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I hereby recommend that the thesis prepared under my supervision by Howard F. Dunholter *entitled* Part 1. THE DESIGN AND CONSTRUCTION OF AN ELECTRON DIFFRACTION APPARATUS. Part 2. ELECTRON DIFFRACTION STUDY OF COPPER OXIDES.

be accepted as fulfilling this part of the requirements for the degree of __________

Approved by:

[signature]

D. A. Wells

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Part 1

THE DESIGN AND CONSTRUCTION OF AN ELECTRON DIFFRACTION APPARATUS

A dissertation submitted to the

Graduate School

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requirements for the degree of

DOCTOR OF PHILOSOPHY

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by

Howard Frank Dunholter

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INTRODUCTION

The modern crystal structure laboratory must contain an electron diffraction apparatus in addition to the usual X-ray equipment; for it is only with the aid of electron diffraction that one can study surface and thin film structure. Due to the low penetrating power of electrons they can yield coherent diffraction effects only from the surface layers extending to a depth of the order of 20 angstroms. If one attempted to use X-rays of such low penetrating power, such a long wave length would have to be used that the equation for diffraction, $\sin\theta = n\lambda/2d$, could not be satisfied for most crystalline material. On the other hand, the great penetrating power of X-rays enables the investigator to study the crystal structure of the mass as a whole. Thus the use of both X-rays and electrons is needed in any complete study of crystal structure.

HISTORY

The theory of electron diffraction was first formulated by Louis De Broglie[1] in 1924. De Broglie, who must have studied the logic of Faraday, reasoned that if it is sometimes useful to assign particle characteristics to light waves, it might also be useful at times to assign wave characteristics to particles. In his theory of the association of guiding wave systems with moving particles, he postulated that the length of the wave associated with a particle would be given by the equation

$$\lambda = h / mv$$

where "mv" is the momentum of the particle and "h" is Planck's constant. Although Elsasser[2] then suggested that the interaction between a beam of electrons and a single crystal should afford a crucial test of the theory, it appears to have been rather the stimulus of an accidental observation which led Davisson and Germer to study the scattering of slow electrons from the surface of a single nickel crystal in March 1927 and Thomson to study the scattering of fast electrons by thin films in May 1927. The results of both experiments confirmed, however, De Broglie's theory. The next progress to be recorded was due to Kikuchi and Nishikawa[3] who transmitted electrons through thin crystals of mica and obtained spot patterns and secondary scattering phenomena (Kikuchi lines).

This was followed by a discovery by Matukawa and Thomson which may be regarded as opening up the field of surface structure research by electron diffraction. They independently discovered that polycrystaline surfaces yielded coherent electron diffraction patterns when grazed by the electron beam, a fact which was correctly interpreted by

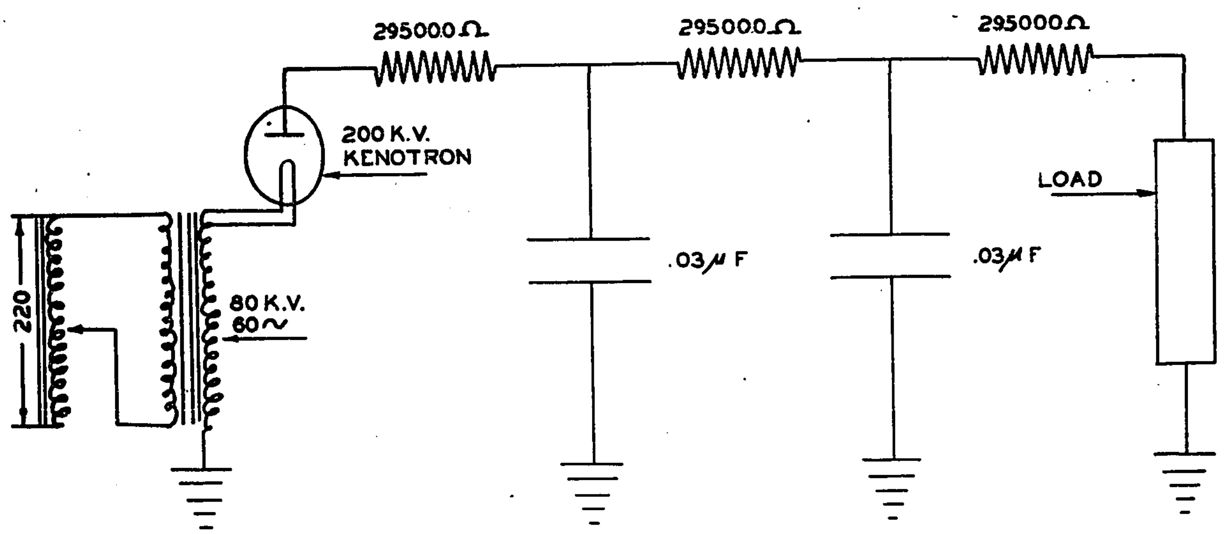
Thomson as being due in effect to transmission through crystalline projections above the mean level of the surface. Another step of historical importance was taken by Wierl[4] when he demonstrated the superiority of the electron beam over X-rays for the study of molecular structure in gases.

APPARATUS

The equipment used in the study of the structure of thin films and surfaces by the diffraction of electrons consists of the camera, in which are recorded the directions and intensities of the rays scattered on impact of a fine beam of electrons, moving at a uniform velocity, on the specimen; together with such subsidiary apparatus as is required for producing the beam and maintaining the necessary vacuum conditions.

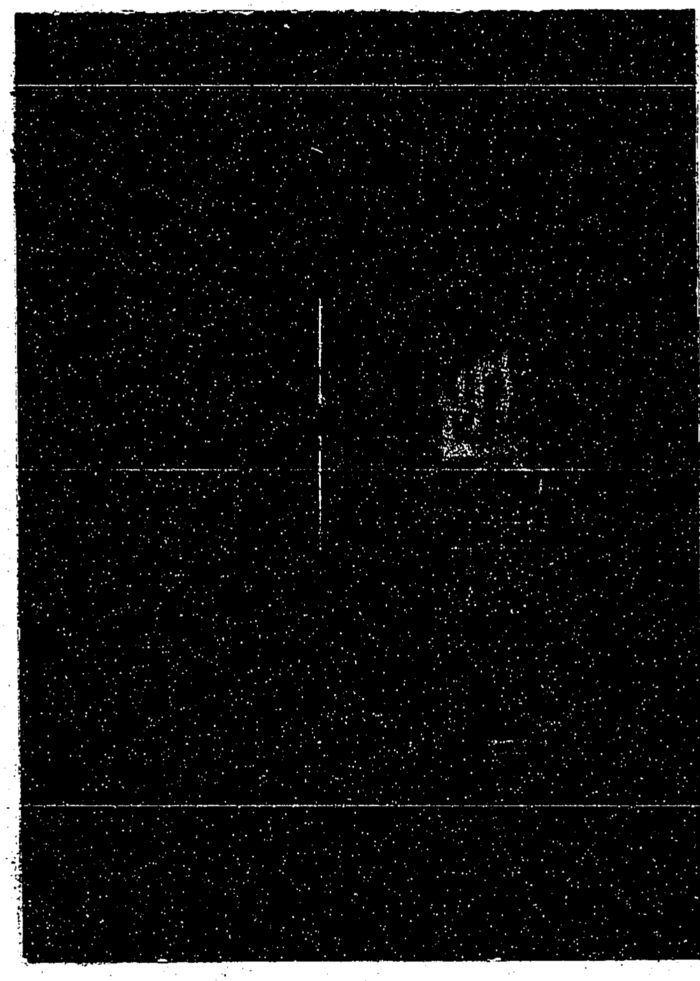
<u>Circuit</u> Since the wave associated with an electron has a length which is a function of its velocity which in turn is a function of the accelerating potential, it is necessary to have a constant potential power supply. Due to some very favorable circumstances, and Dean More's ability to find money in unsuspected places when it is needed for research, the physics department was able to obtain two large mica condensers of 0.03 micro-farads

capacity and 100 peak kilovolts each, together with an end grounded transformer for supplying 5 milliamperes at 80 kilovolts, also a filament transformer and a 200 kilovolt valve tube. These principal units were assembled into the half wave filter circuit shown on page 5. This circuit gave us about a 2000 volt ripple when operating at 80,000 volts and 5 milliamperes; such a ripple is not serious in the operation of the electron tube as will be shown later. Three 29,500 ohm resistors shown in the diagram aid in smoothing the potential ripple; they were the largest resistors which were available for our use although a greater resistance in the circuit would improve the filtering action. The valve tube is rated at 200 kilovolts, over twice the peak potential of the transformer, this is necessary because during every cycle there will be a time when the condensers will be charged to 80 kilovolts above ground potential while the transformer is at 80 kilovolts below ground potential; thus the valve tube will have 160 kilovolts across its terminals. It was found necessary to enclose this tube in a lead house because under varying load conditions X-rays were given off of such intensity as to prove dangerous to persons in its vicinity. See pictures on page 6. Copper tubing, one inch in diameter, was used to connect the various components of the electrical system in order to cut down corona losses. High

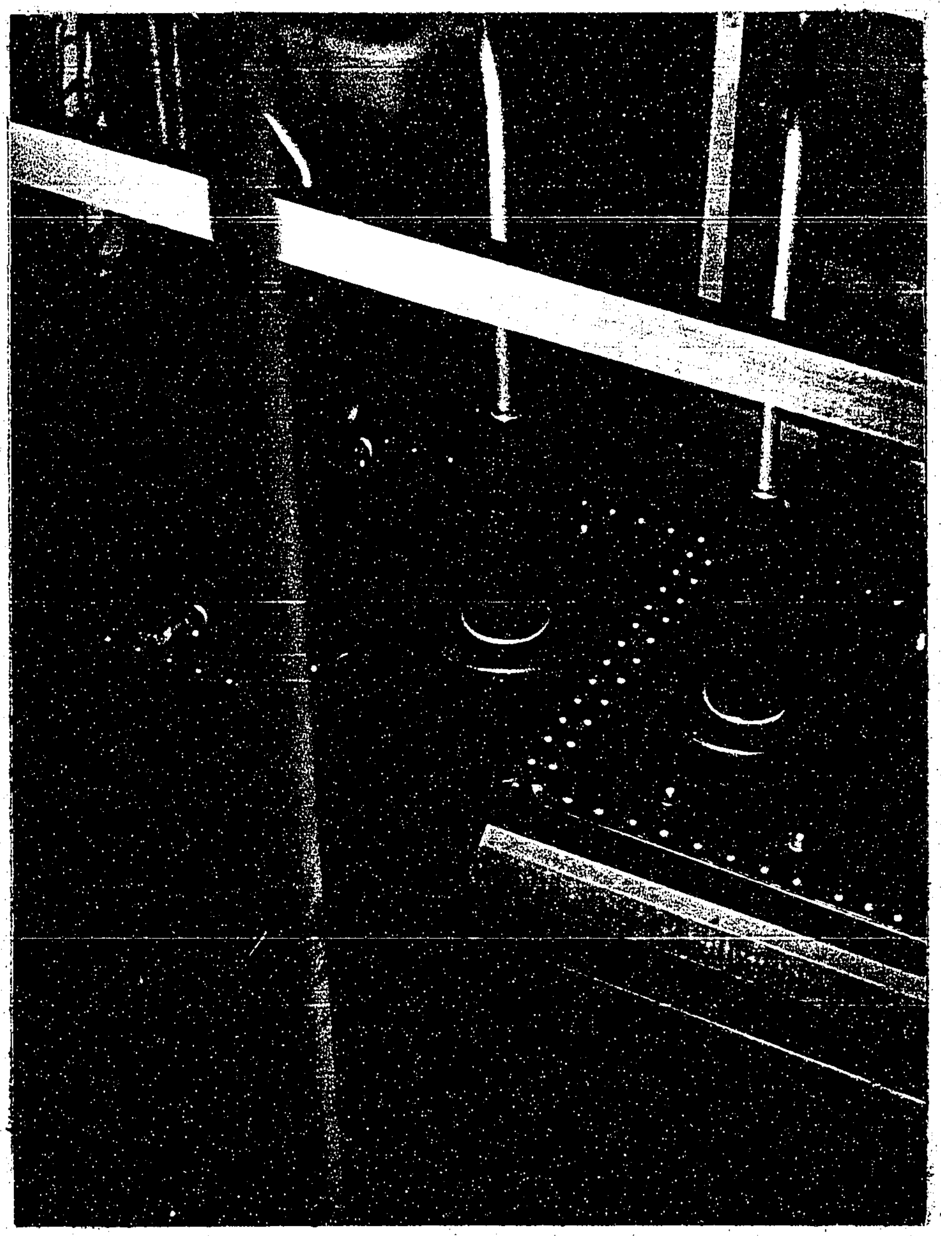


HALF WAVE FILTER CIRCUIT
FOR ELECTRON-DIFFRACTION APPARATUS

This filter circuit gives a 2 kilovolt ripple when the load is at 80 kilovolts and is drawing 5 milliamperes.



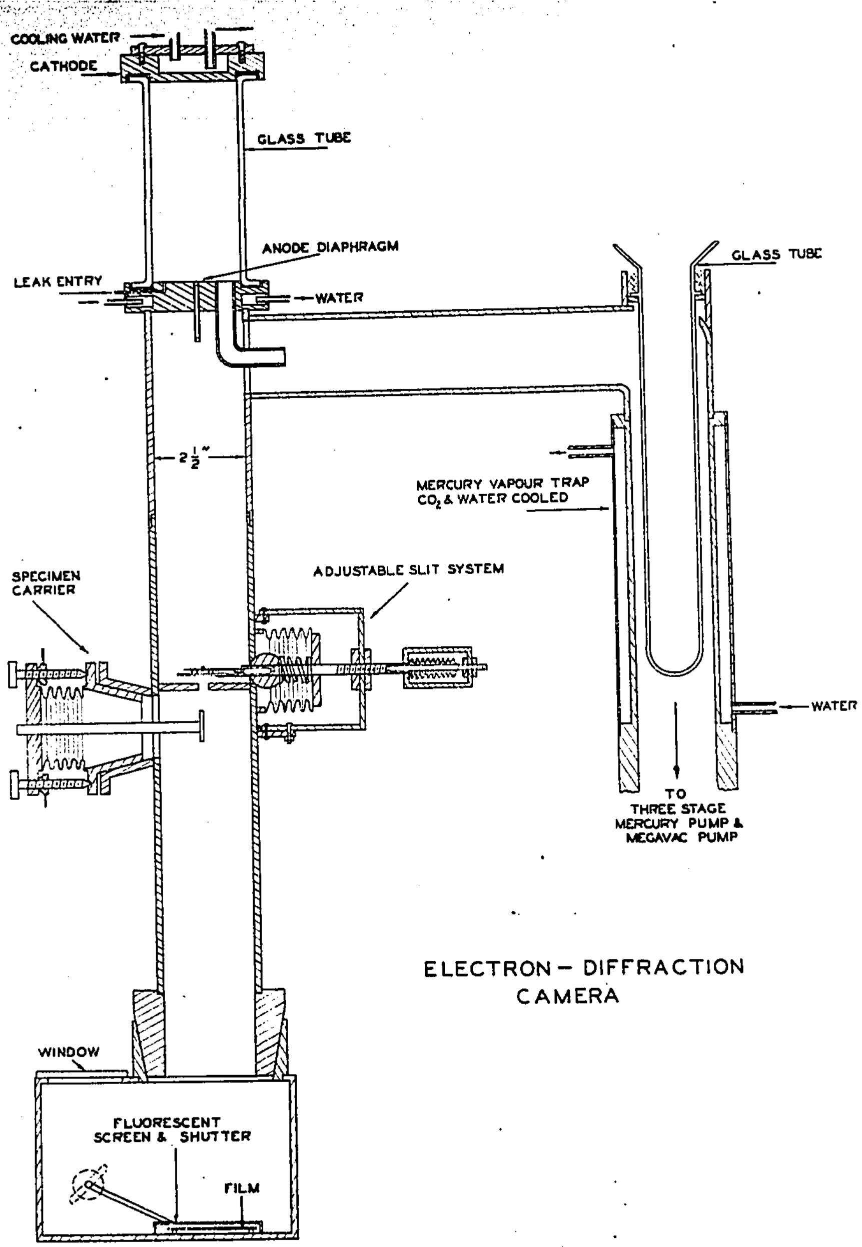
Lead housing for 200 kilovolt valve tube.



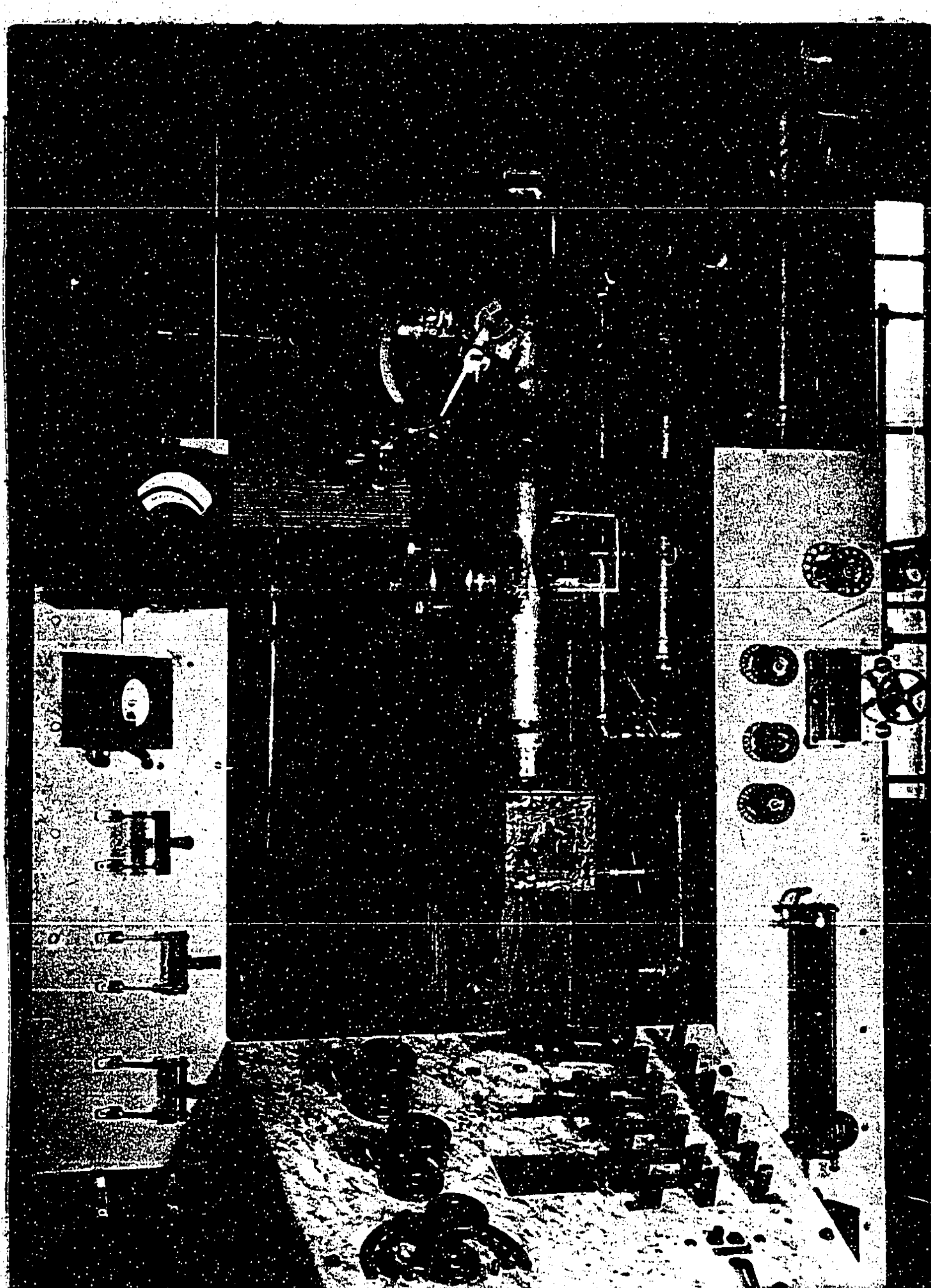
Mica condensers of 100 peak kilovolts and 0.03 microfarads capacity.

voltage insulation for the leads coming from the lead house and the condenser housings was obtained by using bakelite cylinders filled with high dielectric oil; these are shown on page 6. An X-ray control cabinet was used to complete the circuit; it contains an autotransformer, a magnetic switch, a circuit breaker, and a control switch for the filament transformer. To protect the operator from possible charges residing in the condensers after the circuit has been opened, a lever system was connected to the magnetic switch in such a way that when the switch is opened an arm falls on the high voltage end of the condensers, shorting them to ground. See picture on page 9.

Electron Tube A diagram of the electron diffraction tube is given on page 8. The electron beam is obtained in a cold cathode gas discharge tube; the procedure in obtaining the beam is as follows: the tube is evacuated and a low potential drop of about 15 kilovolts is applied across it, air is then leaked into the tube until a discharge is obtained. After having obtained the discharge the leak is decreased and the voltage increased until the desired potential and current are reached. At voltages of 30 kilovolts or over, the electron beam is nicely focused by the induced charges on the cylindrical glass insulator, and takes the form of a thin pencil of light down the axis of the tube.



ELECTRON – DIFFRACTION CAMERA



Electron diffraction camera.

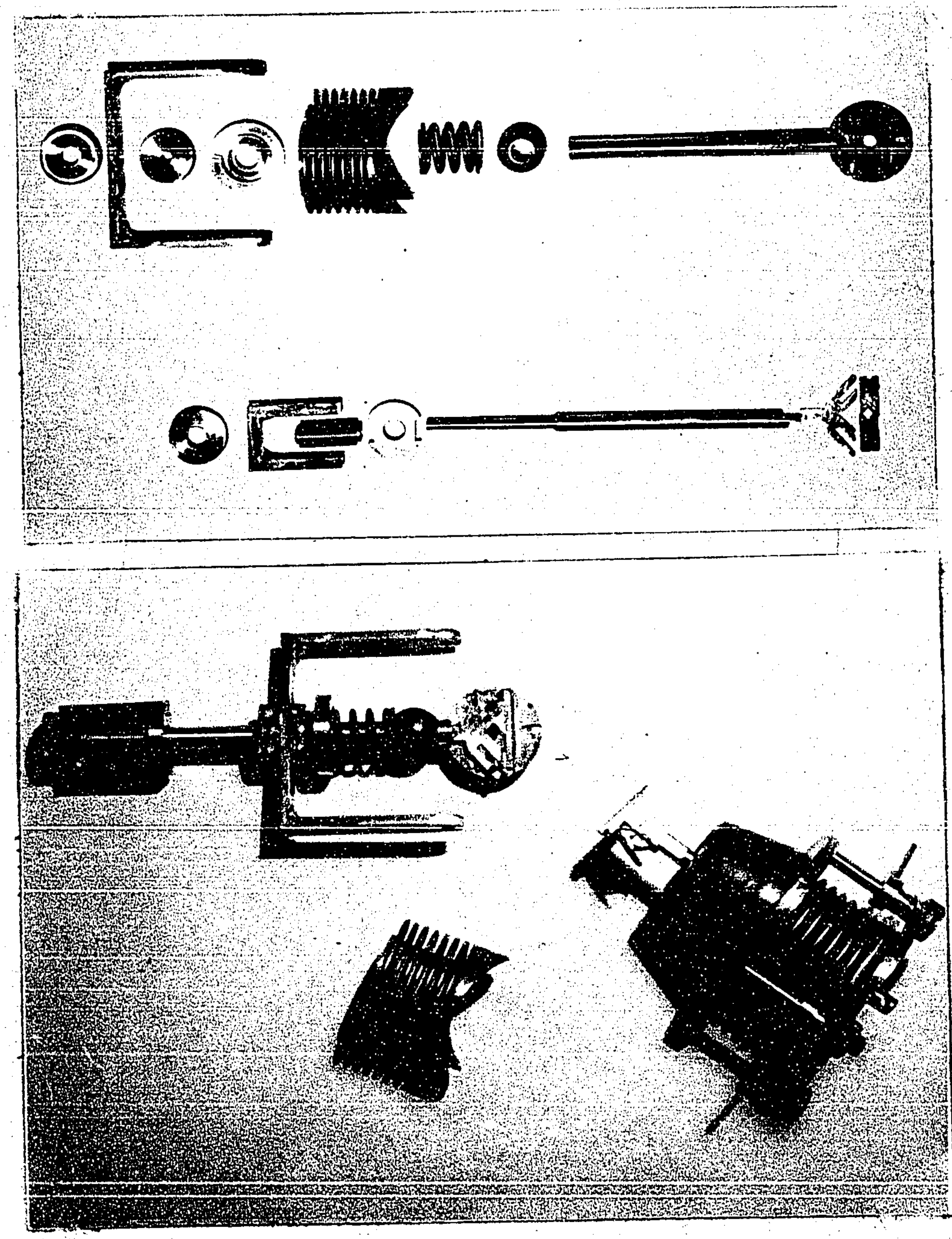
This fine pencil of electrons is then moved slightly by a small permanent magnet so that it falls directly down a small soft iron tube; the beam is shielded from the magnetic field while in the tube. In each end of the tube, which is 1/8 inches in diameter and 2 inches long, is a plug having a hole in its center made by a number 70 drill. This diaphragm serves three purposes; it defines to some extent the direction of the beam, it produces a finer beam, and it helps to produce a monochromatic beam because, when the main beam is bent by the magnet so as to get the maximum intensity down the tube, the slower electrons are sorted from the faster ones. (Since the force on a moving charge in a magnetic field is a function of the velocity of the charge.) After passing the anode diaphragm the stream of electrons again enters the magnetic field produced by the permanent magnet and is again spread into a spectrum of velocities. Just before the electrons strike the specimen an adjustable slit is moved into the most intense part of the velocity spectrum and a monochromatic beam of desired size is allowed to pass through to strike the specimen. The specimen is mounted on the end of a solid rod which can be moved in and out and also tilted through small angles by means of a sylphon bellows. The specimen can also be rotated about the axis of the cone formed by the ground joint of the specimen holder and the port hole.

When the specimen makes the desired angle with the electron beam, a preferred scattering of the electrons is observed which is a function of the velocity of the electrons and of the crystal lattice constants of the specimen. Scattered beams of electrons are observed as spots or lines of light on a fluorescent screen, which is placed at some distance from the specimen or scattering source. It is often possible to improve the diffraction pattern observed on the fluorescent screen by varying the size of the slit, and also by exploring with the beam different parts of the specimen. When the best possible pattern is obtained on the screen, it is lifted out of the way exposing a photographic plate to the electron bombardment. Only a few seconds exposure is necessary for the electrons to leave a permanent trace of their relative positions on the photographic plate. The vacuum is then diminished and the camera detached from the tube by means of a ground joint and the plate developed. The positions of the diffracted spots relative to the undiffracted spot, together with the distance between specimen and film, determines the angles of diffraction or preferred scattering.

<u>Variable Slit</u> A device which proved to be very useful in the successful operation of the electron diffraction tube is the variable slit which is partly shown on page 8.

The variable slit consists of two brass, gold plated, polished, knife-edged "fish tails" which, when moved against one another, form a square hole of variable area. (See pictures on page 13.) These "fish tails" are moved, by means of a sylphon bellows, in a groove on a plate which can also be moved about in the tube by means of another sylphon bellows. Thus they form a variable slit or pin hole whose size and whose position, within the tube, may be changed at any time from outside the tube.

Vacuum System For satisfactory operation of the electron diffraction tube, it is very necessary to have good vacuum conditions. Because of this a very large exhaust tube was used and its connection to the vacuum pumps was made as short as possible. Two pumps are used in tandem, a large Megavac oil pump, and a Leybold three stage mercury diffusion pump. To prevent mercury vapor from diffusing over into the camera, and also to increase the degree of vacuum obtainable; an additional water cooling jacket was built around the exhaust tube and also a glass tube cooled with carbon dioxide snow was inserted in the tube. (See page 8.) Although a very high vacuum is necessary in the diffracting end of the electron tube, in the section of the tube where the electrons originate a very high vacuum is neither necessary nor desirable. For this

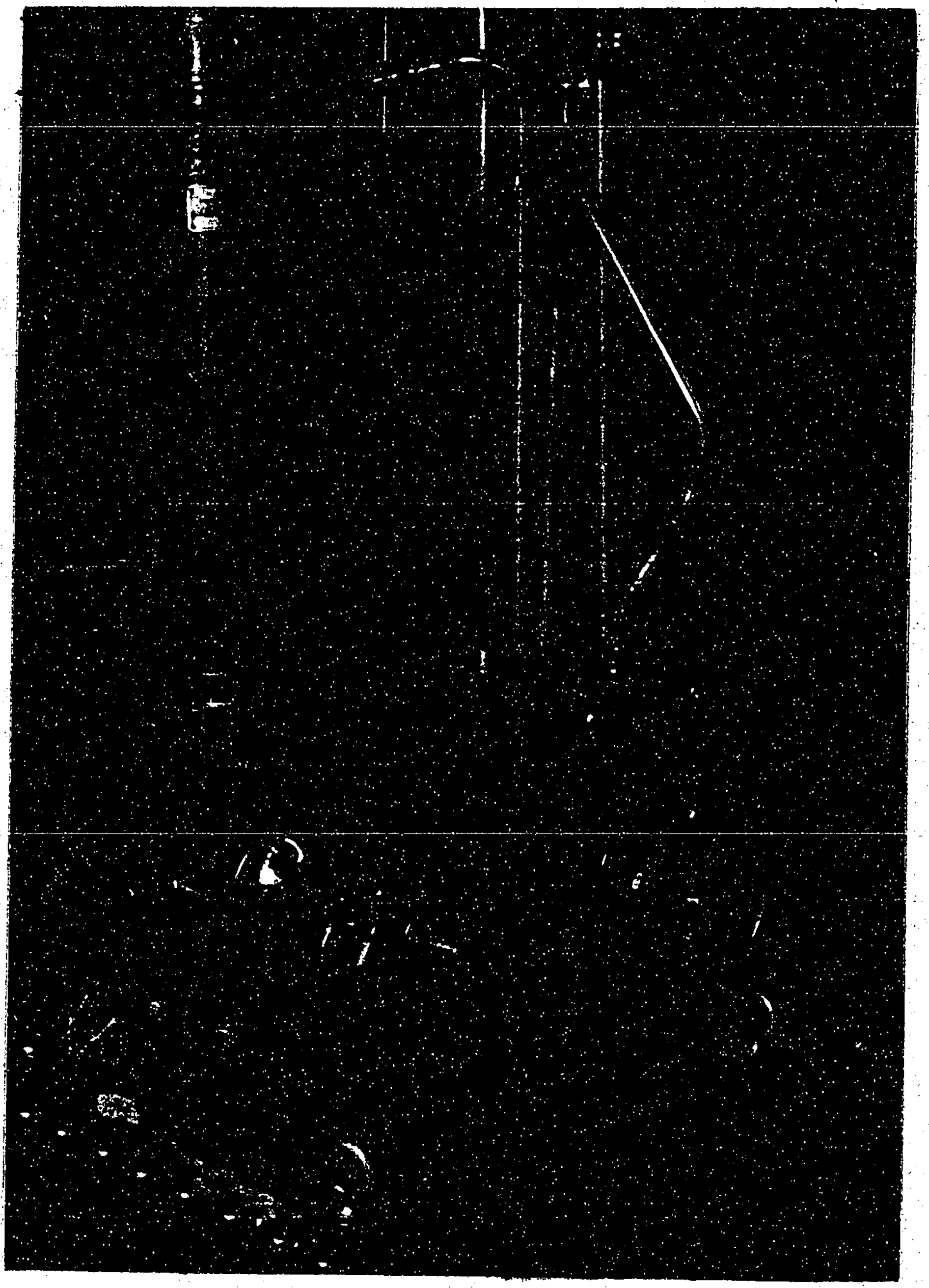


Slit system and specimen holder.

reason the exhaust port for the discharge section of the tube is made small enough to enable a difference of pressure to exist between it and the main section of the tube. Four types of vacuum tight joints are used; Flexible sylphon bellows joints, conical ground joints which can be rotated at all times, permanent solder joints, and semi-permanent joints of piecein wax. When all joints are tight and the mercury pump is warm, the tube can be pumped out in three or four minutes. A picture of the pumping system is shown on page 15.

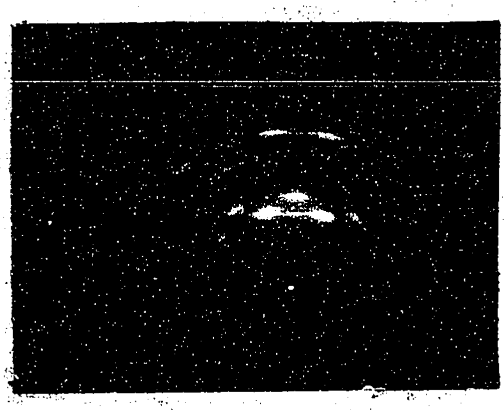
Example Patterns There are two general types of electron diffraction patterns, the transmission type and the reflection type; examples of these are given on page 16. The transmission pattern is obtained by passing the electrons through thin films whose thickness is of the order of magnitude of 10 Angstroms. The reflection pattern is obtained by "reflecting" the electrons at grazing angle from a crystalline plane surface.

Preparation of Specimens It is impossible to place too great an emphasis on the importance of correct preparation of the specimen for electron diffraction investigation. In the case of transmission patterns the difficulty of obtaining a crystalline film thin enough to transmit electrons and strong enough to support itself on a wire frame is easily apparent. In the case of the reflection

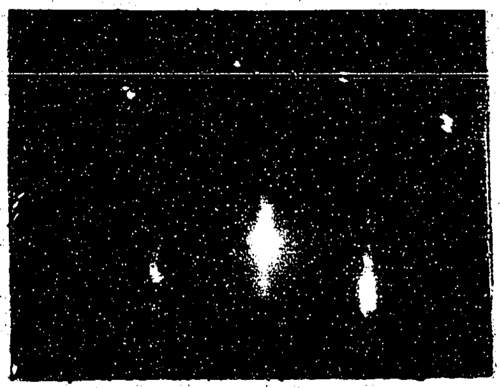


Megavac oil pump and
mercury diffusion pump.

Reflection Patterns

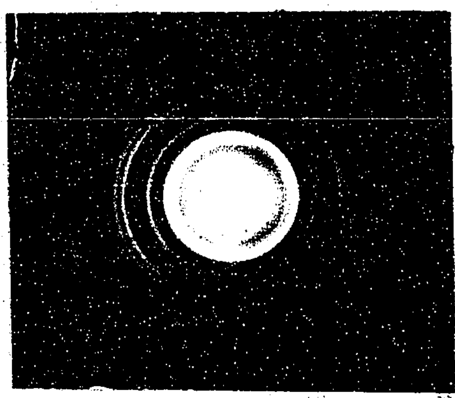


Polycrystalline

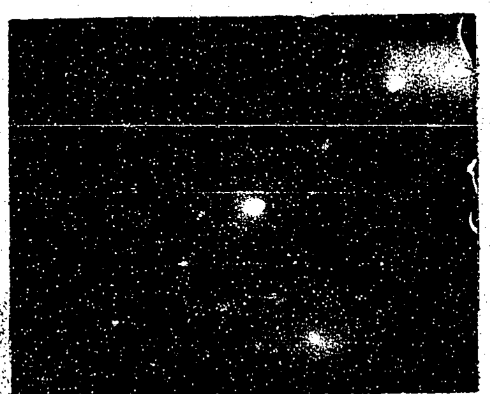


Single crystal

Transmission Patterns



Polycrystalline

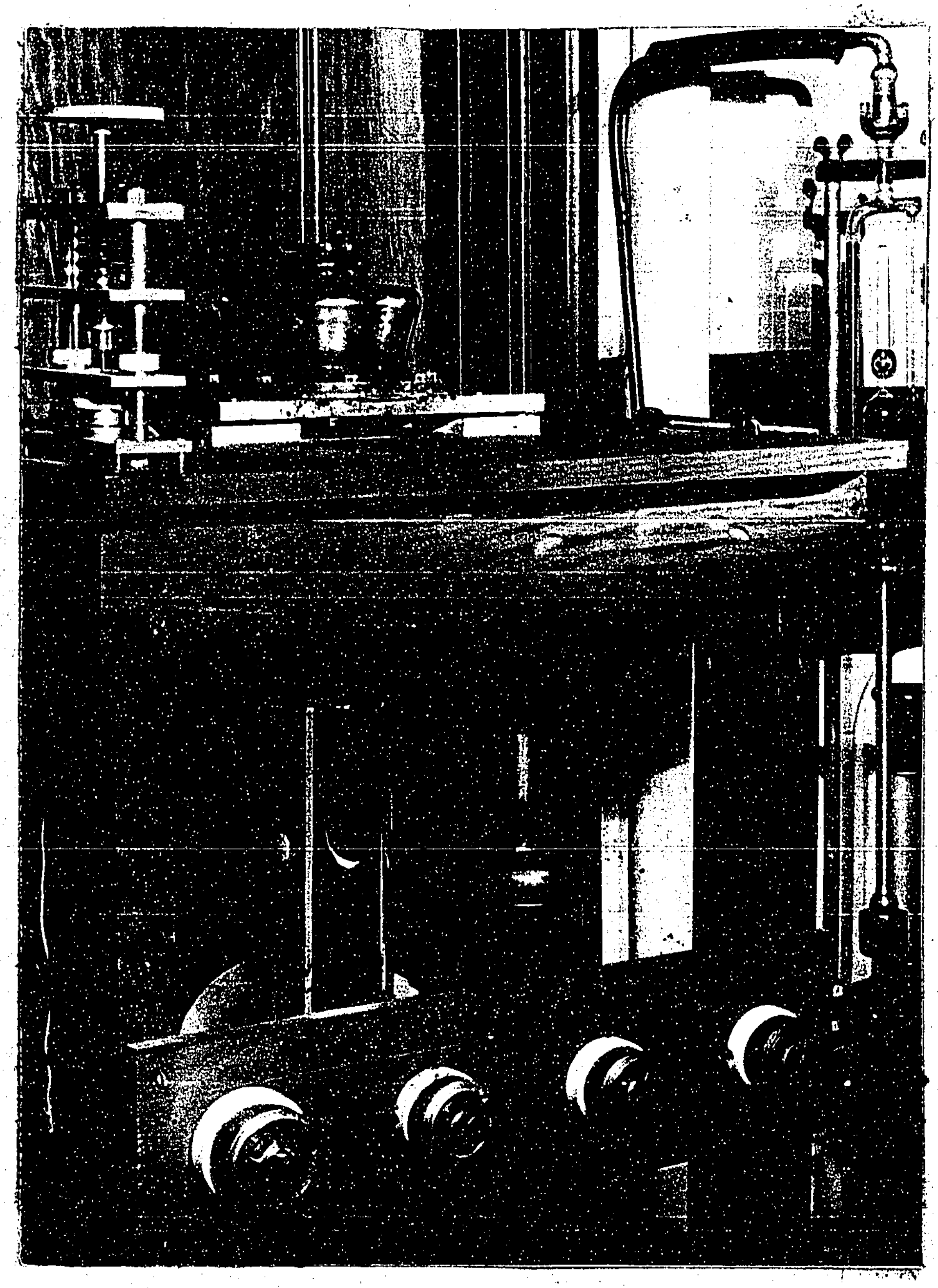


Single crystal

pattern, however, the difficulty in preparing good specimens is not so obvious. The novice is likely to believe at first that a reflection pattern may be obtained from any flat piece of metal if the electron beam is adjusted correctly and strikes the metal at grazing angle. That this is not so, he will soon find out as did G. P. Thomson a few years ago when, because of this fact, he was led to hypothesize that the electrons were not reflected at all but the effect was due to transmission of the electrons through thin crystalline projections above the mean level of the surface. There are three requirements which a good reflection specimen must satisfy: it must have a plane surface; it must have crystals projecting above the surface; and the crystals must be large enough to give good resolution to the diffracting beams and thin enough to transmit the electrons. One of the best means of preparing such specimens is to vaporize the material to be investigated and condense it in vacuo on some plane surface such as a microscope cover glass. The metal (or nonmetal, for that matter) is simply heated in a high vacuum until its vapor pressure is about 10^{-2} mm of mercury or greater, whereupon it emits molecular rays in all directions. The degree of vacuum required for successful carrying out of the process is such that the mean free path of the molecules is larger than the diameter of the vacuum container. Therefore molecular rays propagate from their source without disturbance until they impinge on the walls of the vacuum container or some object within them. The surface to be coated is exposed to these molecular rays which condense on it to form the desired film. An interesting feature of the condensed film is that it apparently exhibits the same degree of polish as the underlying glass and so requires no subsequent burnishing, as do chemical deposits.

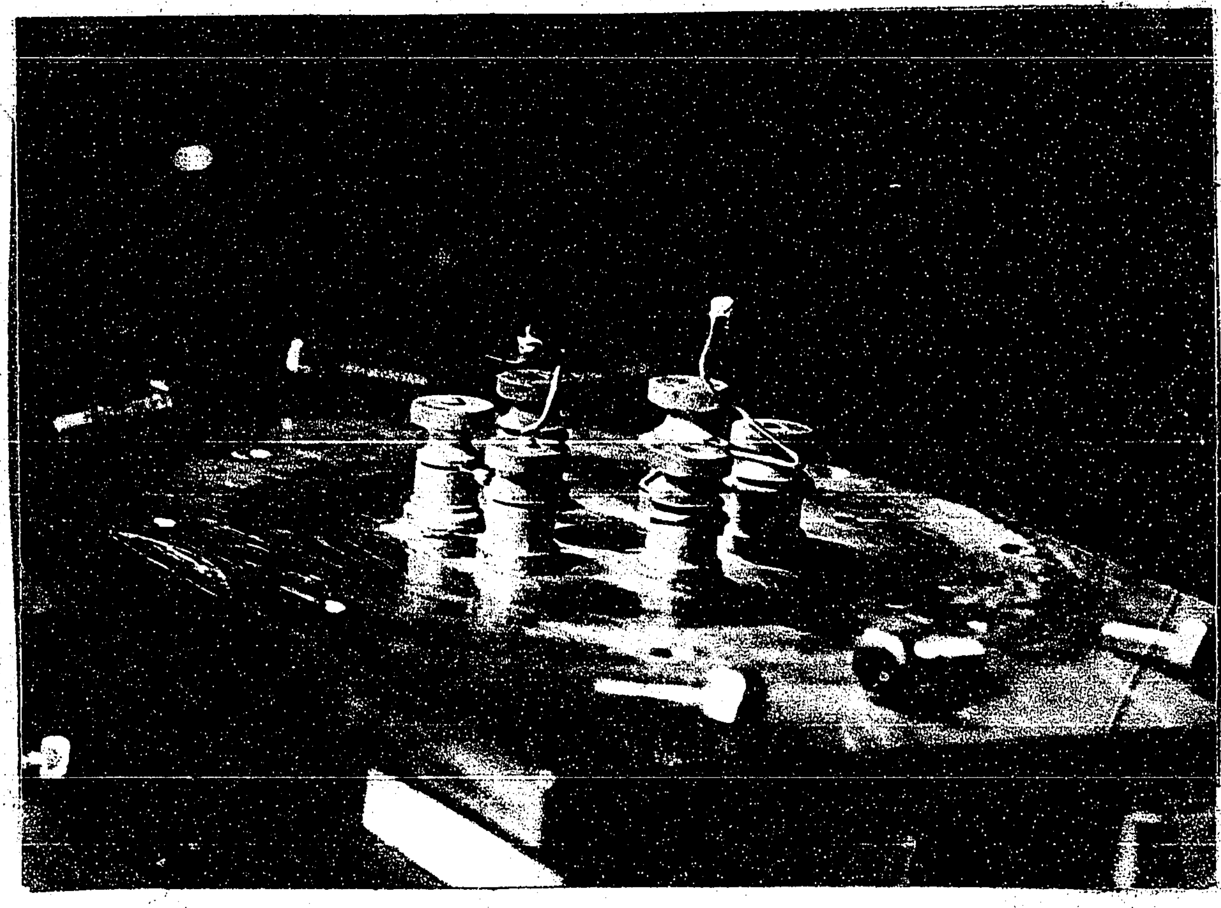
Whether or not a particular material be suitable for giving films by the evaporation process, is determined by the thermal stability and vapor pressure of the material and the practicability of bringing the material to the evaporation temperature in a vacuum. Metals are vaporized by placing them in a conical coil of tungsten wire and passing a heavy current through the coil. Most of the metals melt first before they evaporate, the molten metal being kept from falling out of the coil by surface tension.

Page 19 shows a picture of a vaporizing apparatus which was built for the purpose of providing specimens for electron diffraction studies. The vaporizing chamber is a glass bell jar which is sealed to a large brass ring by means of piecein wax, the ring being clamped by bolts to a flat plate through a rubber gasket. On the plate and



Apparatus for vaporizing
metals in vacuo

within the bell jar are six large copper terminals which can be connected to a transformer of the type used in spot welding, also in the plate are an exhaust port and leak entry. (See page 21.) A glass mercury trap connects the exhaust port to a one stage mercury diffusion pump and a Hyvac oil pump. The leak entry is provided because there are certain metals which can only be brought to fuse to the tungsten wire in an atmosphere of hydrogen or helium. These gases facilitate heat transfer between the tungsten and other metal, and, in addition, they restrain evaporation of the metal. After intimate contact with the tungsten wire has been established, the metal will then vaporize faster in the vacuum, because the heat is transmitted to it more effectively. The pressure in the vaporizing chamber must be 10 microns or less; a McLeod gauge reads this pressure.



Inside view of vaporizing chamber showing the six binding posts and two cover glasses upon which a copper film has been deposited.

References:

[1] De Broglie, L. : Philosophical Mag. 47, 446 (1924).

[2] Elsasser, W. : Naturwiss 13, 711 (1925).

[3] Kikuchi and Nishitawa : Proc. imp. Jap. Acad. 4, 475 (1928).

[4] Wierl, R. : Ann. Physik 8, 521 (1931).

Part 2

ELECTRON DIFFRACTION STUDY OF COPPER OXIDES

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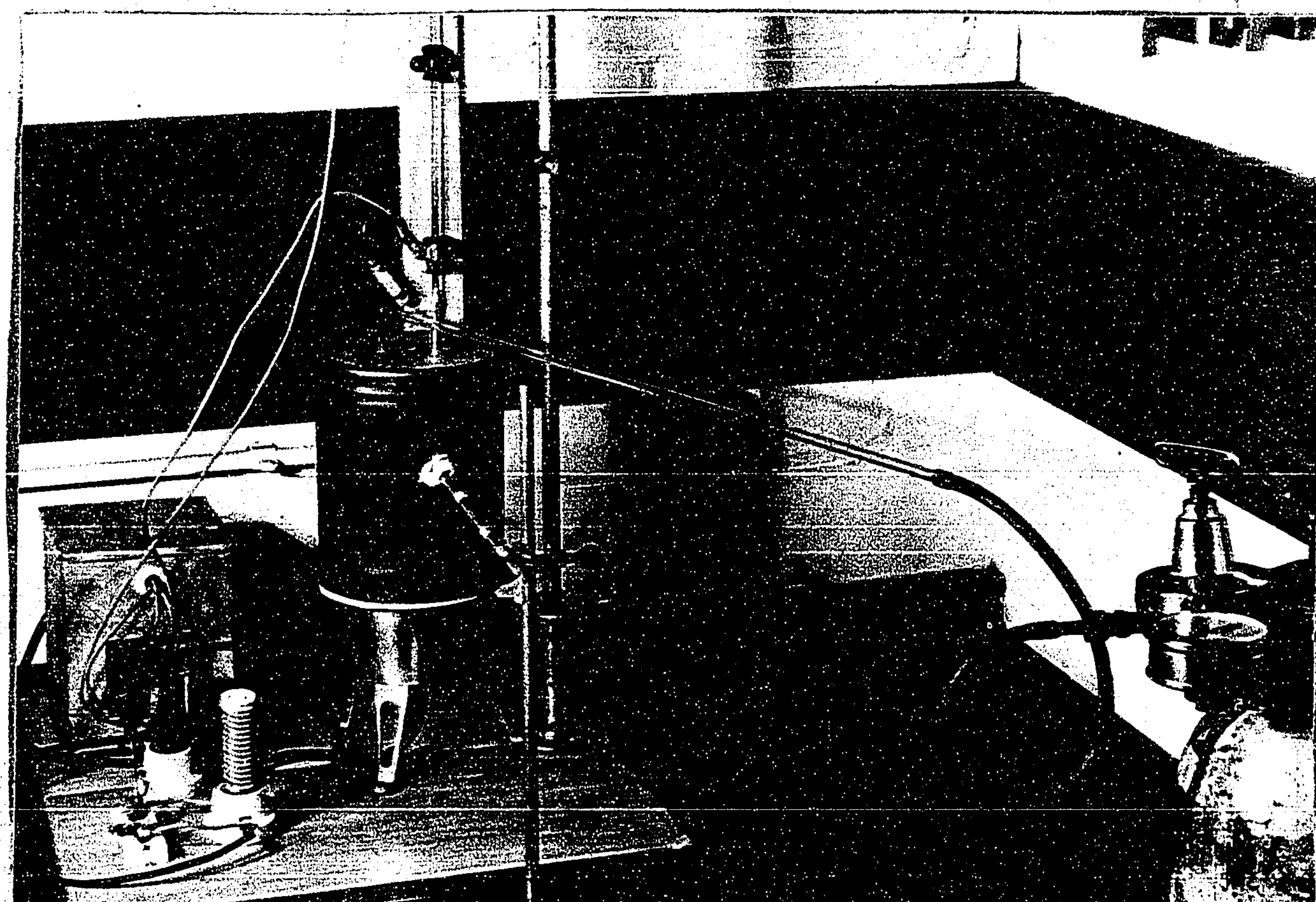
INTRODUCTION

This paper describes an electron diffraction study of copper oxides formed from evaporated copper by exposing it in an oxygen atmosphere at various temperatures and for various lengths of time. It also discusses several of the orientations which were observed in the evaporated copper.

Procedure

The films were prepared by vaporizing the copper in a vacuum of approximately one micron and condensing the vapor on microscope cover glasses. Only deposits thick enough to be opaque to light were used. The oxide was formed on the films by placing them in an adjustable-temperature oxygen-atmosphere electric furnace. A picture of this furnace is shown on page 2. The temperature control device consisted of a long capillary tube connected to a bulb filled with mercury; as the bulb became heated in the furnace, the mercury rose in the capillary and made an electric contact with a tungsten wire which was inserted in the open end of the capillary tube, this closed a relay circuit which in turn opened the heater circuit. Since the tungsten wire could be adjusted to any position in the capillary tube, the furnace could be held to any desired temperature under the boiling point of mercury.



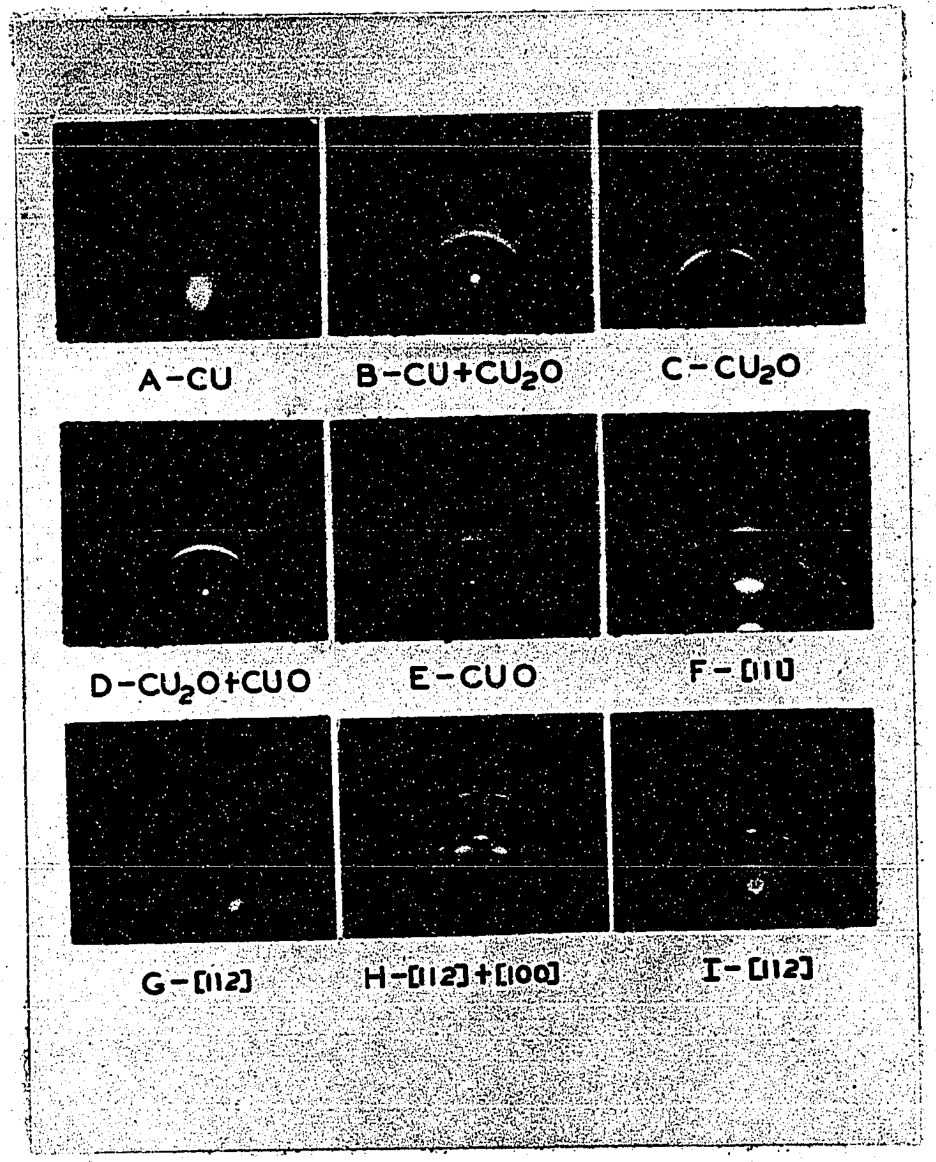
Adjustable-temperature, oxygen-atmosphere
electric furnace.

The thin cover glasses used as a base for the films were a half inch in diameter. These were supported in the furnace by three glass "fingers" directly over the bulb of the thermometer from which the temperature readings were taken. The temperature of the furnace was maintained constant to within plus or minus one degree centigrade. The electron diffraction camera used to obtain the crystal patterns was similar to many described in the literature[1]. All photographs were taken using electrons having a velocity corresponding to a wave length of 0.063 Angstroms and a camera length of 36.5 centimeters.

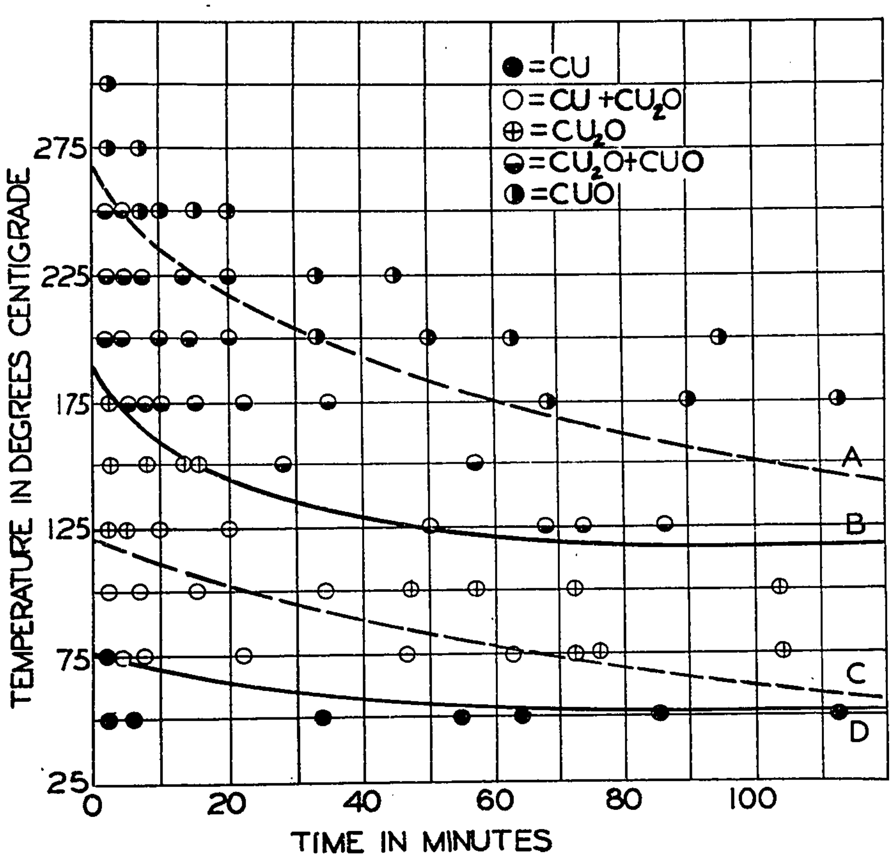
RESULTS

Five types of patterns dependent on the temperature of the furnace and the time of exposure of the films were observed. These are shown in pictures A,B,C,D, and E on page 4. A plot made of these pattern types, showing their relating to time and temperature, is given on page 5.

As may be seen from the graph, rough zones are formed in which only one type of pattern occurs. At temperatures of 50° C or below, the copper films are very resistant to oxidation; exposures in an oxygen atmosphere at these temperatures yield no trace of oxide. (Longer exposures for films prepared by condensation are unsatisfactory since they give very faint patterns.) Above 50°C and below 275°C



Types of electron diffraction patterns obtained from copper and copper oxide films.

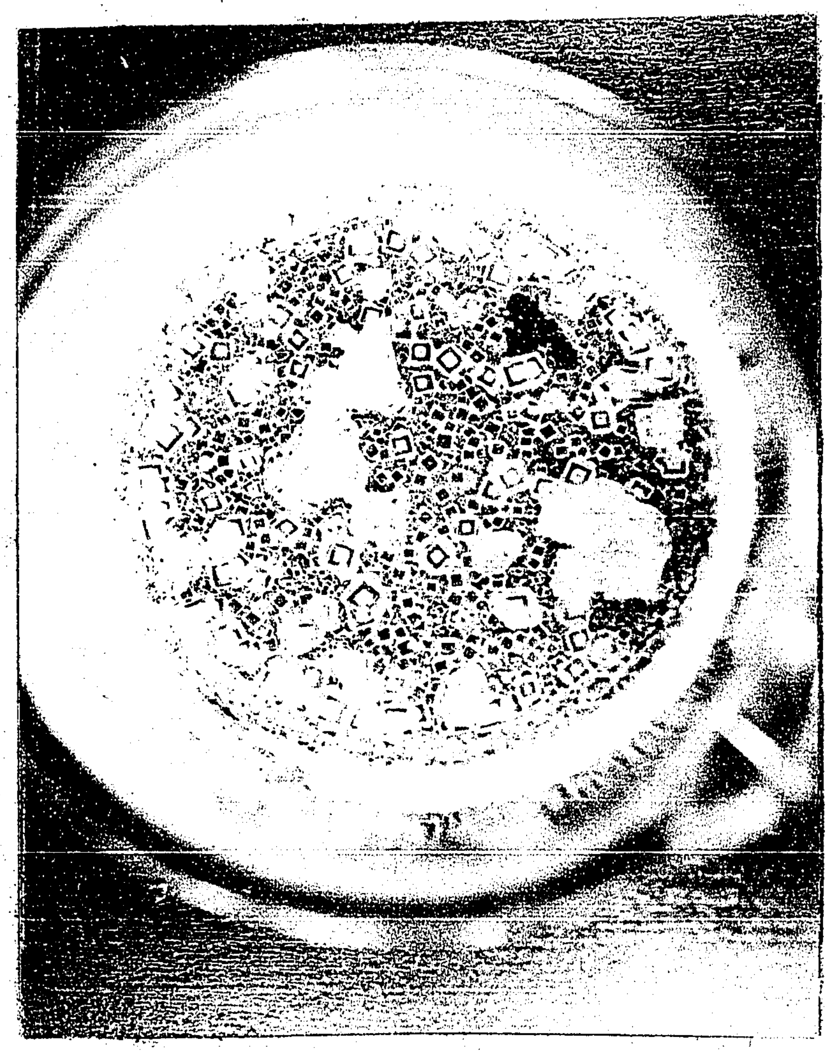


Graph showing the kinds of copper oxides obtained when the evaporated copper films were oxidized at various temperatures for various lengths of time.

cuprous oxide is formed, although at temperatures over 125°C the Cu_2O oxide is unstable and soon changes in an oxygen atmosphere to cupric oxide. At temperatures above 275°C only the CuO form of copper oxide is obtained.

Many of the copper films prepared for this experiment were found to be composed of crystals oriented in such a way as to have one or two sets of planes parallel to the glass base of the films. A picture on page 7 of large sodium chloride crystals which have grown on the bottom of a glass beaker demonstrates this particular type of crystal orientation. Crystal orientations are observed as spots on the diffraction pattern; the geometrical configuration of spots determines the type of orientation. These are shown in pictures F, G, and H on page 4. Deposits in which the (111) planes were all parallel to the glass base were observed more frequently than any other. The (100) orientation was never observed alone but occurred only with the (112) orientation. It would seem from the pattern obtained that the two orientations are equally distinct. If this be so, we have a contradiction to Dr. Dixit's[2] statement in his theory of orientations that "... two equally distinct orientations are never seen."

A few diffraction patterns were obtained which indicated a tilt of the oriented crystal planes. See pictures G and I on page 4. Burges's[3] explanation that this occurs



<u>Example of crystal orientation</u> All the crystals (NaCl) have their (100) planes parallel to the bottom of the glass beaker.

when the vapor beam strikes the glass base at an angle less than 90° is correct as far as we have been able to observe.

References:

[1]Finch, G. I. Pro. Roy. Soc. Lond. A. 141, 399 (1933).
[2]Dixit, Philosophic Mag. 16, 1049 (1933).
[3]Burges, Physica 1. 549 (1934).