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CORROSION AND PASSIVITY STUDIES WITH TITANIUM

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Part 1 Abstract

The distinguishing features of physical and chemical adsorption are discussed. It is concluded that chemisorption must be studied under non-equilibrium conditions and, therefore, that the sticking probability and rate of desorption are the preferable variables for experimental observation. The low-energy electron diffraction method is compared with the flash filament technique and the field emission microscope method as means of making such observations. The dynamic theory of electron diffraction is discussed and the failure of the approximations for the case of low energy electrons is noted. The apparatus and procedures are described with emphasis on recent and projected improvements. Finally, the experimental results are presented and discussed. The crystal face was cleaned by ion bombardment and annealed, and the optimum conditions for this procedure were determined. The experimental results furnish strong evidence in support of the view that this cleaning technique produces a clean titanium surface. It was found that both oxygen and nitrogen are chemisorbed in a hexagonal array with the titanium lattice constant on this surface. This result is consistent with the structures of titanium monoxide, TiO , and titanium nitride, TiN . The average sticking probabilities at room temperature were determined to lie between 3.1×10^{-2} and 10^{-1} for oxygen and between 2.8×10^{-8} and 2.8×10^{-4} for nitrogen. For both gases it was found that the adsorption takes place more readily at higher temperatures. These results indicate that an activation energy is necessary for the adsorption of these gases. Further study of the adsorption of oxygen confirmed the non-equilibrium nature of the adsorption.

Part 2 Abstract

Copper is deposited by evaporation in a controlled manner upon the (00·1) face of a titanium single crystal. Low-energy electron diffraction is used to investigate the structure of the deposit. Before making any deposit, the titanium crystal is cleaned by thorough outgassing followed by argon ion bombardment and annealing. The deposit is found to be in the form of oriented crystallites, with (111) copper planes parallel to the (00·1) titanium plane, and (110) copper planes parallel to the (11·0) titanium planes. The lattice constant of the deposit, in directions parallel to the substrate, is found to be that of bulk copper.

Part 3 Abstract

The low energy electron diffraction apparatus, with no change except in external circuitry, is used to measure secondary electron emission yields. The outgassed titanium surface has a maximum yield of .74 at 210 ev. primary electron energy. The positive ion bombarded surface has a maximum yield of .70 at 180-260 ev. primary energy, and the clean (ion-bombarded and annealed) surface has a maximum yield of .73 at 200 ev. The titanium surface covered with 32 atomic layers of copper has a maximum yield of .91 at 450-650 ev., as compared with the accepted value for bulk copper of 1.26 at 600 ev.

Part 4 Abstract

After prolonged heating of a titanium crystal in high vacuum slightly below the transition temperature, the surface was found to be covered with a stable compound of undetermined structure. This structure was removed by suitable bombardment with positive argon ions, but the underlying crystal lattice was disarranged. Subsequent thermal annealing restored the lattice structure, and resulted in a clean crystal surface without altering the exposed (0001) crystal face.

Part 1

Chemisorption of Oxygen and Nitrogen on Titanium.

INTRODUCTION

The chemisorption of oxygen and nitrogen by titanium has been studied by low-energy electron diffraction and the results will be discussed in terms of the existing theories. Experimental evidence indicates that there are two distinct mechanisms by which gas adheres to solid and liquid surfaces. These are termed physical adsorption and chemical adsorption or chemisorption. As yet there is not complete agreement on the distinguishing features of these two processes. For example, in 1945 S. Brunauer listed the distinctions between physical and chemical adsorption¹, but in 1952 he felt that "some are not convinced even today that it [chemisorption] is really a surface and not a bulk phenomenon."² There are two fundamental reasons for this continuing uncertainty.

The first of these is the problem of isolating the phenomenon to be studied. In any experiment there are at least two competing processes. One is *absorption*, the uptake of gases by the bulk of the solid to form a solid solution or a chemical compound. The other is *adsorption*, the uptake of gases by the surface of the solid. If the distinction is to be made between physical and chemical adsorption, the situation is further complicated. In most experimental methods the process to be studied is isolated by choosing conditions under which the competing processes do not readily take place.

The second difficulty in the study of surface phenomena is the initial state and extent of the surface. Several methods of cleaning the surface have been devised and may be quite effective. However, the usual criteria for determining the effectiveness of the cleaning processes and of measuring the surface area are based on the measurements of surface phenomena.

In both cases a certain amount of previous knowledge is required. Therefore, a large amount of independent data is necessary for the construction and evaluation of adsorption theories. The remainder of this section outlines the principal ideas that have been developed and suggests that several changes in emphasis may be desirable.

THE LANGMUIR ISOTHERM

The fundamental concepts of chemical adsorption were first stated by Irving Langmuir⁸. These are that true chemisorption is unimolecular, the adsorbed gas atoms being held on fixed sites by chemical bonds. The chemical nature of the bonding was stressed. The argument for this is that if the bonds in the interior of a crystal are saturated it follows that the bonds of a surface atom are not. Thus there would be a strong force field at the surface of a crystal and a monolayer of adsorbed gas would serve to terminate the structure. The fixed sites and unimolecular nature of adsorption are clearly inherent in this argument.

These considerations led Langmuir to develop the following kinetic theory of chemisorption³. If the fraction of the surface covered is denoted by θ , then the exposed fraction is $1-\theta$. From kinetic theory⁴ the rate N' at which gas atoms strike a unit surface area is given by

$$(1) \quad N' = P(2\pi mkT)^{-\frac{1}{2}}$$

where P is the pressure of the gas, m the mass of a gas atom, k Boltzmann's constant, and T the absolute temperature. Thus, if α is the probability that an atom striking the surface will stick to it, then the rate of adsorption is

$$(2) \quad \alpha P(1-\theta)(2\pi mkT)^{-\frac{1}{2}}.$$

Assuming the rate of evaporation per unit area is a constant K , the condition for equilibrium is

$$(3) \quad \alpha P(1-\theta)(2\pi mkT)^{-\frac{1}{2}} = K\theta.$$

Finally, if

$$(4) \quad A = \alpha/K\sqrt{2\pi mkT},$$

then equation (2) may be rewritten as

$$(5) \quad \theta = \frac{AP}{AP + 1},$$

the equation of the Langmuir isotherm.

At the time of Langmuir's work the distinction between physical and chemical adsorption had not been made, and he believed that all adsorption was chemical. Since this distinction has an important bearing on the interpretations and extensions of Langmuir's theory, it is preferable to defer discussion of the isotherm for consideration of this point.

CHEMICAL AND ACTIVATED ADSORPTION

In 1931 H. S. Taylor suggested that some adsorption may require an activation energy⁵. In studying the experimentally measured isobars (surface coverage as a function of temperature at constant pressure), he noted that most of these, at low temperatures, are decreasing functions with increasing temperature. However, as the temperature is further increased, the surface coverage begins to rise and passes through a maximum. Investigators had noted that in the lower temperature range the adsorption takes place rapidly and is readily reversible with temperature and pressure. When the surface coverage begins to rise with increasing temperature, this is no longer the case. Taylor pointed out that the low rate of adsorption in the high temperature range might be explained if this adsorption required an energy of activation.

This view is not always accepted even today as has been noted in the introduction. It is suggested that the low rate is actually due to absorption and that the rate determining factor is the speed of diffusion of the gas into the solid. This interpretation is supported by more recent results indicating that irreversible adsorption in the high temperature range can take place quite rapidly. In particular, J. K. Roberts found that when a thoroughly cleaned tungsten filament at a temperature of -190° C. is exposed to hydrogen at pressures less than 10^{-4} mm. Hg. a monolayer of adsorbed gas is formed in a matter of seconds⁶.

These arguments do not actually invalidate the distinction between chemical and physical adsorption as originally introduced by Lennard-Jones⁷. This was based on the further point that the heats of adsorption had been measured for the reversible and irreversible adsorption and found to be of the order of the heats of condensation in the first case and of the heats of chemical bonding in the second. To account for these facts Lennard-Jones plotted the potential energy E of a molecule as a function of its distance s from the surface as shown in Figure 1.

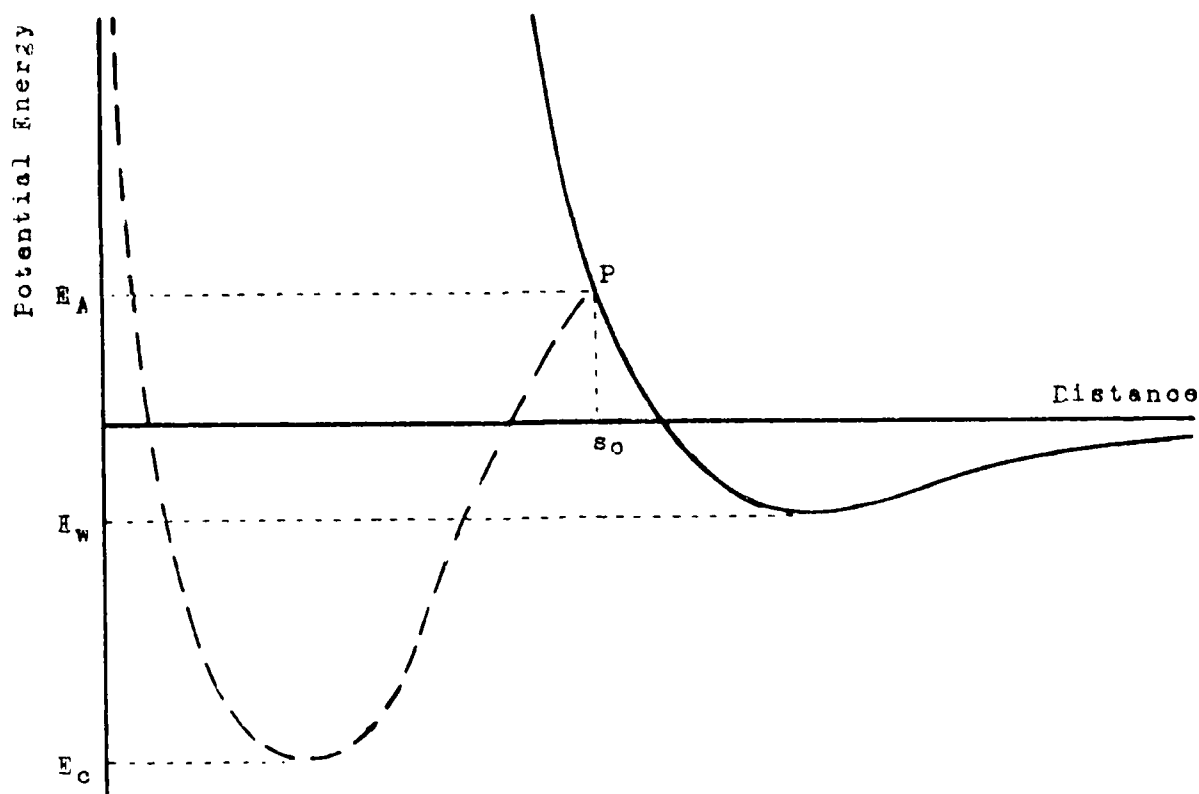


FIGURE 1. POTENTIAL ENERGY OF A GAS MOLECULE APPROACHING THE SURFACE OF AN ADSORBENT

The minimum in the solid curve is attributed to the opposition of Van der Waals' and repulsive forces between the gas molecule and the surface atoms. A molecule trapped in this minimum is regarded

as physically adsorbed with energy of adsorption E_w joules/molecule. If the molecule approaches as close as s_0 , it may shift on to the dashed curve and be chemically adsorbed with heat of adsorption E_c . (Actually, Lennard-Jones drew two separate curves with a point of intersection at P. However, A. Wheeler has pointed out that we are interested in molecules approaching the surface so only the solid curve is of interest for $s > s_0$ ³. Also, for multiatomic molecules there is the possibility of dissociation at P. In this case the plot should be three dimensional to indicate the separate sites for adsorption of the atoms.) Finally, the point P may lie above or below $E = 0$. In the event $E_A > 0$ there is an activation energy necessary for adsorption.

From this picture it is clear that an activation energy need not be an essential feature of chemisorption. Undoubtedly, a good part of the confusion is due to the interchangeable use of the terms chemical and activated adsorption. The existence of the latter as defined above appears to be the issue in question.

HETEROGENEITY AND MOBILITY

Two other factors have been suggested as distinguishing features of adsorption processes. These are "heterogeneity" and the possibility of mobility of the adsorbed atoms.

The concept of heterogeneity was invoked by H. S. Taylor to

explain certain features of the poisoning of catalysts⁹. This has an immediate bearing on adsorption since adsorption is generally accepted as an essential mechanism in catalytically induced reactions. The original idea was simply that the surface of the adsorbent is rough on an atomic scale, and that this results in adsorption sites with varying degrees of binding energy. Only the most energetic sites are thought to be operative in catalysis and these are referred to as active centers.

Although it was proposed as a mechanism for catalysis, Taylor's theory also offers an explanation of an adsorption phenomenon, namely the decrease in the heat of adsorption with increasing surface coverage. This has led to the use of the term heterogeneity in the literature on adsorption, often without its meaning being clearly defined. It appears desirable to follow M. Boudart in taking the property of decreasing heat of adsorption with increasing surface coverage as a phenomenological definition of the term "heterogeneity".¹⁰

Before considering how Taylor's theory of active centers can account for heterogeneity it should be noted that these active centers are no longer regarded as due to surface roughness. At present the favored explanation appears to be crystal faults such as dislocations, vacancies, etc. Taylor has recently put forward the idea that they might simply be impurities on the surface¹¹. Regardless of the proposed nature of active centers, the result is the same.

The gas is adsorbed at the most active centers first. As these are filled up the less active portions of the surface begin to adsorb and the heat of adsorption decreases. For this to be true, chemisorbed atoms must be immobile. If this is not the case, the Boltzmann factor will force the atoms adsorbed at the more active sites to migrate to the less energetic ones. Thus Taylor's explanation at once accounts for heterogeneity and offers a new property, mobility, for further study. This has recently become of interest as the mobility of adsorbed gas atoms may be observed with the field emission microscope¹².

While on the subject of mobility it is worth pointing out that this concept does not repudiate Langmuir's fixed site theory. The fixed sites are simply potential wells as Lennard-Jones has indicated. Atoms trapped in these wells will have vibrational energy states. If the frequency of vibration is ν and the well height E_m , the probability per unit time of an atom moving from one site to the next is given by $\nu e^{-E_m/kT}$. (Note that E_m is not necessarily the same as E_c in Figure 1. In the figure the potential energy is plotted as a function of distance from the surface rather than distance along the surface. Generally E_m is less than E_c .) Thus, there is always some mobility. The magnitude of the transitional probability determines whether it is important or not.

The principal objection to the theory of active centers is the feeling that it should not be necessary to invoke crystal irregularities to explain adsorption. Another mechanism which avoids

this difficulty is the assumption that adsorbed atoms repel each other. The forces involved would be rather weak, affecting only the nearest neighbors. This again requires immobility for, if the atoms are mobile, they would first form a double-spaced structure, and then fill in the holes. Such a procedure gives one constant value for the heat of adsorption for less than half coverage and a second smaller value for more than half coverage. If immobility is assumed, a statistical approach based on the probability, as a function of surface coverage, of a gas atom being adsorbed next to an occupied site may be used. This results in an expression for the heat of adsorption which decreases almost linearly with surface coverage¹³.

This is, of course, a pure adsorption theory and makes no attempt to account for the problems of catalysis. Its only drawback is that it seems unlikely that the repulsive forces would be sufficiently large to account for the observed decreases in the heats of adsorption. M. Boudart has indicated a way out of this difficulty¹⁴. He shows that there should be an induced repulsive interaction between the gas atoms and the surface atoms of the adsorbent which increases with surface coverage and is of the right order of magnitude. In this case the question of mobility is not important.

PHYSICAL AND CHEMICAL ADSORPTION

The foregoing discussion has suggested several possible distinctions between physical and chemical adsorption. It will be convenient to summarize these as follows:

1. BOND STRENGTH. This would appear to be the most clearcut issue. The heats of chemisorption are found to be of the order of 50-150 k cal/mole, while the heats of physical adsorption average close to 3 k cal/mole. This is readily accounted for by assuming chemical bonding in the first case and Van der Waals' attraction in the second. Thus the mechanism of bonding is entirely different in the two cases.

2. SELECTIVITY. The nature of the bonding is confirmed by the observation that chemical adsorption is selective while physical adsorption is not. That is to say, any gas will be physically adsorbed at sufficiently low temperatures. Chemisorption takes place only in cases where the adsorbate and adsorbent have a chemical affinity for one another.

3. NUMBER OF LAYERS. It is established that several layers of gas may be physically adsorbed, but, to be certain that only one monolayer is chemisorbed it is necessary to be certain that the surface was initially clean. Consequently much of the evidence in favor of this distinction is open to question. Also, there is evidence to the contrary.

Schlier and Farnsworth found that outgassing of a copper crystal below 700° C. was insufficient to remove the adsorbed gas layers with no regular structure¹⁵. Outgassing at temperatures in the range 700-900° C. produced diffraction beams from a monolayer

of adsorbed gas. The heat of adsorption could not be measured in these experiments. Still the temperature required to obtain a reasonable rate of evaporation indicates a relatively strong bonding

J. K. Roberts observed the formation of two monolayers of oxygen on tungsten¹⁶. The first of these had a heat of adsorption of 139 k cal/mole and was, he felt, atomic adsorption, one atom of oxygen adsorbing for each tungsten atom on the surface. The second layer appeared to be molecular oxygen, but had a heat of adsorption of 48 k cal/mole. These results might be questioned on the grounds that oxygen is known to diffuse into iron and tungsten to form oxides even at very low temperatures^{12, 17}.

4. RATE OF ADSORPTION. Roberts' results on the rapid rate of chemisorption of hydrogen by tungsten have already been mentioned⁶. More direct evidence by J. A. Becker shows that one out of every two molecules of nitrogen striking a clean tungsten surface at room temperature is adsorbed¹⁸. In view of this it is apparent that the rate of adsorption is no criterion for chemisorption.

5. MOBILITY. It seems probable that a chemisorbed atom, being closer to the surface than a physically adsorbed molecule, would be more strongly affected by the periodic field of the adsorbent. This would require that it be less mobile. However, the theories of heterogeneity have not been developed to the point of establishing relative immobility as a requirement for chemisorption.

A. DISSOCIATION. There is no conclusive evidence that the adsorbate molecules dissociate upon chemisorption. The process seems likely from the nature of the bonding and desirable as part of the mechanism of catalysis, but, lacking further experimental evidence, it cannot serve as a distinguishing factor for chemisorption.

To summarize, the only distinction between physical and chemical adsorption is the nature of the bonding as indicated by the heats of adsorption and the property of selectivity. From the experimental point of view this means that the two differ only in degree, since the energy and not the mechanism of bonding is observed. This point will be developed further by the discussion of the equilibrium condition.

EXTENSIONS OF THE LANGMUIR THEORY

The above remarks are equally applicable to Langmuir's theory. Although it is often listed as a theory of chemisorption, no assumption is made which depends on the mechanism of bonding. The sticking coefficient α and the rate of desorption K will, of course, vary with the energy of bonding, but these have not been evaluated theoretically.

Many extensions of Langmuir's theory have been made. For example, if several layers are adsorbed, allowance must be made for

varying values of α and K for the different layers. If α and K are of nearly the same order of magnitude for different layers, the effect of competition between these layers must be considered. Again, if dissociation is assumed, the rate of adsorption and desorption must be suitably modified. The type of analysis given readily leads to

$$(6) \quad \theta = \frac{(AP)^{\frac{1}{2K}}}{(AP)^{\frac{1}{2K}} + 1}$$

in this case¹⁹.

For some modifications a different approach is indicated. The Langmuir isotherm may also be obtained by writing an expression for the Helmholtz free energy F_g for N_g atoms in the gas phase, an expression for the Helmholtz free energy F_a for N_a adsorbed atoms, and applying the equilibrium condition

$$(7) \quad \left. \frac{\partial F_g}{\partial N_g} \right|_{T, V} = \left. \frac{\partial F_a}{\partial N_a} \right|_{T, V}.$$

This treatment is readily extended to include the effects of interaction between adsorbed atoms, and the heat of adsorption as a function of surface coverage may be obtained²⁰.

THE EQUILIBRIUM CONDITION

Each of the above theories rests on the same fundamental ideas as the original Langmuir theory, but corrects for certain additional factors. Although their assumptions appear sound, such theories have been only partially successful. It is suggested that the

failures have been due to failure to satisfy the equilibrium condition and/or failure to take account of the possibility of multi-layer chemisorption.

The violation of the equilibrium condition experimentally is implied in the references to "irreversible" adsorption. This must mean that the pressures at which the experiments were carried out were so high that the equilibrium state was complete coverage, or that the times involved were too short compared to the rate of desorption for equilibrium to be reached. From the practical viewpoint the equilibrium pressures for partial coverage and the time to establish equilibrium may be unobtainable in such cases.

To make these considerations a little more concrete it is interesting to estimate the equilibrium pressure for half coverage. Assuming the Langmuir isotherm, equation (5), or the Langmuir isotherm modified for dissociation on adsorption, equation (6), the condition $\theta = \frac{1}{2}$ requires $P = 1/A$. A was defined as $a/K\sqrt{2\pi mkT}$. The rate of desorption K should be given by the probability per unit time of an atom escaping from the surface multiplied by the number, n , of adsorbed atoms per unit area. Thus the equilibrium pressure for half coverage is given by

$$(8) \quad P = \frac{n\nu}{a} (2\pi mkT)^{\frac{1}{2}} e^{-E_c/kT}$$

Assuming one adsorbed atom for each surface atom there are approximately 10^{15} sites/cm² on most crystal faces, so, for $\theta = \frac{1}{2}$,

$n \approx 5 \times 10^{14}$. The heat of chemisorption runs about 50 - 150 k cal/mole or approximately 2 - 6 ev/particle. Therefore, $E_c = 4$ ev will be a reasonable value. The vibrational energy must then be less than 4 ev if the adsorbed atoms are to be trapped, so take $\nu = 2\text{ev/h} \approx 5 \times 10^{14}$ cycles per second. At room temperature $kT \approx 1/40$ ev, and, if the calculations are made for nitrogen, $m = 4.65 \times 10^{-23}$ gm. For α , Becker's value of $\frac{1}{2}$ may be used since this was obtained experimentally for a clean surface. Finally, if the answer is to be in mm.Hg., the relation

$$(9) \quad P \text{ in dynes/cm}^2 = 1.33 \times 10^3 \quad P \text{ in mm.Hg.}$$

must be used. When these values are substituted into equation (8) the equilibrium pressure 4.1×10^{-41} mm.Hg. or roughly 10^{-41} molecules per liter is obtained.

This result indicates that even for much smaller sticking probabilities the equilibrium pressures will be unobtainably low. (Gomer has claimed a residual gas pressure of 10^{-30} mm.Hg. or approximately 10^{-10} molecule/liter when his experimental tube is immersed in liquid helium¹². As there is no method of measuring such a pressure, this claim is presumably based on an extrapolation of the vapor pressures to liquid helium temperatures. Thus, while the procedure offers great attractions for the attainment of low pressures, it is not suited to measurement of the isotherms even if the time to attain equilibrium is sufficiently short.)

CONCLUSIONS

In view of these facts it is apparent that to be of value

chemisorption observations must be made under non-equilibrium conditions but at pressures where the number of residual gas molecules striking the surface will not appreciably contaminate it in the time necessary to make the observations. In such circumstances, if the surface can be thoroughly cleaned, there can be no question about the results. The maximum allowable pressure will, of course, depend on the sticking probability and the time necessary for observation. Fortunately, even for unit sticking probability such pressures may be achieved with conventional high vacuum apparatus.

To be specific, the pressure for 10% coverage by nitrogen in one hour will be calculated assuming the sticking probability is one. From equation (1) the number of nitrogen molecules striking a square centimeter of surface per second is $3.9 \times 10^{20} P$, where P is the pressure of the gas in mm. Hg. As nitrogen is diatomic, the number of atoms striking a square centimeter of surface per hour is $1.4 \times 10^{24} P$. Taking the number of sites as 10^{15} per square centimeter, an answer of slightly less than 10^{-10} mm. Hg. is obtained.

On this basis the chemisorption isotherm is at best a theoretical device for calculating the variation of the heat of adsorption with surface coverage. The experimental quantities to be measured are the sticking probability and the heat of chemisorption as functions of surface coverage under non-equilibrium conditions. At higher temperatures it might be possible to measure rates of

desorption. Actually, experimental values of these quantities might be preferable from the theoretical viewpoint. They should have a direct bearing on the Lennard-Jones potential energy curve, and lead to a clearer understanding of the state of the surface and of the chemisorbed gas.

In conclusion, it should be noted that this approach is not new, but it is only since the introduction in 1950 of the Bayard-Alpert gauge²¹ for the measurement of very low pressures that it has been completely practical. Thus, while Roberts'^{6, 16} work was carried out by admitting the gas to be adsorbed in amounts which could only partially cover the surface, the results cannot be taken as conclusive since the residual gas pressures were not known. Becker's work¹⁸ does not suffer from this difficulty, and he has emphasized the importance of the sticking probability. His technique is discussed in the following section.

ELECTRON DIFFRACTION

INTRODUCTION

There are several experimental methods which are suited for measurement of the sticking probability. Of these, Becker's flash filament technique¹⁸ is probably the best known and certainly the simplest. The apparatus consists solely of a ribbon filament and a Bayard-Alpert gauge²¹. The filament is thoroughly outgassed by heating, allowed to cool to the desired temperature, and exposed to a gas at very low pressure for a short time interval. The pressure and time of exposure may be chosen so that the number of gas molecules striking the surface during exposure is less than the number necessary to form a monolayer. Thus, at the end of the time interval, the filament is only partially covered, the exact extent of coverage depending on the sticking probability. The filament is then flashed at high temperature, thus desorbing the gas. The fast response of the Bayard-Alpert gauge makes it possible to measure the pressure surge and, hence, for a known experimental volume, the amount of gas adsorbed may be calculated and the sticking probability deduced.

Several refinements on this basic technique have been used by Becker but the method must always suffer from one intrinsic disadvantage. This is that the filament is inevitably polycrystalline so that what is measured is the average sticking probability for

several undetermined crystal faces. Ultimately, a theoretical description of the surface states is desired and for such a theory more precise information as to the sticking probability for particular crystal faces is required.

The problem is further complicated, in the case of titanium, by the existence of a structure transition from hexagonal close-packed to body-centered cubic at a temperature slightly above 800° C., so another method is required. Two possible methods are observations with a field emission microscope and by low-energy electron diffraction.

The field emission microscope consists of a small cathode, the tip of a finely pointed wire, placed at the center of a spherical glass bulb. The hemisphere in front of the tip is coated with a phosphor and a conductor, which serves as the anode. The bulb is evacuated and a large potential difference applied to the electrodes. For a microscopic tip the resulting field at the tip is sufficient to produce cold cathode emission and this current forms an image of the tip on the screen. Magnifications of 10^6 are possible. Examinations of the Nordheim-Fowler equation²² shows that cold cathode emission is strongly dependent on the work function ϕ . Since ϕ varies with crystal faces and the tip is generally so small that it is a single crystal, the pattern observed consists of a number of light patches from those crystal facets which have greatest emission for a given applied fields. From the symmetry and angles between

such patches the crystal faces may be identified. As adsorbed gas layers also affect the work function, the effect of gases can be observed directly. The preferential adsorption by particular faces has been observed. Also, the temperature dependence of adsorption is readily studied by providing a small filament to heat the tip. With Gomer's technique of submerging the entire experimental tube in liquid helium¹² the temperature of the tip may be varied from 4° A. to evaporation temperature in this manner.

The principal difficulty of adsorption studies with the field emission microscope lies in the determination of the extent of surface coverage. This may be estimated from the emission provided that the emissivities from the clean and fully covered surfaces are known. Aside from this, the instrument seems particularly suited for measurements of sticking probabilities, offering the advantage that several crystal faces could be studied simultaneously and over a wide temperature range. Gomer has planned to make such observations.

In comparison, the low-energy diffraction technique provides far more detailed information, though with a correspondingly increased period of time required for the observations. Specifically with this method it is possible to determine the surface structure of the crystal and the adsorbed gas layer. The determination of the surface structure of the crystal is of interest since observation of the crystal structure serves as a check on the effective-

ness of the cleaning procedure. This feature in itself establishes the importance of the method. In addition, a knowledge of the structure of the adsorbed gas layer is significant for a complete understanding of the adsorption process.

It is not meant to imply that the electron diffraction method is unsuitable for the observation of sticking probabilities. With this method the partial surface coverage can be determined and the present results include calculations of sticking coefficients. The measurements are necessarily slower than would be possible with the field emission instrument and restricted to one crystal face, but are otherwise completely equivalent. In this connection it is worth noting that modern techniques have made automatic operation of a diffraction tube a distinct possibility. Some of these improvements will be discussed in the section on apparatus and procedure. Automatic operation would reduce the time necessary to obtain sufficient data on the adsorption of a gas for the determination of the sticking probability from several weeks to several days.

THEORY OF ELECTRON DIFFRACTION

In 1928 H. Bethe developed a dynamic theory of electron diffraction²³ analogous to that for X-ray diffraction. Unfortunately, this is not completely valid for low-energy electrons (20 - 200 eV) and no further work appears to have been done on this special case

other than a criticism²⁴ by von Laue of the applicability of Bethe's analysis. In the following discussion the problem is stated for the general case following von Laue. Bethe's treatment of the boundary conditions is then given. This is applicable to the general case and brings out the essential features of low-energy diffraction. Finally, the difficulties of the general solution are indicated and the implications of Bethe's simplifying assumption are pointed out.

As the first step to a mathematical description, the experimental arrangement must be summarized. The procedure is to direct a collimated, mono-energetic beam of electrons onto the face of a single crystal and measure the current density of reflected electrons as a function of a polar angle θ , and an azimuthal angle ϕ . θ is measured from the normal to the crystal face and ϕ from a direction fixed in the surface lattice. The experiment is conducted in a field-free region except for a small negative bias at the entrance to the collector to prevent measurement of inelastically scattered electrons.

Theoretically this situation may be approximated by a semi-infinite crystal occupying the region $z > 0$. The region $z < 0$ is field-free so that electrons in this region satisfy the Schrodinger equation

$$(10) \quad \Delta\psi(\underline{r}) + K^2\psi_f(\underline{r}) = 0,$$

where K is defined by

$$(11) \quad K^2 = 8\pi^2 m F / h^2.$$

Within the crystal there exists a potential $V(\underline{r})$ so the appropriate Schrodinger equation is

$$(12) \quad \Delta \psi_e(\underline{r}) + \{ K^2 + U(\underline{r}) \} \psi_e(\underline{r}) = 0,$$

where $U(\underline{r})$ is introduced for $2me V(\underline{r})/\hbar^2$. The problem is to obtain the solutions of equations (10) and (12), and then to match them at the boundary $z = 0$ by applying the boundary conditions

$$\psi_f|_{z=0} = \psi_e|_{z=0}, \text{ and}$$

$$(13) \quad \frac{\partial}{\partial n} \psi_f|_{z=0} = \frac{\partial}{\partial n} \psi_e|_{z=0}.$$

The solutions of equation (10) are well known. Any plane wave of the form $e^{i\mathbf{K}_m \cdot \mathbf{r}}$ is acceptable if the relation

$$(14) \quad \mathbf{K}_m \cdot \mathbf{K}_m = K^2$$

is valid:

Solutions of equation (12) are not so readily obtained. To facilitate the discussion it is necessary to expand the potential function. From symmetry considerations the function $U(\underline{r})$ is perfectly periodic with the crystal lattice in any direction normal to the z -axis. This is not completely true in the z direction since the condition

$$(15) \quad \lim_{z \rightarrow 0} U(\underline{r}) = 0$$

must be satisfied. However, the deviation from periodicity should be negligible except in the immediate vicinity of the surface. Therefore, it is possible to expand the function $U(\underline{r})$ in a triple Fourier series with the same periods as the crystal lattice if the

coefficients are regarded as functions of z .

For this purpose it is convenient to introduce the direct lattice vectors $\underline{a}_j$ defined as having the magnitude a_j of the lattice constants and the direction of the unitary base vectors $\underline{a}_j$ of the lattice coordinate system. Thus an arbitrary position vector $\underline{r}$ may always be resolved as

$$(16) \quad \underline{r} = r_j \underline{a}_j = \underline{r}_0 + n_k \underline{a}_k,$$

where $\underline{r}_0$ is the position of a point in a lattice cell referred to the origin of that cell, and the n_k are integers. Summation convention is used with this notation. The volume V_a of a unit cell in the direct lattice is given by the triple scalar product $\underline{a}_1 \cdot \underline{a}_2 \times \underline{a}_3$.

Associated with every direct lattice is a reciprocal lattice whose vectors $\underline{b}_j$ are defined by the relations

$$(17) \quad \underline{b}_1 = \underline{a}_2 \times \underline{a}_3 / V_a, \text{ etc.}$$

From this definition it follows immediately that

$$(18) \quad \underline{a}_i \cdot \underline{b}_j = \delta_{ij}.$$

Finally, it is desirable to define the vectors $\underline{g}$ and $\underline{h}$ by the equations

$$(19) \quad \underline{g} = 2\pi g_j \underline{b}_j, \text{ and } \underline{h} = 2\pi h_j \underline{b}_j,$$

with the understanding that the g_j and h_j are integers. For brevity the notation Σ_g and Σ_h will be used to indicate triple summation over these integers.

(25)

With the above notation the triple Fourier expansion of the function $U(\underline{r})$ may be written as

$$(20) \quad U(\underline{r}) = \sum_g C_g(z) e^{i\mathbf{g} \cdot \underline{r}},$$

so equation (12) becomes

$$(21) \quad \Delta \psi_e(\underline{r}) + \{K^2 + \sum_g C_g(z) e^{i\mathbf{g} \cdot \underline{r}}\} \psi_e(\underline{r}) = 0.$$

The form of the potential function suggests that this equation has as its solution a superposition of plane waves with z -modulated amplitudes. Since any arbitrary propagation vector $\underline{k}_n$ with magnitude $2\pi/\lambda$ may be written as

$$(22) \quad \underline{k}_h = \underline{k}_0 + \underline{h},$$

such a solution takes the form

$$(23) \quad \psi_e(\underline{r}) = \sum_h \psi_{e,h}(z) e^{i\mathbf{k}_h \cdot \underline{r}}.$$

When this is substituted in equation (21) the result is

$$(24) \quad \sum_h \{ \psi_{e,h}'' + 2i\mathbf{k}_h \cdot \underline{a}_s \psi_{e,h}' + (K^2 - k_h^2) \psi_{e,h} \} e^{i\mathbf{k}_h \cdot \underline{r}} + \sum_{g,h} C_g \psi_{e,h} e^{i(\mathbf{k}_h + \mathbf{g}) \cdot \underline{r}} = 0,$$

where the primes indicate differentiation with respect to z . If this is rewritten collecting terms with the same exponential factor, there results the infinite set of simultaneous differential equations

$$(25) \quad \psi_{e,h}'' + 2i(\mathbf{k}_h \cdot \underline{a}_s) \psi_{e,h}' + (K^2 - k_h^2) \psi_{e,h} + \sum_g C_g \psi_{e,k-g} = 0.$$

Thus (23) is the desired solution if the amplitudes are chosen in accord with these conditions.

THE BOUNDARY CONDITIONS

To grasp the full significance of this result the effect of

the boundary conditions (19) must be considered. Having introduced a superposition of plane waves inside the crystal, it is necessary to use a superposition of plane waves outside. However, experimentally a mono-energetic primary beam of electrons is used and only those electrons with very nearly this energy are collected. Therefore, outside the crystal only those waves with propagation vectors $\underline{K}_m$ such that

$$(26) \quad \underline{K}_m^2 = K^2$$

can be allowed. That is, the solution for $z < 0$ must be of the form

$$(27) \quad \psi_f = \sum_m \psi_{f,m} e^{i \underline{K}_m \cdot \underline{r}}.$$

Thus, the conditions (23) become

$$\sum_m \psi_{f,m} e^{i \underline{K}_m \cdot \underline{r}'} = \sum_h \psi_{e,h} e^{i \underline{k}_h \cdot \underline{r}'}, \text{ and}$$

$$(28) \quad \sum_m \underline{K}_m \cdot \underline{n} \psi_{f,m} e^{i \underline{K}_m \cdot \underline{r}'} = \sum_h \underline{k}_h \cdot \underline{n} \psi_{e,h} e^{i \underline{k}_h \cdot \underline{r}'},$$

where $\underline{n}$ is a unit vector normal to the surface and $\underline{r}'$ is any position vector lying in the surface.

These conditions may be further simplified by resolving the propagation vectors as

$$(29) \quad \underline{K}_m = A_m \underline{T}_m + B_m \underline{n}, \text{ and } \underline{k}_h = a_h \underline{t}_h + b_h \underline{n},$$

where $\underline{T}_m$ and $\underline{t}_h$ are unit vectors tangent to the surface. In this notation, condition (28) becomes

$$(30) \quad K^2 = \underline{K}_m^2 = A_m^2 + B_m^2.$$

From this it is seen that for any given tangential component A_m there are only two possible propagation vectors $\underline{K}_m$ and $\underline{K}_m'$

(27)

related by

$$(31) \quad B_m = -B_m'.$$

There is, of course, no corresponding condition on the waves in the crystal since their energies are not fixed.

Substituting this result in the boundary conditions (28) yields the relations

$$(32) \quad \begin{aligned} \sum_m (\psi_{f,m} + \psi_{f,m}') e^{i A_m T_m \cdot \underline{r}'} &= \sum_h \psi_h e^{i a_h t_h \cdot \underline{r}'}, \text{ and} \\ \sum_m B_m (\psi_{f,m} - \psi_{f,m}') e^{i A_m T_m \cdot \underline{r}'} &= \sum_h b_h \psi_{e,h} e^{i a_h t_h \cdot \underline{r}'} \end{aligned}$$

There is only one possible non-trivial solution of these equations. With each wave with propagation vector $\underline{K}_m$ striking the surface, there must be associated a reflected wave with the propagation vector $\underline{K}_m'$ and a set of waves in the crystal whose propagation vectors have tangential components satisfying the condition

$$(33) \quad A_m T_m = a_h t_h.$$

For every value of m there exists a set of values of h for which this relation is true, and these will be indicated by h' . Using this fact, the terms of equation (32) may be collected and set equal to zero. In this way the boundary conditions are reduced to two sets of equations,

$$(34) \quad \begin{aligned} \psi_{f,m} &= \sum_{h'} \frac{B_m + b_h}{2B_m} \psi_{e,h}, \text{ and} \\ \psi_{f,m}' &= \sum_{h'} \frac{B_m - b_h}{2B_m} \psi_{e,h}. \end{aligned}$$

Therefore, the amplitudes of the reflected waves are determined by the solutions of equations (25). Before returning to the consideration of this equation, one additional point should be de-

veloped from the boundary conditions.

THE SURFACE GRATING CONDITION

If the angle between the normal and the reflected wave propagation vector is denoted by θ_m and that between the normal and the propagation vector of a wave in the crystal by θ_h , equation (33) may be written

$$(35) \quad A_m = K \sin \theta_m = k_h \sin \theta_h = a_h.$$

This is just a statement of the law of refraction for an electron crossing a potential barrier at oblique incidence. In the geometrical theory of electron diffraction this condition requires that the surface grating condition holds regardless of the shape of the potential barrier.

The same result may be deduced from the present argument in the following manner. Let the primary beam be described by

$$(36) \quad \psi_{f,o} e^{i \underline{k}_o \cdot \underline{r}} = \psi_{f,o} e^{i(A_o \underline{T}_o + B_o \underline{n}) \cdot \underline{r}}.$$

Then the primary beam in the crystal has the form

$$(37) \quad \psi_{e,o} e^{i \underline{k}_o \cdot \underline{r}} = \psi_{e,o} e^{i(A_o \underline{T}_o + b_o \underline{n}) \cdot \underline{r}}.$$

The only permissible periodic modulations of this wave are those with the lattice period. Thus, the only waves this primary beam can induce in the crystal are described by

$$(38) \quad \psi_{e,g} e^{i \underline{g} \cdot \underline{r}} e^{i(A_o \underline{T}_o + b_o \underline{n}) \cdot \underline{r}}.$$

Hence the only reflected waves will be those for which

$$(39) \quad A_m \underline{T}_m = A_o \underline{T}_o + \underline{g} \cdot \underline{t} \text{ tang}.$$

The angle of incidence θ_o and reflection θ_m have already been defined and may be used to write tangential components as

$$\begin{aligned} A_o &= K \sin \theta_o = \frac{2\pi}{\lambda} \sin \theta_o, \text{ and} \\ (40) \quad A_m &= K \sin \theta_m = \frac{2\pi}{\lambda} \sin \theta_m. \end{aligned}$$

Thus, if we take the vectors $\underline{T}_o$ and $\underline{g}$ tang to have the same direction and, for convenience, choose this to be the lattice direction $\underline{a}_2$, then it follows from the definition of $\underline{g}$, equation (19), that

$$(41) \quad \frac{1}{\lambda} \sin \theta_m = \frac{1}{\lambda} \sin \theta_o + \frac{g_2}{a_2}, \text{ or}$$

$$(42) \quad g_2 \lambda = a_2 (\sin \theta_m - \sin \theta_o),$$

where g_2 is an integer and a_2 is the lattice constant. Therefore, the observed diffraction beams should obey the plane grating formula in any case.

CONCLUSION

The wave length λ is related to the energy of the electron by

$$(43) \quad \lambda = \frac{h}{p},$$

where p is the momentum of the electron. If λ is given in Angstroms and the accelerating potential V in volts, this relation reduces to

$$(44) \quad \lambda = \sqrt{150/V},$$

so the plane grating condition may be plotted as a function of accelerating voltage. When the colatitude angles at which experimental maxima occur are plotted as a function of voltage, they are found to coincide with the surface grating curve. The intensities of these maxima fluctuate as a function of voltage and this should

be related to the lattice constant a_g and the manner in which the periodic potential goes to zero. This is the information to be obtained by substituting the solutions of equations (25) into equations (34).

Bethe approached this problem by regarding the inner potential as perfectly periodic for $z > 0$ and going discontinuously to zero at $z = 0$. In this case the coefficients C_g and $\psi_{g,h}$ are no longer functions of z , and, consequently, condition (27) reduces to an infinite set of linear algebraic equations. This is still a difficult problem and must be attacked by approximation methods. The answers obtained indicate that the intensity of the maxima should fluctuate strongly with voltage, and that the maxima as a function of voltage should be displaced slightly from the point predicted by a purely geometrical theory. This is, of course, the effect of the step potential at the surface.

These results do not agree well with the results of low-energy electron diffraction, but are quite satisfactory for electron energies in excess of 200 - 300 electron volts. Von Laue pointed out that the assumption of a step potential is quite unreasonable from electrostatic considerations. The error is negligible for higher energy electrons since few of these are diffracted by the first few atomic layers. Most of these electrons traverse the potential barrier and enter a region of truly periodic potentials before they are diffracted.

Von Laue attempted to estimate the error for low-energy electrons by making a very approximate solution of equation (27). Unfortunately, he appears to have neglected the second term so his results are open to question. In any event, to make an accurate approximation it is necessary to know how the coefficients of the Fourier expansion of the potential function vary with z . This problem is under active consideration today but as yet the problem has not been satisfactorily solved for the case of covalent bonding²⁵. Therefore, a reasonably accurate solution of the general problem is not available. Such a solution would add considerable value to low-energy electron diffraction data by making it possible to determine the distance between surface planes and, perhaps, to measure the variation in potential as a function of distance normal to the surface.

APPARATUS

THE DIFFRACTION TUBE

Figure 2 shows a cross-sectional drawing of the experimental tube and a photograph of the assembled parts. Three distinct operations can be carried out with this equipment. These are heating the crystal to outgas or anneal it, cleaning the crystal face by ion bombardment, and electron diffraction. They will be discussed in that order.

For each of these operations the crystal must be placed in a different position. This is made possible by mounting the crystal on a shaft which rides in two V-bearings. The movement of the shaft is controlled from outside the vacuum tube by magnetic coupling to the nickel slug attached to the far end of the shaft. The electrical connections to the crystal are maintained by concentric, helical, molybdenum springs reaching back from the far end of the shaft to wire presses in the envelope. This arrangement allows rotation about the axis of the shaft as well as lateral travel.

To heat the crystal, the shaft is placed as shown in Figure 2. The molybdenum block to which the crystal is attached lies directly beneath the bombarding filaments. Thus, this block may be heated by electron bombardment while the crystal and the shaft are pro-

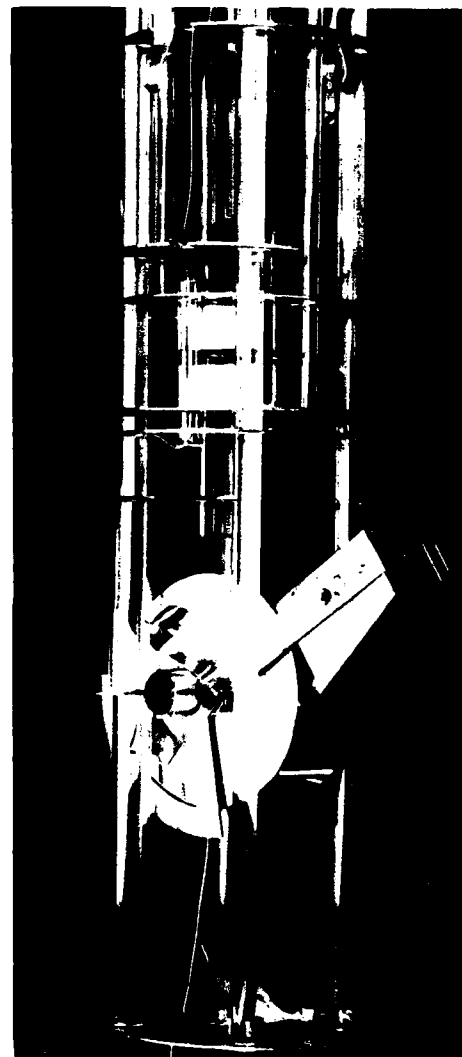
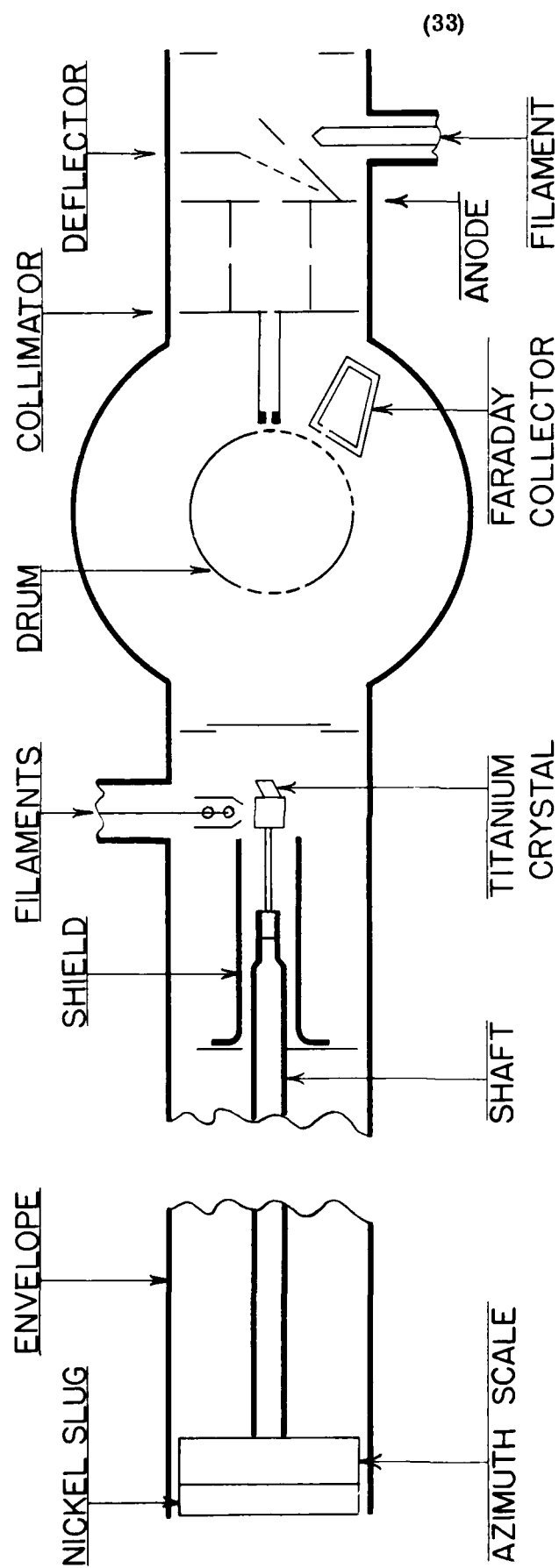


Figure 2. DRAWING OF THE EXPERIMENTAL TUBE AND PHOTOGRAPH OF THE ASSEMBLED PARTS

ected by shields on the filaments. The shaft is Pyrex tubing except for a short segment of molybdenum rod attached to the molybdenum mounting. The rod has a small diameter, and is shielded from the electron bombardment to prevent heat conduction to the Pyrex portion of the shaft. The crystal, on the other hand, has a large area of contact with the mounting block and only a quarter of the mass, so it is heated by conduction to the temperature of the block. This temperature is measured by making the block the junction of a molybdenum-titanium thermocouple, the leads for which travel through the Pyrex shaft. Consequently, the cold junction lies at the far end of the shaft where connection is made to the helical molybdenum springs.

For ion bombardment the mounting is withdrawn into the Pyrex shield to limit bombardment to the crystal face. The ions are produced in the region in front of the crystal by using the bombardment filament as an electron gun. It is equipped with a grid for this purpose. The ions thus formed are accelerated toward the crystal face by placing the bombardment filaments and other tube parts at a positive potential with respect to the crystal.

Finally, for electron diffraction, the shaft is moved forward so that the face of the crystal contains the axis of rotation of the Faraday collector. The conditions for electron diffraction have already been given in the discussion of the theory. The basic construction and operation of the present apparatus is similar to

that originally used by Farnsworth²⁶ and has been described elsewhere²⁷. The two significant improvements of the original apparatus are an electron gun devised by Farnsworth²⁸ in 1950 and a mechanism to control the rotation of the collector. The latter is original with this work and is a significant step toward automatic operation. Therefore, its purpose and operation merit further consideration.

The diffraction current density is a function of three variables, the azimuth and colatitude angles and the energy of the incident electron beam. The azimuth angle is not a useful variable for automatic operation since there are only a few crystal orientations for which the surface grating is sufficiently large for diffraction of low-energy electrons. Therefore, the usual procedure is to fix the azimuth angle and study the diffraction current density as a function of the colatitude angle and the energy of the incident beam. An electronic circuit to sweep the range of electron energies would be simply arranged, but would not be sufficient in itself for practical automatic operation as the sweep period need be no more than fifteen minutes. Thus, the need for precise control of rotation of the collector is indicated.

The usual method for rotating the collector is to mount the tube so that the rotation takes place in a horizontal plane, and to attach a vertical shaft with a nickel slug to the collector. An external magnetic field may be used to rotate the slug, and, hence the collector, but this field must be removed during the diffrac-

tion measurement. With this arrangement friction holds the collector in place while the magnetic field is removed. Since the friction of unlubricated parts in high vacuum is erratic, at best, it is difficult to adapt this control to automatic operation. Therefore, in the present apparatus the operation is controlled by a gear arrangement.

This arrangement operates in the following manner. The tube is mounted so that the collector rotates in a vertical plane, the acceleration of gravity supplying the driving force. The collector is connected by a rigid, horizontal shaft to the control mechanism in a side tube. This mechanism consists of an escapement and reduction gear which allow the collector to move in half-degree steps. The connection between the collector shaft and the reduction gear is made by ratchet working in 24° steps, so the collector may be reset when it reaches the end of its travel. Both the escapement and the reset are controlled from without by magnetic coupling.

THE ELECTRICAL CIRCUITS

The basic electrical circuits are shown in Figure 3. For electron diffraction the gang switch is put in the central position. With this setting, the crystal, drum, and collimator are maintained at the accelerating potential as previously noted. This accelerating voltage is adjustable stepwise by means of a switch at the battery bank, and also continuously variable over a smaller range

(37)

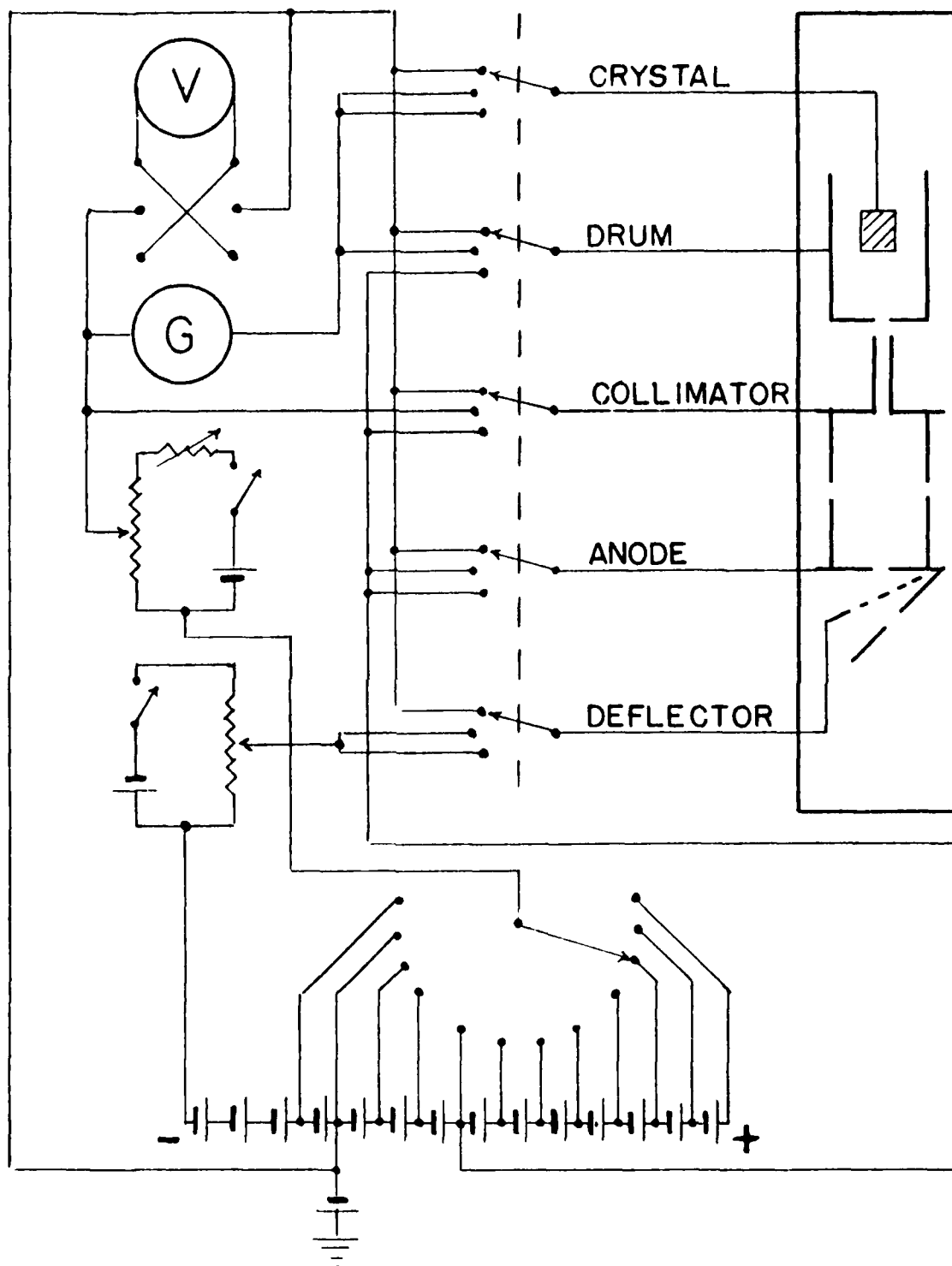


FIGURE 3. BASIC ELECTRICAL CIRCUITS.

by means of a voltage divider. When it is changed the deflector voltage must also be adjusted by means of a voltage divider.

The current from the crystal drum is monitored by a galvanometer. To insure that readings taken at different times will be comparable, this current must be held constant by regulating the electron gun filament current. For automatic operation this adjustment must be maintained, and an electronic circuit has been constructed which accomplishes this. The galvanometer, with its scale replaced by a dual element photo-tube, serves as the sampling circuit. The error signal from the photo-tube is amplified and fed into the control winding of a saturable reactor. This element serves as a variable impedance in the primary circuit of the electron gun filament transformer.

The remaining circuits needed for automatic operation are synchronizing circuits and an accelerating voltage sweep circuit. The latter must be coupled with the drive motor of a d.c. amplifier-recorder system measuring the collector current. This equipment was not available for the present measurements, so the collector current was measured with a modified DuBridge circuit d.c. amplifier²⁹. This has ample sensitivity and stability for manual operation, but insufficient stability for automatic operation.

THE VACUUM SYSTEM

The vacuum system is an all glass and mercury system with

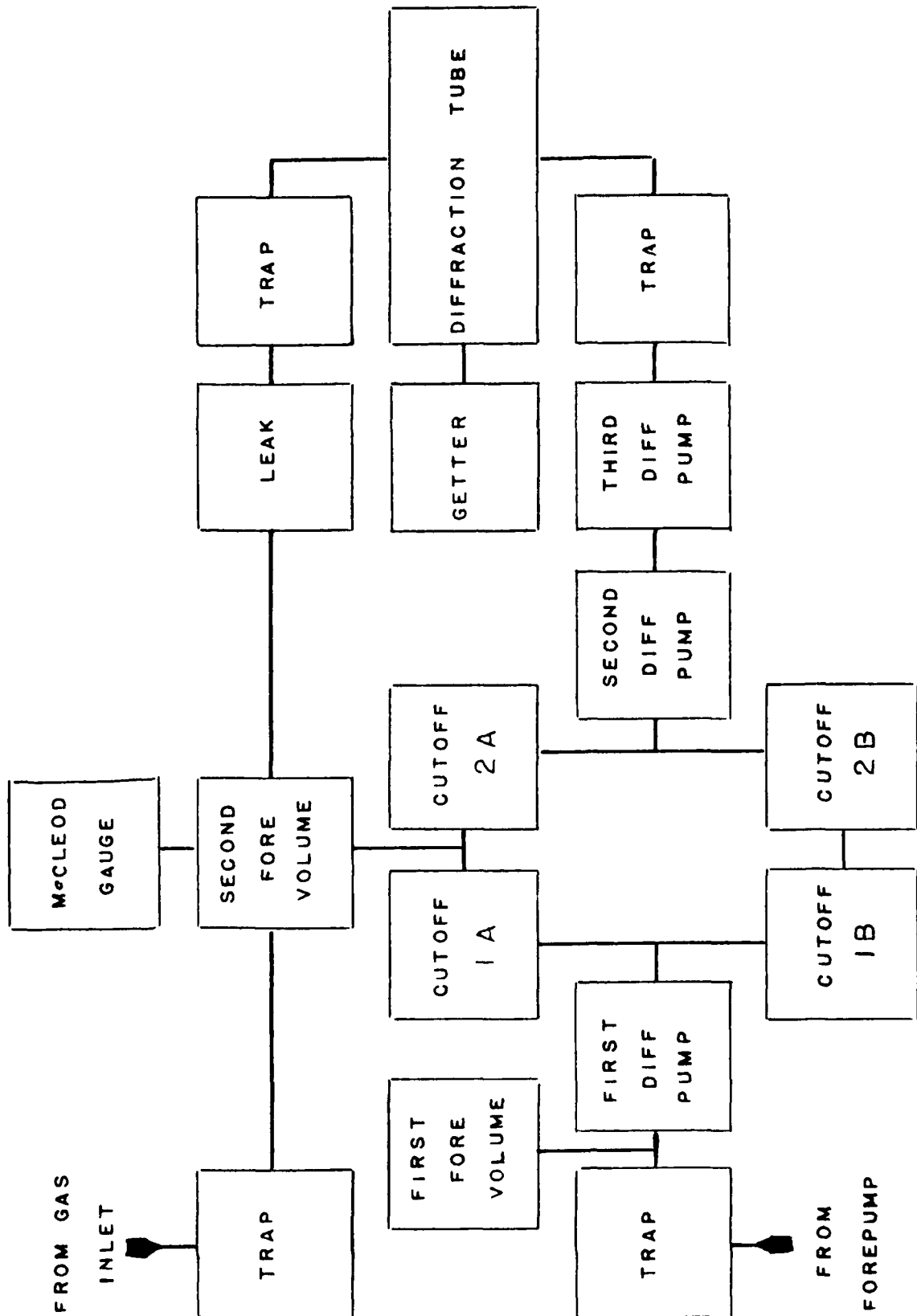


FIGURE 4. BLOCK DIAGRAM OF THE VACUUM SYSTEM.

liquid nitrogen traps to prevent mercury vapor from reaching the experimental tube. Figure 4 is a block diagram of the components of this system. The first fore volume is provided so that the mechanical pump may be run intermittently. The second fore volume and McLeod gauge may be used for calibrating ion gauges on the experimental tube, and measuring pumping speeds and build-up rates to analyze operation of the system. Also, with the aid of the cut-offs, this second volume may be isolated for storage of gases whose adsorption is to be studied. When this is done, the gas may subsequently be admitted to the experimental tube by means of the porcelain tube leak^{30, 31}.

Although this is a kinetic system, it is equipped with a getter. This is a side tube containing several molybdenum filaments which may be heated to deposit a molybdenum film by evaporation on the walls of the side tube. Such a film rapidly chemisorbs active gases, particularly oxygen. The getter increases the pumping speed several fold and, consequently, is extremely effective in reducing the time necessary to obtain very low pressures. It does not appear to affect the ultimate obtainable vacuum. This suggests that the limiting factor is diffusion of helium through the walls of the Pyrex envelope. In any case, the getter should continue to operate, keeping the partial pressures of the active gases substantially lower than the residual tube pressure.

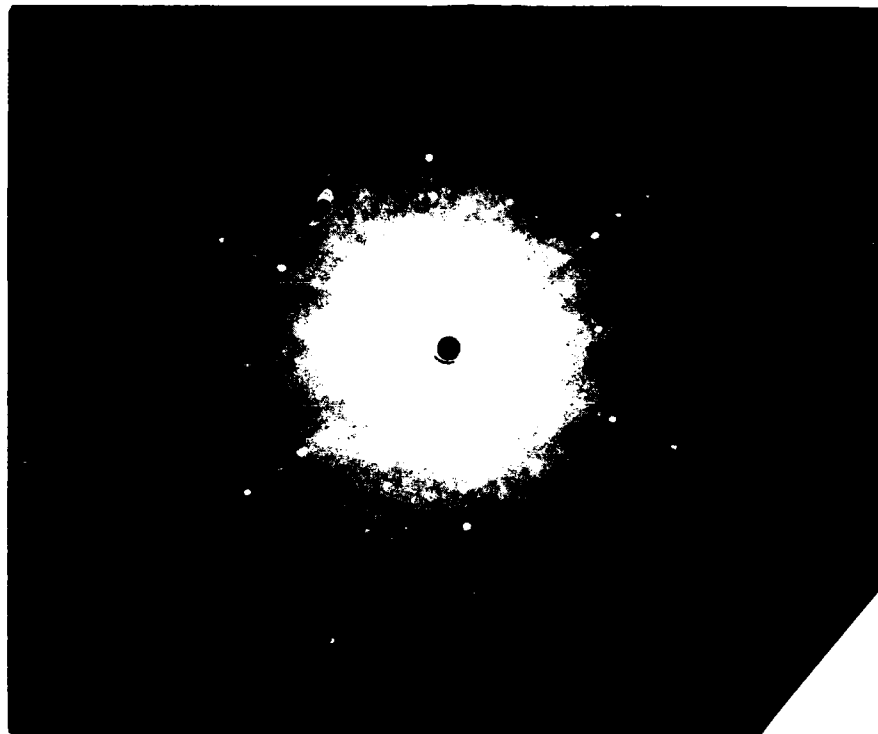
PROCEDURE

CLEANING AND ASSEMBLY

The parts of the experimental tube are made from Pyrex glass, chromel, nickel, molybdenum, and tungsten filament wire. The glass was cleaned with a saturated solution of potassium dichromate in concentrated sulfuric acid. All of the chromel parts with the exception of the scales and the collector rotation mechanism parts were electro-polished in a solution of 40% ortho-phosphoric acid and 60% glycerine. All the metal parts except the collector rotation mechanism parts were outgassed at 800° C. in a vacuum furnace. The collector rotation mechanism parts were excepted from these treatments to avoid enlarging the bearings and warping the gears. Instead, these parts were cleaned for 12 hours or more in a degreaser using acetone or trichloro-ethylene as the solvent. After all the parts had been cleaned as thoroughly as possible, they were assembled and placed in the Pyrex envelope. Precautions were taken to prevent exposure to dust and lint during this final assembly.

THE CRYSTAL PREPARATION

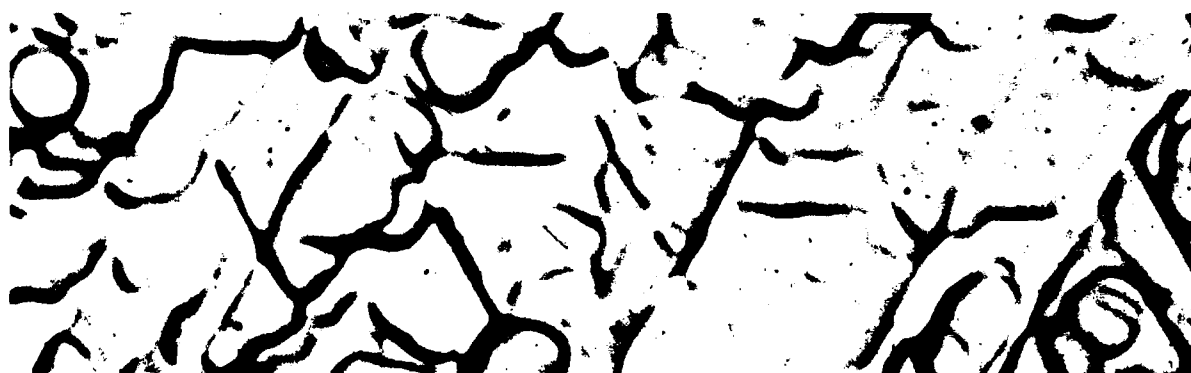
The titanium single crystal used in these experiments was grown at the New Jersey Zinc Company by the strain-anneal method. Upon receipt by this laboratory, the crystal was X-rayed for orientation, then cut, polished, and etched parallel to the (00-1) crystal plane. The etchant used was 50% glycerine and 50% hydro-



X-Ray of the Crystal Taken after the Experiment



Photomicrograph of the Crystal Face before the Experiment x1000



Photomicrograph of the Crystal Face after the Experiment x1000

FIGURE 5 . PHOTOGRAPHS OF THE CRYSTAL

fluoric acid. The prepared face was photo-micrographed previous to the final assembly of the experimental tube.

The experimental work on, and vacuum treatment of, this crystal may be divided in two parts. The first of these has already been reported in part^{27, 32} and in full³³. The second part of the work is the subject of the present report. During the first part of the work it was attempted, with only partial success, to outgas the crystal by heating alone. While this work was in progress a separate experiment being carried out in this laboratory indicated that the crystal face could be successfully cleaned by positive ion bombardment³⁴. Therefore, the experiment was halted and the apparatus modified to make this procedure possible. When operation was resumed, the first project was to determine the optimum conditions for ion bombardment. This phase of the procedure will be discussed in the results. Other than this, the techniques used to obtain the vacuum and prepare the crystal were to torch the experimental tube, heat the filaments, and heat the crystal. These operations were repeated cyclicly until the desired vacuum was obtained. Also, during the second part of the work the getter previously described was used to facilitate the procedure.

At the end of the present experiments the crystal was removed and its structure checked by X-ray analysis. A second photomicrograph was made to determine the effects of the ion bombardment. Figure 5 is composed of X-rays of the crystal taken after the completion of the experiments and two photomicrographs of the crystal

(44)

face which was studied. One was taken before the tube was assembled and the second after the completion of the experiments. Both are X1000.

RESULTS

INTRODUCTION

The experimental work may be divided conveniently into three phases. The first of these was the determination of the optimum method of cleaning the surface. The effectiveness of the cleaning procedure is, of course, of primary importance in all adsorption studies and the low-energy electron diffraction method is unique in that it gives a positive check on this operation. The second phase consisted of studies of the adsorption of the residual gases. This work in itself is not of great interest since the exact composition of the residual gases was not determined. It is, however, essential to the interpretation of the results of the final phase of the experiment, the study of the adsorption of pure gases. Certain of these measurements required a considerable amount of time. In such cases the residual gases might have an appreciable effect. The study of the adsorption of residual gases alone either eliminates this possibility or determines the appropriate corrections for it.

THE SURFACE CLEANING TECHNIQUE

The earlier work with this apparatus and crystal has already been mentioned. It was found possible to clean the surface sufficiently by heating in high vacuum to produce diffraction beams. These beams were, however, not typical of the titanium structure. It was concluded that the surface was still covered by an adsorbed

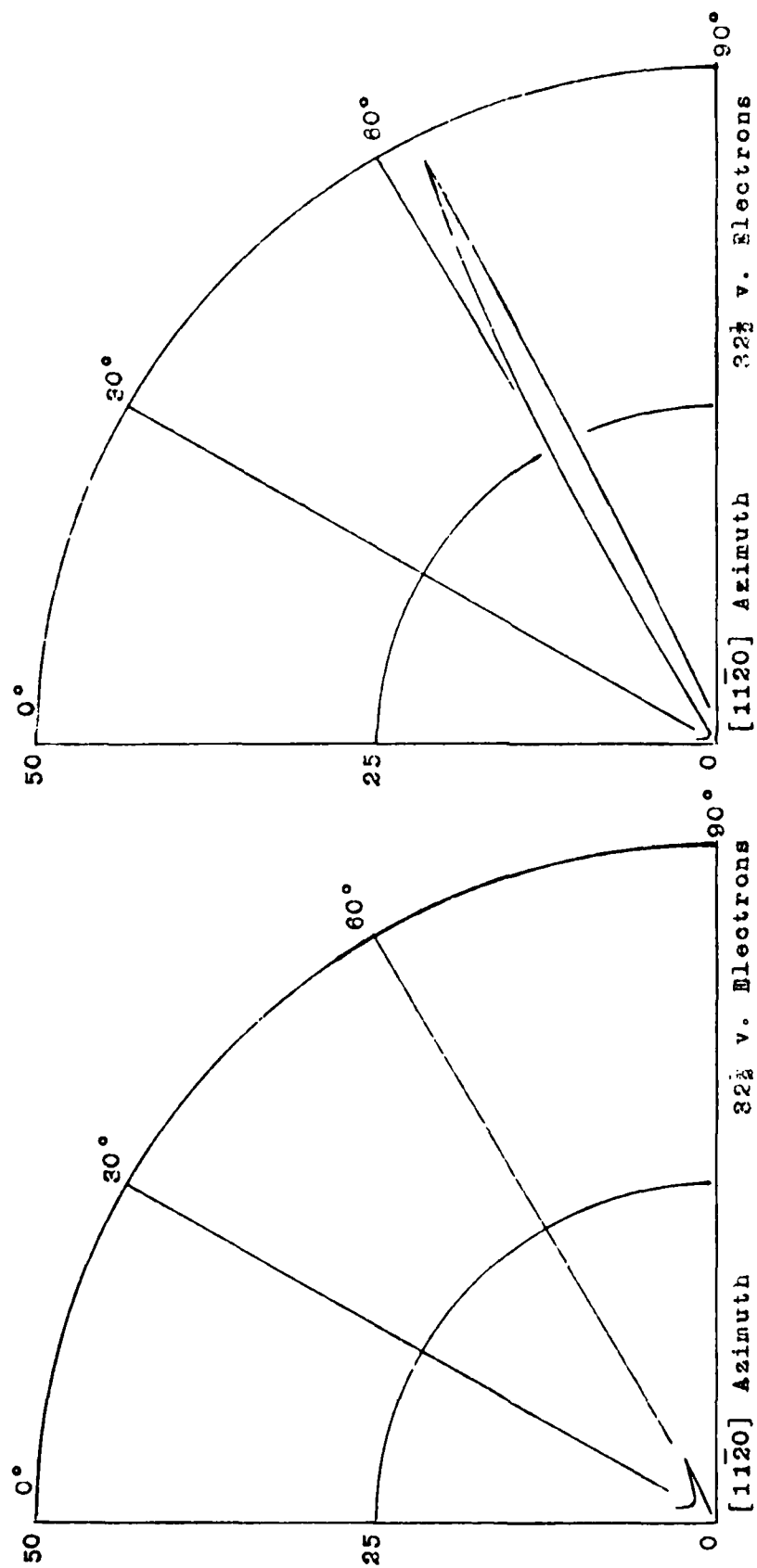
gas layer, a stable compound, or other contaminants. The latter could be present if impurities in the crystal diffused to the surface or if the etchant was not fully removed by the rinsing procedure. In any event, holding the crystal at 750° C. for over 100 hours in a vacuum of the order of 10^{-9} mm.Hg. had no effect on this surface layer³³. The use of higher outgassing temperatures is precluded by the structural transition.

This same difficulty was encountered by Dr. R. E. Schlier of this laboratory in his attempts to clean the face of a titanium crystal for another experiment. He tried admitting argon into the experimental tube and running a self-maintained discharge using the crystal face as the cathode. This resulted in annihilation of the diffraction beams, but heating the crystal to 500° C. for a short period produced the theoretical titanium diffraction pattern³⁴. This pattern, while typical of titanium, was weak and poorly defined

The present work began with the object of improving this cleaning procedure. The first step was to introduce the electron accelerator to sustain the discharge. Such a sustained discharge can be maintained at low bombarding energies and current densities. In this manner, it was hoped, the surface damage could be minimized. Furthermore, this procedure can be carried out at lower pressures. This is desirable as it increases the mean free path of the sputtered atoms, allowing them to leave the immediate vicinity of the crystal face.

The inclusion of the electron accelerator made it necessary to open the experimental tube, and this opportunity was taken to make several other repairs and modifications. These included installation of the getter and the collector rotation mechanism. In all, the crystal was exposed to dry air for several weeks. This meant that the cleaning procedure would be the same as that for a freshly prepared sample. Therefore, it was decided to determine the effectiveness of the ion bombardment alone. As Dr. Schlier's work showed it necessary to anneal the crystal at 500° C. following ion bombardment, the crystal was outgassed at this temperature.

After the crystal had been outgassed, an attempt was made to clean it by ion bombardment. The bombarding current used was one microampere. This could be controlled by adjusting the argon pressure and the electron gun emission. The procedure was to bombard with low energy ions for five minutes and then try several annealing times. The bombarding energy was increased from 200v. to 700v., but no improvement in the results was noted for energies above 500v. The best annealing time was found to be on the order of 5 minutes, longer times having an adverse effect. The results at this stage were still relatively poor, so higher bombarding currents were used. Ion bombardment for one minute at 100 microamperes gave distinctly better results than 100 minutes at one microampere. Finally, the crystal was heated to 750° C. until pressure fell to 10^{-8} mm.Hg. This treatment partially restored the structure originally observed. After this outgassing the ion bombardment was particularly successful.



AFTER ION BOMBARDMENT

AFTER ANNEALING

FIGURE 6. EFFECT OF ANNEALING THE CRYSTAL AFTER ION BOMBARDMENT.

Subsequent experience in removing adsorbed gas has shown that the best results are obtained by heating the crystal to 750° C. until the pressure can be reduced to less than 10^{-8} mm.Hg., then ion bombarding for five minutes with a 100 microampere current of 500 volt ions. The outgassing operation generally requires 10 to 12 hours with the present vacuum system. The argon pressure used for ion bombardment is on the order of 5×10^{-3} mm.Hg. Following the ion bombardment, this gas is pumped out and the crystal is annealed at 500° C. for five minutes. After prolonged exposure of the crystal to active gases this entire procedure must be carried out twice to achieve satisfactory results.

Figure 8 shows the strongest diffraction beams from the titanium structure plotted as a function of the colatitude angle θ . This beam is obtained from the $[11\bar{2}0]$ azimuth with an incident beam of 32½ volt electrons. The graph on the left shows the beam after ion bombardment. The plot on the right shows this same beam after the crystal has been annealed. The improvement is apparent. The beam shown on the right is a typical strong diffraction beam. Its maximum in intensity is roughly 50 times the maximum background intensity. Its width at half the maximum intensity is four degrees. This corresponds to the limiting resolution of the apparatus.

The term $[11\bar{2}0]$ azimuth is used above to indicate a particular azimuthal orientation ϕ . It has been mentioned that there are only a few such orientations for which the surface grating spacing is large enough for the diffraction of low-energy electrons. In the

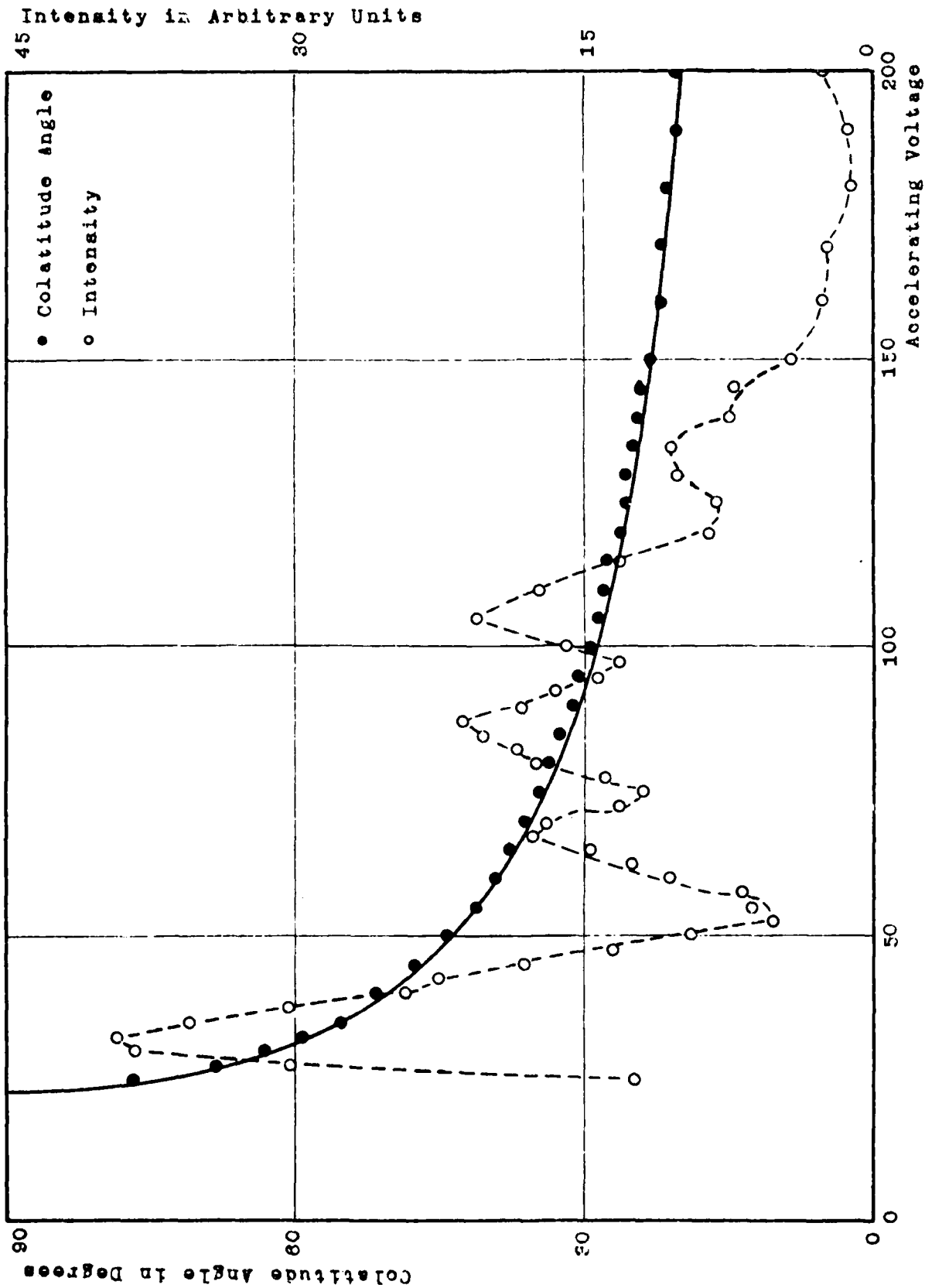


FIGURE 7. (1120) AZIMUTH, FIRST ORDER SURFACE GRATING CONDITION AND EXPERIMENTAL RESULTS FROM THE CLEANED SURFACE.

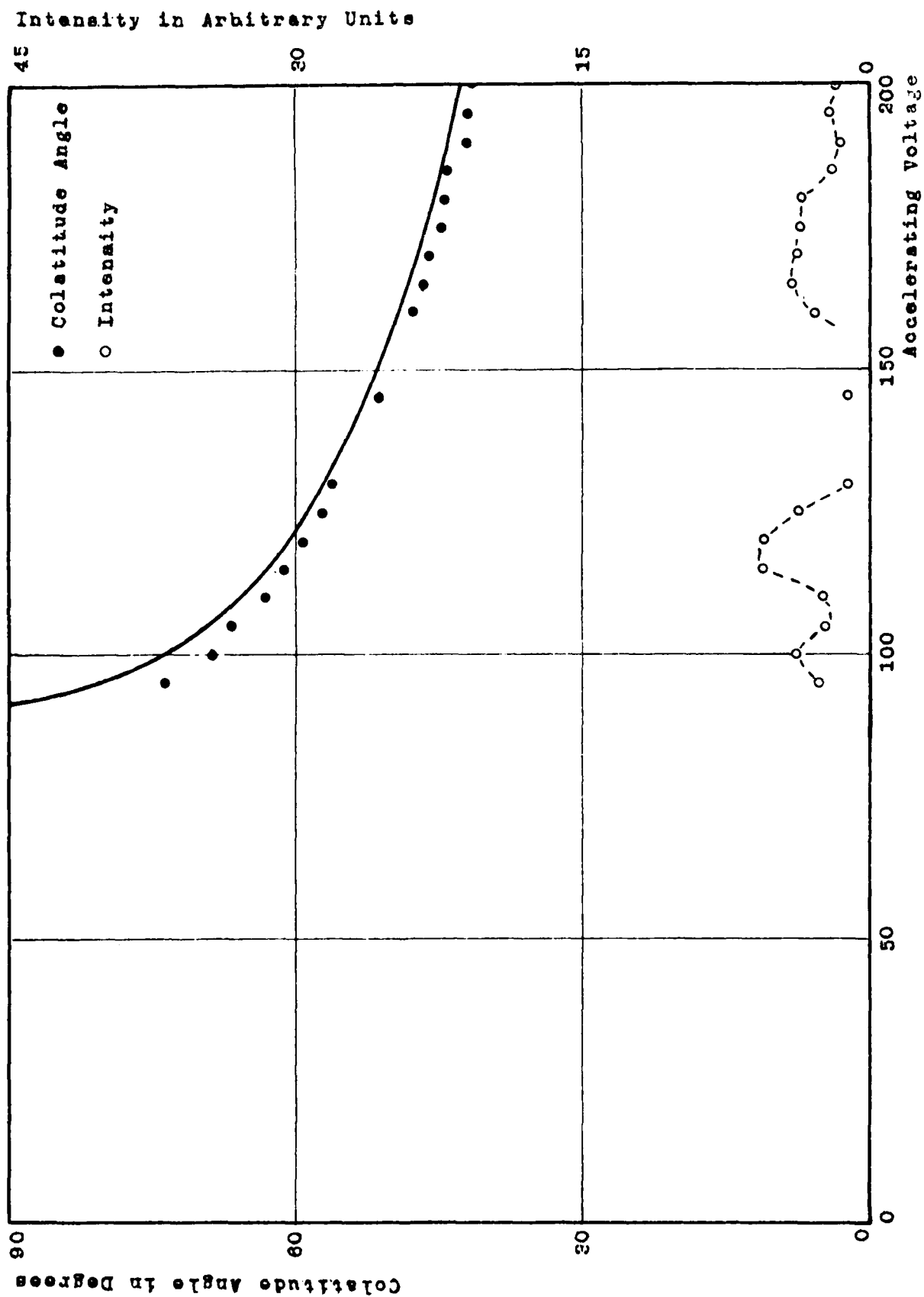


FIGURE 8. ($11\bar{2}0$) AZIMUTH, SECOND ORDER SURFACE GRATING CONDITION
AND EXPERIMENTAL RESULTS FROM THE CLEANED SURFACE

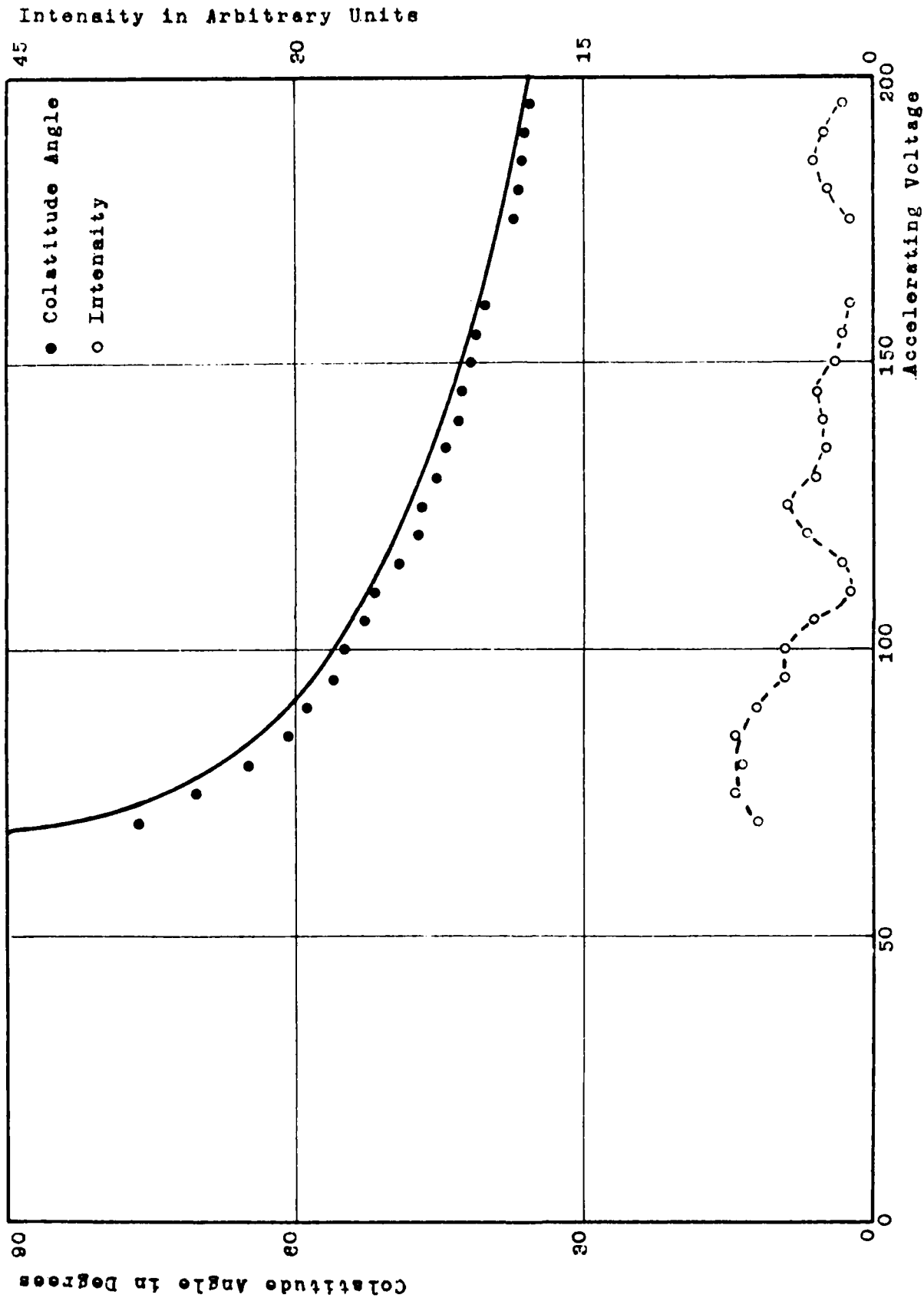


FIGURE 9. (0110) AZIMUTH, FIRST ORDER SURFACE GRATING CONDITION
AND EXPERIMENTAL RESULTS FROM THE CLEANED SURFACE

case of titanium six of these orientations correspond to the alignment of one of the six $[11\bar{2}0]$ crystal planes within the plane of rotation of the collector. Each of these orientations is equivalent for the purposes of electron diffraction, so the notation is sufficient to fix the orientation. There is also another set of six equivalent orientations from which diffraction beams may be observed. These correspond to the alignment of one of the $[01\bar{1}0]$ planes with the plane of rotation of the collector.

STUDIES OF THE CLEAN SURFACE

Having developed a method of cleaning which produced a theoretical titanium diffraction beam, detailed surface studies were undertaken. These consisted of studying the diffraction current as a function of the accelerating voltage V and the colatitude angle θ . The results for the $[11\bar{2}0]$ azimuth are shown in Figures 7 and 8 and those for the $[01\bar{1}0]$ azimuth in Figure 9. In these figures the solid curve is a theoretical plot of a surface grating condition. The $[11\bar{2}0]$ azimuth has a large surface grating spacing so parts of the first and second order surface grating conditions lie within the region $20 < V < 200$ volts, $15^\circ < \theta < 90^\circ$. The first order condition is shown in Figure 7 and the second order condition in Figure 8. The $[01\bar{1}0]$ azimuth has a smaller spacing, and only the first order condition falls in the prescribed region. This is shown in Figure 9.

The solid points in the figures represent the angular positions

of the diffraction maxima as illustrated in Figure 6. The open circles indicate the intensity of these maxima in terms of the arbitrary intensity scale shown on the right in the graphs. It was pointed out in the discussion of the theory of diffraction that the intensity of the maxima as a function of accelerating voltage can not be predicted. Accordingly, dashed curves have been drawn through these experimental points. No maxima were found which did not satisfy the theoretical surface grating conditions.

These results were observed in several of the equivalent azimuths and were found to be identical in form. Slight shifts in the experimental surface grating curves were noted. It was found that these were due to an error in the angle of incidence. By further study of the equivalent azimuths the deviation from normal incidence was determined to be one degree and correction tables were computed for the azimuths studied. All the data shown have been corrected for this factor.

Theoretical consideration shows that a change of one degree at a colatitude angle of 80° results in a change of three tenths of one percent in the determination of the lattice constant. For the titanium lattice constant this is approximately 0.01 angstroms. On this basis the experimental results indicate that the lattice constant of the surface grating differs by less than one per cent from that determined for bulk titanium by X-ray diffraction. Therefore, the structure of the cleaned surface has the symmetry and lattice constant of the hexagonal plane of titanium. This does not

positively identify it as a clean titanium surface. For example, oxygen and nitrogen were found to adsorb in the same structure. However, the fact that this surface actively chemisorbs gases suggests that it is actually clean. Lacking evidence to the contrary, this viewpoint was adapted and the experiments continued on this basis. The dashed intensity curves in Figures 7, 8, and 9 are taken as identifying features of the cleaned surface.

ADSORPTION OF RESIDUAL GASES

The adsorption of residual gases is a possible source of contamination. The best conditions achieved in this work were to keep the residual gas pressure less than 5×10^{-9} mm.Hg. This was done by outgassing the crystal at 750° C. until the residual tube pressure was less than 5×10^{-9} mm.Hg. with the crystal at this temperature. The crystal face was then cleaned as previously described. The pressure rose slightly above 5×10^{-9} during the annealing, but, in view of the thorough outgassing, it is felt that this must be due to argon driven into the crystal during the ion bombardment. Thus, it seems reasonable to assume the partial pressure of the active gases was less than 5×10^{-9} mm.Hg. during the entire cleaning procedure. Allowing for the action of the getter, this estimate should be quite conservative. Using the calculations developed in the discussion of adsorption, the minimum time for complete coverage is 15 minutes, or roughly the time from the end of the ion bombardment to the beginning of observation. As this computation assumes the sticking probability is unity, it is unlikely that the

surface would actually be more than half covered at the start of observation. Under these conditions the completion of a monolayer would be easily observable. In fact, no change was observed in the diffraction patterns for the first few hours after cleaning, so it may be assumed that the results shown were not due to adsorbed gases.

This conclusion seems relatively sound for the studies of the clean surface. The situation is not so favorable for the adsorption measurements. In this case the argon must be removed from the gas handling system before the gas to be studied can be introduced. This requires at least an hour between the end of the ion bombardment and the exposure of the crystal to the gas. In addition, some of the later adsorption measurements required observation periods of six hours or more. For these reasons the adsorption of residual gases was carefully observed. At first it was found that after 5 hours the contamination became observable. The earlier adsorption measurements required only an hour for observation, so the residual gas effect was considered negligible. When the longer observations were undertaken, the residual gas adsorption was rechecked. At this time it was found that observable contamination did not take place for 24 hours. Thus, the partial pressure of the active gases was several orders of magnitude less than the residual gas pressure of 2×10^{-9} mm.Hg. indicated by the ion gauge. Since several months had elapsed between these checks, this seemed a reasonable improvement in the vacuum. Therefore, the possibility of contamination by residual gases was ruled out.

THE STRUCTURE OF ADSORBED OXYGEN AND NITROGEN LAYERS

The studies of the adsorption of oxygen and nitrogen were made by the same methods and the results are very similar for the two gases. Therefore, it is convenient to discuss them simultaneously. The procedure was to clean the surface, expose it to the gas for 10 minutes, and then obtain the diffraction pattern. In the case of nitrogen, exposures at gas pressures of 10^{-7} and 10^{-5} mm.Hg. had little effect, but when the procedure was repeated with a gas pressure of 10^{-2} mm.Hg. a definite change in the diffraction pattern was noted. In contrast to this, exposure to oxygen at 10^{-7} mm.Hg. produced a distinct change in the diffraction pattern. Repeating the procedure with the oxygen pressure increased to 10^{-5} mm.Hg. gave the same result.

Both of these gas structures were found to be stable and were studied extensively. They have hexagonal symmetry and the titanium lattice constant. The distinguishing feature is the form of the intensity vs. accelerating voltage curves. The results for the first order surface grating conditions in the two azimuths are shown in Figures 10 and 11 for the oxygen structure and in Figures 12 and 13 for the nitrogen structure. The diffraction beams from the gas-covered surface are generally weaker than those from the clean surface. This, plus the fact that the intensity decreases with increasing order and accelerating voltage, made it impossible to observe more than a few scattered points on the second order surface grating condition. Therefore, these graphs have been omitted.

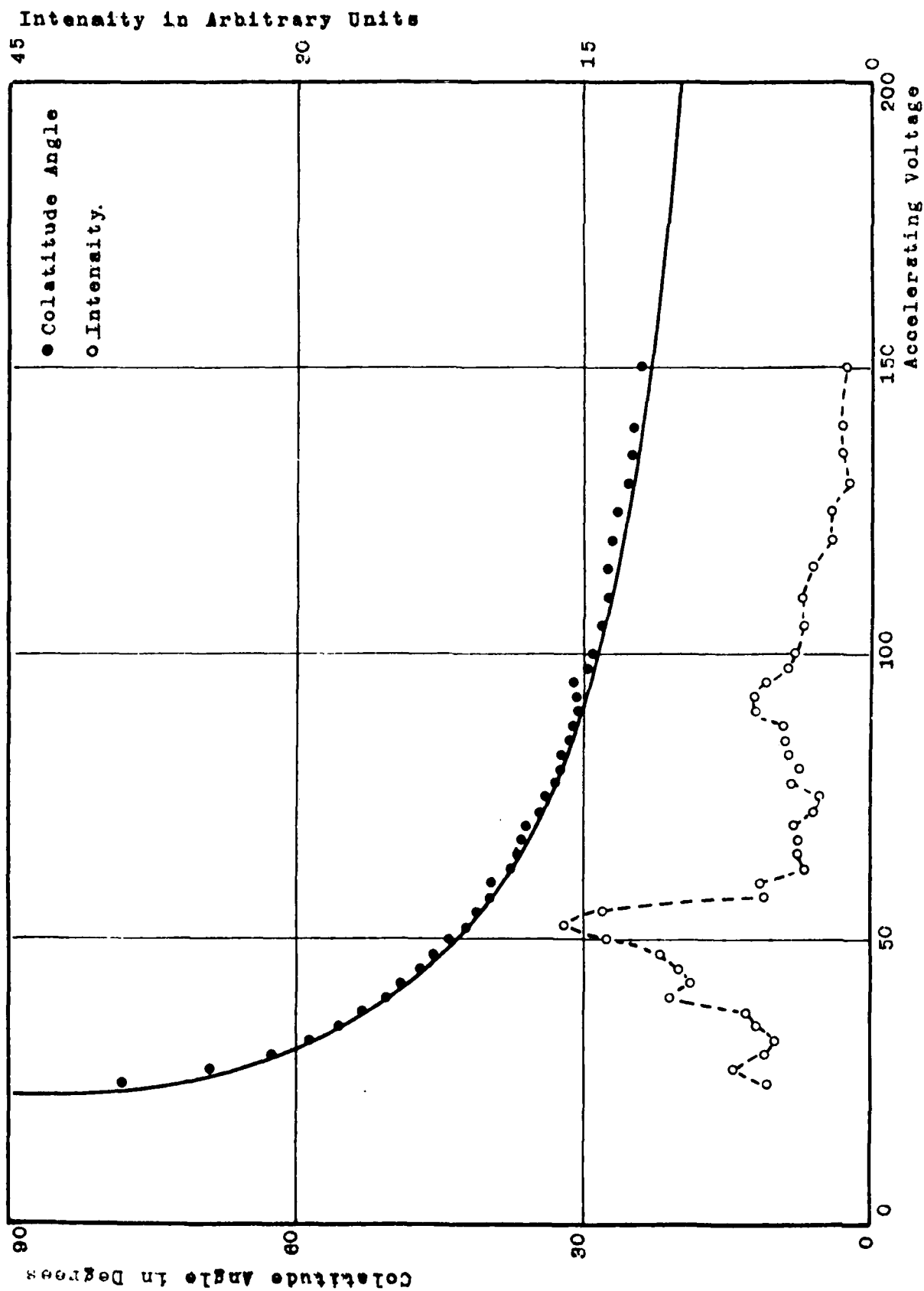


FIGURE 10. $(11\bar{2}0)$ AZIMUTH, FIRST ORDER SURFACE OPERATING CONDITION, EXPERIMENTAL RESULTS FROM THE OXYGEN COVERED SURFACE

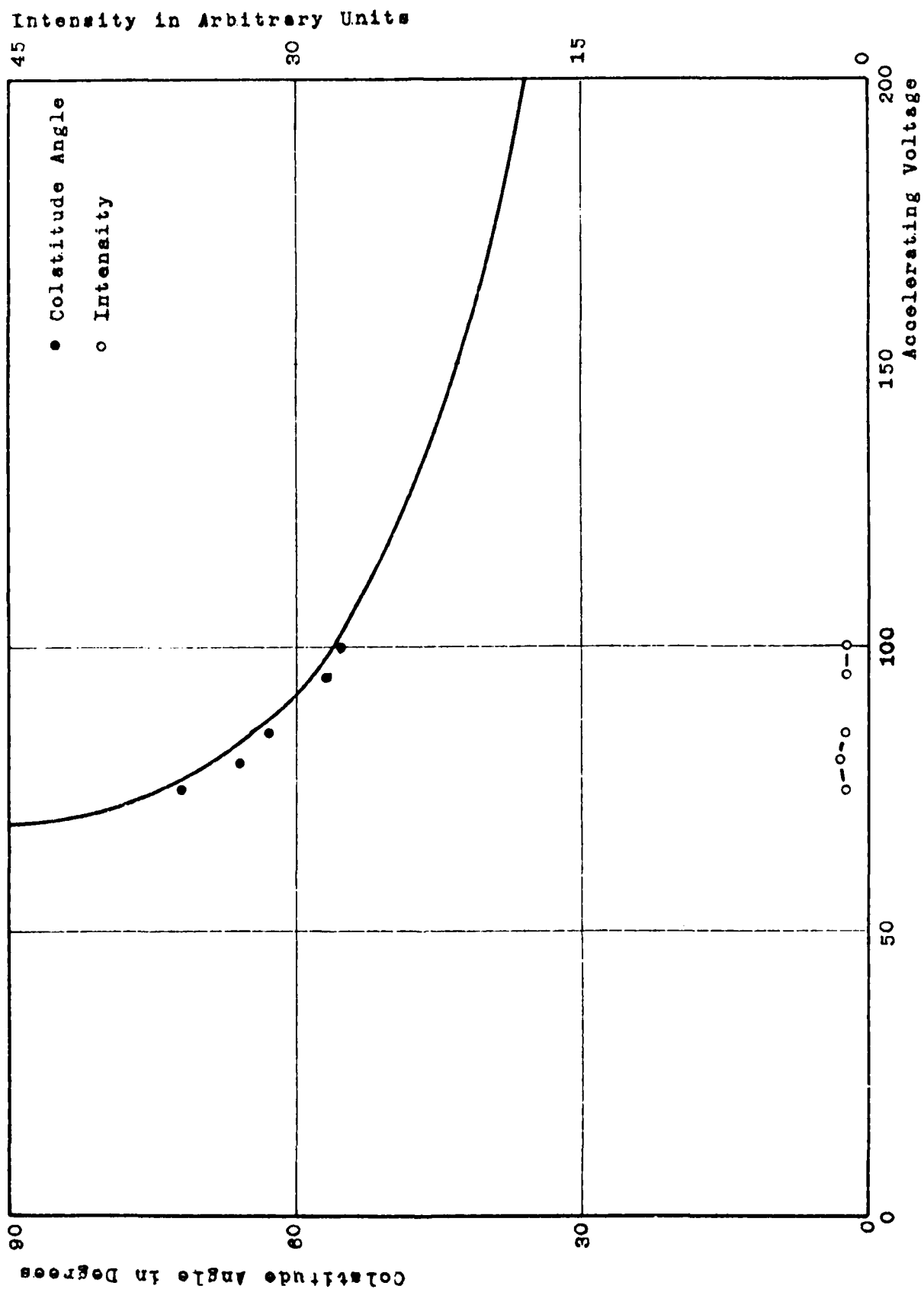


FIGURE 11. $(01\bar{1}0)$ AZIMUTH, FIRST ORDER SURFACE GRATING CONDITION, EXPERIMENTAL RESULTS FROM THE OXYGEN COVERED SURFACE

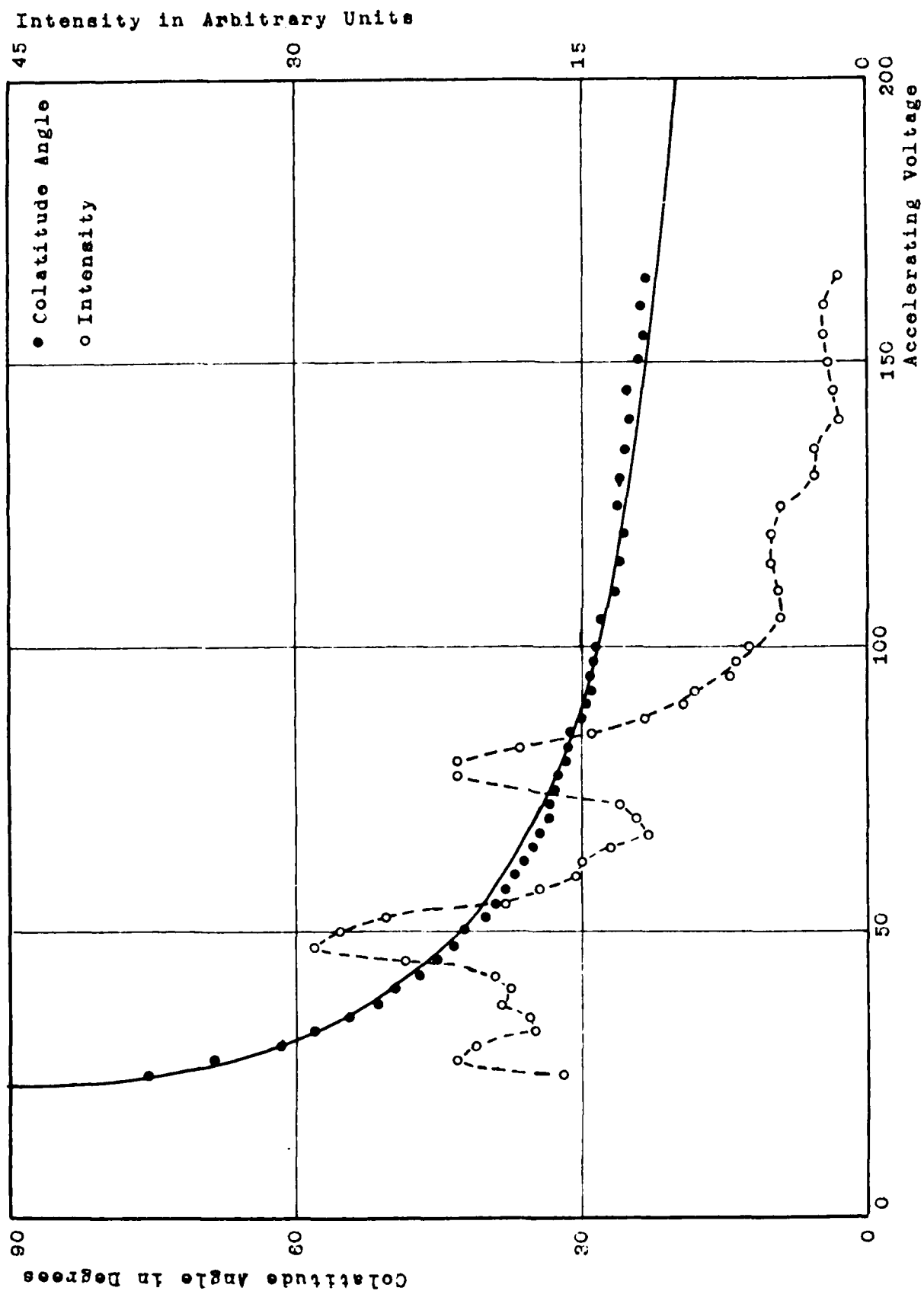


FIGURE 12. (1120) AZIMUTH, FIRST ORDER SURFACE GRATING CONDITION,
EXPERIMENTAL RESULTS FROM THE NITROGEN-COVERED SURFACE

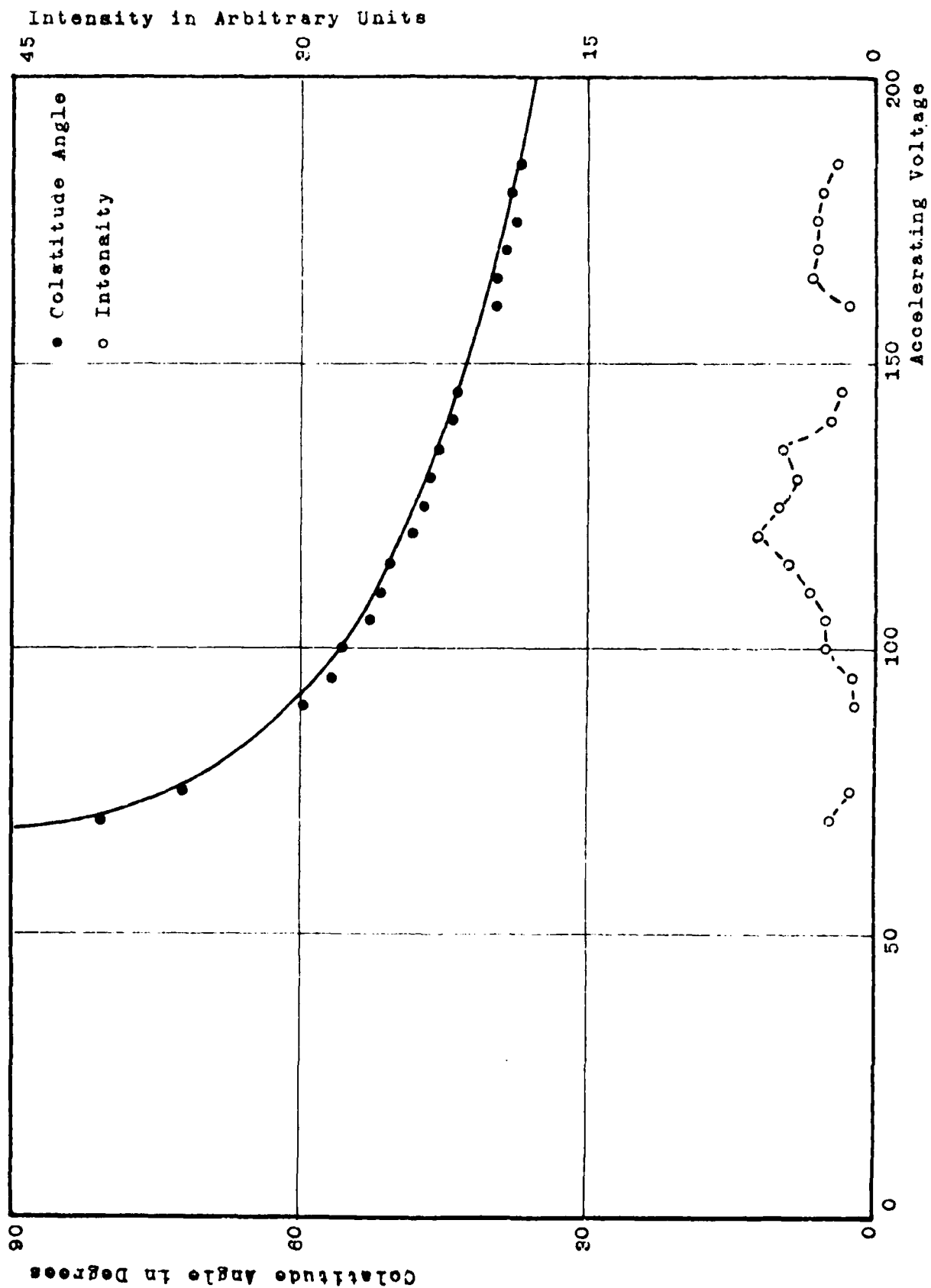


FIGURE 13. (0110) AZIMUTH, FIRST ORDER SURFACE GRATING CONDITION
EXPERIMENTAL RESULTS FROM THE NITROGEN COVERED SURFACE.

Even in the data given there are gaps in the readings at higher voltages where no maxima could be found.

The results appear to be completely consistent with the known crystal structure of titanium monoxide, TiO , and titanium nitride, TiN . Both of these are face-centered cubic lattices similar to the Rock Salt structure. Therefore, their (111) planes are hexagonal nets and alternate (111) planes are composed entirely of gas atoms or entirely of titanium atoms. In both cases the length of the sides of the hexagons differs from the titanium lattice constants by less than 2%. The one significant difference is that the distance between adjacent (111) planes of the compounds is almost exactly half the distance between adjacent (00·1) planes in the pure titanium lattice. Thus, it appears reasonable that oxygen or nitrogen would be adsorbed by the (00·1) face of a pure titanium crystal in a hexagonal array but with a smaller distance between the gas layer and the surface than that between adjacent (00·1) titanium planes. This decrease in the distance between planes should account for the change in the intensity vs. accelerating voltage curves. Unfortunately, part of this change must also be attributed to possible changes in variation of the periodic potential at the surface and to possible differences in the scattering power of the gas atoms as compared to the titanium atoms. Significant numerical considerations are therefore precluded.

While the gas structures observed are entirely consistent with the considerations above, they offer no explanation of the surface

structure observed in the earlier work. In an attempt to account for this earlier structure, the crystal was heated to 500° C. for 10 minutes while exposed to nitrogen at a pressure of 10^{-7} mm.Hg. This procedure was also tried with oxygen. In this case the crystal temperature was 300° C. and the gas pressure 10^{-8} mm.Hg. In both cases the previously observed gas structures were formed. It is significant that the gas pressures used were at least an order of magnitude lower than those necessary to form the gas structure in the same time interval with the crystal at room temperature. These results indicate a definite increase in the sticking probability with increasing temperature, and, consequently, a positive activation energy for the adsorption of these gases by titanium.

This procedure was repeated using the same gas pressures and intervals of exposure, but at higher temperatures. For exposure to nitrogen the temperature was 700° C. The resulting diffraction patterns showed some traces of the earlier beams characteristic of the unknown structure. The result is not regarded as significant as such traces were always noted after heating the crystal to this temperature. In the second trial with oxygen, the crystal temperature was only 550° C. This treatment completely extinguished all the diffraction beams. To achieve this result with a ten minute exposure and the crystal at room temperature the oxygen pressure must be greater than 10^{-1} mm.Hg. This large difference in pressure, a factor of 10^7 , seems to be conclusive evidence for the activated adsorption of several layers of gas in an amorphous structure.

THE STICKING PROBABILITIES

After the determination of the basic features of the diffraction patterns from the cleaned, oxygen-covered, and nitrogen-covered surfaces was completed, studies of the sticking probabilities for oxygen and nitrogen on titanium were undertaken. For this work attention was confined to those first order beams from the $[11\bar{2}0]$ azimuth which are obtained for accelerating voltages in the range 20 - 125 volts. The procedure used was to expose the crystal to the gas at low pressure for a ten minute interval. After such an exposure the diffraction beams from the prescribed region were observed. The entire procedure was repeated several times using successively higher gas pressures. By comparing the several observations, the decrease in the titanium beams and increase in gas beams can be observed.

In Figure 14 the decrease in the intensity of the titanium beam at 32.5 volts is plotted as a function of the oxygen pressures used. The solid points are experimental and have been connected by solid lines. In the same figure the increase of the oxygen at 52.5 volts is shown. Open circles are used for the experimental points and they have been connected by dashed lines. In Figure 15 the same information has been plotted for the adsorption of nitrogen. The nitrogen beam used is that occurring at 47.5 volts.

The interpretation of these data is complicated by the fact that for partial coverage the intensity of the diffraction beams is

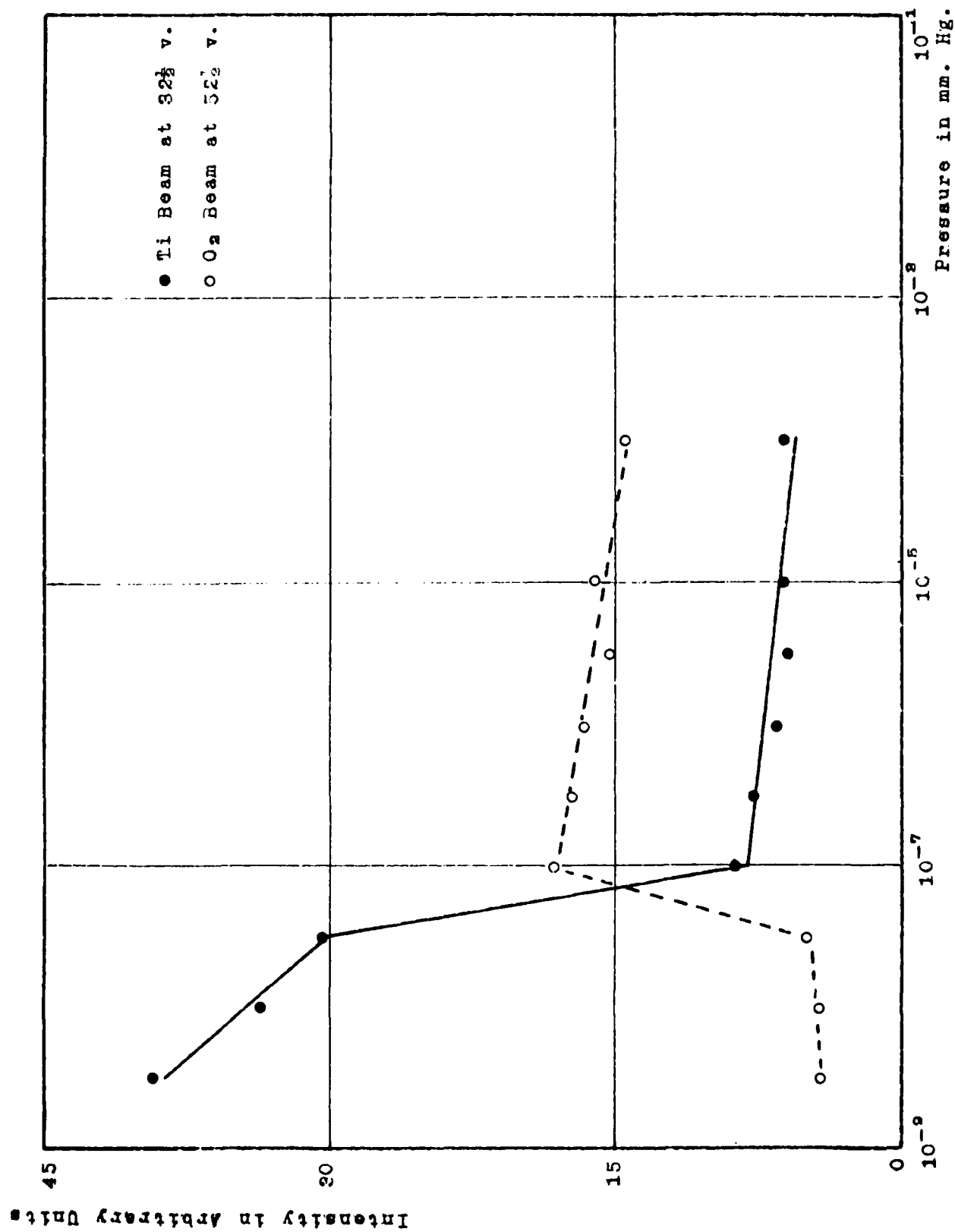


FIGURE 14, (1120) AZIMUTH, CHANGE IN FIRST ORDER DIFFRACTION BEAM INTENSITIES AFTER 10 MINUTE EXPOSURES TO OXYGEN AT THE PRESSURES SHOWN.

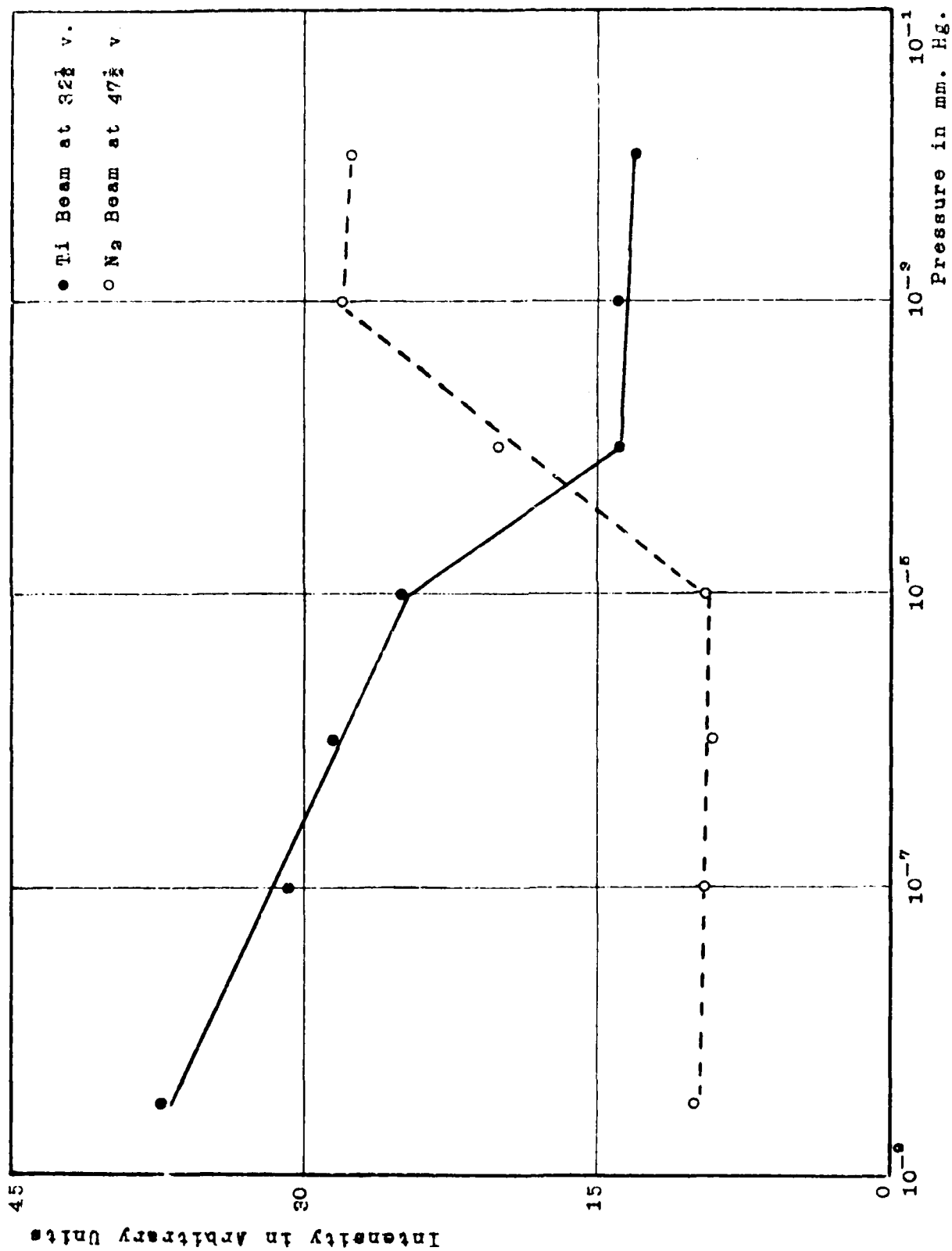


FIGURE 15, (1120) AZIMUTH, CHANGE IN FIRST ORDER DIFFRACTION BEAM INTENSITIES AFTER TEN MINUTE EXPOSURES TO NITROGEN AT THE PRESSURES SHOWN.

due to the superposition of diffracted waves from the exposed titanium surface and from the gas layer. These effects are not readily separated. Consequently, it is not possible to determine the partial coverage with much accuracy. It should be noted that this is an exceptional case. Usually the gas structure is not identical with the surface structure of the adsorbent. When this is so, diffraction beams occur which are due entirely to the gas structure and, therefore, the square roots of their intensities vary directly with the surface coverage.

In view of the difficulty described above the analysis of the results shown in Figures 14 and 15 must be severely curtailed. It is possible to estimate the average sticking probability. Figure 14 indicates that the diffraction pattern obtained following a ten minute exposure to oxygen at a pressure of 3×10^{-8} mm.Hg. is typical of the cleaned surface. The diffraction pattern obtained following a ten minute exposure to oxygen at a pressure of 10^{-7} mm. Hg. is the strongest one obtained from the oxygen layer. In the discussion of adsorption it was indicated in equation (1) that the total number of molecules striking the surface is proportional to the integral of the pressure over the time of exposure. Thus the data imply that the fraction of the cleaned surface exposed, $1-\theta$, falls to $1/e$ of its initial value for some value of Pt between 3×10^{-7} and 10^{-6} mm.Hg. - min. Consideration of the results for nitrogen adsorption shows that $1-\theta$ falls to $1/e$ of its initial value for some value of Pt between 10^{-4} and 10^{-2} mm.Hg. - min.

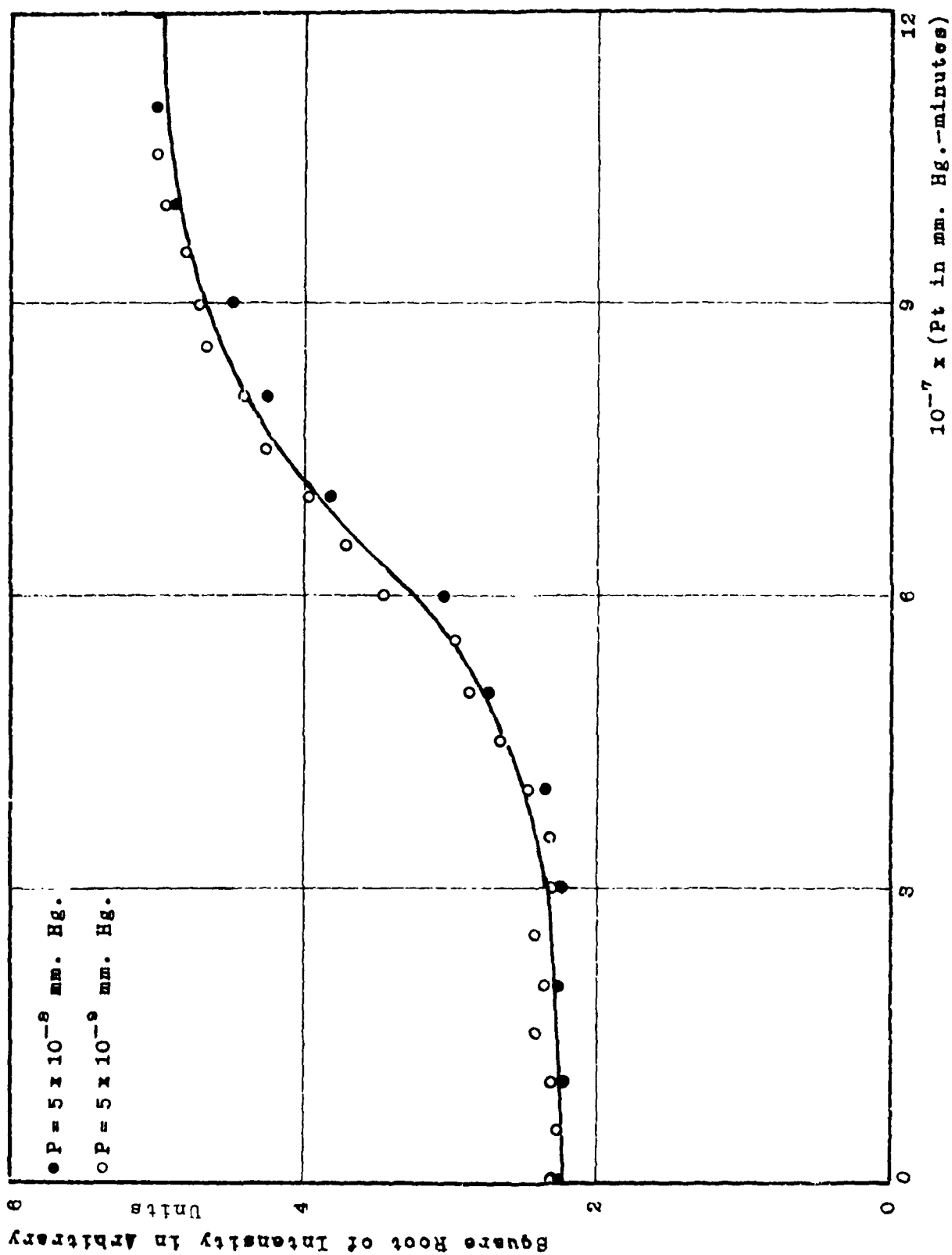


FIGURE 16. SURFACE COVERAGE AS A FUNCTION OF THE TOTAL NUMBER OF GAS ATOMS WHICH HAVE STRUCK THE SURFACE.

Langmuir's assumption may be used to relate the results to the sticking probabilities. As the measurements were made at room temperature it will be assumed that the rate of desorption is negligible. Therefore, if M is the number of sites/cm², the rate of adsorption of gas atoms is $M \frac{d\theta}{dt}$. From the discussion of Langmuir's theory, it follows that

$$(45) \quad M \frac{d\theta}{dt} = \alpha N' (1-\theta),$$

where N' is defined by equation (1). Generally, α is a function of θ . If the average sticking probability $\bar{\alpha}$ is used, integrating and applying the initial condition $\theta = 0$ when $t = 0$ yields

$$(46) \quad \theta = 1 - e^{-\bar{\alpha} N' t / M}.$$

Therefore, the fraction of the cleaned surface exposed falls to $1/e$ of its initial value when $\bar{\alpha} N' t / M = 1$. From these arguments the average sticking probability for oxygen is found to lie between 3.1×10^{-2} and 10^{-1} . The average sticking probability for nitrogen is found to lie between 2.8×10^{-6} and 2.8×10^{-4} .

Both of these results, particularly the last, are substantially smaller than the sticking coefficient for nitrogen on tungsten observed by Becker¹⁸. This is consistent with the fact that this adsorption requires an activation energy.

One additional set of observations has been made on the adsorption of oxygen. This confirms the assumption that the rate of desorption is negligible at room temperature. These measurements consisted of exposing the cleaned surface to the same low pressure of oxygen many times and observing the intensity of the 52.5 volt

gas beam from the $[11\bar{2}0]$ azimuth after each exposure. Figure 16 shows the results of this experiment. The square root of the diffraction beam intensity is plotted as a function of the product of the gas pressure and the total time of exposure. The solid circles represent points obtained by this method for oxygen at a pressure of 5×10^{-8} mm.Hg. The open circles represent the experimental points obtained when a pressure of 5×10^{-8} mm.Hg. of oxygen was used. From the figure it is seen that the surface layer is completely formed for either pressure. Therefore, the rate of desorption is negligible at these pressures.

In considering Figure 16 it is worth noting that from this type of measurement the sticking probability as a function of θ is readily computed when suitable diffraction beams are available. Specifically, the square root of the intensity of a gas beam which is not superimposed on a titanium beam is directly proportional to the surface coverage. Therefore, data for the variation of the square root of intensity for such a beam plotted as in Figure 16 would represent θ as a function of Pt. From such a curve the quantities θ , $1-\theta$, and $\frac{d\theta}{dt}$ could be determined as functions of Pt. These results could be substituted in equation (45) to determine α as a function of θ .

SUMMARY

The ion bombardment and annealing technique removed contaminations from the surface which prolonged heat treatment in an excel-

lent vacuum failed to effect. The resulting cleaned surface has the titanium structure and lattice constants within the error of measurement. Studies of the adsorption of oxygen and nitrogen on this surface showed that they form structures typical of titanium monoxide and titanium nitride. Also, while there is evidence that chemisorption can take place on a previously adsorbed layer, this evidence suggests that the succeeding layers lack definite structure. These results are strongly indicative that the cleaned surface is actually an uncontaminated titanium surface.

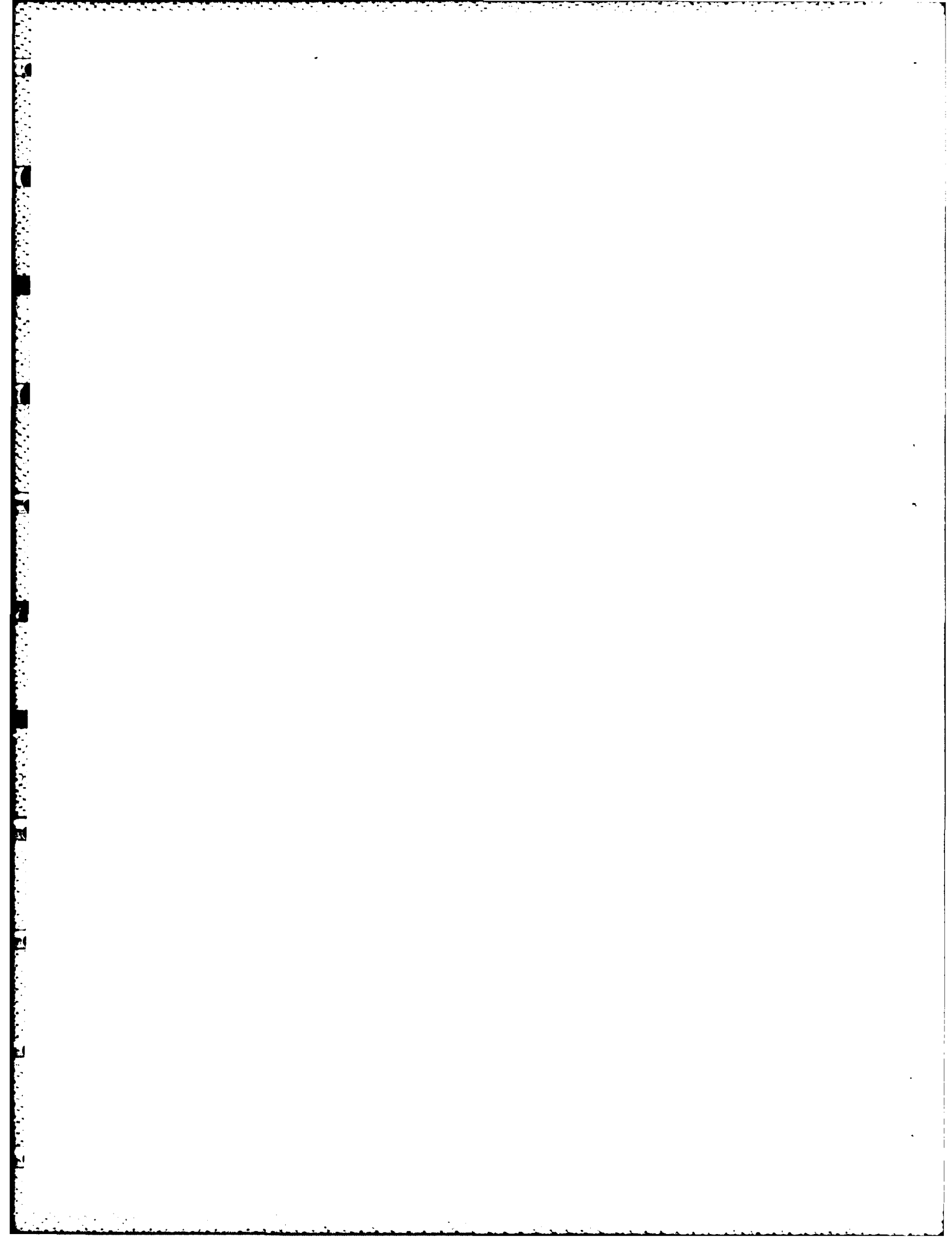
The low sticking probabilities observed in these experiments, $8.1 \times 10^{-2} < \bar{\alpha} < 10^{-1}$ for oxygen and $2.8 \times 10^{-6} < \bar{\alpha} < 2.8 \times 10^{-4}$ for nitrogen suggest that an activation energy is needed for the gas adsorption. This was substantiated by measurements made at higher temperatures. A further result of the adsorption studies was the observation that the equilibrium coverage at pressures as low as 5×10^{-9} mm.Hg. is complete surface coverage. This implies that the rate of desorption is very low at room temperatures, and, therefore, that the bonding forces are very strong, probably chemical in nature. This result justifies the attempts to keep the residual gas pressure as low as possible.

The complex surface structure observed in the earlier work has not been completely recovered or explained. It seems most probable that it was due to impurities in the crystal.

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PART 2
STRUCTURE OF EPITAXED COPPER DEPOSITED BY EVAPORATION
ONTO THE (00•1) FACE OF A TITANIUM SINGLE CRYSTAL

INTRODUCTION

Epitaxy is most often studied by examining the growth from solution of one material upon a crystalline substrate of a different material, using light microscopy¹. More recently, the techniques used have included growth from the vapor phase and high energy electron diffraction. Both of these methods are limited. The optical methods require visible overgrowths; high energy electron diffraction generally requires overgrowths at least several atomic layers thick. Thus there is little direct experimental evidence concerning the nature of the first few atomic layers of the overgrowth and the relationship of these layers to the substrate.

Low-energy electron diffraction, on the other hand, is quite sensitive to even one mono-layer of adsorbed gas. Farnsworth² reported that at least 50 percent of the diffracted electrons arise from the first atomic layer of silver, for electron energies of less than 300 ev. The low-energy diffraction technique should therefore be very useful when investigating very thin epitaxed layers.

It has been reported by Uhlig³ that the addition of copper ions to solutions attacking titanium has an inhibiting affect on the corrosion rate. One suggestion is that the copper forms a monolayer upon the surface, which has the effect of passivating the surface. This part of the experiment was intended to determine the structure of such a monolayer.

APPARATUS

EXPERIMENTAL TUBE

The apparatus is quite similar to that used in the experiments on the adsorption of gases by titanium. The only major difference is the inclusion of a source of copper vapor. Therefore only a brief description of the apparatus is given here.

Figure 1 is a schematic of the experimental tube, which consists of an electron gun, a crystal mounting, a movable Faraday collector, and a source of copper vapor. Provision is made for the cleaning of the crystal surface by positive ion bombardment⁴, and for the outgassing of the crystal by electron bombardment.

(2)

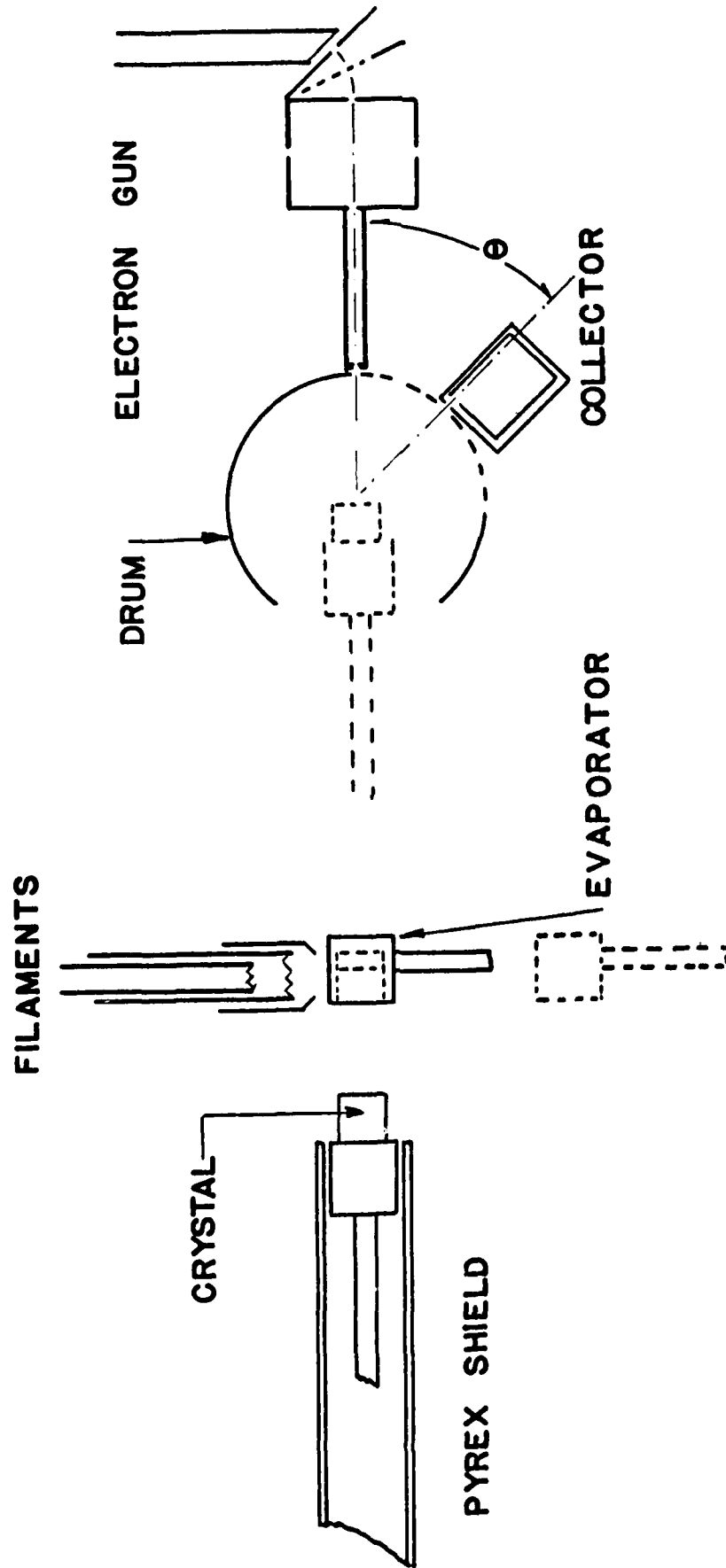


Fig. 1. Experimental Tube

(3)

The dotted outlines on the figure show the positions of the crystal and the evaporator when the diffraction data are obtained. An essentially mono-energetic beam of electrons is incident normally on the (00·1) face of a titanium single crystal. Rotation of the crystal and collector permits detection of electrons scattered into nearly the entire forward hemisphere about the crystal. The circuitry allows variation of the incident beam energy from 10 to 250 electron volts, and limits the collected electrons to those which have lost less than 3 ev energy. The crystal can be rotated or translated by means of an external magnet; the collector is rotated in one-half degree steps with a solenoid actuated escapement mechanism.

The crystal is clamped on a molybdenum cylinder. The cylinder can be placed directly under the filaments, and heated by electron bombardment, using the lower of the two filaments as an electron source. The solid outlines on the figure show the positions of the crystal and evaporator when a deposit is being made. In this case the evaporator is heated by electron bombardment.

In order to clean the crystal surface by positive ion bombardment, the crystal is placed in the position shown by the solid outline; the evaporator is placed in the position shown by the dotted outline. The upper of the two filaments is used as a source of ionizing electrons, and the lower is used as a grid. The ions formed in the region in front of the crystal are attracted to the crystal by the application of a negative potential to the crystal. Ion currents of about 100 micro-amperes can be obtained with this arrangement, using a tube pressure of about 5×10^{-3} mm. Hg. of argon.

The vacuum system consists of two single stage mercury diffusion pumps in series, separated from the experimental tube by a dry ice and a liquid nitrogen cooled trap. The dry ice cooled trap is constructed so that mercury is returned to the pump when the trap is warmed. This arrangement prevents mercury from choking the liquid nitrogen cooled trap. A porcelain tube leak is used to control the argon (or other gas) pressure in the tube. The leak is separated from the tube by a liquid nitrogen cooled trap. Mercury cut-offs placed between the diffusion pumps allow the use of the higher pressure stage pump to evacuate the gas inlet system. The tube, after sealing it to the vacuum system, is evacuated and baked out for several hours at 350°C. After the bake-out, a molybdenum filament in a side tube is heated until a visible film forms on the sides of the tube. The film acts as a getter, reducing the pressure in the tube below that which can

(4)

be obtained with the pumps alone. After several flashings of the filament, a vacuum of between 5×10^{-10} and 10^{-9} mm. Hg. can be attained, and maintained for several weeks without further flashing of the getter. The results of adsorption studies on the titanium⁵ indicate that the pressure of active gases in the tube is below 10^{-10} mm. Hg.

EVAPORATION SOURCE

The evaporator consists of a molybdenum cup into which a piece of pure copper has been previously vacuum melted. The cup is mounted on a carriage with the open end facing the crystal. The carriage is mounted in a side tube so that the evaporator can be placed in front of the crystal or withdrawn into the tube. A movable shield between the cup and the crystal allows the time of deposit to be controlled.

The evaporator was calibrated in an auxiliary vacuum system by weighing the amount of copper which passed through a hole 14 mm. in front of the cup. This distance was that used in the experimental tube. The weighing was done with a quartz beam vacuum microbalance⁶, of sensitivity $(1.40 \pm .04) \times 10^{-4}$ gm./mm., as determined from the period and moment of inertia of the balance. One millimeter deflection of the balance corresponded to a deposit density of $(6.67 \pm .20) \times 10^{18}$ atoms/cm². The calibration data were obtained in the form of balance deflections, time of deposit, and evaporator temperature. These data were plotted as the logarithm (base 10) of the deflection per minute versus the inverse of the temperature in degrees Kelvin. A straight line passing through or near the points was determined by the method of least squares. Each point was weighted by the amount of the deposit. The result of the calibration was that the rate of deposit followed the equation

$$\log_{10} R = 34.33 - 2.20 \times 10^4 / T^\circ \text{K.} \pm 0.085,$$

where R is the rate of deposit in atoms/cm.²/min.

A thermocouple was originally placed in the cup to determine the temperature of the evaporator. It was found that the thermocouple readings, as a consequence of the design of the apparatus, were consistently low. Therefore it was necessary to obtain temperatures by means of an optical pyrometer. The same pyrometer and corrections were used in both the calibration and the experiment, so that, although the absolute temperature of the evaporator is probably in error, the error in the deposit rate is not felt to be more than that caused by a five degree error in temperature. At the evaporator temperature used in the experiment, the deposit rate was

(5)

$$R = (1.58^{+0.5}_{-0.4}) \times 10^{15} \text{ atoms/cm.}^2/\text{min.},$$

with a consistency of 20 percent for different deposits.

The above-mentioned possible error in the evaporator temperature may account for the fact that the latent heat of evaporation of copper, as calculated from the observed deposit rate, is 100,000 cal./mole, a value considerably greater than the 72,810 cal./mole given by Dushman⁷.

CRYSTAL PREPARATION

The titanium single crystal used in the experiment was prepared from iodide titanium, by Prof Nielson of New York University, using the strain-anneal method. The crystal was received in the form of a cylindrical bar 6 mm. in diameter. The bar was oriented by the laue back-reflection X-ray method, and cut, using a thin composition grinding wheel, so that the (00·1) face of the crystal was exposed. The crystal was then polished on 4/0 emery paper, lapped with Fisher Alumina and Fisher Gamal, and etched with a solution of 60 percent glycerine-50 percent hydrofluoric acid. This treatment did not give a smooth surface under the microscope, but rather one containing a large number of triangular etch pits, the bottoms of which appeared to be smooth and parallel to the (00·1) face. The crystal was then washed thoroughly with distilled water, and clamped to the molybdenum mounting cylinder.

OUTGASSING AND SURFACE CLEANING

Diffraction patterns were observed after outgassing the crystal at temperatures above 500°C. The patterns were not indicative of the titanium lattice constant, however. Further outgassing at temperatures up to 750°C. strengthened the diffraction beams, but did not produce the patterns that were expected from the titanium crystal. Higher temperature heating could not be used, since titanium undergoes a phase transition at a temperature of about 850°C. It was felt that the titanium crystal surface, after outgassing, was covered with a contamination of some complex, as yet undetermined structure. Accordingly, it was decided to attempt to clean the surface by positive ion bombardment⁴. It was found that ion bombardment definitely removed the surface layers, but resulted in a disturbed surface, since the diffraction patterns after the bombardment were weak, although indicative of the expected titanium spacing. Annealing the crystal by heating for several

minutes at 500°C. greatly strengthened the beams, and confirmed the result that the surface spacing of the crystal was that of titanium. The surface obtained after this treatment was found to be partially covered with oxygen. After more thorough outgassing followed by ion bombardment and annealing, the overall diffraction patterns indicated a clean surface, which reverted to the oxygen covered surface after a period of from several hours to several days, depending on the thoroughness of the outgassing and the residual gas pressure. It appears that several hundred hours of outgassing and a residual gas pressure of less than 10^{-9} mm. Hg. are necessary to obtain and maintain a clean surface (as indicated by the diffraction patterns). It is also necessary that the argon be as free of active gases as possible. In the present experiment, the argon used was obtained from Linde Air Products, and is spectroscopically pure. In any case, it was found that exposure of the crystal to argon at the pressures used during ion bombardment caused no change in the diffraction patterns, indicating that there was little or no danger of contamination of the crystal by the argon. After lengthy outgassing followed by ion bombardment and annealing, the titanium crystal remained detectably gas free for at least two days.

RESULTS AND DISCUSSION

After ion bombardment and annealing, the surface was examined by electron diffraction to make certain that it had been sufficiently cleaned. The crystal was then placed in position to receive the deposit, copper was deposited, and the diffraction patterns were again observed. The cleaning, deposition, and examination were carried out in a time which was as short as possible in order to minimize effects of residual gas adsorption. After the copper covered surface was examined, the crystal was again ion bombarded to remove the copper, and heated for several hours. Before another deposit, the crystal was again ion bombarded and annealed. The diffraction data indicated that very little if any copper remained on the crystal surface after this procedure.

Figure 2 is a plot of the positions of the diffraction beams caused by a copper deposit of $(3.0 \pm 0.3) \times 10^{16}$ atoms/cm.². These beams lie in the (11·0) and (10·0) titanium azimuths; that is, the planes of the incident and diffracted beams are (11·0) and (10·0) planes, respectively. The sine of the colatitude angle is plotted against the wave length of the electron beam. The circles represent experimental points. Diffraction beams are also present due to the titanium substrate. These beams are not shown, but lie on or close to the dotted lines in the figure.

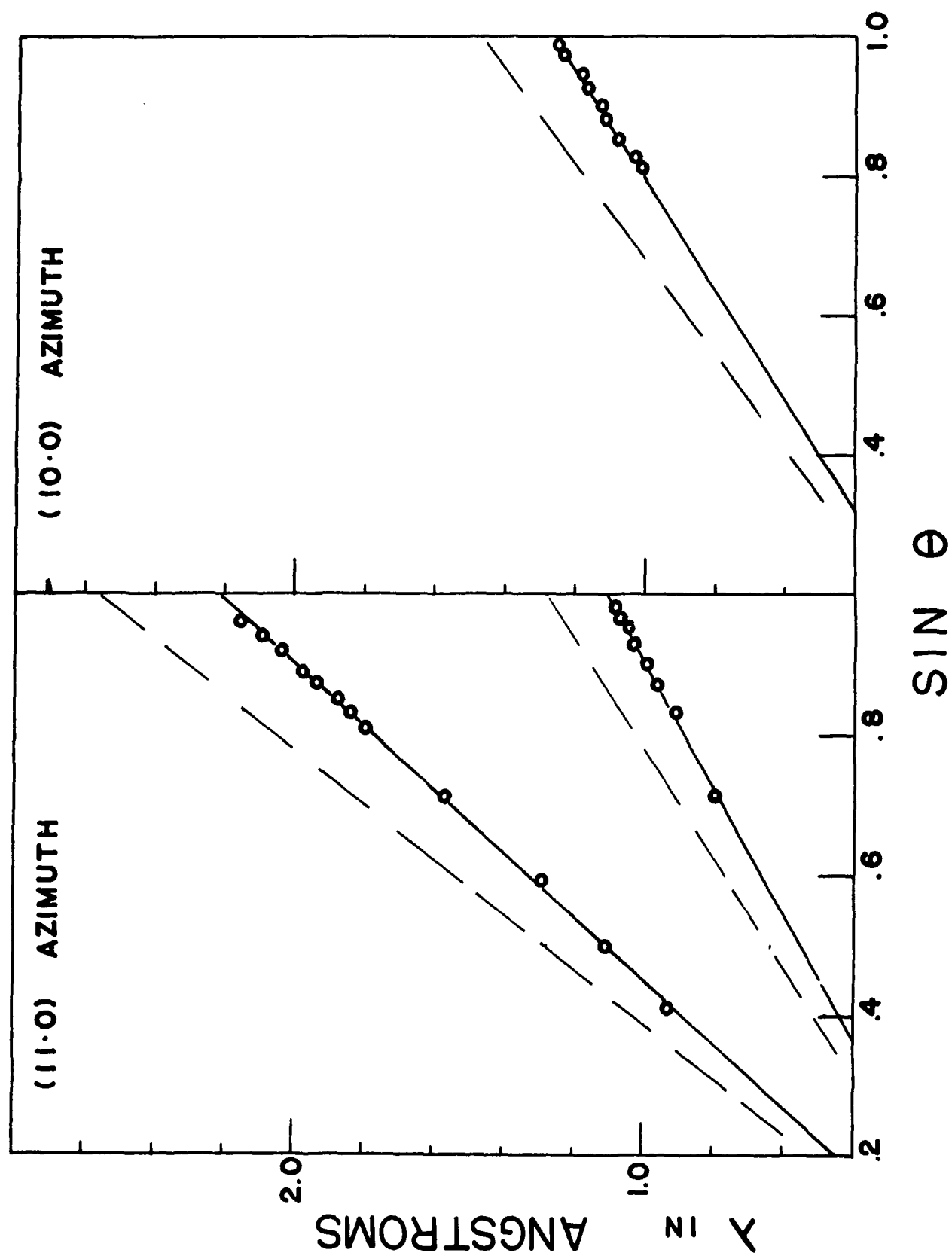


Fig. 2. Positions and Wave Lengths of Diffraction Maxima after Deposition of Copper

(3)

One of the consequences of the low penetration of low-energy electrons is that, if the surface atoms of the crystal lie in planes perpendicular to the incident beam, the angular positions of the diffracted maxima should satisfy the simple grating equation,

$$N \lambda = a \sin \theta,$$

where N is the order of the diffracted beam, λ is the wave length, a is the separation of rows of atoms in the azimuth being considered, and θ is the angle between the incident and diffracted beam (the colatitude angle). Thus a plot of $\sin \theta$ versus λ should be a straight line passing through the origin, and with the intercept equal to the separation of rows of surface atoms, at $\sin \theta$ equal to unity.

The solid lines on figure 2 are calculated from the lattice constant of bulk copper for an orientation of the deposit such that (111) copper planes are parallel to (00.1) titanium planes, and (110) copper planes are parallel to (11.0) titanium planes. The fact that the experimental points follow these straight lines indicates that the surface of the deposit is predominantly parallel to the substrate, and that the hexagonal lattice constant of the copper, in directions parallel to the surface, is that of bulk copper. On the basis of the observed orientation, the average thickness of the deposit shown here is 17 ± 5 atomic layers.

Figure 3 shows some representative diffraction beams for various thicknesses of deposit. Collector current is plotted against colatitude angle. The beams shown are in the (11.0) titanium azimuth. The voltage of the beam is such as to give a maximum diffracted current associated with the copper lattice. The peak at the left, for each thickness of deposit, is that due to the titanium substrate; the peak at the right is produced by the deposit. In each case where a definite copper peak is seen, the hexagonal lattice spacing corresponding to the angular position of the peak is 2.55 ± 0.01 A., which is the hexagonal spacing found in bulk copper. In the one-half layer deposit, no peak is observed, but the shoulder also corresponds, with somewhat greater error, to the above spacing. Thus, no transition spacing between the copper and the titanium has been found in the directions parallel to the substrate surface, although the mismatch between the copper and titanium is -13 percent. The deposits made were between one-half to 25 atomic layers in thickness, assuming a uniform distribution.

The diffraction maxima corresponding to the titanium lattice spacing are decreased in intensity by the addition of the deposit, but the maxima are not shifted in either

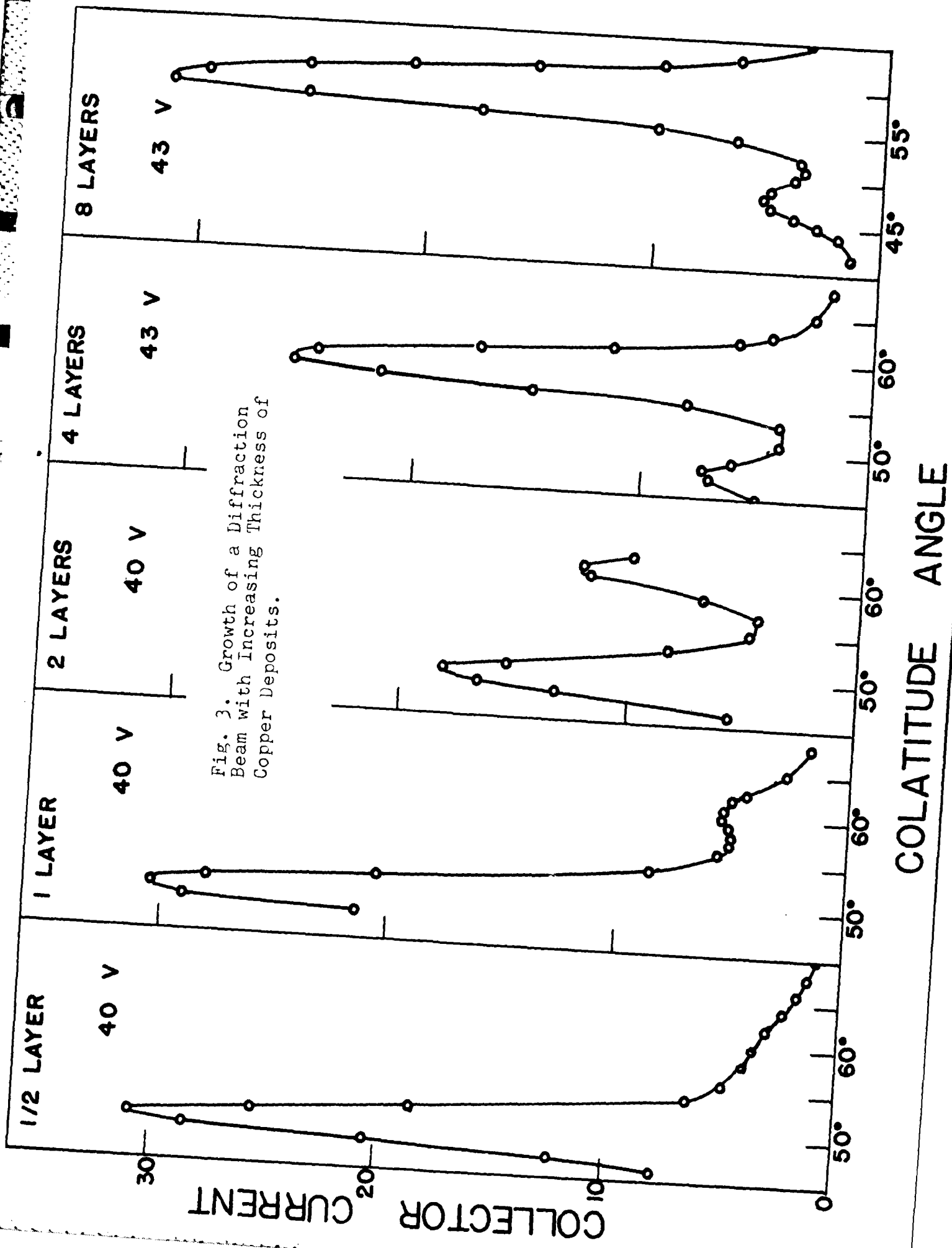


Fig. 3. Growth of a Diffraction Beam with Increasing Thickness of Copper Deposits.

angle or wavelength. This indicates that no true monolayer of copper has been formed on the substrate. If a true monolayer were formed, even if strained to fit the surface lattice spacing of titanium, it would be expected that the wavelength of the diffraction maxima would be altered, by either a change in the surface potential barrier and/or a change in the separation of the surface plane of atoms from the plane immediately below.

A uniformly distributed deposit should cause an exponential decrease in the intensities of the diffraction beams from the titanium substrate as the thickness of the deposit is increased. The observed decrease is more nearly inversely proportional to the thickness of the deposit. This behavior can be qualitatively explained on the assumption that the deposit is composed of oriented crystallites, with relatively uncovered areas of titanium between the crystallites.

Annealing the deposit at temperatures of about 350°C. causes a large decrease in intensity of the diffraction beams corresponding to the copper lattice, without greatly changing the titanium beams. This indicates that the orientation of the deposit is reduced by the annealing without removing the deposit. This disorientation with annealing is more apparent for the thicker deposits. The experimental method is not capable of determining whether or not the above decrease in the beams from the copper deposit is to be associated with a loss of crystal structure in the crystallites, or a disorientation of the crystallites with respect to the titanium substrate.

During the time of deposit, the crystal was exposed to radiation from the evaporator. The temperature of the crystal during the deposit is not known, but an upper limit can be estimated, and is found to be approximately 100°C. at equilibrium. Most of the deposits were made in a time too short for equilibrium to be established, and the highest temperature was probably much less than 100°C. Thus the temperature of the crystal during the time of deposit was considerably below the temperature at which the deposit becomes disoriented.

After making some of the deposits, the crystal was exposed to a controlled oxygen atmosphere, at pressures below 10^{-7} mm. Hg. The effect of the adsorption on the diffraction beams from the titanium substrate is the same as the effect on the beams from a clean surface⁴. Thus the copper deposit has little effect on the adsorption of oxygen by titanium. This behavior is a confirmation of the conclusion that the deposit consists of oriented crystallites, with incomplete coverage of the titanium surface. The deposit appears to mask only the regions of the crystal that are covered by the copper crystallites.

The effect of the copper deposit on the diffraction beams is not precisely reproducible. That is, the intensities of the beams is not reproduced, although the angular positions are. Examination of the data on the beams from the copper and titanium indicate that the irreproducibility is not caused by errors in the amount of the deposit, but is rather a result of disorientations in the deposit. Part of this effect is caused by the state of the surface when the deposit is made. A cleaner surface generally results in a more oriented deposit. Deposits on a deliberately gas covered surface were not carried out, however, so the question of whether or not any oriented overgrowth of copper would have been observed on a completely gas covered surface cannot be answered.

Finally, it should be stated that no information can be given on the separation of the atoms of the deposit in the direction perpendicular to the surface. The inner potential of the crystal causes a displacement in wave length of the diffraction maxima. The low penetration of the electrons causes this effect to be complex, so that it is not possible to readily separate the effect of the inner potential from the displacement caused by changes in the lattice dimensions in a direction perpendicular to the surface. The inner potential, however, does not affect the determination of lattice dimensions in directions parallel to the surface.

CONCLUSION

The results indicate that the deposited copper is in the form of oriented crystallites, with a lattice spacing in the directions parallel to the substrate equal to the lattice spacing in the (111) plane of bulk copper. Little or no variation in the lattice spacing has been observed for all thicknesses investigated. These results do not support a monolayer hypothesis, such as that of Van der Merwe⁸, but are in agreement with a nucleation hypothesis¹; in which the substrate tends to orient nuclei of the deposited material. As the nuclei grow, the role of the substrate is relegated to that of a mechanical support. It would be expected that the forces attaching the nuclei to the substrate would not be large; this is born out by the disorienting caused by annealing.

It should be mentioned that the type of overgrowth observed may well be dependant on the method used. In the present case, there was a great difference between the temperature of the evaporator and the temperature of the crystal. The results might be considerably different if the deposit was grown from the vapor phase by a more nearly equilibrium process, or grown from solution.

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PART 3 SECONDARY ELECTRON EMISSION FROM THE TITANIUM CRYSTAL, AND FROM THE COPPER-COVERED TITANIUM CRYSTAL.

With no change in the tube parts and only minor changes in the electrical circuits, the electron diffraction apparatus can be used to measure total secondary electron emission yields from the titanium single crystal. The method is to measure the total incident electron current, as a function of electron energy, by measuring the total current to the drum and crystal. The current to the drum alone is the secondary electron current. Thus the ratio of the drum current to the combined drum and crystal current is the secondary electron yield per unit primary current.

Secondary emission ratios were observed after various surface treatments of the crystal. These ratios, or yields, are plotted in Fig. 1 as a function of the energy of the primary electron beam. The zeros of the several curves have been displaced along the vertical axis by varying amounts to minimize overlapping at the low-energy end of the curves. Circles and crosses denote experimental points.

The curve labeled "OUTGASSED" was obtained after heating the crystal at 750° C. for 16 hours. The electron diffraction data indicate that the crystal surface was somewhat contaminated. Since the crystal had been previously cleaned by positive ion bombardment many times, the degree of contamination was not as great as that on a crystal which had been outgassed but not ion bombarded.^{1,2} The maximum yield for the outgassed crystal was found to be 0.74 at 200 ev. primary energy.

The curve labeled "POS. ION BOMB." was obtained after bombarding the crystal with positive argon ions for five minutes, using a current of 100 micro-amperes and an ion energy of 500 ev. (assuming singly ionized argon ions). The surface so obtained is presumably free of the stable layer of contaminant, but is disturbed enough to greatly broaden and weaken the electron diffraction beams. It is also likely that some argon has been driven into the surface by the ion bombardment.³ The maximum yield for the ion bombarded crystal was found to be 0.70 for primary energies in the range of 160 to 220 ev.

The curve labeled "CLEAN" was obtained after annealing the ion bombarded crystal at a temperature of 500°C. for 10 minutes. The annealing removes any argon which has been driven into the crystal, and also the defects in the disturbed surface lattice³. The maximum yield for the clean surface was found to be 0.73 at primary energies from 180 to 200 ev.

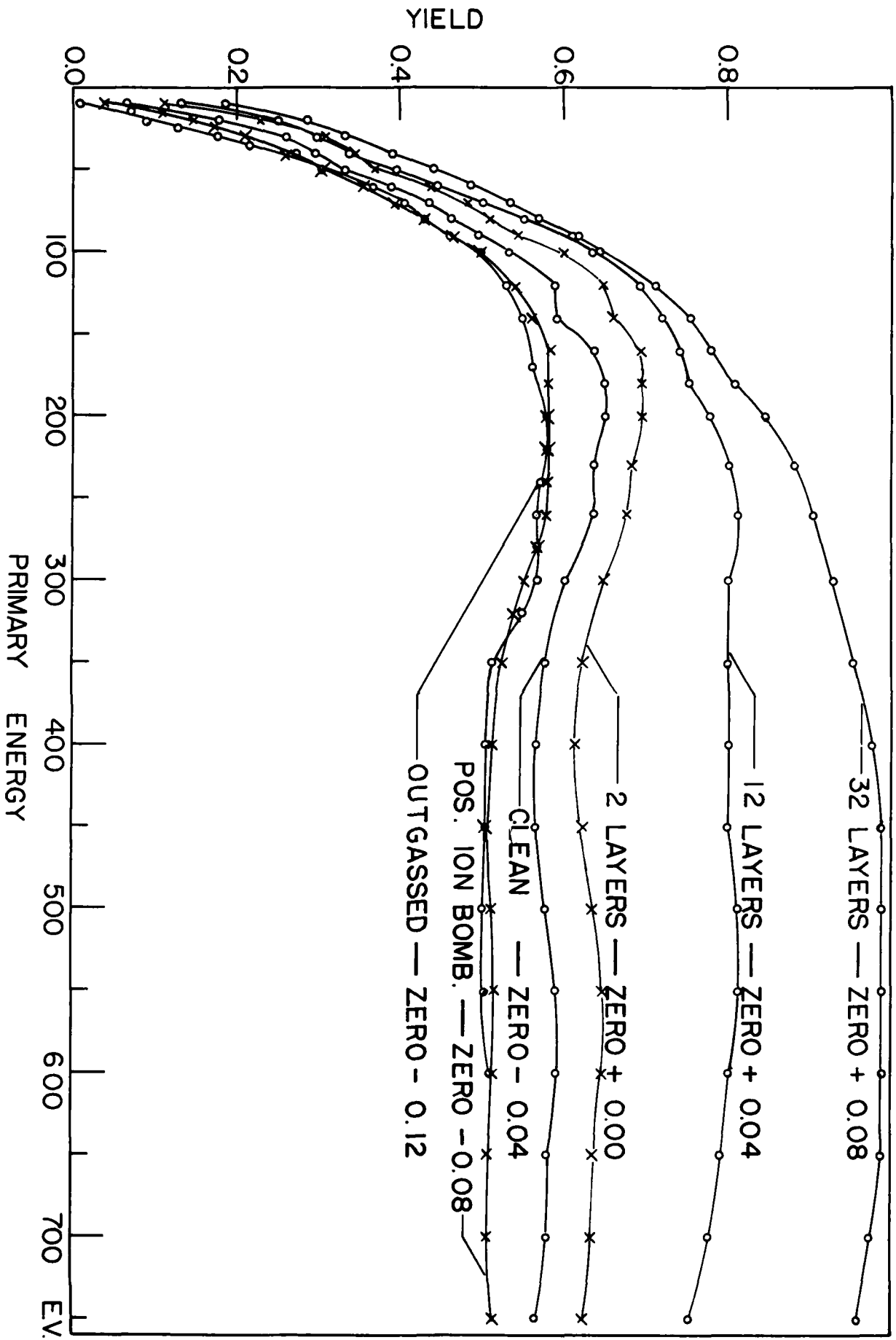


Fig. 1. Secondary Electron Emissions Ratios vs. Primary Electron Energy

The remaining curves were taken after making deposits of copper on the titanium surface. In addition to the thicknesses as shown, two others were used, --22 and 42 atomic layers. The yields for these deposits are not shown in Fig. 1. The thickness of the deposit was calculated from the orientation of the copper on titanium found by low-energy electron diffraction, and reported in detail in Part 2 of this report. The thicknesses given are average values, assuming a uniform deposit. Actually, the deposit is not uniform, but is composed of oriented crystallites. The titanium surface is not completely covered by the deposit, except for very thick deposits. The maximum yields for the copper covered surface were found to be 0.735 at 160 to 200 ev. (2 layers), 0.82 at 260 ev. and 0.82 at 500 to 550 ev. (12 layers), 0.88 at 500 to 550 ev. (22 layers), 0.91 at 450 to 650 electron volts, and 0.95 at 550 ev. (42 layers). This may be compared with the yield of 1.26 at 600 ev. reported for bulk copper.⁴ The discrepancy is accounted for by considering that the secondaries have a maximum depth of origin much greater than 42 atomic layers within the crystal for primary energies as high as 500 ev.

Figure 2 is a plot of yield versus thickness of the deposit for various primary electron energies. The experimental points at A and B are for the outgassed and ion bombarded crystals (without annealing), respectively. Straight lines connecting the experimental points are drawn for identification of points belonging to the different primary energies. The yield at 500 ev. is still increasing after a deposit of 42 layers, whereas the yields at 10 and 20 ev. tend to be constant after the deposit of 32 layers. The maximum depth of origin of the secondaries is therefore probably less than 32 atomic layers, for a primary energy of 10 and 20 ev. and greater than 42 layers for a primary energy of 500 ev. These conclusions do not apply to the depth of origin of secondary electrons in bulk copper, since the copper deposit is non-uniform.⁵

The electron diffraction data in Part 2 and the secondary electron emission data in Part 3 are not contradictory, but may not be mutually substantiating. This is because the electron diffraction data are obtained by using only elastically reflected (or full energy) electrons, while the secondary emission data include all of the reflected and emitted electrons. The electron diffraction data are useful in connection with the secondary electron emission experiments because they furnish information on the surface conditions of the crystal being investigated.

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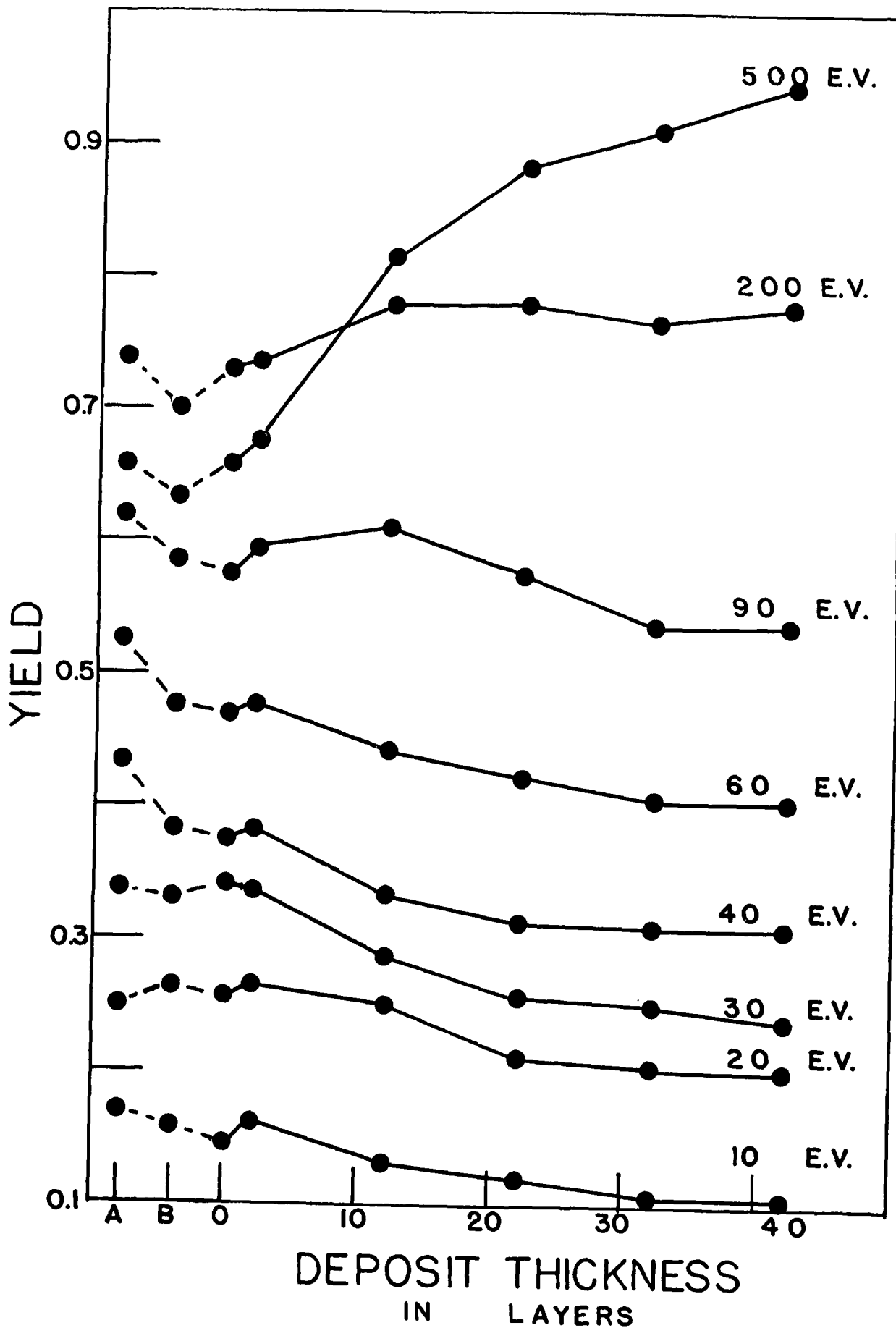


Fig. 2. Secondary Electron Emission Ratios vs. Surface Treatment

PART 4

Ion Bombardment-Cleaning of Germanium* and Titanium† as Determined by Low-Energy Electron Diffraction

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IN the process of carrying out adsorption experiments using germanium and titanium crystals by means of low-energy electron diffraction experiments, it has, of course, been necessary to obtain clean surfaces in high vacuum. After many attempts it became apparent, with both of these crystals, that the usual method of outgassing at elevated temperatures for long periods of time was not sufficient to produce clean surfaces which contain considerably less than one monolayer of gas, as in the case for many metals.

With the titanium crystal, a complicated, hexagonal, single crystalline surface structure was observed after heating at 700° to 750°C for many hours which was oriented on the (0001) hexagonal titanium face. In an attempt to remove this structure, the crystal surface was bombarded by argon ions in a low pressure discharge. After bombardment of a few minutes the diffraction pattern was nearly obliterated. Subsequently, a short annealing of a few minutes at 500°C resulted in a new diffraction pattern whose surface spacing was the same as that of titanium.¹ Later experiments showed that this is probably a titanium surface which can be maintained for a few hours at sufficiently low pressures. It was further established, by means of the low-energy electron diffraction technique,² that the new surface was etched parallel to the (0001) plane, i.e., the one which was parallel to the geometrical boundary, and the same as that which was present originally. This, of course, is one of the most significant aspects of this method of cleaning, where one wishes to expose a desired set of crystal facets. However, it should be emphasized that these results are dependent on the discharge conditions. One is not justified in assuming that the same discharge conditions will produce equally desirable results with surfaces parallel to other crystal planes, until tests have been made by the low-energy electron diffraction method. The annealing conditions are also critical and depend on the mass of the crystal and its mounting.

It was observed in the above experiments that during the short annealing subsequent to bombardment, the residual pressure in the tube was increased to a considerably higher value than that produced by a similar annealing not preceded by bombardment. This is interpreted as an indication that argon penetrates the crystal lattice during bombardment.

In order to obtain a clean surface of titanium it was necessary to precede the ion bombardment by a thorough high temperature outgassing to remove absorbed gas. When this was not done the

diffraction pattern obtained after bombardment and annealing was inferior.

In the experiments on the (001) face of a germanium crystal, it was observed that a weak diffraction pattern could be obtained after outgassing the crystal for several hours at 600° to 700°C. This diffraction pattern appeared to be characteristic of the germanium lattice. It was never possible to increase the intensities of the small number of observed beams to the point where the identification could be made with assurance. In fact, in many cases of prolonged heating near the melting point, the pattern became weaker or disappeared entirely. It was, therefore, concluded that the surface structure was not that of clean germanium but of a compound with a relatively imperfect crystal structure resembling germanium to some extent.

Subsequently, the aforementioned method of cleaning by ion bombardment and annealing was attempted for the germanium crystal. In the first attempt hydrogen ions were used instead of argon, since the experimental tube was equipped with a palladium tube. The results were negative. A gas-handling system was then installed so that argon could be admitted under controlled conditions. The results obtained after argon ion bombardment are very similar in nature to those obtained with titanium. The contaminating surface layer was removed by the ion bombardment, but the diffraction pattern was obliterated. After a subsequent short annealing at 500°C, a sharp intense diffraction pattern was observed which we believe to be characteristic of a clean germanium crystal surface. This surface can also be kept stable under best vacuum conditions for periods of several hours before adsorption effects from the residual gases become observable.

The structures of these adsorbed gases are now being investigated for both germanium and titanium with the use of gas handling systems for known gases.³

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† This part of the research was supported by Office of Ordnance Research, U. S. Army.

¹ This observation was first made with a diffraction unit operated by R. E. Schlier.

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³ We are aware of the fact that ion bombardment has been used previously to clean surfaces, but to our knowledge the method of low-energy electron diffraction has not been used to determine the condition of the surface after low-temperature annealing. For information on penetration of low-energy diffracted electrons and gas adsorption on copper and nickel crystals, see the following: H. P. Farnsworth *Phys. Rev.* **49**, 605 (1936); **35**, 1133 (1930); R. E. Schlier and H. E. Farnsworth, *J. Appl. Phys.* **25**, 1333 (1954); two papers in *Bull. Am. Phys. Soc.* **29**, 35 (1954).

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