The Crystal of Tungsten obtained by Deposition

By

Takeo Fujiwara

(Received March 4, 1930)

Abstract

The tungsten deposits were made on a tungsten ingot of square cross section by passing sufficient electric current through it in an atmosphere of wet hydrogen, and the same kind of depositions were also made on an electrolytically etched surface of a single crystal of tungsten and on the tungsten crystals previously deposited in hexagonal prismatic forms. The crystals thus made were examined by means of microphotographs and X-rays.

In the first case most of the deposited crystals of tungsten presented the form of a hexagonal prism or of a rhombic dodecahedron or of granules and their clusters. The crystals thus deposited in the form of a hexagonal prism or of a rhombic dodecahedron were so formed that they would be rhombic-dodecahedrons with crystal faces whose indices are (110), but most of them took the prismatic form with an equiangular hexagonal cross section and a pyramidal top formed by the crystal faces (110), by taking one of the trigonal axes of the crystal, in the direction parallel to the axis of the prism. The single crystals thus obtained by deposition were not always perfect and sometimes a lamellar structure composed of many parallel thin sheets of the crystal, which were separated from each other by certain narrow intervals, were detected at some part of the crystal. In the case of the specimens composed of granules and their clusters, they were composed of somewhat large micro-crystals arranged rather at random.

When the deposition was made on an electrolytically etched surface of the single crystal of tungsten or on the tungsten crystal previously deposited in the form of a hexagonal prism as stated before, most of the crystals thus formed by new deposition took on the same form—dodecahedron or hexagonal prism—as the mother crystal by being enveloped also by the crystal faces (110), and one of their crystal faces (110) was so deposited on the same kind of crystal face of the mother crystal that the lattice structures of the two crystals were united to make a unique lattice.

Introduction

The arrangement of the crystals in deposited metals has already

been studied by many investigators. The electrolytically deposited metals[1] are composed of micro-crystals which have a tendency to arrange themselves in a regular manner, and the sublimated metal in vacuo[2] which was formerly supposed to be a single crystal is not necessarily composed of such a single crystal. H. Alterthum[3] was the first to study the tungsten deposits, and he deposited the tungsten on a tungsten ingot of square cross section by passing sufficient electric current through it in an atmosphere of hydrogen saturated with water vapour at room temperature. According to his opinion, if a tungsten ingot is heated by an electric current in an atmosphere of wet hydrogen tungsten is removed from the hotter part as WO_2 and is deposited as metallic tungsten on the colder part. This deposition is marked when the hydrogen is saturated with water vapour at room temperature. R. Hayami[4] has found fine crystals having the form of a rhombic dodecahedron in such deposits with the microscope.

In the present experiment, tungsten was deposited, by Alterthum's method, on the tungsten ingot, on the electrolytically etched surface of a tungsten single crystal and on the single crystal of tungsten obtained by deposition, and the tungsten crystals thus obtained were examined by means of micro-photographs and X-rays.

Materials and Experimental Method

Numerous tungsten crystals of considerable size were deposited on many tungsten ingots of square cross section by the method stated above, and then the same kind of depositions were made on the electrolytically etched surface of an ingot composed of several single crystals of tungsten, and on the previously deposited crystals of tungsten. In the first case the deposited crystals present the appearance of prismatic forms with natural crystal faces, dodecahedrons or granules and their clusters as seen as in Fig. 1 in Plate I, which is a micro-photograph of the tungsten deposits on the surface of a tungsten ingot. When the tungsten is deposited on a comparatively large crystal on

1 H. Hirata: These Memoir, **10**, 95 (1926);
„ **11**, 429 (1928);
S. Tsuboi: These Memoirs, **11**, 271 (1928);
„ **12**, 209 (1929)
2 T. Yamamoto: These Memoirs, **11**, 39 (1928)
3 H. Alterthum: Zeits. Phys. Chem. **110**, 1 (1924)
4 R. Hayami: Mazda Kenkyu-Jiho, **1**, 199 (1926)

the electrolytically etched surface of a tungsten ingot or on the surface of the tungsten crystals obtained by previous deposition, most of the crystals newly deposited take the forms of prisms or of dodecahedrons. The micro-photographs of typical crystals thus obtained are shown in Plates I, III and IV.

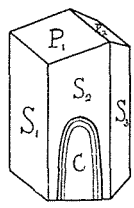
The angular distribution of the normals to the crystal faces of each crystal thus obtained was measured by the optical goniometer, and then the Laue-photographs were taken by using parallel or convergent X-rays, as the case might be, which radiated from the focus on the Mo-target of a Coolidge tube. Generally the photographic plates were placed perpendicularly to the beam of the X-rays. The potential applied to the tube was about 40 K. V. s, the current passed through, 10 milliamperes, and the duration of the exposure of each photograph varied from 25 to 60 hours according to the specimen. Some of the Laue-photographs thus taken are shown in Plates I, II and III.

Discussion of the Results

A. Crystal deposited in Prismatic Form

All the prismatic tungsten crystals deposited on the surface of a tungsten ingot take the form of a hexagonal prism, and their tops are truncated by two or three planes so as to form pyramids; and some of the crystal faces forming the sides of the prism have cavities at their lower parts, as shown in Fig. 1, where the cavity is denoted by C, and the planes forming the sides of the prism and the pyramid are denoted by S_1, S_2, S_3, S_4, S_5, S_6, P_1, P_2 and P_3 respectively.

Fig. 1



In the examination of these prismatic tungsten deposits, first the angular distribution of the normals to various faces was determined by using an optical goniometer which was essentially the same as that used by B. Fujita[1] in his research on the structure of the etched surface of the metallic crystals of Al and Zn. But in the present experiment a microscope with low magnification was used for observing the reflected light, and the angle was measured within a limit of accuracy of $\pm 2^\circ$ Next the crystallographic axes were determined by treating a Laue-photograph, taken with that specimen by using convergent X-rays[2], with

1 B. Fujita: These Memoirs, **12**, 159 (1929)
2 T. Fujiwara: These Memoirs, **11**, 283 (1928)

the crystallographic globe devised by Prof. U. Yoshida[1]. Then the indices of the crystal faces formed by deposition were obtained by comparing the orientation of the normals of the crystal faces with that of the crystallographic axes thus determined. About twenty-five crystals of the form of hexagonal prisms were examined by this method.

It was found in the above way that every one of the crystals of the hexagonal prism was a perfect single crystal which was enveloped by the crystal faces of the indices (110) at its side and at its pyramidal top, so that one of the trigonal axes of the crystal was oriented in the direction parallel to the axis of the prism. By illuminating with parallel light, the wall of the cavity on a side of the prism was found to be composed of many parallel layers of the crystal faces having the same indices as the side of prism to which the cavity belongs, as if these parallel layers were piled up in a stepwise manner, as seen in Fig. 4 in Plate I.

Some of the micro-photographs and the Laue-photographs taken are reproduced in Figs. 2, 3, 4 and 5 in Plate I, where Figs. 2 and 3 are the micro-photographs of the crystals of the hexagonal prism form and Fig. 4 is an enlarged photograph of the cavity shown in Fig. 2 in Plate I. Fig. 5 in Plate I is the Laue-photograph taken with the crystal shown in Fig. 2, Plate I, by using convergent X-rays, and in this case the beam of incident X-rays was made to strike the crystal perpendicularly to the axis of the prism and to a photographic plate. The arrow in the same figure indicates the direction parallel to that axis of the prism. The indices of the crystal faces of the crystal shown in Fig. 2, Plate I, are tabulated in Table I, where the notations of the crystal faces are just the same as those used in Fig. 1, and the axis of the prism was taken as a vertical axis. In this table ϕ represents the angle between the direction of the axis of the prism and the normal to a crystal face, and θ the angle of inclination of the normal to a crystal face against the normal to the standard crystal face S_1. The result was just the same in both crystals shown in Figs, 2 and 3 in Plate I, i. e. the indices of all the crystal faces forming the sides and the pyramidal top of the hexagonal prism were (110) in both cases.

---

1 U. Yoshida: Japanese, J. Phys., **4**, 133 (1927); S. Takeyama: These Memoirs, **12**, 257 (1929)

In all Laue-photographs taken with the caystals deposited in the prismatic form with hexagonal cross section by using convergent X-rays, there were always some spectral lines with fine structures, as seen in some lines in Fig. 5 in Plate I. The appearance of such a spectral line with a fine structure is slightly different from that of the doublets of K lines of molybdenum caused by an ordinary perfect single crystal.

In order to examine the origin of such fine structure two photographic plates were placed perpendicularly to the undeflected beam of X-rays at different distances from the specimen, and two Laue-photographs were taken by using convergent X-rays at the same time. The typical photographs taken in this way are shown in Figs. 6 and 7 in Plate I, where the distances of the photographic plate from the specimen are 2.03 and 2.95 cms. respectively.

Table I

No. of crystal face		By optical method	By X-ray analysis	Indices of the crystal faces
S_1	Φ	90°	90°	$10\bar{1}$
	θ	0°	0°	
P_1	Φ	34°	35°	110
	θ	30°	30°	
S_2	Φ	90°	90°	$01\bar{1}$
	θ	60°	60°	
S_3	Φ	90°	90°	$\bar{1}10$
	θ	120°	120°	
P_2	Φ	34°	35°	011
	θ	151°	150°	
S_4	Φ	90°	90°	$\bar{1}01$
	θ	180°	180°	
S_5	Φ	90°	90°	$0\bar{1}1$
	θ	240°	240°	
P_3	Φ	36°	35°	101
	θ	270°	270°	
S_6	Φ	90°	90°	$1\bar{1}0$
	θ	300°	300°	

In these photographs it can be seen that the distribution of the spots and the spectral lines is, in general, similar in both cases, and that Fig. 7, in Plate I is an enlargement of the other in the ratio of the respective distances of the photographic plates from the specimen. Though, in the case of each spectral line which has a fine structure, its distances from the other spectral lines and its length are enlarged in the photograph taken at a greater distance, yet its total width, the number of its components, the distances between any two components and their intensity-distribution are nearly the same in both photographs, taken at different distances from the specimen. Thus it was easy to find any corresponding components in two corresponding spectral lines in two photographs taken at different distances.

Fig. 1 in Plate II, is an enlarged photograph of the spectral lines I and II in Fig. 7 in Plate I, and Fig. 2 in Plate II is an enlarged photograph of the spectral lines I and II in Fig. 6 in Plate I.

By measuring, with Hilger's travelling micrometer, the distances of the components of all the spectral lines from the intense nucleus of the central spot which is impressed by the undeflected beam of X-rays on the photograph, the glancing angle of the X-rays to various atomic planes and consequently the kinds of these spectral lines and the indices of the atomic planes to whose reflections the spectral lines are due, were determined as in the former method;[1] then the distance between any two consecutive components of the spectral lines were also obtained. For the value of the wave length of the $K_{\alpha'}$, K_{α}, K_{β} and K_{τ} lines $\lambda_{\alpha'}=0.712 \times 10^{-8}$ cm., $\lambda_{\alpha}=0.708 \times 10^{-8}$ cm., $\lambda_{\beta}=0.631 \times 10^{-8}$ cm. and $\lambda_{\tau}=0.620 \times 10^{-8}$ cm.[2] were respectively used. Some of the results thus obtained are tabulated in Tables II, III and IV, which deal respectively with the spectral lines denoted by I, II and III, Fig. 6 in Plate I. In these tables the indices of the atomic planes by whose reflections the individual spectral lines are caused, are represented in brackets. In each table the notations l_1, l_2, l_3, etc., and L_1, L_2, L_3 etc., in the 1st and 3rd columns, represent the numbers of the components of the spectral lines in two corresponding photographs; and l_1, l_2, l_3 etc. correspond to the photograph taken at the greater distance. These notations of the components of the spectral lines are the same as those used in the enlarged photographs of Figs. 1 and 2 in Plate II. The lines tabulated in the same horizontal row are the corresponding components in two corresponding photographs, the distances between any two consecutive components are represented in the 2nd and the 4th columns of each table in mm. and the symbols α', α, β, etc, in the 5th column show that the components in the corresponding horizontal rows are the spectra of $K_{\alpha'}$, K_{α} or K_{β} lines respectively.

From the table it can be seen clearly that the distance between any two components belonging to the same spectral line in the first photograph is just the same as that between the corresponding components in the second photograph within the limit of experimental errors. It is also found from the tables that the distance between any two components belonging to two different spectral lines and which

1 T. Fujiwara: loc. cit.

2 W. Duane and Kang-Fuh-Hu: Phys. Rev., **9**, 489 (1918);
„ **14**, 369 (1919)

Table II, Line I, (321)

Distance of the plate from the specimen, a_1=2.03cms.		Distance of the plate from the specimen, a_2=2.95 cms.		Kinds of the spectral lines	Ratio of the distances between any two components [a_2/a_1=1.45]
No. of the component	Distance between two consecutive components	No. of the component	Distance between two consecutive components		
l_1		L_1		α′	
	0.11		0.11		(1–3)=1.46
l_2		L_2		α′	
	0.02		0.08		(2–4)=1.53
l_3		L_3		α	
	0.11		0.12		
l_4		L_4		α	
	0.20		0.21		
l_5		L_5		α	
	0.11				
l_6		faint	0.25	α	
	0.15				
l_7		L_7		α	
	1.75		2.71		
l_8		L_8		β	(3–8)=1.42
	0.11		0.10		
l_9		L_9		β	(4–9)=1.41
	0.21				
l_{10}		faint	0.44	β	
	0.23				
l_{11}		L_{11}		β	

Table III, Line II, (310)

Distance of the plate from the specimen, a_1=2.03 cms		Distance of the plate from the specimen, a_2=2.95 cms		Kinds of the spectral lines	Ratio of the distances between any two components [a_2/a_1=1.45]
No. of the component	Distance between two consecutive components	No. of the component	Distance between two consecutive components		
l_1		L_1		α	
	0.11		0.12		
l_2		L_2		α	
	0.16		0.15		
l_3		L_3		α	
	0.07		0.08		
l_4		L_4		α	
	0.10		0.10		
l_5		L_5		α	
	0.10		0.10		
l_6		L_6		α	(2–7)=1.42
	1.00		1.60		
l_7		L_7		β	

seem to be caused by the same atomic layer is larger in the 2nd photograph than in the other, and that the ratio of these distances in two photographs is nearly the same as that of the distances of the corresponding photographic plates from the specimen, as shown in the last column of each table. Thus it can be understood clearly, from the facts stated above, that even with a monochromatic X-ray the spectral lines can have a complex structure due to the reflection of the X-ray from the parallel atomic planes in different thin sheets of crystal layers arranged parallel at certain small intervals. Moreover the facts above stated teach us that the tungsten crystals examined are not entirely perfect, and at least at some part of them the crystal is composed of several thin sheets of crystal layers arranged parallel at certain small intervals, even though the atomic arrangement in all the sheets belongs to a unique lattice of the body-centered-cube of the tungsten crystal.

Table IV, Line III (211)

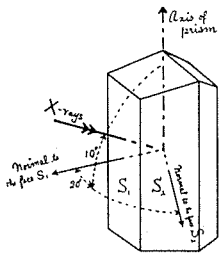
Distance of the plate from the specimen $a_1=2.03$ cms.		Distance of the plate from the specimen $a_2=2.95$ cms.		Kinds of the spectral lines
No. of the component	Distance between two comsecutive components	No. of the component	Distance between two consecutive components	
I_1		L_1		α
	0.06		0.07	
I_2		L_2		α
	0.08		0.09	
I_3		L_3		α
	0.11		0.09	
I_4		L_4		α
	0.16		0.16	
I_5		L_5		α
	0.06		0.08	
I_6		L_6		α

The correctness of this consideration will be seen from the appearance presented by the inner surface of the cavity as shown in Fig. 4, Plate I. This was also confirmed by a Laue-photograph taken with the specimen by using parallel X-rays. Though the distribution of Laue-spots in this case was explainable by considering that the spots were due to a single crystal having the body-centered cubic lattice[1], yet the shape of every spot was different from that of the ordinary one due to a perfect single crystal. As seen in Fig. 3 in Plate II, each one of most of the Laue-spots obtained in the present case consists of a number of smaller fragments separated by some weak

1 M. Majima and S. Togino: Sci. Papei, Inst. Phys. and Chem. Tokyo, **7**, 259 (1927)

and diffuse narrow dark lines. The photograph shown in Fig. 3 in Plate II, was taken by sending the X-rays in the manner shown in Fig. 2, and a photographic plate was set perpendicularly to the beam of X-rays about 2.8 cms. behind the specimen.

Fig. 2



B. Crystal deposited in the Form of a Dodecahedron

The tungsten deposits made on the tungsten ingot and presenting the appearance of a dodecahedron were examined in the same way as the former case, and it was found that the indices of all the crystal faces of such dodecahedrons were (110) as in the case of the hexagonal prism. In most of them the actual form of the crystal was not a regular rhombic-dodecahedron owing to unequal growth of the crystal faces, and the crystals forming the regular rhombic-dodecahedron were generally small in size and few in number. The Laue and microphotographs taken with these crystals are reproduced in Figs. 1, 2 & 3 in Plate III, where Fig. 1 was taken by using convergent X-rays, and Fig. 2 by using parallel X-rays. In Fig. 2 in Plate III we can detect clearly that each Laue-spot consists of small fragments separated by some weak and diffuse narrow lines as seen in Fig. 3, Plate II. This fact seems to indicate that the crystal is not entirely perfect, as in the case of the hexagonal prism, but that at least at some part of it the crystal is composed of several thin sheets of crystal layers arranged at certain small intervals.

So far as is known, from the present investigation, all tungsten deposits, which have a regular crystal form, belong to either the hexagonal prism or the rhombic dodecahedron category. Though in outward appearance these two crystal forms are entirely different, yet they are both bounded by the same crystal faces having indices of (110), and the hexagonal prism is nothing but a modified form of the dodecahedron, obtained by a predominant growth of the crystal in the direction of the trigonal axis which is parallel to the crystal faces forming the sides of the prism.

Finally, powder photographs of hexagonal prism and of dodecahedron crystals were taken, and it was ascertained that they have the

body-centered cubic structure, as was observed by other authors.[1]

C. Granular Crystals and their Clusters

In the case of granular crystals and their clusters which were deposited on the tungsten ingot, it was found, by taking the Laue-photographs, that they are composed of somewhat large micro-crystals oriented rather at random; some of their micro-photographs are shown in Figs. 4 & 5 in Plate III. In some of the clusters somewhat large micro-crystals arranged in a regular manner, having one of their trigonal axes as their common axis and rotated several degrees about it, were found. The micro-and Laue-photographs of this cluster are shown in Figs. 6 & 7 in Plate III, where the latter was taken by using convergent X-rays.

D. Crystal deposited on Etched Crystal-faces of a Single Crystal of Tungsten

First the tungsten ingot composed of several single crystals oriented in different directions were etched electrolytically in a 10% solution of sodium carbonate with current density of 0.15 amp./cm^2, and the indices of the crystal-facets thus developed by etching were obtained by comparing the orientation of the normals of each facet with that of the crystallographic axes of the single crystal. The former was determined by using the optical goniometer mentioned above, and the latter by means of the rotating crystal method devised by S. Takeyama.[2] It was found that the indices of the crystal facets developed by etching were (110), and this is concordant with those observed by previous investigators[3] with the microscope.

Next the deposition was made on the etched crystal surfaces of known orientation of the crystal facets. Most of the crystals thus obtained present the form of the prism or the dodecahedron, and they lie on the surface of the mother crystal or stand at its edge, as seen in Figs. 8, 9 and 10 in Plate III, where Figs. 9 and 10 are the

---

1 P. Debye: Phys. Z. S. **18**, 483 (1917)
A. W. Hull: Phys. Rev. **18**, 88 (1921)

2 S. Takeyama: These Memoirs, **11**, 469 (1928)

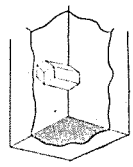
3 I. Langmuir: Phys. Rev., **23** 374 (1923)
R. Hayami: loc. cit.
M. Mayeda: Mazda-Kenkyu-Jiho, **4**, 9 (1929)

enlargements of some parts of the photograph shown in Fig. 8 in Plate III.

The crystals thus obtained were also examined in the same way as in the former cases, and it was found that all of them are formed with crystal faces whose indices are (110); and that they are entirely the same kinds of hexagonal prism or dodecahedron as in the former cases. It was also found, by comparing the orientations of the crystallographic axes of the mother and the new crystals, that the crystal lattice of the latter is nothing but the extension of that of the former, so that they form an entirely unique crystal lattice of tungsten atoms. This relation will be seen clearly in Figs. 1 and 2 in Plate IV. Fig. 1 in Plate IV was taken by illuminating the surface of the specimen from one direction and Fig. 2, Plate IV by illuminating the same surface from another direction. It can be seen from these photographs that all crystals deposited in the same domain bounded by a crystal-boundary have certain parallel crystal faces which do or do not shine brightly at the same time as the back ground.

The writer was able to observe a very interesting case of the growth of the new prismatic crystal formed by deposition on an edge of a mother prismatic crystal, as shown in Fig. 3. From the optical and the roentgenographical examination described before, he was able to ascertain that the new crystal was also bounded by crystal faces (110), and that the lattice structure of the new crystal was nothing but a unique extension of the lattice structure of the tungsten atoms in the mother crystal.

Fig. 3



The phenomenon that the channels at the boundaries of the etched crystal become deeper as the deposition proceeds, and that the depositions become marked at the edges, as seen in Figs. 1 and 2 in Plate IV, is explainable by Alterthum's hypothesis. The tungsten removed from the inner part of the ingot through the boundary is liable to be deposited on the cooler parts such as edges and boundaries. This phenomenon has also been seen in the crystals deposited in a prismatic form, which have cavities at their lower parts and sharp edges formed by two crystal faces.

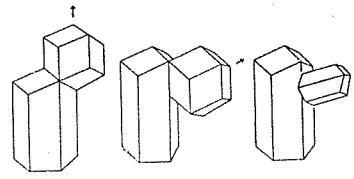
Finally the deposition was made on a single crystal whose surface had previously been cleaned by electron bombardment, and entirely the same results were obtained as in the case of the electrolytically etched surface.

E. Crystal deposited on a Mother Tungsten Crystal deposited in a Prismatic Form

Now a new deposition as in the former cases was made on the mother crystals formed previously by deposition in the prismatic form with hexagonal cross sections, and about twenty five crystals thus deposited were examined by the same method as that previously described. In this case several X-ray photographs were taken with different parts of each specimen, and the relative crystallographic orientation of the different parts of the specimen were determined. The micro-photographs of several different types of the depositions are shown in Figs. 3, 4, 5, 6 and 7 in Plate IV.

It was found that all the new crystals thus obtained by deposition on the mother crystals in the form of the hexagonal prism were the same kind of crystals as the mother crystals, and the new crystals took the form of the rhombic dodecahedron or of the hexagonal prism as was described before; the lattice structure of the new ones is nothing but a unique extension of that of the mother crystal. This point will be seen more clearly in Fig. 4. Among the new crystals those which took the hexagonal prism form by the growth of six crystal faces (110), which are parallel to one of the trigonal axes, in the direction parallel to that axis, were predominant. The arrow in Fig. 4 indicates the direction of such growth.

Fig. 4



Thus so far as the writer's investigation goes, all tungsten crystals deposited by the method before stated are bounded by crystal faces of the indices (110). This is concordant with the result obtained theoretically by M. Yamada[1].

In conclusion, the writer wishes to express his sincere thanks to Prof. U. Yoshida, of Kyoto Imperial University for the interest he has taken in this research. He is also very grateful to Mr. M. Mayeda

1 M. Yamada: Sci. Rep. Tohoku Imp. Univ., **13**, 53 (1924)

of this laboratory for his kind help in arranging the apparatus with which the deposition was done.

Research Laboratory,
Tokyo Electric Co.,
Kawasaki, Kanagawaken,
Japan.

Plate I

Fig. 1

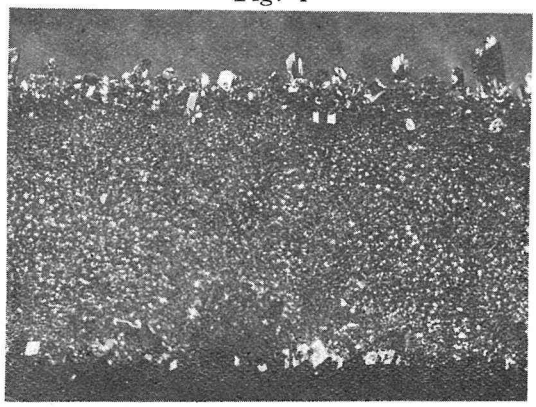
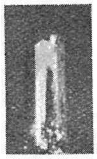
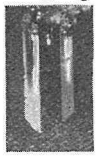


Fig. 2



X 25

Fig. 3



X 25

Fig. 4

X 48

Fig. 5

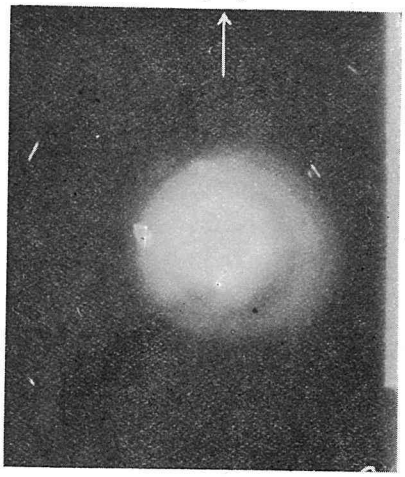


Fig. 6

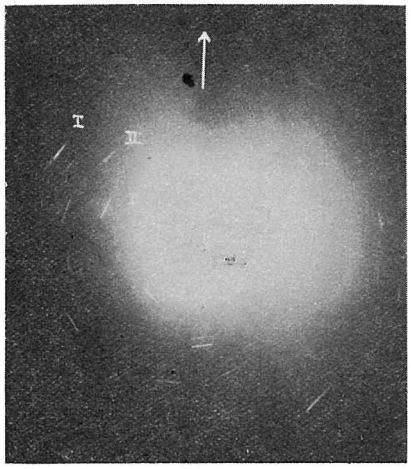


Fig. 7

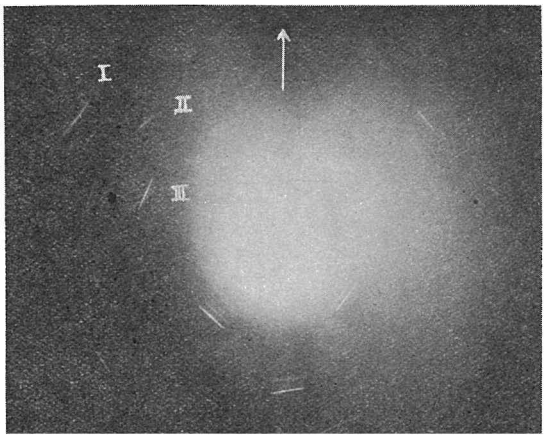


Plate II

Fig. 1

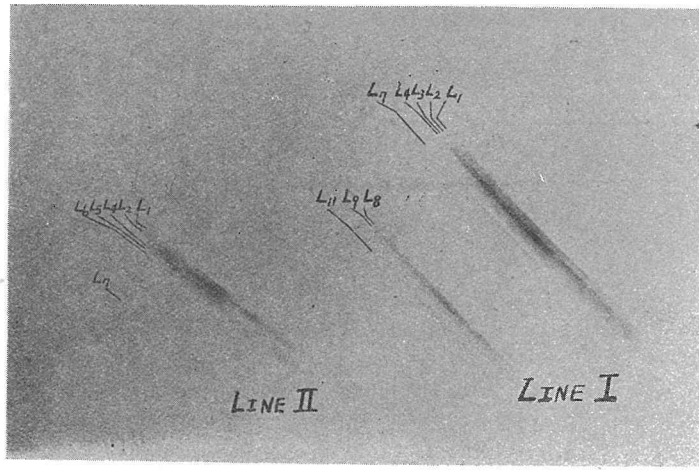


Fig. 2

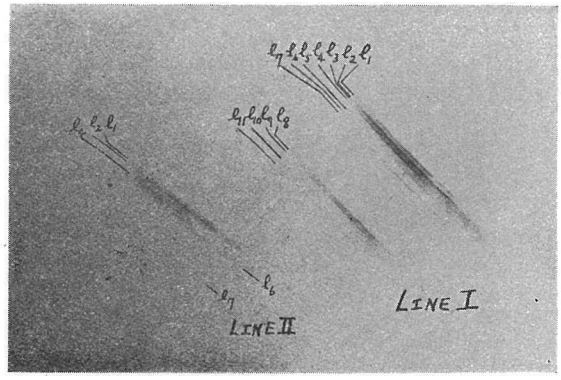


Fig. 3

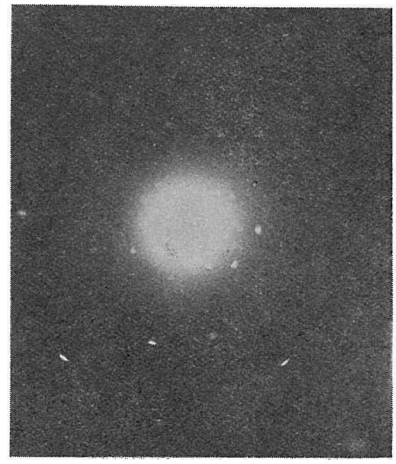


Plate III

Fig. 1

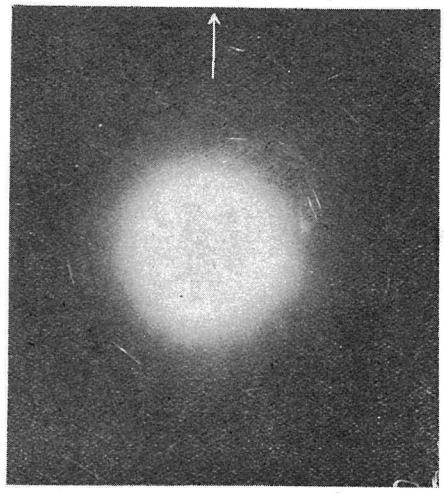


Fig. 2

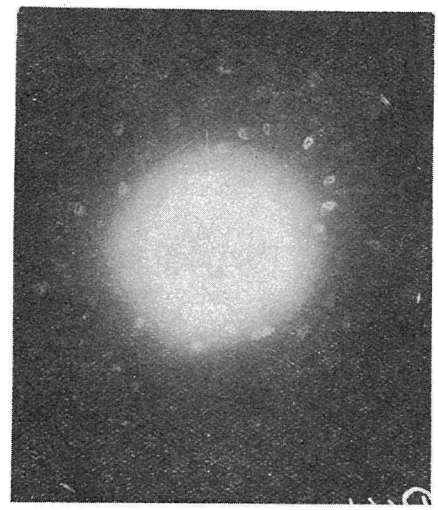
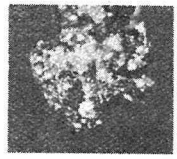


Fig. 3

X 25

Fig. 4



X 25

Fig. 5

X 20

Fig. 6

X 20

Fig. 7

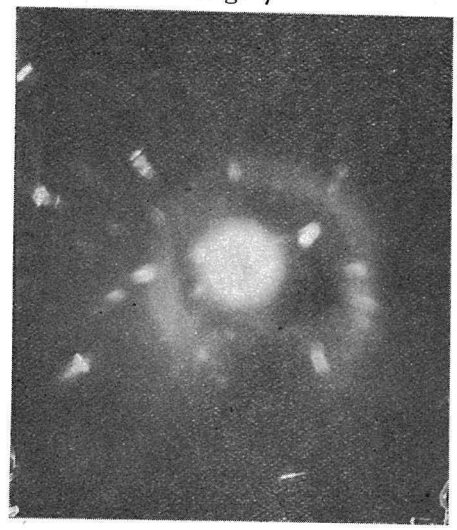
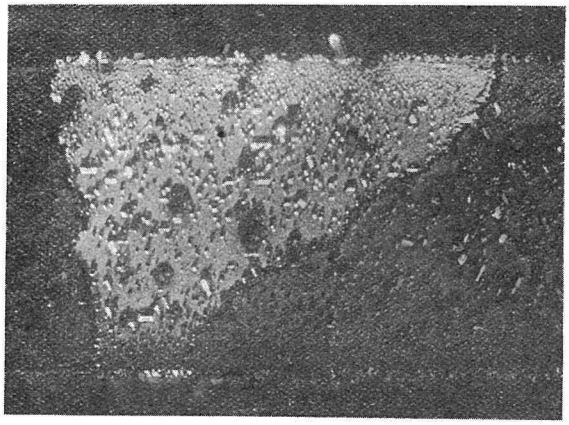


Fig. 8



X 8

Fig. 9

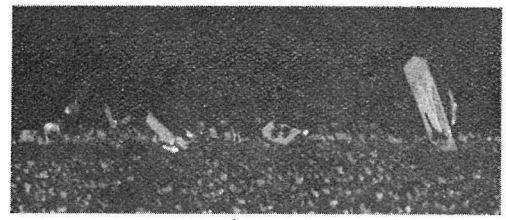


Fig. 10

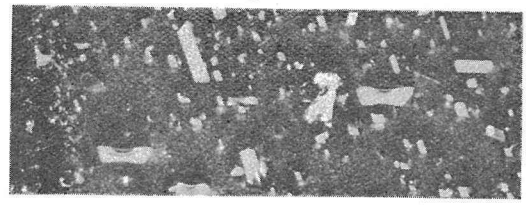
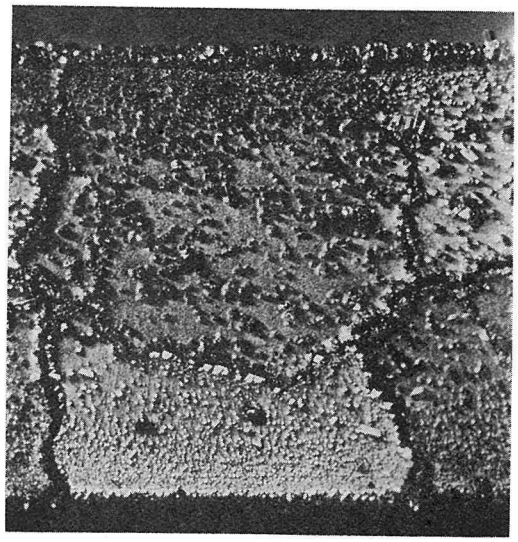


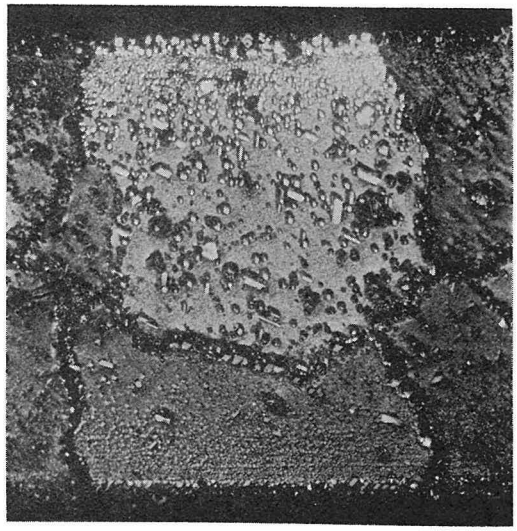
Plate IV

Fig. 1



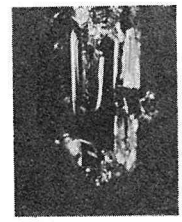
X 12

Fig. 2



X 12

Fig. 3

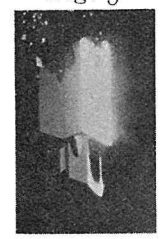


X 20

Fig. 4

X 20

Fig. 5



X 20

Fig. 6

X 25

Fig. 7

X 25