The latter is in contradiction with the results found in lanthanum and in bismuth.

In order to account for only six lines an attempt has been made to assign three sub-levels to the initial and final states. Although the relative intensities and separations are about what one should expect in certain cases, the frequency separations definitely show that this cannot be the explanation.

In conclusion we wish to express our appreciation of the many favors shown us by various members of the Mt. Wilson Observatory Staff and to acknowledge the invaluable assistance rendered us by the facilities that they so generously placed at our disposal.

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A METHOD OF PRODUCING LONG SINGLE-CRYSTALS OF METAL AND A STUDY OF THE FACTORS INFLUENCING CRYSTAL-ORIENTATION AND PERFECTION

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The apparatus described in the following was to serve the purpose of studying the influence on the orientation of the gradient of temperature along a single crystal during its growth, and the effect of strong magnetic fields applied at the exact point of transition of the two phases of the metal. It was found that the particular method of growing crystals of great length, developed for this investigation, was superior to any others known to the authors. It became evident that the influence of a magnetic field applied to a zone of crystallization is of such complexity that it seemed to be better to describe these effects in a separate paper, especially since the method has practically nothing to do with the special purpose, and therefore, may be of more general interest.

There are three principal methods known which have been used for the production of large single-crystals, and they vary considerably in the results obtained.

(1)   The progressive crystallization of molten metal in a glass or quartz tube, the lower end of which ends in a sharp point from which the first grain starts, the heat of crystallization being drawn off mainly through that end.[1,2,3]   The very largest crystals (Cu) of several kilograms weight have been obtained by that method.[4]

(2)   The pulling of a single-crystalline thread out of the molten metal.[5,6]

(3)   The recrystallization of a metal in a fluidal state[7] or at a transformation of an allotropic modification (Fe).   The speed of crystallization regulated by the motion of the specimen is kept below the natural speed by a constant progression of a fixed gradient of temperature along the wire.

The first two methods require the molten state of the metal, the last avoids this condition, which is a very delicate one for many metals, because of the fast evaporation of many substances in the molten state, and because some metals have one or more allotropic transformations between the melting point and room temperature.   In passing through these transformations the monocrystalline structure is very easily destroyed.

The methods (1) and (3) have in common that the orientation of the crystal[†] depends more or less on accidental conditions, although the direction of the heat gradient across the rod seems to determine the situation of the plane with the best thermal conductivity.   The method (2) permits one to obtain any desired orientation by means of a seed-crystal.

The first method involves large difficulties as soon as long crystals ($^1/_2$ meter and more) of sufficient homogeneity are desired, as is necessary for thermal and electrical measurements where the constancy of the cross-section over greater lengths is needed.   The difficulties arise because of the impossibility of filling thin glass capillaries of several meters length without occlusion of gas and oxide.   Further it produces large difficulties to cool these long rods under exactly constant thermal conditions.   Similar difficulties are involved in the second method, mainly concerning the constancy of the cross-section of the crystal.

The method of recrystallization gives the possibility of obtaining long thin crystals, but one is never sure that the rod really consists of one individual crystal throughout its whole length.

It is well known that the progression of the constant gradient of temperature over the crystal has to be kept constant to get a constant speed of crystallization.   There cannot be any doubt that under ideal conditions the orientation of the crystal depends on that and on the direction of the gradient of temperature in the zone of growth, but just this last condition

[†] The term orientation shall define the angle between the main axis of the crystal and the axis of the rod.

is very hard to fulfil in the method (1) and (2) as soon as one has long crystals, because the orientation of the gradient changes with the growth
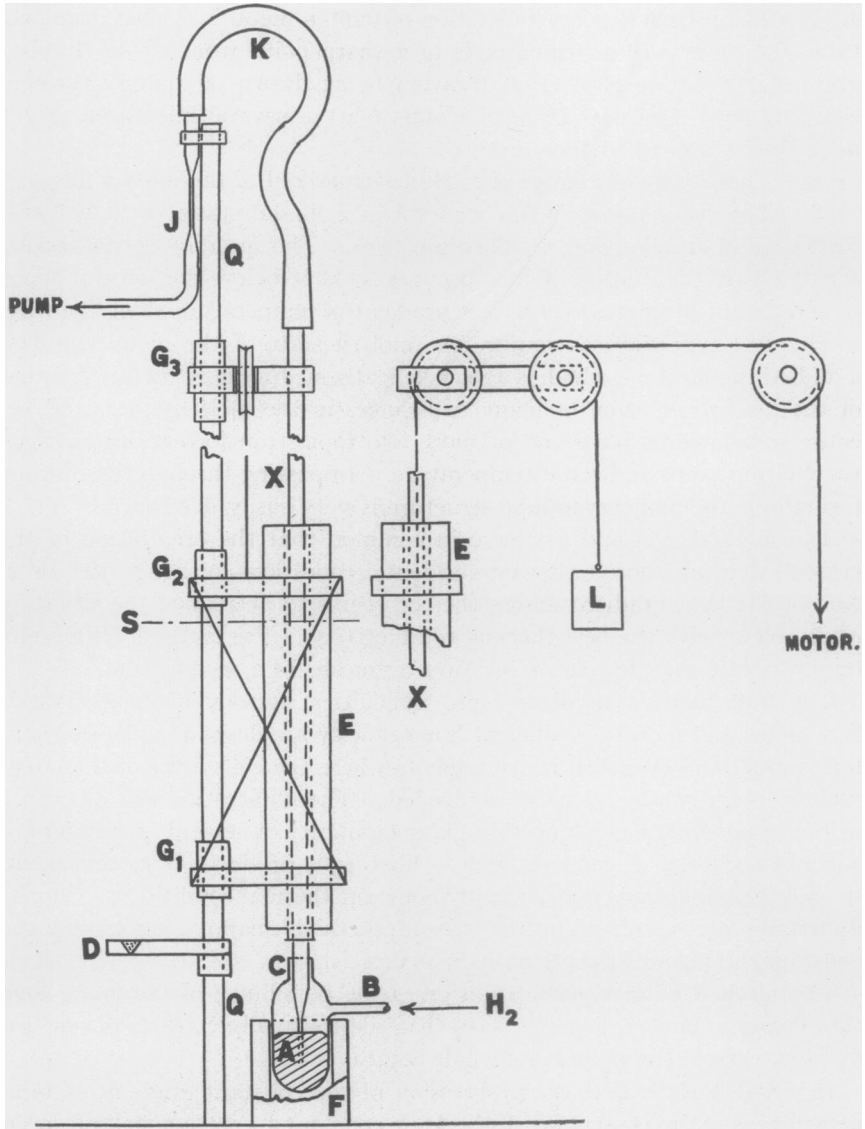

FIGURE 1

of the crystal. One part of the heat of crystallization goes along the crystal either to the cooled edge (method 1) or to the cooled clamp of the drawing mechanism (method 2); the other part leaves the crystal normal

to the axis of the rod into the surrounding air.   But the longer the crystal grows the larger grows its thermal resistance, i.e., the smaller becomes the amount of heat carried parallel to the rod, and the larger the transversal part.   This means a change in the orientation of the gradient in the crystal.   Thus may be explained the phenomenon of a continuous change of orientation along the crystal, where, for instance, the cleavage-plane has an increasing or decreasing angle with the axis of the rod over its length without any detectable discontinuity as was observed on zinc-crystals by Linder.[8,9]   Experiments showed that this effect can be avoided by making one of these two paths of the heat in the crystal as small as possible.

The only way of satisfying all these conditions was to use the first method, which produced a single crystal of 15 to 20 centimeters length, and 5 to 15 mm. diameter.   Then the glass tube was heated again above the melting point of the metal, enough at the same time to soften the glass, and then was drawn by means of a mechanical device out to the desired length and diameter, keeping the cooling conditions during this process as constant as possible.   The latter portion of this process was first described by Taylor,[10] who thus produced very thin metal fibers without considering their crystalline structure.   In fact, it was observed that there is no difficulty in obtaining very uniform wires of diameters below 0.05 mm., but these wires are of little use as soon as one is interested in the determination of the nature of the crystalline structure.   To obtain wires with larger diameters up to 1–2 mm., this simple method was found not to work satisfactorily;   mainly, because of the lack of uniformity of the cross-section and of the occlusion of gas bubbles which sometimes interrupted the metal core, so that a new crystal started.

The process which was finally used to produce crystals of any desired length with a constancy of diameter of less than 2% was the following: for producing crystals from Bi with a melting point of 271°, a soda-glass had to be used because of its appropriate softening temperature of 320°. The glass tube had to be rather thick-walled, about 5 mm. inside diameter, and of a good cylindrical shape.   It was found that the gas bubbles, which appear so easily at the metal-glass surface when the metal crystallizes in the tube, are mainly caused by contaminations on the walls of the tube. Thus, they had to be cleaned inside with hot chromic acid, distilled water and alcohol to destroy these layers.   The glass tube was then heated in an electric tube-furnace above the melting point of the Bi while being evacuated for several hours.   The metal was molten in a pyrex vessel A (Fig. 1).   This crucible had a side-arm B through which a flow of highly purified hydrogen was sent.   The purification was done with palladium-asbestos and liquid air.   Thus the hydrogen reduced the surface of the metal, the gas was finally burned in the chimney C.   The metal in A had to

be heated by means of a furnace F up to 500° to get a reasonable speed of reduction. In the case of Bi, one hour was in general sufficient to reduce the oxide and to obtain a mirror-like surface. The glass tube X was, as mentioned above, heated by the furnace E and evacuated. This furnace was supported by the stand Q by means of the gliding sleeves G_1 and G_2. As soon as the metal was reduced, X was lowered into C, its tip being broken off and its end immersed into the metal. Then the metal was sucked slowly into X through the hose K and the capillary J up to the point S. It is important that the speed of sucking the metal be very small in order to avoid irregularities at the glass-metal surface. After this, the tube was lifted, A replaced by the carrier D, having an asbestos-filled hole in which the end of the capillary rested thus preventing the liquid metal from running out. The lifting of the glass tube out of A brought the level S just up to the upper rim of the furnace, so that all the metal was kept molten at a uniform temperature.

The furnace E was connected by means of a cable with the balancing weight L and a worm-gear arrangement driven by an electric motor which lifted E upward with a speed of 5 mm. per min. The carrier D was cooled by a gentle air blast, so that the crystallization started at the capillary portion and proceeded uniformly over the whole glass tube. This method does not differ in principle from method 1; but it is necessary for the successful application of the next process to use the described additional precautions in order to obtain a perfect contact of metal glass as indicated by the mirror-like appearance of the surface and the absence of gas bubbles.

The next process consisted mainly in melting the metal in the tube again and drawing out tube and metal together, thus starting a new crystallization. The arrangement fulfilling the required conditions was as follows:

Figure 2 shows a side view and a top view of the apparatus. D is a claw holding one end of the glass tube filled with the crystal X; the other end of which goes through the electric furnace C and is fastened to the car A. This car rolls on four wheels on the tracks B. The whole apparatus is driven by the motor F (compound wound) and transmits its motion by means of two worm gears to the shaft L. At the lower end, the shaft has a pinion which moves the rack N and herewith the claw D which glides on the tracks E. The motion of the claw can be regulated from 0.2 to 10 mm. per min.

The car is moved by the same mechanism but at a different speed by means of the inextensible chain K running over the three trolleys M_1, M_2 and M_3. The chain is wound around the drum G. Thus the ratio between the motion of the claw D which brings the crystal into the furnace and the motion of the car A which draws the crystal Y out of the furnace
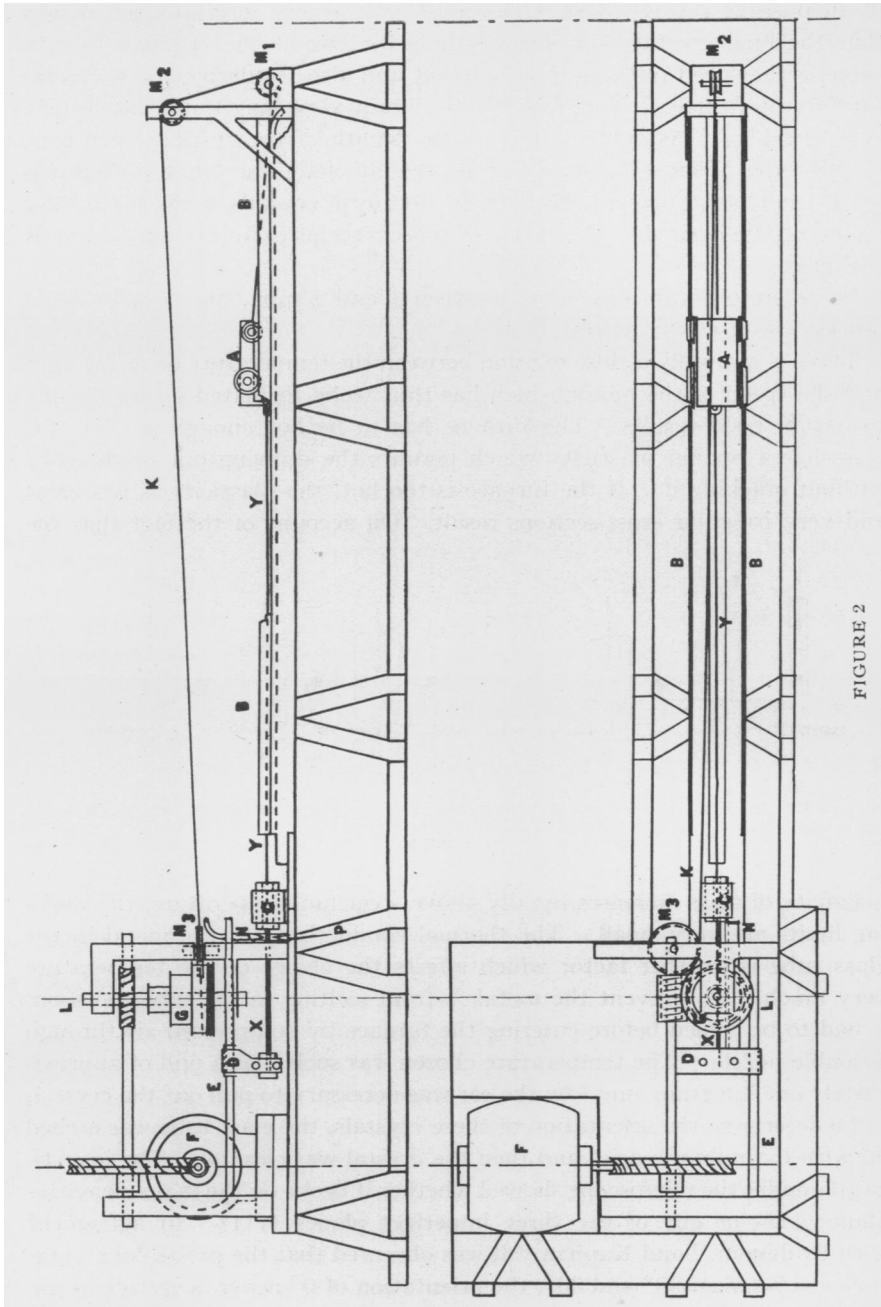
FIGURE 2

is constant even if the speed of the motor varies. It was found that out of all possible ratios 1:3 gave the most satisfactory results which means that the final crystal Y was three times as long as the original X. By keeping the speed of the motor constant and also regulating the temperature of the furnace it was possible to obtain very long uniform crystals. The length of Y is only limited by the length of the tracks which was, in this case, about $1^1/_2$ meters. On account of the fact that the ratio is fixed, one has to recrystallize these obtained crystals again if smaller diameters are desired. The repeated process seems to improve the crystals still more.

In order to obtain diameters between 1 and 2 mm., only one drawing process was used, in general.

There is naturally a close relation between the temperature of the furnace and the speed of the motor which has thus to be regulated very carefully to obtain good results. The furnace has to be hot enough so that the glass has a certain plasticity which permits the drawing out of the tube without cracking it. If the furnace is too hot, the plasticity is too great and very irregular cross-sections result. On account of the fact that the
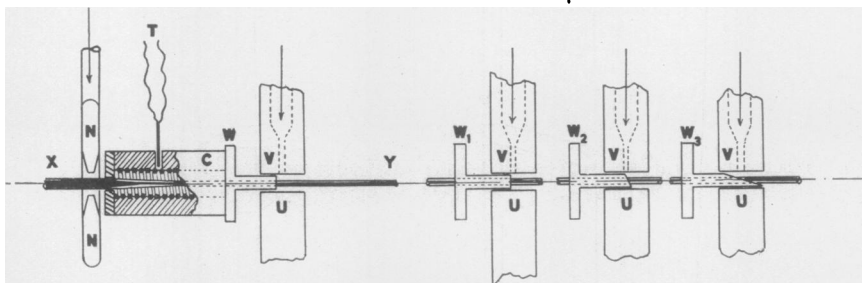

FIGURE 3

plasticity of glass increases rapidly above a certain temperature, the working limits are very small. The thermal conductivity of the metal in the glass tube is another factor which affects the choice of the temperature very much. To prevent the metal X from melting in the tube too soon, it had to be cooled before entering the furnace by compressed air through a double nozzle. The temperature chosen was such that a pull of approximately one kilogram/mm.[2] by the car was necessary to pull out the crystal.

To determine the orientation of these crystals, the glass tube was etched off with hydrofluoric acid, and then the crystal was cleaved. The investigation under the microscope showed whether it broke on the main-cleavage-plane (111) or one of the three imperfect planes (11$\bar{1}$). In agreement with Bridgman,[11] and Kapitza,[12] it was observed that the probable orientation was between 90° and 30°, the orientation of 0° never occurring at all.

The described arrangement gives the opportunity of locating rather

exactly the zone of crystallization, i.e., the section in the drawn tube where the metal solidifies. If all conditions are kept constant (speed, ratio and temperature), this solidification takes place at a certain and constant distance behind the furnace; hence, it is possible to study the effect of certain influences on the act of crystallization. One of these applications was a strong magnetic field which produced on the crystal effects too complex to be described in this paper. Another was the temperature gradient over this zone and its effect on the orientation. To investigate this, it was only necessary to put at the outlet of the furnace C guard-tubes W of different shapes (W_1, W_2, W_3) as shown in figure 3. The jet in the block V blew compressed air at a pressure of 20 cm. of water against the face of the guard-tube W thus determining the angle of the gradient with the axis of the rod. The length of the guard-tube was such that the zone of crystallization was a few mm. in front of the face, so that the metal was still molten when it came in the region of the blast.

Two main questions seemed to be of interest: (1) Is the orientation of the crystal entirely determined by the direction of the gradient, no matter in which orientation the crystal started originally (the first part of the thick crystal fixed in the claw of the car not having been liquefied in general and thus having the effect of a seed-crystal)? (2) Is it possible to obtain a certain orientation with a certain gradient if the crystal has no starting orientation inforced by a seed-crystal?

The experiments gave no strict answer to these questions; nevertheless, it was evident that a variation of the gradient caused a variation in the orientation in general, so that the plane (111) grows more or less parallel to the direction of the gradient down to an orientation of $30°$. In case the crystal was started by a seed-crystal, the orientation of which was different from the gradient, a change of the orientation in the crystal started at the point where the air-blast was applied. The smaller the orientation the more irregular became the changes, i.e., the weaker the influence of a change in the orientation of the gradient. Below $30°$, it was impossible to observe any influence. This shows that *the orientation of the gradient is not the only factor determining the orientation of the crystal.*

FIGURE 4

The other influence can only be considered as resident in the strain, applied to the crystal during the act of crystallization by the glass walls and due to the expansion of the metal (3.3% of its volume from data given by Endo[13]) at the melting point. Hence, the volume of crystallizing region reaches a maximum and then decreases due to the thermal con-
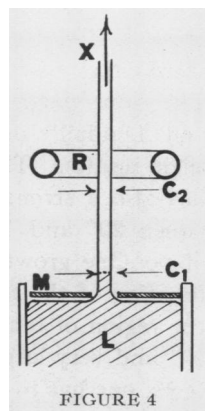
traction during the cooling process. From the observations by the authors, it is probable that the orientation of the crystal becomes rigidly determined at the instant when a decided contraction appears, preceded by the above expansion indicating that the properties of the crystal (orientation, perfection, etc.) are determined by the forces acting at the time of this contraction to a large extent. This may be observed in certain cases by watching an upright glass tube, filled with molten Bi, as the crystal grows upward from a cooled tip. The crystallization is seen to take place in blocks which contract visibly from the glass at the instant of formation. If one considers that the stresses, induced by previous expansion, are present at the moment of contraction, then the difficulty of obtaining crystals with small orientations may be explained as follows. As it is known that the coefficient of thermal expansion is largest parallel to the trigonal axis and smallest normal to it ($\parallel$ 0_4162; $\perp$ 0_4120 between 20° and 240°C.[14]) it could be expected that the crystal prefers an orientation in the glass tube where the maximum contraction would be parallel to the direction of maximum compression. Thus large angle-orientations are preferred.

This argument explains also the changes in orientation of crystals grown with the Czochralski-method (method 2). The only difference is that there is instead of a transversal pressure in the glass tube a stress along the crystal which affects it almost the same and is caused by the weight of the column of the liquid metal suspended at the point where the crystal is formed. One of the authors (G.) studied the possibilities of growing Bi-crystals in various orientations by this method without getting satisfactory results for small orientations, Kapitza[12] did not succeed either. The same particular question was studied carefully recently by Hoyem and Tyndall[15] on zinc-crystals, without their finding an explanation of their results. They can be compared with the results on Bi because Zn has also a strong anisotropic thermal expansion ($\parallel$ 0_4639; $\perp$ 0_4141 between 20° and 100°).[16] Hoyem and Tyndall studied mainly the limits of possible growth, in a certain orientation given by a seed-crystal, as a function of the temperature of the liquid metal. It could be shown that the region of temperature was very small for orientations between 0° and 50° and very large between 50° and 90°. To find an explanation of these facts, one has to consider the effects produced by a change in temperature in method 2. It is evident that two factors are changed here simultaneously by a change of temperature, first, the size and orientation of the gradient, second, the stress applied to the zone of formation. If X in figure 4 is the crystal pulled out of the liquid metal L, M the perforated mica-plate floating on L, R the ring-nozzle cooling the crystalline thread by an air blast, the gradient of temperature between X and L depends on the difference of temperature between these two points, the arrange-

ment of R and the speed of pulling the thread.   As soon as only the temperature of L is changed the position of the zone of crystallization changes also (for instance, it may be for a low temperature at C_1, for a higher one at C_2); hence, also, the weight which hangs on X and therewith the stress applied to the zone of formation.   The observation that for small orientations only low temperatures can be used (which means that the axis of maximum contraction can be forced to grow in the direction of the tension only if it is very small) is therefore in perfect agreement with the observations by the authors.   •

The influence of the orientation and the size of the gradient is independent of the stress but can only be effective without stress.   This may explain why there exists also a lower limit for the temperature below which a crystal of a certain orientation cannot grow.   Here the stress is so small, that its influence on the crystal is almost negligible.   The change in temperature means then nothing else than a change of the gradient of temperature in the zone of crystallization, which depends entirely upon the apparatus and is hard to define exactly in the Czochralski arrangement.

In conclusion, the authors would like to state that the experiences made in the study of growth of metal single-crystals reveal the fact that the strain applied to the crystal "in statu nascendi" has an important bearing upon its final orientation, which leads to serious doubt concerning the actual perfectibility of crystals grown under such circumstances.   Experience shows that the chosen orientation is that in which the work done by the applied forces is a minimum, but we know that this minimum in all the described methods is far from zero.   Hence any method of crystal growth which does not eliminate these strains appears to have a serious fault in adding a fundamental distortive force to the building forces of the growing crystal, which should be reflected to some degree in the investigations carried out with them.   This may partially account for deviations from the Voigt-Thomson law that have been observed by various investigators (f.i., for the Peltier effect on Bi by Bridgman) especially in case of two of the most delicate crystals, Bi and Sn.[2]   The fact that other functions like the conductivity of these crystals follow the $\cos^2$-law does not necessarily contradict, because the mechanism of electric conductivity and thermoelectricity is so much different that the same basal imperfectibility may affect these processes to a different degree.

This investigation is being continued and more quantitative results will be published soon.

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HIGHER SPARK SPECTRA OF NEON AND ARGON IN THE EXTREME ULTRA-VIOLET

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The first spark spectra of neon[1] and of argon[2] were reported last year. Using conditions of controlled electron excitation it was possible to bring out arc and first spark spectra of these and other gases. With such a discharge it was impossible to get spectra of higher stages of ionization beyond the first spark spectrum even though the voltage was raised to more than double the theoretical voltage for doubly ionizing the atoms. This year an electrodeless ring discharge has been used very successfully in bringing out the extreme ultra-violet spectra of higher stages of ionization of these gases. The discharge tube was a tube of glass or quartz 2 inches in diameter, wound with 12 turns of heavy copper wire. This was attached to the slit of the vacuum spectrograph by a side tube between the middle pair of turns, so that the light observed came from the region of most intense ionization. Power was usually supplied by a 3.5 kw. mercury gap oscillator, though a smaller 0.25 kw. outfit was used at times, both at about 300,000 cycles. Gas was circulated through the apparatus and purified by a misch metal discharge tube as in the previous investigations.[3] The arrangement of the spectrograph was the same as previously, but the focus was somewhat improved by the use of Schumann plates on thinner glass, permitting greater bending to the focal circle.

When a gas such as neon was excited the strongest lines were those due to Ne III, with Ne II and Ne IV less intense and Ne I practically missing, indicating complete single ionization and much multiple ionization, the higher stages of it by cumulative action. In all photographs lines of oxygen