at high temperatures ($T > 750^\circ\text{C}$). More careful surface preparation eliminated the need for excessive ion sputtering. Usual conditions of ion bombardment were 2×10^{-5} torr Ar or Xe, 340-eV accelerating potential for 2 h. Heating the samples to $T > 900^\circ\text{C}$ has also produced diffraction features without ion bombardment. At these elevated temperatures, however, the ringlike diffraction patterns which are characteristic of the disordered surface structure formed irreversibly and therefore studies of the platinum surface structures which are present at lower temperatures could not be made. Thus, ion bombardment and subsequent heat treatment was necessary to generate the clean substrate structure or the low-temperature surface structures. All of the surface structures reported in this paper were reproducible under all conditions of surface preparations and ion-bombardment treatments unless otherwise noted.

EXPERIMENTAL PROCEDURE

The low-energy electron-diffraction apparatus which was used in these experiments was of the postacceleration type.²² The electrostatically focused electrons ($1 \mu\text{A}$, $5\text{--}450 \pm 0.2$ eV) are back reflected from the crystal surface and after separation of the inelastically scattered fraction, by a retarding potential, the elastic electrons are accelerated and strike a fluorescent screen. Although better focusing²³ and energy-selection²⁴ techniques have been reported which could give almost an order-of-magnitude better resolution with some sacrifice of the beam intensity, the electron

optics proved to be adequate for these studies. Figure 1 shows the fraction of elastically reflected electrons as a function of electron energy. It is seen that just as in the case of silicon surfaces²⁵ the platinum surface becomes more reflecting to low-energy electrons with decreasing accelerating potential. Other physical characteristics of the system are not reported here since it is outside the scope of this paper. After bakeout and degassing diffraction-chamber pressures of the order of 5×10^{-10} torr were obtained. During heat treatments or annealing of the samples the pressure remained in the 5×10^{-10} to 2×10^{-9} range.

In order to monitor the composition of the ambient and detect the presence of possible surface contaminants a quadrupole mass spectrometer (Electronics Association Inc., Model 210) was permanently mounted on the diffraction chamber. This way we could continuously monitor the background ambient composition during heat treatments and the composition of the gases used for ion bombardment.

In order to further probe the nature of the different surface structures, they were heated in oxygen and in hydrogen in their temperature range of stability. In this manner, surface contaminants which form volatile oxide products or react in a reducing atmosphere could be detected by the mass spectrometer and eliminated from the surface.

The diffraction patterns yield a great deal of information as to the structures of the surface. Intensity analysis of the diffraction features is necessary, however, to distinguish between several structures which could yield similar diffraction patterns.² This is carried

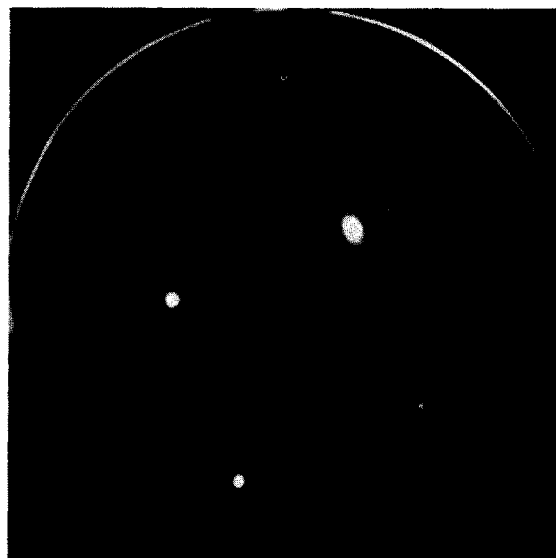


Fig. 2. Diffraction pattern of the clean Pt(100) substrate at $E_i = 73$ eV.

²² LEED by Varian Associates.

²³ J. A. Simpson, Rev. Sci. Instr. **35**, 1698 (1964).

²⁴ C. W. Caldwell, Jr., Rev. Sci. Instr. **36**, 1500 (1965).

²⁵ J. J. Lander and J. Morrison, J. Appl. Phys. **34**, 3517 (1963).

out by monitoring the intensity of the diffracted beam as a function of electron energy and scattering angle. Variation of the intensity of a given diffraction spot with heat treatment or in the presence of gases can give information on the kinetics of surface diffusion or adsorption. Intensity measurements were made using a telephotometer with fiber optics (Gamma Scientific Instruments Model 2000) which allowed highly reproducible measurements of intensity fluctuation with beam voltage which were plotted on an X-Y recorder. These were then taken at various angles of incidence. The fluorescent screen has also been photographed directly to obtain the diffraction patterns. The relative intensities could then be obtained by using a densitometer.

CLEAN SUBSTRATE STRUCTURES

In order to investigate the structure and the chemistry of platinum single-crystal surfaces the intensity of the diffracted low-energy electrons is to be analyzed as a function of electron energy and diffraction angle. For this purpose the preparation of the clean single-crystal substrate which has reproducible diffraction characteristics is of major importance. Therefore, we describe the procedure used to obtain the clean (100) substrate of platinum which produces reproducible diffraction features. After the surface preparation and mounting of the platinum sample in the diffraction chamber (which was described above), the system was evacuated and baked out. When the partial pressure of different reactive gases (O_2 , H_2 , CO , H_2O) was reduced below 10^{-10} torr, the surface was ion bombarded with high-purity argon or xenon using 340-eV accelerating potential at a gas pressure of 2×10^{-5} torr for 2h. After the first ion bombardment most of the surface damage which was introduced during the crystal preparation has been removed. Subsequent ion bombardments which were carried out to remove the unwanted sur-

TABLE II. List of surface structures which were detected on the different low-index surfaces of platinum and their approximate temperature range of stability.

Substrate	Surface structure	Approximate temperature range of stability
Pt(100)	(5 \times 1)	350°–500°C
	(2 \times 1)	300°–500°C
	⊙ ^a	>700°C
Pt(110)	⊙ ^a	>600°C
Pt(111)	(2 \times 2)	800°–1000°C
	(3 \times 3)	800°–1000°C
	⊙ ^a	>900°C

^a The notation ⊙ indicates a ringlike diffraction pattern.

face structures which were formed, required less than 30 min ion bombardment under identical conditions. The initial ion bombardment was followed by vacuum annealing (10^{-10} torr, 600°C for 1 h. The diffraction pattern of the clean (100) substrate obtained this way is shown in Fig. 2. The intensity and the size of the diffraction spots and other physical properties (oxygen adsorption, for example) were found to be reproducible. The parameters which may affect the production of this pattern are the accuracy of crystal orientation, polishing, etching, and the ambient during the heat treatment.

The clean (111) substrate could also be prepared reproducibly by using the same procedures which were described above for the preparation of the (100) crystal face.

The (110) crystal face, however, showed faceting when heating above 600°C in vacuum. This face has a more open structure which was found to undergo reconstruction readily. The surface appears to have a high degree of disorder since the background intensity was always high when compared to the spot intensity. Extended heating of the (100) face above 1000°C in vacuum has also produced faceting. The facets are characterized by the appearance of four extra specular reflections. The angles between these specular reflections and the (100) surface normal is 15.5 deg. The new crystal planes which seem to form have Miller indices (410). The highest-density (111) surface remains stable even under severe heat treatments near the melting point (<1769°C). On some of the (111) crystal faces there is a doubling of the diffraction spots, i.e., two sets of diffraction spots appear near each other as a result of heat treatment close to the melting point. This is similar to the mosaic structures which are frequently observed in electron-diffraction studies²⁶ and which are due to a small angle slip of the surface planes.

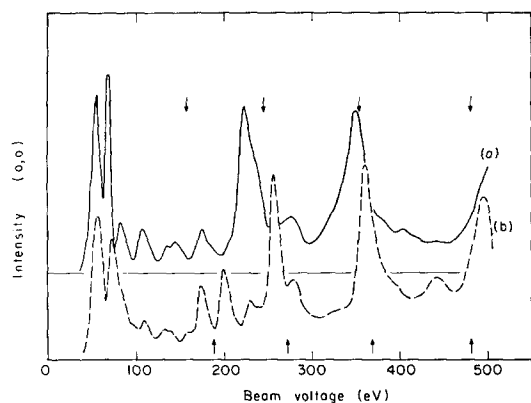


FIG. 3. The intensity of the (00) reflection as a function of beam voltage for the (a) Pt(100) and (b) Pt(111) substrates. The arrows are at the positions of the calculated Bragg reflections. The incident beam is at 12 deg to the surface normal.

²⁶ B. K. Vainshtein, *Structure Analysis by Electron Diffraction* (Pergamon Press, Inc., New York, 1964).

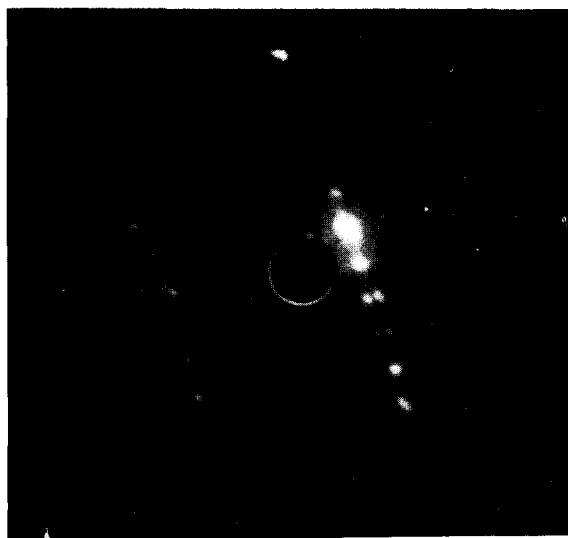


FIG. 4. Diffraction pattern of the Pt(100)-(5 \times 1) surface structure at $E=73$ eV.

Figures 3(a) and 3(b) show the I_{00} -vs-beam-voltage curves obtained for the (100) and (111) clean platinum substrate. These curves are for an angle of incidence of 12 deg.

SURFACE STRUCTURES

The surface structures which were observed on the different platinum substrates are summarized in Table II. The notation which was adopted is that suggested by Wood.²⁷ These surface structures can be easily reproduced on all of the single-crystal samples used unless otherwise noted. The structures are divided into two types, ordered and disordered. The properties of the different surface structures are described below.

Properties of the Ordered Surface Structures

Pt(100)-(5 \times 1)

This structure was formed by heating the crystal in the temperature range 350°–500°C after ion bombardment. Figure 4 shows a characteristic diffraction pattern at 70 eV. The pattern has appeared with the fractional order diffraction spots in one direction, i.e., (01), more intense than those in the other (10) direction.¹⁵ The intensity of the rows of extra spots varies independently along the two perpendicular axes on all of the samples. Thus, the intensity of the fractional order diffraction spots for a given sample may be stronger in one direction (x axis, for example)

than in the other direction. There are also no diffraction spots in between the rows which emanate from the (00) reflection. These observations lead us to propose that the pattern is due to a surface structure with a unit cell of dimensions five times that of the substrate along one principal axis and the same as the substrate along the other. These are surface domains in which the large spacing of the surface structure is along the x axis while in other domains it is along the y axis. The pattern as seen in the photograph is due to the superposition of two patterns rotated 90 deg to one another. As long as the size of the domains is much smaller than the electron-beam size (~ 1 mm²) many domains will contribute to the observed diffraction pattern.¹⁵

The (5 \times 1) structure is observable only at low electron energies (<150 eV). The I_{00} -vs- E curve of the clean (100) substrate remains virtually unaffected by the presence of this new structure on the surface. The doubling of some of the fractional order diffraction spots may be due to mosaic structure effects. The surface structure is resistant to heating in hydrogen or oxygen in its temperature range of stability. The surface structure which is due to oxygen and was re-

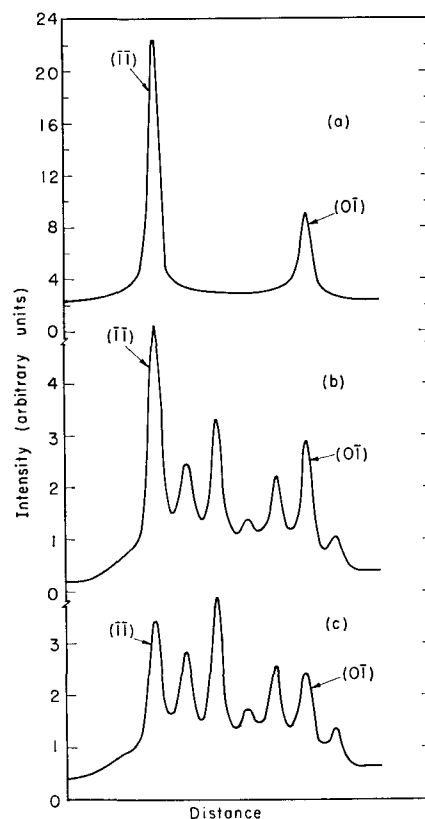


FIG. 5. The intensity variation of the diffraction spots along the (11)-(01) direction as a function of heating time at 500°C ($t_a=0$, $t_b=20$ min, $t_c=30$ min).

²⁷ E. A. Wood, J. Appl. Phys. **35**, 1306 (1964).

ported by Tucker²⁸ for the Pt(100) face was found to coexist with the (5×1) diffraction pattern.

The pattern will slowly anneal out if the sample is left at room temperature. After 5 to 12 h the extra diffraction spots have completely disappeared. Reheating the sample to 350°–500°C causes the pattern to reappear. Once heated above its temperature range of stability the surface structure disappears irreversibly, i.e., cannot be regenerated without repeated ion bombardment.

The rate of formation of the (5×1) surface structure can be measured by monitoring the intensity variation of the diffraction spots as a function of time at a given temperature. This is displayed in Figs. 5(a)–5(c). Since the intensity of the diffraction spots on the fluorescent screen was found to be a linear function of the electron-current density, such intensity data, when taken at different temperatures, may be used to determine the activation energy for the formation of surface structures. It was found to be roughly 38 kcal/mole for the (5×1) structure.

The intensity of the $(\frac{5}{2}, 0)$ spot seems to be independent of heating temperature within the stability range of the (5×1) surface structure provided that the conditions of surface preparation (ion bombardment, etc.) which are carried out prior to heating the (100) substrate, are standardized. When the ion-bombarded sample is heated above 500°C the (5×1) diffraction pattern appears rapidly then slowly disappears. This effect is shown in Fig. 6 at $T=515^\circ\text{C}$.

Analysis of the intensity of the (5×1) diffraction features has been carried out to find out what arrangement of surface atoms gives rise to this pattern. This structure is not complex, is easily reproducible, and the relative intensities of the different order diffraction spots are well defined. The model which was used in the computations of the structure factor was a face-centered-cubic crystal lattice of 10 planes, 50 atoms in each plane. Only single-electron scattering was considered. The attenuation of the electron beam with penetration depth was also taken into account by the use of suitable transmission coefficients. Possible lattice expansion or contraction has also been allowed. The atomic scattering factor was computed via the partial wave method. The detailed structure analysis will be reported elsewhere.²⁹ Preliminary results indicate that the observed intensities give a somewhat better fit to a model in which there are arrays of vacancies in every fifth row of surface atoms in the almost completely filled substrate plane. The intensities of the diffraction spots which are attributed to the (5×1) surface structure are of the same order of magnitude as the intensities due to the substrate unit mesh. This can be seen from Fig. 5(c). If extra atoms would be present on top of the

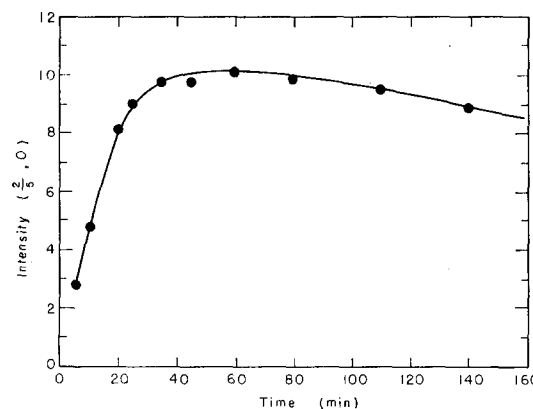


FIG. 6. The intensity variation of the $(\frac{5}{2}, 0)$ diffraction spot of the (5×1) surface structure as a function of heating time at 515°C.

platinum substrate the intensity ratio would be much larger ($I_{00}/I_{(5\times 1)} \simeq 10^2$).

Pt(100)–(2×1)

This surface structure was observed to develop prior to the formation of the (5×1) structure. Its temperature range of stability overlaps with that of the (5×1) pattern.

Pt(111)–(2×2)

This diffraction pattern forms as a result of the same type of heat treatment used to obtain the surface structures on the (100) substrate. The surface structure did not cover the entire face of the crystal, however, as did the (100) surface structures. It was reproducible on that portion of the (111) substrate where a steep temperature gradient existed. Upon remounting the sample to reduce this gradient the pattern was not reproducible. The intensity of the fractional order diffraction features decreases slowly when the sample is allowed to stand at room temperature. The diffraction spots will disappear in about six days. They can be regenerated again when reheated in their temperature range of stability. This pattern, as all the other surface structures, is not detectable at high electron energies (>150 eV). Similar surface structure can be obtained when the (111) substrate is heated in oxygen. The conditions of its formation, however, are different from the experimental conditions which were necessary to produce the pattern on the clean substrate.

Pt(111)–(3×3)

Prolonged heating of the (2×2) surface structure above 800°C causes it to convert into the (3×3) structure. The temperature range of stability of these

²⁸ C. W. Tucker, Jr., J. Appl. Phys. **35**, 1897 (1964).

²⁹ A. Chutjian and G. A. Somorjai (to be published).

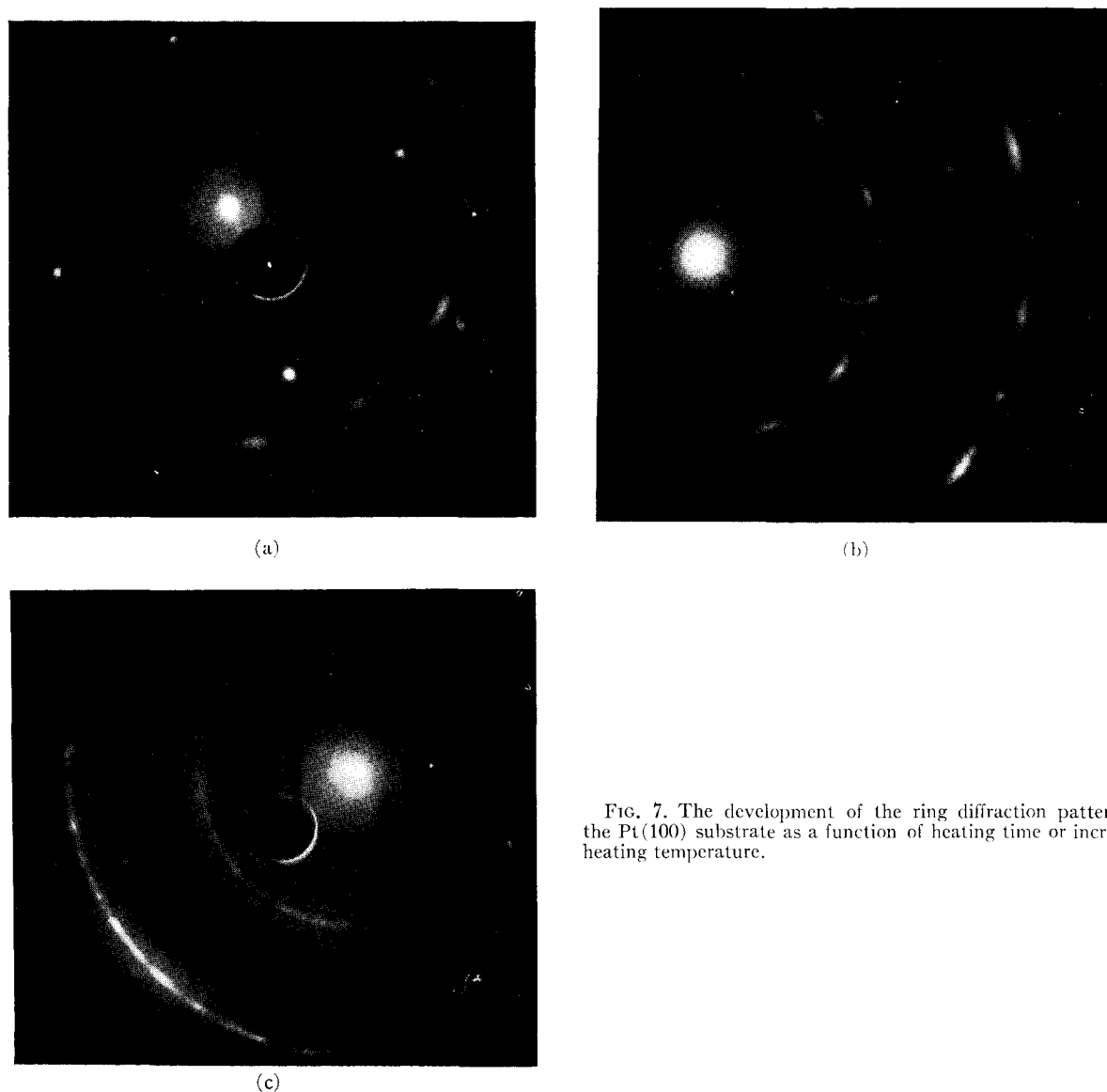


FIG. 7. The development of the ring diffraction pattern on the Pt(100) substrate as a function of heating time or increased heating temperature.

two ordered structures is the same as that of the disordered surface phase which gives rise to ringlike diffraction patterns, are discussed below. Thus, the ordered and disordered surface structures were often found to coexist on the (111) substrate.

The following statements summarize the experimental information concerning the ordered surface structures which appear on the different platinum substrates.

(a) The surface structures which appear on the different crystal faces of platinum are stable only in well-defined temperature ranges. The stability range of two structures may overlap on the given substrate.

(b) The surface structures are not affected by heat treatments in oxygen or hydrogen in their temperature range of stability.

(c) The structures are in registry with the substrate (not rotated) and are characterized by lattice parameters which are integral multiples of that of the substrate $[(5 \times 1), (2 \times 1), (2 \times 2), (3 \times 3)]$.

(d) The surface structures anneal out at temperatures below their range of stability but reappear readily when reheated in their stability range. Once heated above this temperature range they disappear irreversibly.

(e) The surface structures were obtained only after ion bombardment. The properties of the surface struc-

tures, however, were independent of the type of ions which were used in the ion bombardment.

(f) The surface structures could rapidly be obtained by applying a steep temperature gradient along the substrate surface. The structures could also be formed on the (100) substrate by heating the crystals in a well-defined temperature range.

(g) The intensity of the diffracted beams emanating from the surface structures is of the same order of magnitude as the intensity of the substrate reflections.

(h) The different heat treatments have not resulted in any appreciable rise in the ambient pressure or in the appearance of volatile impurities either when the heating was commenced or during the heating period.

(i) The presence of these surface structures causes no change in the positions of the intensity maxima in the I_{00} -vs- E (electron volts) curves which were taken for the clean substrates.

(j) Several surface structures were found to exist on the (100) face of silver, gold, and palladium single crystals.^{16,17} The ordered surface structures on the gold substrate are similar to those found on the (100) face of platinum.

Properties of the Disordered Surface Structures

$$[Pt(100)-0, Pt(111)-0, Pt(110)-0]$$

When the (100) substrate was heated in the temperature range 500°–700°C no extra surface structure was formed and the diffraction pattern was that of the clean substrate unit mesh. Above 700°C, however, a new diffraction pattern slowly appears. This is characterized by narrow, circular segments. Six such segments appear at first [Fig. 7(a)], then with increased heating time or higher heating temperature 12 and then 24 segments form [Fig. 7(b)] which finally join into a ring [Fig. 7(c)].

The ringlike patterns can be obtained without ion bombardment, only by heating the sample between 700°C and the melting temperature (1769°C). Their formation is irreversible, i.e., once they have been created they are stable indefinitely at any temperature below the melting point and can only be removed by ion bombardment. They remain unchanged during heat treatment in oxygen and/or hydrogen.

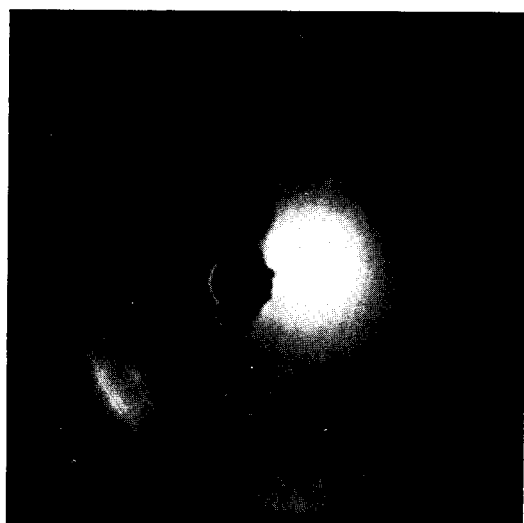
If the sample is heated above 1000°C for an extended period (4–6 h), the intensity of the diffraction features which are due to the substrate unit mesh and which coexist with the ring pattern decreases while the intensity of the rings increases. When heated near the melting point, the ringlike diffraction pattern finally remains the only diffraction feature on a presumably greatly disordered surface.

The rings are concentric about the (00) reflection, have sharp outlines, and show the usual diffraction features of other surface structures, (a) appear only at low electron energies (5–150 eV) and (b) appear at decreasing angles with respect to the (00) spot with increasing electron energy. One striking feature of the ring pattern is that it does not overlap with any of the diffraction spots which are due to the substrate unit mesh.

Ringlike diffraction patterns were also found to exist on both the (111) and (110) platinum surfaces as well. They also form in narrow segments which show sixfold symmetry. The rate of ring formation is somewhat slower on the (111) face, one has to heat to temperatures above 1000°C to obtain formation rates comparable to that on the (100) face at 750°. Figure 8(a) shows the disordered surface structure on the (111)



(a)



(b)

FIG. 8. The development of the ring diffraction pattern on the Pt(111) substrate as a function of heating time or increased heating temperature.

TABLE III. The ratio of the lattice parameters d_0/d_{111} for the different sets of rings on the (100), (111), and (110) substrates of platinum.^a

		d_0/d_{111} (experimental)	d_0/d_{111} (corrected)
Pt (100)	First	0.75 ± 0.03	0.87 ± 0.03
	Second	0.43 ± 0.03	0.50 ± 0.03
	Third	0.41 ± 0.03	0.47 ± 0.03
Pt (111)	First	0.89 ± 0.03	0.89 ± 0.03
	Second	0.51 ± 0.03	0.51 ± 0.03
Pt (110)	First	0.78 ± 0.03	0.90 ± 0.03

^a d_0 is the apparent lattice parameter which can be assigned to a diffraction ring and d_{111} is the interplanar distance in the substrate.

face in its first stages of development. There are six twin segments which are symmetrically positioned between the first-order diffraction spots of the substrate. There are six additional segments near the diffraction spots. The segments which appear in twins we have also observed separately. Figure 8(b) shows the ring pattern in a later stage of development. Under no conditions did the ring segments overlap the first-order substrate diffraction spots.

The ring structure formed on the (110) face at temperatures much lower than the other faces. This face has shown disorder as the background intensity was always high with respect to the spot intensity. Faceting, which occurs simultaneously, gives rise to complex diffraction patterns.

Several rings were found to form on the (100) and (111) substrates. All of the rings were concentric about the (00) reflection of the substrate. They do not appear to be higher-order reflections of the first ring which is nearest to the (00) reflection of the substrate. The apparent lattice parameter which may be assigned to these ringlike patterns is smaller than the interplanar distance in the substrate plane on all platinum surfaces. There are uncertainties in the measurement of the lattice parameter which are due to several factors. These are: (a) Angular distortion due to stray magnetic or electrostatic fields, (b) possible expansion or contraction in the substrate plane with respect to the bulk lattice spacing, (c) inaccurate positioning of the sample in the chamber, or (d) inner potential corrections. In order to overcome these difficulties in characterizing the ringlike diffraction patterns we give our data instead as an apparent lattice parameter in terms of the ratio d_0/d_{111} . d_{111} is the interplanar spacing in the different crystal faces in real space and d_0 is the real space lattice dimension which is characteristic of the diffraction ring. They are calculated from the ratio, $\sin\theta_{111}/\sin\theta_0$. It should be noted that for the (100) and (110) crystal faces the interplanar spacing is equal to the nearest-neighbor distance. In the (111) face the interplanar spacing is $\frac{1}{2}\sqrt{3}$ times the nearest-neighbor distance. Thus, it is appreciably smaller than in the

other two crystal faces. The first column in Table III gives a summary of the observed ratios. We designate as "first" the ring which is nearest to the (00) reflection. The ratios were found to be independent of beam voltage.

There is no noticeable change in the positions of the maxima in the I_{00} -vs- E (eV) curves of the clean platinum (100) and (111) substrates due to the presence of the ring patterns.

The following statements summarize some of the important properties of the disordered surface structures and other pertinent information which could be used to interpret these structures.

(a) The ringlike diffraction patterns form on the (111), (110), and (100) substrates of platinum via sets of radially symmetric segments at elevated temperatures.

(b) Their formation is irreversible and they become the only diffraction feature of the surface as the melting point is approached. They may be formed without the use of ion bombardment by heating the substrate in their temperature range of stability.

(c) The ring patterns are unaffected by heat treatment in hydrogen or oxygen atmospheres.

(d) The rings appear to have apparent lattice parameters which are smaller than the smallest interplanar distance in the substrate plane.

(e) The surface structure which gives rise to the ring pattern is parallel to the surface upon which it forms and shows diffraction features similar to other surface structures.

(f) The ringlike patterns are narrow and well defined and always appear in the same position on a given substrate. They are unlike the radial distribution functions observed by neutron-diffraction³⁰ or x-ray-diffraction studies of liquids near the melting point.³¹

(g) The formation of these ring patterns reflects the gradual loss of long-range order at the surface as heating time or temperature is increased.

(h) Ringlike diffraction patterns were also found to form on other metal surfaces.^{16,17} They have apparent lattice dimensions which are smaller (Ir, Au) or larger (Ag) than the distance of closest approach in the ordered substrate.

(i) There is no evidence of any macroscopic change in the surface structure of platinum as observed in a photomicrograph (1000 \times magnification) when the ringlike diffraction pattern is formed.

DISCUSSION

Two types of surface structures were found to exist on the studied low-index platinum surfaces. One type

³⁰ H. A. Levy, P. A. Agron, M. A. Bredig, and M. D. Danford, *Ann. N.Y. Acad. Sci.* **79**, 762 (1960).

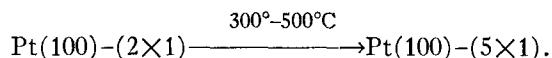
³¹ N. W. Gingrich, in *Liquids; Structure, Properties, Solid Interactions*, T. J. Hughel, Ed. (Elsevier Publ. Co., Inc., New York, 1965).

is ordered and stable only at lower temperatures, roughly below one-half the melting temperature. The other type is disordered and appears at high temperatures. All of the experimental observations seem to indicate that both types of surface structures are the property of the clean platinum surfaces. No single impurity could produce the variety of diffraction features which were observed as a function of substrate temperature in the high-purity platinum surfaces.³² The surface structures show a broad range of different physical properties (stability range, long- or short-range order, different types of surface structures on each substrate).

Heat treatments in ultrahigh vacuum, in oxidizing or reducing ambients have not produced any new volatile species which could be detected by the mass spectrometer.

ORDERED SURFACE STRUCTURES

All of the ordered surface structures were obtained after ion bombardment although their formation was not a function of the type of ions which were used. Bombardment by high-energy ions can create high concentrations of defects at the surface and can produce a nonequilibrium distribution of surface atoms.³³ This is easily discernible from the diffraction patterns one obtains after such treatment. The ordered surface structures seem to represent intermediate steps in the annealing process during which the surface atoms diffuse to their equilibrium atomic positions. The surface structures appear to be made up of ordered arrays of vacancies in the substrate plane. The vacancy model is supported by the following observation. If the stability ranges of two surface structures overlap, increased heating time or temperature favors the formation of the more open structure. For example,



Thus, if we assume that all of the ordered surface structures are composed of ordered arrays of vacancies we find that the nonequilibrium vacancy concentration is reduced as would be expected to occur with increasing annealing time or temperature.

The formation of the surface structures is reversible as long as they are not heated above their temperature range of stability. It appears that at low temperatures, below the stability range of a given surface structure,

vacancy clustering takes place which destroys the long-range order. The pattern can be regenerated at will, by heating repeatedly in its temperature range of stability. The reappearance of the surface structures indicates that, in a well-defined temperature range, the long-range ordering of vacancies represents the more stable configuration.

When the surface structures are heated above their temperature range of stability they anneal out irreversibly. Thus, the surface atoms attain a more stable configuration which may be characterized by the absence of any surface structure or by a structure which is compatible with the equilibrium concentration of vacancies.

The properties of the ordered surface structures coupled with the vacancy model indicate that (a) a nonequilibrium concentration of vacancies in the platinum surface could be maintained at room temperature, (b) these vacancies are randomly distributed or clustered at room temperature so as to show no diffraction features, (c) at elevated temperatures long-range ordering of the vacancies takes place which gives rise to surface structures of remarkable stability. The formation of these structures is likely to be surface diffusion controlled, (d) at temperatures above the stability range of the surface structures the vacancy concentration approaches its equilibrium value and the surface structures are removed irreversibly.

The activation enthalpy for surface diffusion seems to be higher for the (111) than for the (100) face of platinum. All of the surface structures form in a higher temperature range on the (111) substrate.

If the presence of a nonequilibrium concentration of disordered surface atoms is needed for the formation of the ordered surface structures, they may not form at all when the surface is at equilibrium at the onset of the heat treatments. In order to study the stability of the platinum surface structures in equilibrium, substrates with equilibrium vacancy concentrations should be prepared (without the use of heat treatments).²

DISORDERED SURFACE STRUCTURES

The disordered surface structures are characterized by ringlike diffraction patterns. These develop gradually via segments which have sixfold symmetry. When the substrate is heated near the melting point they remain the only diffraction feature of the platinum surface. They form irreversibly on all of the platinum substrates which were studied and could be obtained without ion bombardment. It appears that the ring diffraction patterns are characteristic of a disordered surface phase which seems to be the equilibrium surface structure of platinum near its melting point. At elevated temperatures, above the stability range of all of the ordered surface structures the substrate atoms undergo an order-disorder transition. Once formed

³² An impurity to cause the observed diffraction features must have large bulk and surface concentrations ($>10^{17} \text{ cm}^{-3}$) in platinum which are uniform from sample to sample. It should be able to form a variety of surface structures ordered and disordered which are stable in only certain temperature ranges. It should also be nonvolatile in oxidizing or reducing medium or in vacuum.

³³ R. L. Jacobson and G. K. Wehner, *J. Appl. Phys.* **36**, 2674 (1965).

there is apparently a large activation energy required to restore the long-range order; hence the disordered surface structures are "frozen in" below the transition temperature.

The apparent lattice parameters which can be assigned to the disordered surface structures are extremely reproducible from sample to sample. Closer inspection of the ratios, d_o/d_{is} , obtained for the different platinum surfaces, reveals that the values computed for the (100) and (110) substrates are identical within the accuracy of the measurements. The ratios obtained for the (111) face are larger. These ratios, however, were obtained by using the interplanar spacing in the (111) plane which is $\frac{1}{2}\sqrt{3}$ times smaller than the interplanar distance in the (100) and (110) planes.

If we assume that the surface structures which give rise to the ring patterns in the (100) and (110) surfaces have the same interplanar spacing as in the (111) substrate of platinum their ratios, which are listed in the first column of Table III, should be multiplied by $2/\sqrt{3}$. The corrected values are shown in the second column of Table III. The ratios now have identical values for all three substrates within the accuracy of our measurement. Also, the ratio of lattice spacings which can be assigned to the different rings are $d_o^I/d_o^{II}=\sqrt{3}$ and $d_o^I/d_o^{III}=2$ within our accuracy. The data suggest that the ringlike diffraction patterns are due to domains of (111) surface structures on all faces of platinum with reduced nearest-neighbor spacing. These hexagonal surface structures appear at preferred orientations at first as shown by the presence of ring segments. After extended heating time or as the melting temperature is approached they can be freely rotated in the substrate plane. If we assume that the disordered hexagonal surface structures show an 11% contraction with respect to the interplanar spacings in the (111) substrate, this model gives ratios, d_o/d_{is} , for the first three rings, 0.89, 0.51, and 0.45, respectively. This is in good agreement with the values listed in Table III.

In addition to the ringlike patterns on the platinum surfaces, ring or segmented ringlike surface structures have been observed on gold (100), silver (100), and iridium (111) surfaces.^{16,17} In no case do the diffraction rings coincide with the diffraction spots of the substrate but show "contraction" or "expansion" of different magnitudes. For example, in silver the ap-

parent lattice parameter which can be assigned to the ring pattern indicates a 13% expansion with respect to the nearest-neighbor distance in the ordered substrate while gold shows a "contraction" which is similar to that of platinum. It is likely that the disordered phase is present at high temperatures on many face-centered-cubic metal surfaces which have a low enough evaporation rate so as not to permit the removal of the new phase into the vapor as soon as it forms.

The formation of a disordered surface structure at temperatures where no such disorder is apparent in the bulk of the platinum single crystals is not very surprising. Surface Debye temperature measurements⁷ indicate large mean-square displacements of surface atoms with respect to that of the bulk. Lindeman's theory of melting which has been extended recently^{34,35} predicts that the melting temperature is proportional to the mean-square displacement of atoms. Thus, it may be possible that melting at the surface occurs at temperatures appreciably below the melting temperature for the bulk. It should be pointed out, however, that the ringlike diffraction patterns are always narrow and well defined and do not resemble the radial distribution functions obtained by x-ray and neutron-diffraction studies of liquids near the melting point.^{33,36} The observed closed-packed-hexagonal surface structure on the different platinum surfaces may be the precursor of the "random-close-packed structures" which have been postulated³⁷ to exist in the melt.

The irreversible nature of the observed order-disorder phase transformation has been considered by Ubbelohde,³⁸ when he postulated the presence of "noncrystallizable clusters" in addition to the crystalline clusters to explain the undercooling phenomena.

ACKNOWLEDGMENTS

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³⁴ F. A. Lindeman, *Physik. Z.* **11**, 609 (1910).

³⁵ J. J. Gilvary, *Phys. Rev.* **102**, 308 (1956).

³⁶ G. W. Brady and J. T. Krause, *J. Chem. Phys.* **27**, 304 (1957).

³⁷ J. D. Bernal, in *Ref. 30*.

³⁸ A. R. J. P. Ubbelohde, *Advan. Chem. Phys.* **6**, 459 (1964).