On the Crystalline Configurations of Electrolytic Lead deposited from Nitrate Solutions[1]

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Abstract

The arrangement of the micro-crystals in electrolytic specimens of lead, deposited from nitrate solutions was examined with X-rays by the Laue method. From the diffraction patterns obtained, it was confirmed that the micro-crystals of lead have a tendency to be electrolytically deposited in a fibrous way, with one of their [211] axes arranged parallel to a definite common direction, as was the case in the experiments previously made by other investigators with various electrolytes of different chemical composition. But the present examination has shown that in certain respects, *conclusions drawn from previous experiments must be reconsidered; e. g., the direction* of the maximum growth of deposited lead and the relative orientation of the micro-crystals in the specimen.

Introduction

The crystalline configurations of electrolytic lead have already been examined with X-rays by Frölich, Clark and Aborn,[2] and also by Hirata, Tanaka and Komatsubara.[3] As a consequence of these investigations, it has become an accepted fact that the micro-crystals of lead tend to be deposited electrolytically, having one of the normals to their (211) faces in common. But in some respects, the conclusions drawn from these two investigations do not harmonize with each other. Frölich and his co-operators, who made their experiment with electrolytic specimens of lead deposited from the solutions of perchlorate, fluorate, fluosilicate and others, have made no report on the direction of the maximum growth of these electrolytic specimens, which was supposed from the universal argument of Glocker and Kaupp[4] to coincide with the direction of the fibrous axis: while the experimental results obtained by Hirata and his co-operators with the electrolyzed lead deposited from several acetate solutions, showed that though these two directions described above are crystallographically equivalent, they do not always coincide with each other, as was previously found by the same investigators[5]

1. This paper was read at the meeting of the Institute for Metals of Japan, April, 1938.
2. Zeits. f. Elektrochem., **32**, 295 (1926).
3. Bull. Chem. Soc., Japan., **10**, 391 (1935).
4. Zeits. f. Phys., **24**, 121 (1924).
5. H. Hirata and Y. Tanaka; These Memoirs, A, **15**, 9 (1932).

with some electrolytic copper specimens. To make clear the cause of such disharmony, more experimental data may be needed with regard to the crystalline configuration of electro-deposited lead.

The writers were therefore led, by way of supplement to the aforesaid X-ray investigations, to repeat essentially the same experiment with electrolytic lead deposited from its nitrate solutions. Utilizing the heterogeneous X-rays emitted from the molybdenum anticathode, the Laue figures were taken on photographic plates which were always placed perpendicularly to the incident beam at a distance of 3 cms. behind the specimens. The experimental results thus obtained are briefly described below.

Specimens

In the present experiment, specimens of electro-deposited lead prepared by Mr. T. Ishida at the Industrial Research Laboratory of Osaka Prefecture were examined. We are not precisely informed of the procedure adopted in the electrolysis at the Industrial Research Laboratory, but it is known that the specimens were deposited at the room temperature (20°C) with a constant current density (1 amp./1 dm.^{2}), a sheet of copper 4 cms. × 2.5 cms. in area being used as cathode. The conditions under which these specimens were prepared are given in the following Table I.

Table I.

Number of Specimens	Electrolyte	Pot. applied to the electrodes (volts)
A B	$Pb(NO_3)_2$ HNO_3	0.18～0.17
C D E	$Pb(NO_3)_2$ $NaNO_3$	0.14～0.15

As a result of the electrolysis, the lead specimens came to appear in a foliated form 0.5～1.5 mms. in diameter, having the largest surface parallel to the stem of the foliage (i. e., to the direction of maximum growth of deposited lead). The micro-structure of some of these specimens is reproduced in Figs. 1 and 2, Plate I.

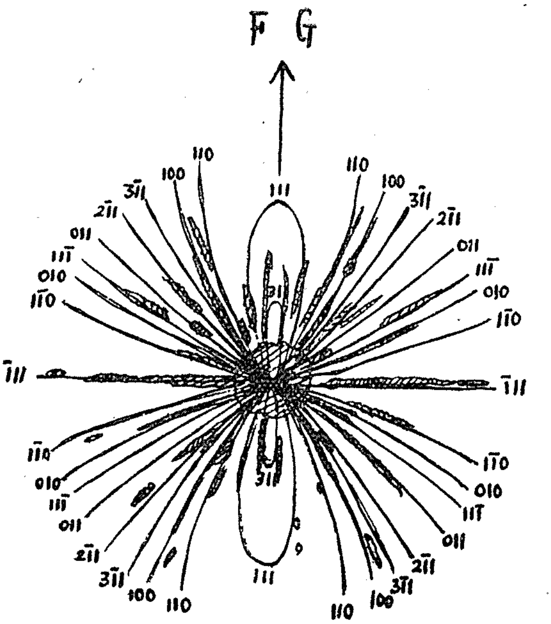
Experimental Results

With a fragment of the specimens above mentioned, the diffraction parttern was taken, by setting its foliated surface perpendicular to the incident X-ray beam. The diffraction patterns thus obtained are reproduced in Figs. 3, 4, 5, 6 and 7, Plate I. To take these diffraction patterns, the stems of the foliated specimens were always placed in the vertical direction as is represented by the arrow G. As will easily be seen in these figures, the diffraction phenomena investigated with all the specimens were found to be essentially the same: Each one of the specimens gave rise to a diffraction pattern consisting of a set of short radiating bands. This shows without doubt, that the lead specimens under examination are of a fibrous nature.

Having confirmed this point, the writers tried to determine the fibrous axis in these specimens. This could be done by the aid of an improved Yoshida's crystallographic globe.[1]

In the annexed Figs. 8, 9, 10, 11 and 12, the full lines represent diagramatically the theoretical positions of the prominent radiating bands, which are expected to appear when a lead crystal is rotated around a direction parallel to one of its [211] axes (represented by the arrow F), and the incident X-ray beam is made to strike this crystal taking the direction perpendicular to the axes of rotation mentioned above. The shaded parts of the same figures are copies of the original plate of Figs. 3, 4, 5, 6 and 7. To transcribe these copies, the original plates of Figs. 3, 4, 5, 6 and 7 were respectively placed upon Figs. 8, 9, 10, 11 and 12, in such a way that the direction represented by F and the centre of the central spot in both figures coincide. As may be seen from Figs. 8, 9, 10, 11 and 12, the agreement between the calculated curves and those observed is satisfactory. Consequently, it seems legitimate to presume that the specimen giving the diffraction patterns reproduced in Figs. 3, 4, 5, 6 and 7 are in the main at least, composed of micro-crystals having one of the [211] axes in common.

Fig. 8



1. U. Yoshida; Japanese J. Phys., 4, 133 (1927), and S. Takeyama; These Memoirs, A, 11, 467 (1928).

Fig. 9

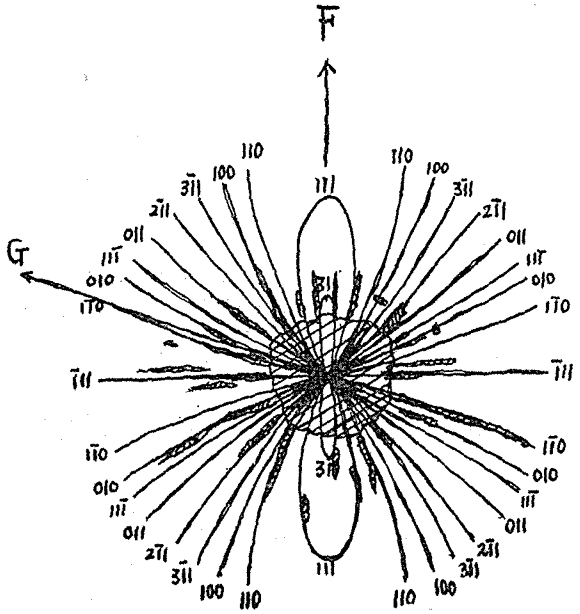


Fig. 10

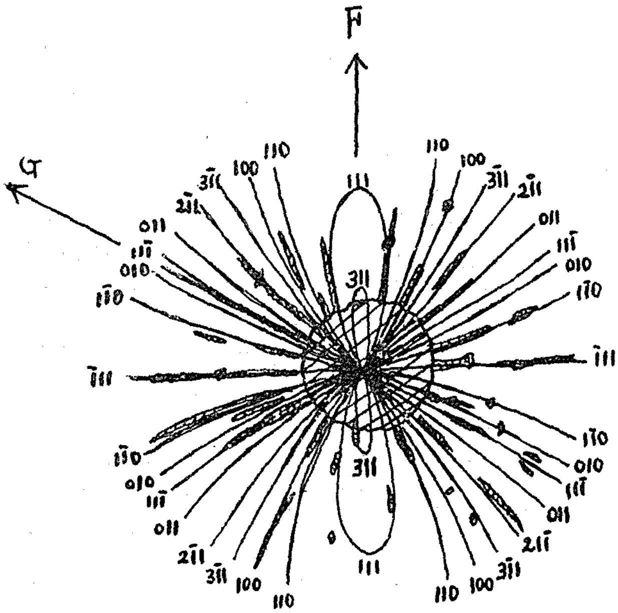


Fig. 11

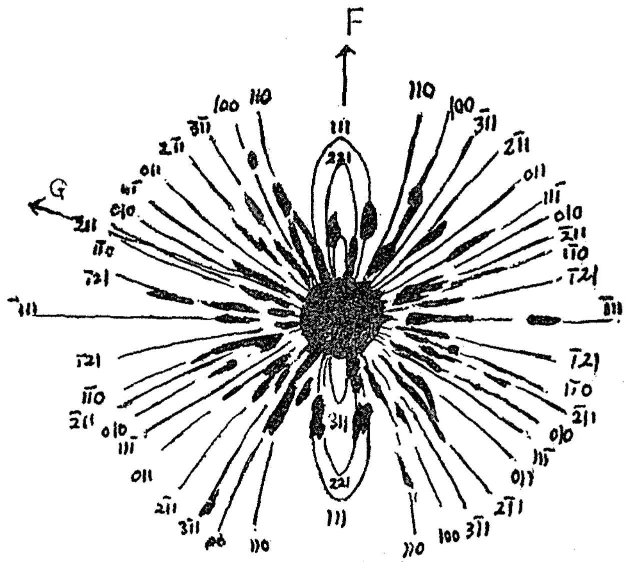
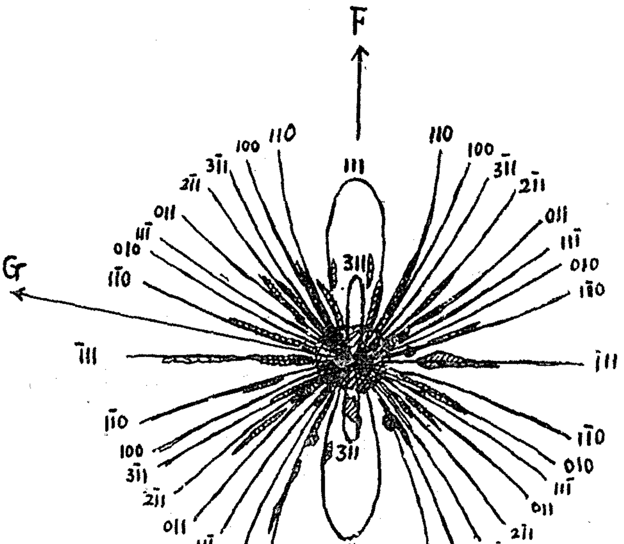
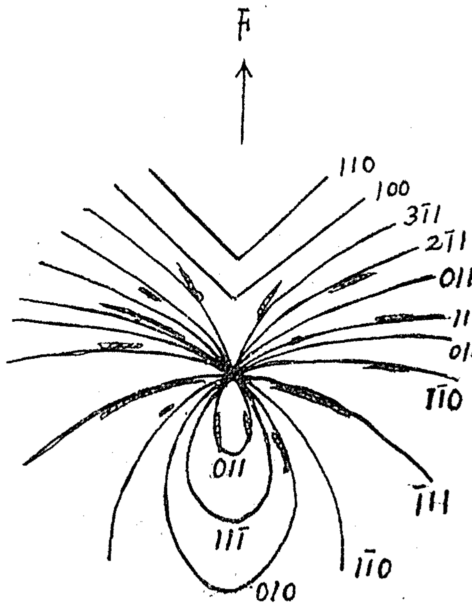


Fig. 12



The above assumption, made on the basis of the diffraction phenomena due to the normal incidence of X-rays to the fibrous axes, was also found by calculation to hold good in the case of oblique incidence. Fig. 13, Plate I shows the diffraction patterns taken with the same specimen used in the case of Fig. 8, Plate I, when the axis of the fibre was tilted 45° from its vertical position towards the incident X-ray beam. In the annexed Fig. 14, this diffraction pattern is represented by the shaded parts, while the full lines in the same figure are the theoretical positions of the prominent radiating bands, expected to appear in the present configuration. As can be seen from Fig. 14, the agreement between the calculated curves and the observed ones is satisfactory. Accordingly, our foregoing assumption was confirmed as correct, and we may conclude that the micro-crystals of lead have a tendency to be electrolytically deposited in fibrous manner with one of the [211] axes arranged parallel to a definite common direction. This is in no way different from the experimental results previously obtained by the other investigators already cited.

Fig. 14



But it is noticed that the direction of fibre thus determined, does not always coincide with the direction of maximum growth of deposited lead, contrary to our expectation derived from the universal argument of Glocker and Kaupp. We have already seen that the diffraction patterns reproduced in Figs. 3, 4, 5, 6 and 7 arose when the directions represented respectively by F and G were parallel to the photographic plate. Consequently, it can be concluded, on one hand that these two directions F and G coincide with each other in specimen A, which produced Fig. 3; while on the other hand, both directions F and G being situated in specimens B, C, D and E parallel to their foliated surface, the angle between these two direcions is found by measurement from Figs. 5, 4 and 6, 7 to be about 60,° 70,° 80° respectively.

The angles between some of the [211] axes of a lead crystal, which belongs to the cubic system, are generally confirmed by calculation to be 60,° 70°33′ and 80°24′.[1] Thus it may be inferred that the direction of the maximum growth of deposited lead examined in the present experiment, also coincides roughly with one of the normal of the [211] axes of the micro-crystals forming the considerable part of the specimen. This inference is consistent with the experimental results previously obtained by Hirata and his co-operators.[2]

Having ascertained these facts, the writers tried to analyze the crystalline configuration of the specimens more precisely. It is noticed that all the diffraction patterns obtained in the present experiment, as can be seen in Figs. 3, 4, 5, 6 and 7, Plate I, are similarly made up by a set of comparatively short and straight radiating bands, which had already been known to be given rise to by the micro-crystals arranging themselves with one of their [211] axes in common. Thus we may naturally anticipate that all the specimens examined are essentially of the same crystalline configuration, in which the micro-crystals are rotated within a certain small angle around their common axis [211] which lies parallel to the foliated surface. From the calculation, as will be described below, the crystalline configuration of the specimens above mentioned was found to be realized by incomplete rotations of two lead crystals (named for the sake of convenience crystals I and II respectively) with their atomic plane 211[3] in common, around the normal to this common atomic plane, in the vicinity of a certain ideal orientation. Here it should be stated that these two crystals I and II were so situated in this ideal orientation that the atomic plane $21\bar{1}$ of crystal I coincided with the atomic plane $2\bar{1}1$ of crystal II.[4]

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1. If we designate the atomic plane of micro-crystals with its normal parallel, to a definite direction (e. g. to the direction of fibre) to be of the indices 211, the normals to the atomic planes 121 and $1\bar{1}2$, $2\bar{1}\bar{1}$, $\bar{1}21$ and $1\bar{2}1$ should incline to this direction by the angles 60°, 70°33′, 80°24′ respectively.

2. *Loc. cit.*

3. In this paper, the indices of an individual atomic plane and crystallographic axis are respectively given following Miller and Nigglie by the symbols *hkl* and ⟨*abc*⟩; while those of a family of them are represented by (*hkl*) and [*abc*].

4. It can easily be seen in such a case, that the orientation of one of these two crystals may be realized on rotating the other crystal through an angle 120° around the normal to their common atomic plane 211.

Now to make clear our foregoing statement, let us provisionally assume that the incident X-ray beams were made to strike these rotating crystals perpendicularly to the axis of rotation, taking the direction normal to the atomic plane $11\bar{3}$ of crystal I (i. e., roughly to the atomic plane $1\bar{3}1$ of crystal II) in the ideal orientation. Then the radiating bands as shown by the full lines in Figs. 8, 9, 10, 11 or 12, would be expected to appear partly on the photographic plate. Examining Fig. 6, Plate I for illustrations, it was found that the theoretical positions of the radiating bands are represented by a superposition of two figures, Figs. 15_a and 15_b; each one of these two figures, Figs. 15_a and 15_b, is produced by the rotation of the lead crystals I and II in the counterclockwise and clockwise senses respectively. To draw these figures Figs. 15_a and 15_b, the angle of rotation of these two crystal was equally taken as $16.^\circ$ In Fig. 16, the theoretical positions of the radiating bands obtained by combining Figs. 15_a and 15_b are compared, similary as in

Fig. 15_a

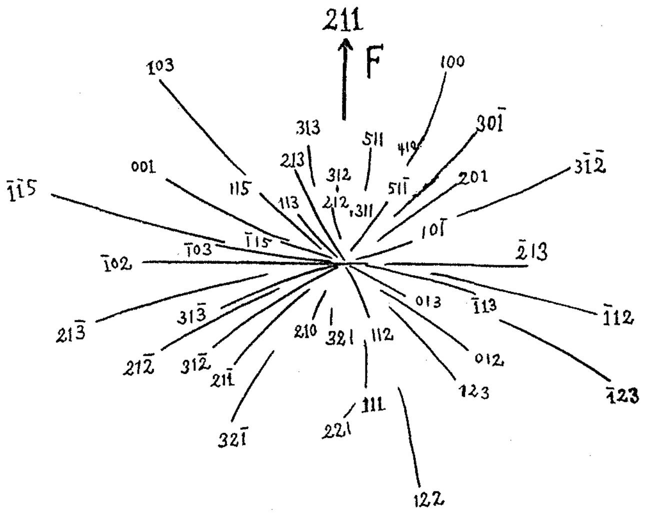
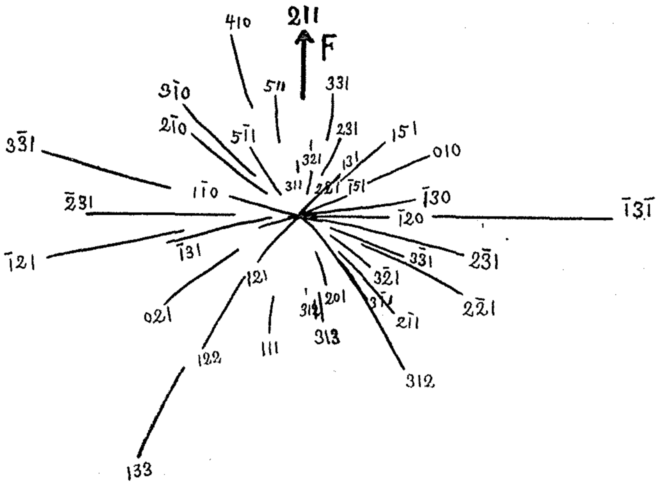


Fig. 14, with the observed ones reproduced from the original plate of Fig. 6, Plate I. As may be seen from Fig. 16, the agreement between the calculated and the observed positions of the radiating bands is satisfactory. This shows us that the orientation of each micro-crystal in Specimen D, which gave rise to Fig. 6, Plate I, is in fine accordance with the prediction from the foregoing general statement. Similar agreements between the theoretical and observed results were also

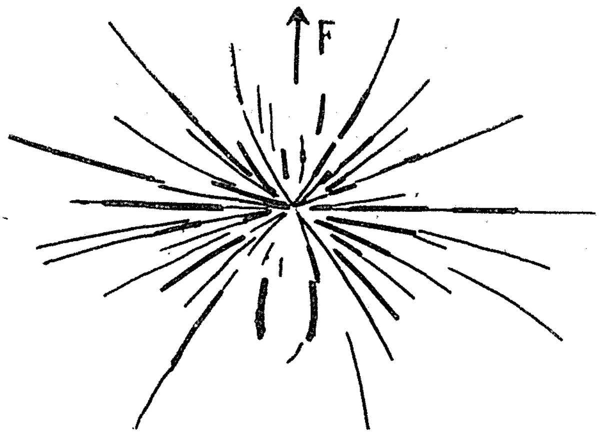
Fig. 15b



found to hold good with regard to all diffraction patterns within the scope of our calculation.

Accordingly, our foregoing statement being confirmed, we may conclude that the specimens examined in the present experiment, con-

Fig. 16



sist mostly of micro-crystals of lead rotated within a certain small angle from two initial orientations, around the axis normal to one of their (211) planes; in each of these two initial orientations, the micro-crystal is so situated that another of its planes (211) which is parallel to the axis of rotation above stated, may coincide roughly with that corresponding to the other. Moreover, it can also be inferred from the above illustration, that the foliated surface of the specimen coincides roughly with one of the (113) planes of micro-crystals incompletely rotated from both initial orientations.

Conclusion

The arguments which have hitherto been advanced with respect to electrolytic lead deposited from nitrate solutions, lead us to the following conclusions :—

(1) As was already known, the micro-crystals of lead have a tendency to be electrolytically deposited in a fibrous-like manner, having one of the [211] axes in common.

(2) The direction of maximum growth of electro-deposited lead does not always coincide with the direction of the fibrous axis. But even in such a case, it was found to coincide with some one of the [211] axes, which make an angle 60°, $70^\circ 33'$, $80^\circ 24'$ respectively with the fibrous axis, as was suggested by Hirata and his co-operators.

(3) Most of the specimens of electrolytic lead, if not all, consist of two groups of micro-crystals incompletely rotating around the same common axis [211]; a micro-crystal belonging to one of these groups is so situated that one of its (211) planes which is parallel to this axis of rotation, may roughly coincide with that of another micro-crystal belonging to the other.

In conclusion, the writers wish to express their sincere thanks to Prof. Denzo Uno and Ass. Prof. Hideki Hirata for the efficacious suggestions and interest they have taken in this investigation. Thanks are also due to Mr. Takeo Ishida who kindly supplied many samples required for the present experiments.

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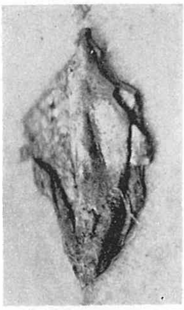
Plate I

Fig. 1

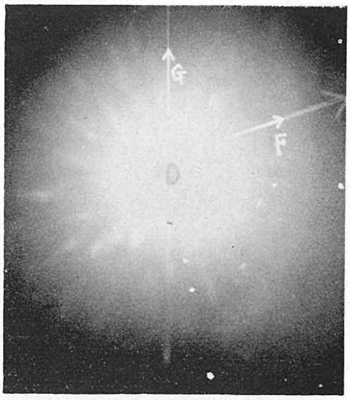
Specimen B
×13

Fig. 2



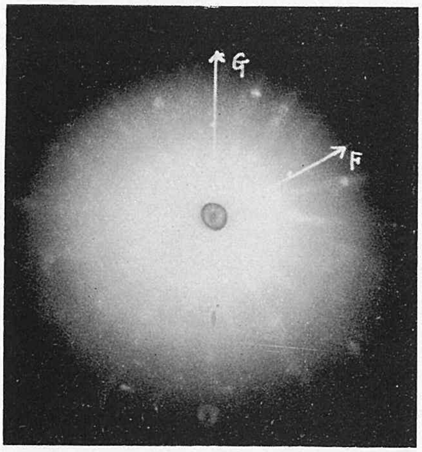
Specimen C
×13

Fig. 4



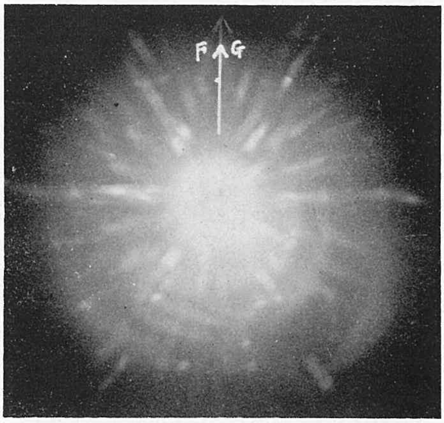
Specimen B

Fig. 3



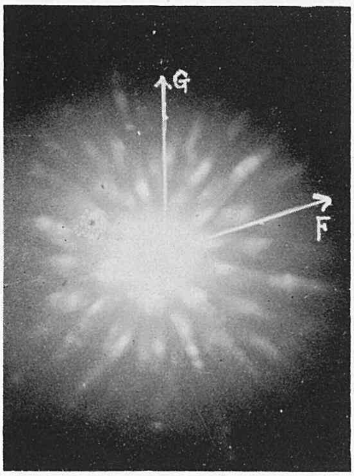
Specimen A

Fig. 5



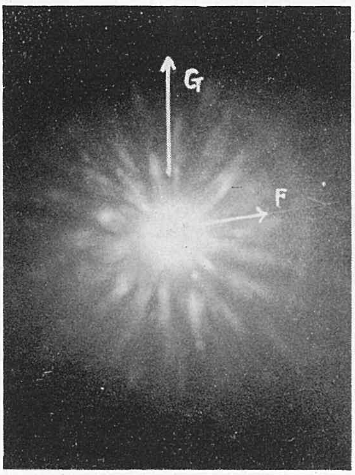
Specimen C

Fig. 6



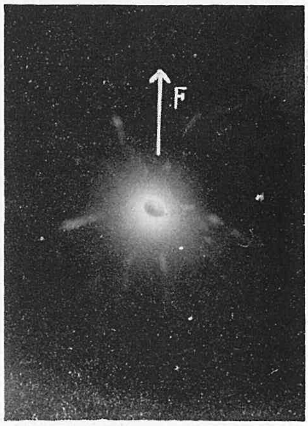
Specimen D

Fig. 7



Specimen E

Fig. 13



Specimen A