# ON THE ARRANGEMENTS OF THE MICRO-CRYSTALS IN LEAD DEPOSITED BY ELECTROLYSIS.

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**Introduction.** By way of continuity with our previous investigations[1] on the crystalline structure in various electro-deposited metals, essentially the same experiment has been repeated with electrolysed specimens of lead. The heterogeneous X-rays emitted from the molybdenum anticathode were also utilized in the present experiment.

Here it should be stated that the crystal form of lead belongs to $\Gamma'c$ of $a_0 = 4{,}983$Å.[2]

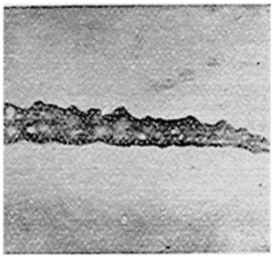
**Specimens.** To prepare the specimens used in this experiment, a platinum wire was steeped by 2 cm. into the electrolyte as the cathode. At a distance of 3–5 cm. from the cathode, a thin plate of lead, 1.5 cm. × 3 cm. in area and serving as anode, was placed. The conditions under which these specimens were obtained, are given in Table 1.

Table 1.

| No. of speci-mens | Composition of electrolyte | Current of electrolysis (amperes) | Potential applied to the electrodes (volts) | Distance between the electrodes (cm.) | Temp. °C. |
|---|---|---|---|---|---|
| A | 6 g. $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ was dissolved in 200 c.c. $H_2O$. $C_2H_4O_2$ sufficient for clearing the solution was added. | The current was gradually increased from about 0.1 ampere, with the augment of deposit. | 4 | 5 | about 20 |
| B | 10 g. $Pb(C_2H_3O_2)_2 \cdot 3H_2O$<br>5 c.c. $C_2H_4O_2$<br>195 c.c. $H_2O$ | 0.1 | 3.5 | 3 | 20 |
| C | 5 g. $Pb(C_2H_3O_2)_2 \cdot 3H_2O$<br>2.5 c.c. $C_2H_4O_2$<br>197.5 c.c. $H_2O$ | 0.1 | 3.5 | 3 | 20 |
| D | 2.5 g. $Pb(C_2H_3O_2)_2 \cdot 3H_2O$<br>1.3 c.c. $C_2H_4O_2$<br>198.7 c.c. $H_2O$. | 0.08 | 4 | 3 | 14 |

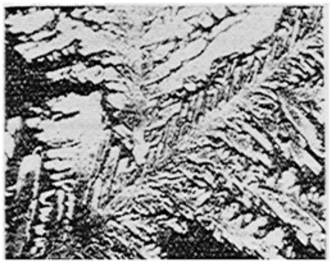
(1) For example, H. Hirata and Y. Tanaka; *Mem. Coll. Sci., Kyoto Imp. Univ.*, A, **17** (1934), 143.
(2) E. A. Owen and G. D. Preston, *Proc. Phys. Soc.*, **35** (1923), 101.

Though powdery or needle-shaped deposits of lead were often detected at the beginning of the electrolysis, the specimens of lead which appeared after several hours, usually had a foliated form with many branchlets. But some of the needle-shaped specimens were observed to remain unaltered, when electrolysis proceeded for a comparatively long time. The micro-structures of these two types of specimens are reproduced in Fig. 1 and 2.



Specimen C (needle-shaped). ×50.

Fig. 1.



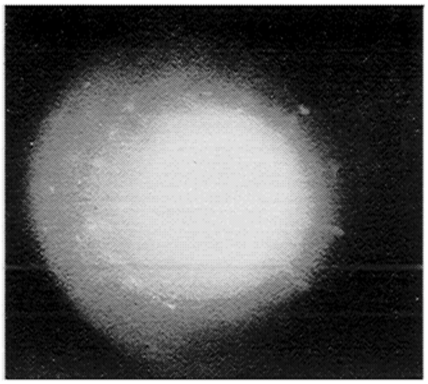
Specimen C (foliated). ×50.

Fig. 2.

**Experimental Results.** The crystalline structures of the specimens mentioned above were examined by means of Laue's method. To take a diffraction pattern of the foliated specimens, a piece of them was so placed that the foliated surface was perpendicular to the incident X-ray beam, while, with a fragment of the needle-shaped specimens, the interference figure was obtained by setting its longitudinal axis perpendicular to the direction of the incident beam. In doing so, the photographic plate was always placed perpendicularly to the incident beam in a position 3.2 cm. behind the specimen.

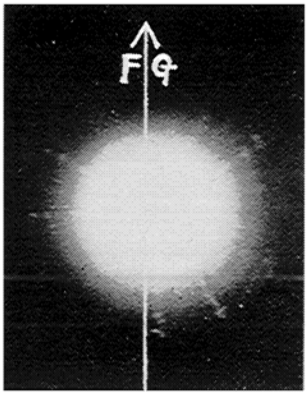
Some of the diffraction patterns thus obtained with the foliated and needle-shaped specimens are reproduced respectively in Fig. 3, 4, 5, 6, and 7. In these figures, the direction of the maximum growth of deposited lead (i.e., the direction of the longitudinal axis or the stem of the foliage) is represented by an arrow G.

Not only the patterns here reproduced, but also most of the diffraction figures given by these specimens, were found to be essentially the same: i.e., all the figures, except Fig. 3 were observed to be made up with a set of radiating bands. On the other hand, Fig. 3 consists of several Debye-Hull rings due to the reflections of the prominent atomic planes of the lead crystal. This shows that a considerable portion of the specimen giving Fig. 3, is composed of an irregular aggregation of microcrystals of lead, but the other specimens are mostly of a fibrous structure.



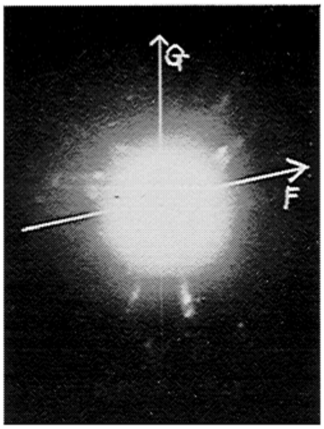
Specimen C (foliated). $\beta = 90°$.

Fig. 3.



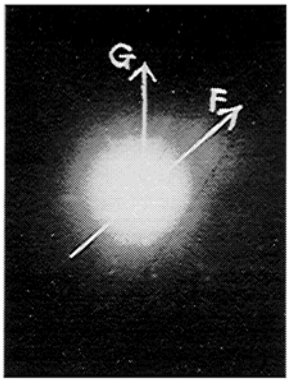

Specimen C (needle-shaped). $\beta = 90°$.

Fig. 4.



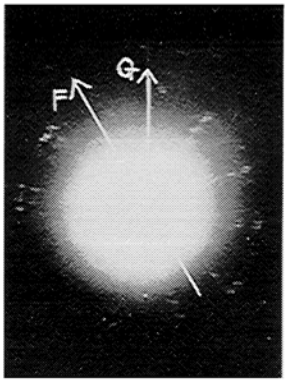

Specimen C (foliated).
$\beta = 90°$.

Fig. 5.




Specimen B (foliated).
$\beta = 90°$.

Fig. 6.




Specimen A (foliated).
$\beta = 90°$.

Fig. 7.

Having thus ascertained these facts, the writers tried to determine the direction of the common axis of the micro-crystals in the fibrous specimens mentioned above. This was done in the same manner as in our previous investigations.(1)

In the annexed figures, Fig. 8, 9, 10, and 11, 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 an arrow F), and the incident X-ray beam is made to strike this crystal taking the direction perpendicular to the axis of rotation mentioned above. The shaded parts of the same figures are copies of the original plates of Fig. 4, 5, 6, and 7.(3) To transcribe these copies, the original plates of Fig. 4, 5, 6, and 7 were respectively placed upon Fig. 8, 9, 10, and 11, in such a way that the direction represented by F and the centre of the central spot in both figures coincide with each other. As can be seen from Fig. 8, 9, 10, and 11, the agreement between the calculated curves and those observed is satisfactory. Consequently, we may infer that the specimens giving the diffraction patterns reproduced in Fig. 4, 5, 6, and 7 are, in the main at least, composed of micro-crystals having one of the [211] axes in common.

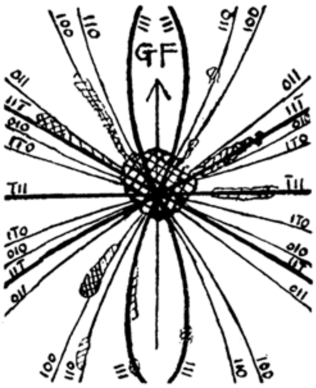



Fig. 8.

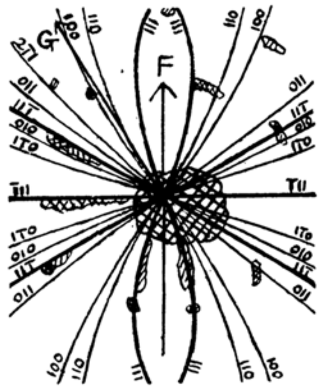



Fig. 9.

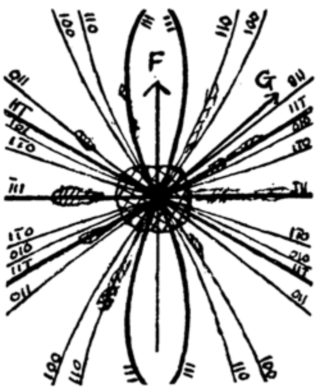



Fig. 10.

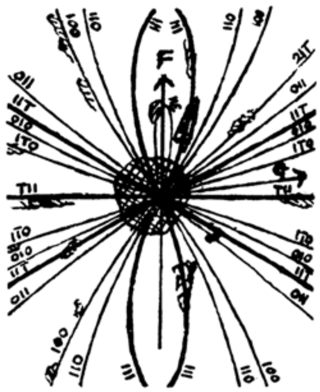
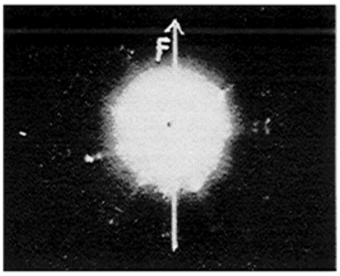



Fig. 11.

(3) It is to be noticed that the diffraction patterns reproduced in Fig. 3–7 and 12 interchange from right to left as compared with those of the original plates.

Next, to confirm the above inference, the writers investigated the interference phenomena due to an oblique incidence of the X-ray beam to the fibrous direction of the same specimen as was used in the case of Fig. 4. Fig. 12 is the diffraction figure taken when the axis of fibre was tilted 45° from its vertical position towards the incident beam. To take this diffraction figure, the photographic plate was also placed 3.2 cm. behind the specimen.




Specimen C (needle-shaped).
$\beta = 45°$.

Fig. 12.

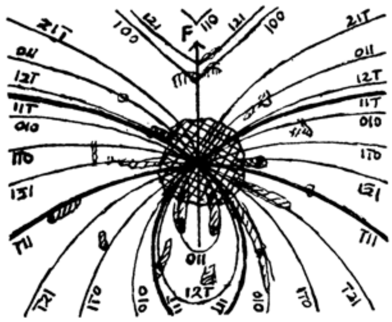



Fig. 13.

In the annexed figure, Fig. 13, the theoretical curves traced out by calculation are compared with Fig. 12. As may be seen from Fig. 13, the agreement between the calculated curves and the observed ones is rather satisfactory. Accordingly, our foregoing inference was confirmed as correct, and we may conclude that the micro-crystals of lead have a tendency to be electrolytically deposited with the normals to their icositetrahedral faces (211) arranged parallel to a definite common direction. This is in no way different from the experimental results given by Frölich, Clark, and Aborn.(4)

But, it is noticed that the direction of fibre thus determined, does not always coincide with the direction of maximum growth of deposited lead. As has already been seen, the diffraction patterns, Fig. 4, 5, 6, and 7, were produced, when the directions, represented respectively by F and G, were parallel to the photographic plate. Consequently we may conclude, on the one hand, that these two directions F and G coincide with each other in the needle-shaped specimen, which produced Fig. 4, while, on the other hand, both directions F and G being situated parallel to the largest surface of the foliated specimen, the angles between them are found by measurement from Fig. 5, 6, and 7 to be about 33°, 48°, and 80° respectively.

(4) *Z. Elektrochem.*, **32** (1926), 295.

The angles between the [211] axes of a crystal belonging to the cubic system, are generally confirmd by calculation to be 33°34′, 48°12′, 60°, and 80°24′. Thus, it may be inferred that the direction of the maximum growth of deposited lead G also coincides roughly with one of the [211] axes of the micro-crystals forming the considerable part of the specimens. This inference may explain why the branchlets of the foliated specimen make angles of about 33°, 48°, and 60° with one another, as shown in Fig. 2.(5)

**Summary.** The arrangements of the micro-crystals in electrolytic specimens deposited from acetic acid solutions, were examined with X-rays, by the so-called "transmission method". From the diffraction patterns obtained, it was confirmed on the one hand, that the micro-crystals of lead have a tendency to be electrolytically deposited in a fibrous way, with one of the normals to their (211) faces arranged parallel to a definite common direction, as was the case in the experiments of Frölich, Clark, and Aborn. On the other hand, the direction of the growth of deposited lead, was found to coincide roughly with any one of the [211] axes, which make an angle 0°, 33°34′, 48°12′, and 80°24′ respectively with the common axis of the micro-crystals.

In conclusion the writers wish to express their best thanks to Professor D. Uno for the interest he has taken in the experiments. Their thanks are also due to the Imperial Academy of Japan for the fund granted for the investigation.

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(5) As all the branchlets of the foliated specimens were found not to lie in the same plane, the writers were obliged to flatten each specimen by placing it between two glass plates, before its micro-photograph was taken. Thus, the angles between some of the branchlets, especially those between the big branchlets and the stems of the foliage seen in Fig. 2, are different from the actual angles.