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On the Crystalline Configurations of Zinc and Cadmium Deposited by Electrolysis[1]

By **Hideki Hirata, Hajime Kotô** and **Mituo Hara**

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Abstract

To make clear the geometrical peculiarities of the inner structures of zinc and cadmium deposited electrolytically, the crystalline configurations of the electrolytic specimens of these two metals were examined with X-rays by the Laue method. From the diffraction patterns obtained, it was found that some of these specimens are composed mostly of a few crystals of considerable size; but the others are of an incomplete fibrous nature in which the micro-crystals of zinc or cadmium rotate within a certain angle around the direction normal to their common plane. In either case, the crystals forming these specimens were proved to be so arranged that each of them has one of its $(2\bar{1}\bar{1}0)$ planes in common. Moreover, it was also found that the normal either to this common plane or to another $(2\bar{1}\bar{1}0)$ plane inclined by an angle 60° to the aforesaid common plane of the crystals, coincides with the direction of the maximum growth of these electrolytically deposited specimens. This seems to explain why electrolytic specimens of zinc and cadmium grow in a dendritic form with many branchlets, which make an angle of 60° to each other.

Introduction

During the last ten years and more, the crystalline configurations of various electro-deposited metals have been investigated with X-rays by Glocker, Kaupp,[2] Bozorth[3] and many others.[4] But in connection with the metals belonging to the hexagonal system, as zinc and cadmiun, very few X-ray examinations have been carried out up to the present time.[5] So the late Mr. Y. Tanaka,[6] who had previously found in our

1. This paper was read at the meeting of the Japan Institute of Metals, April, 1940.
2. R. Glocker & E. Kaupp: Zeits. f. Phys., **24**, 121 (1924).
3. R. M. Bozorth: Phys. Rev., **26**, 390 (1925).
4. e. g., P. K. Fröhlich & G. L. Clark: Zeits f. Elektrochem., **31**, 649 (1925), P. K. Fröhlich, G. L. Clark & R. A. Aborn: Zeits. f. Elektrochem., **32**, 295 (1926), H. Hirata & H. Komatsubara: Zeits. f. anorg. allg. Chem., **158**, 137 (1926). H. Hirata: These Memoirs, **11**, 429 (1928).
5. As is well known from the experimental results of numerous investigators (e. g., E. A. Owen & J. Iball: Phil. Mag., **16**, 479 (1933). E. A. Owen & E. L. Yates: Phil. Mag., **17**, 113 (1934). J. Weigle: Helv. Phys. Acta., **7**, 51 (1933). W. Stenzel & J. Weerts: Zeits. f. Krist., **84**, 20 (1932).), the crystal structures of zinc and cadmium belong to the hexagonal closed-pack of the lateral axes $a_0=2.6589$ Å and 2.9736 Å long, and of the axial ratios $c'=1.856_3$ and 1.885_9 respectively.
6. H. Hirata & Y. Tanaka: Rep. Chem. Res. Inst., Kyoto Imp. Univ., **3**, 45 (1933).

laboratory that under a certain condition the micro-crystals of zinc have a tendency to be electrolytically deposited in a fibrous way, with one of their lateral axes ‹100›—i. e., the normal to one of the lateral faces $(2\bar{1}\bar{1}0)$ of the hexagonal prism of the second order—arranged parallel to a definite common direction, was induced to give a more complete report of his investigation. But as he died young before the completion of his work, the present writers undertook to repeat his investigation, in order to make the report he would have made had he lived to write it. Accordingly before going into detail, it should be emphasized that the main part of this work is the record of the efficient and painstaking labour of the late Mr. Tanaka.

Specimens

In the present experiment, specimens of electro-deposited zinc and cadmium prepared at the laboratory of the Imperial Mint, Osaka, were examined similarly as before. It was reported that these specimens were deposited by applying 3 volts to both electrodes of the electrolytic bath, under the following conditions:—

Zinc

Specimen A:

Electrolyte; H_2O solution of $Zn(C_2H_3O_2)_2$ containing 9.13% of Zn.

Anode; zinc plate of 3 cm. × 4 cm. in area.

Cathode; platinum wire 1 mm. in diameter and 4 cm. long.

Electrolytic current; initially amounting to 0.3 ampere, but gradually increased up to 1.0 ampere due to the augmentation of the electrolytic deposition.

Temperature; 13.5°C.

Cadmium

Specimen A:

Electrolyte; H_2O solution of $Cd(C_2H_3O_2)_2$ containing 12.31% of Cd.

Anode; cadmium wire 5 mm. in diameter, and 10 cm. long.

Cathode; platinum wire 1 mm. in diameter, and 1.5 cm. long.

Electrolytic current; 0.2 amp.~1.0 amp.

Temperature; 13.5°C.

Specimen B

Electrolyte; H_2O solution of $CdSO_4$ containing 11.00% of Cd.

Anode; the same as in the case of Specimen A.

Cathode; platinum wire 1 mm. in diameter and 3 cm, long.
Electrolytic current; 0.5 amp.~1.0 amp.
Temperature; 15.0° C.

The specimens of zinc and cadmium thus obtained from the solutions of acetic acid (called Specimen A for convenience sake), were observed to have a dendritic form with many branchlets which make an angle of 60° with one another in one plane; while the specimen of cadmium deposited from the solution of sulphuric acid (called Specimen B), is of an acicular form without any branchlet. In Figs. 1, 2 and 3, Plate I, the macro-structures of some of these two kinds of specimens are reproduced.

Experimental Results

(i) Zinc

With a fragment of Specimen A of the electrolytic zinc above indicated, the present experiment was begun after the Laue method, making use of the heterogeneous X-ray beam emitted from the molybdenum anticathode. To take a diffraction pattern, the specimen was so situated, unless otherwise stated, that the face of the dendrite took the orientation perpendicular to the incident X-ray beam, having its stem parallel to the vertical direction: while the photographic film was always placed perpendicular to the incident beam, 3 cm. behind the specimen.

The diffraction patterns thus obtained are usually seen to consist of a number of short radiating bands as shown in Figs. 4 and 5, Plate I. But the figures made up of a set of Laue spots as reproduced in Fig. 6, Plate I, were also found to be given rise to by some specimens belonging to this category. This shows us without doubt, that most of these specimens under examination are of an incomplete fibrous nature, in which the micro-crystals of zinc rotated within a certain angle around their common axis: but some of the specimens are seen to be composed of one or a few single crystals of considerable size.

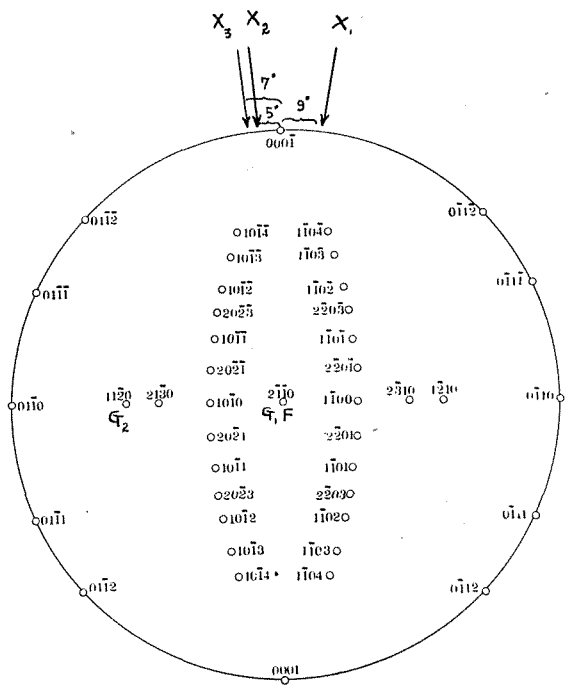
Having thus ascertained these facts, the writers tried by the aid of an improved Yoshida's crystallographic scale,[1] to determine more precisely the crystalline configurations corresponding to the various figures. As the consequence of this determination, each micro-crystal

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

in the fibrous specimens which gave rise to Figs. 4 and 5, Plate I, was confirmed to arrange itself having the normal to one of its $(2\bar{1}\bar{1}0)$ planes—i. e., one of the lateral faces of hexagonal prism of the second order—parallel to a definite common direction. Moreover, it also became clear that either this common axis of the micro-crystals or the normal to another $(2\bar{1}\bar{1}0)$ plane inclined by an angle 60° to the aforesaid common axis, coincides with the direction of the maximum growth of deposited zinc.

To give a particular account of the foregoing statements, the orientations of the micro-crystals of zinc, confirmed to produce Figs. 4 and 5, Plate I, are projected stereographically in the annexed figure, Fig. 7, with reference to the directions of the incident X-ray beams. These directions of incident X-ray beams corresponding to the diffraction patterns, Figs. 4 and 5, were respectively found parallel to the directions of the arrows X_1 and X_2 in this figure, the common axis of the micro-crystals being assigned to take the direction projected at the point F. Further, G_1 and G_2 are the projections of the direction of the maximum growth of the zinc, which coincide respectively with the vertical directions marked by the arrows G in Figs. 4 and 5, Plate I. In Figs. 8 and 9, the theoretical curves representing the positions of the prominent radiating bands expected to appear due to the incomplete rotation of the micro-crystals from the initial orientations projected in Fig. 7, are compared with the copies of the diffraction patterns reproduced from Figs. 4 and 5, Plate

Fig. 7



I.[1] To draw the theoretical curves in these two figures, Figs. 8 and 9, the micro-crystals were assumed to rotate to the angles 20° and 17° respectively in the clockwise sense form the intial orientations above stated, around the direction represented by F. The fair agreement between the theoretical positions of the radiating bands and those observed, as may be seen in Figs. 8 and 9, seems to confirm our foregoing statements, that the electro-deposited specimens of zinc giving rise to the diffraction patterns, Figs. 4 and 5, are of an incomplete fibrous structure in which the micro-crystals rotate within a certain angle around the direction normal to their common plane of the indices $(2\bar{1}\bar{1}0)$. Here, it is noticed that the rotations of micro-crystals now under consideration take place in the vicinity of the orientation, in which (0001) plane of the micro-crystals coincides with the largest face of the specimen situated perpendicular to the incident X-ray

Fig. 8

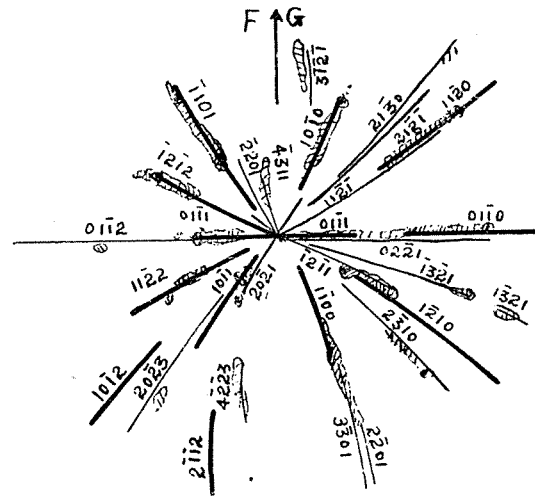
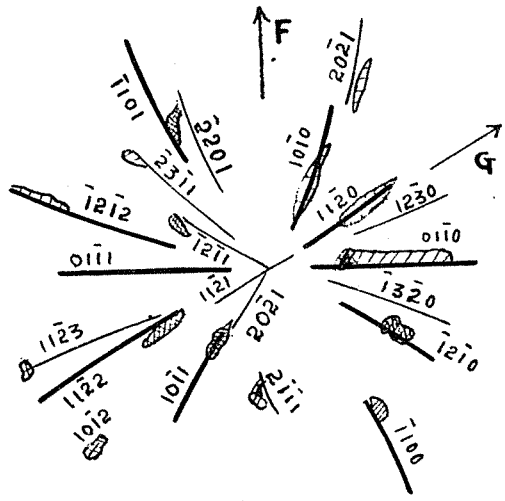


Fig. 9

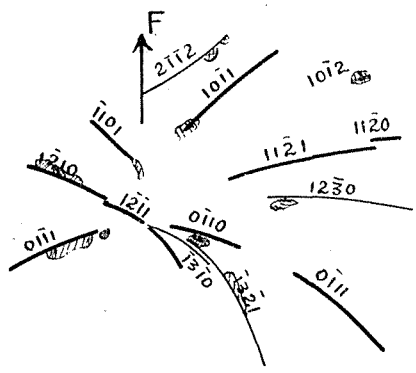


1. To transcribe these copies, the original films of Figs. 4 and 5 were respectively placed upon Figs. 8 and 9, in such a way that the direction represented by F and the centre of the central spot in both figures coincide with each other.

beam. Furthermore, from Fig. 4, Plate I, it is also found that the direction of the maximum growth of electrolytic-deposited zinc is roughly parallel to the direction of the common axis of micro-crystals, as was previously suggested by Tanaka; but this direction of the maximum growth is seen in Fig. 5, Plate I, to coincide with the normal to another $(2\bar{1}\bar{1}0)$ plane, which makes an angle 60° with the aforesaid common axis.

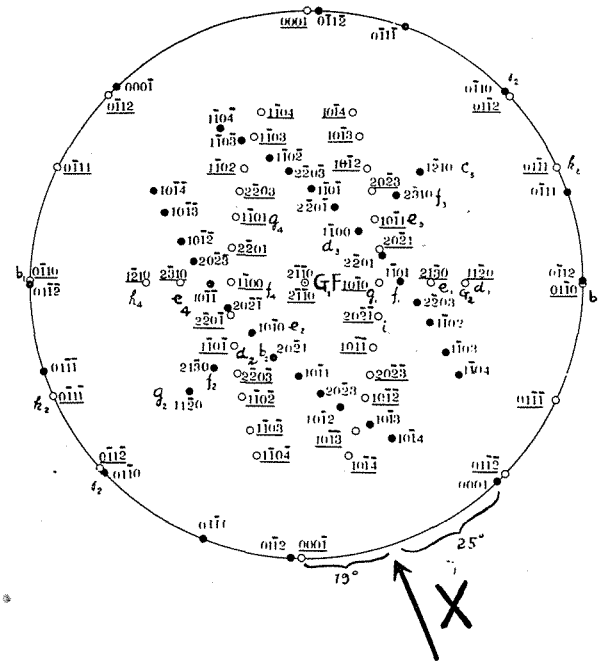
The above consideration in connection with the inner structures of the electro-deposited zinc, deduced from Figs. 4 and 5, Plate I, was also found to be consistent with the other diffraction patterns corresponding to the different orientation of the specimens. Fig. 10, Plate I shows the diffraction pattern taken with the same specimen used in the case of Fig. 5, Plate I, when the common axis of the micro-crystals was tilted 45° from its normal direction towards the incident X-ray beam. In the annexed figure, Fig. 11, this diffraction pattern is reproduced 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. 11, the agreement between the calculated positions and those observed is quite satisfactory. The slight discrepancy of the positions found in Fig. 11, is fully explained by the difficulty of setting the common axis of the micro-crystals in the strictly right position. Accordingly, the above consideration was again confirmed, and we may conclude that our foregoing statements are correct, at least with regard to the inner structures of the specimens responsible for the formation of Figs. 4 and 5, Plate I.

Fig. 11



Next, the writers extended their consideration to the specimen giving rise to the diffraction figure, Fig. 6, which consists of a number of Laue spots. By a procedure similar to that used before, it was concluded that the specimen under consideration is mostly composed of two crystals of zinc, situated with reference to each other, in the way shown in the annexed figure Fig. 12.

Fig. 12



In Fig. 12, various atomic planes belonging to these two crysals are projected stereographically, as in Fig. 7. To distinguish the atomic planes of one of these two crystals from those of the other, their points of projection are indicated in Fig. 12 by white circles, and those corresponding to the other by black ones. The point F in this figure is the projection of the direction normal to the common plane of these two crystals, which was confirmed to coincide with the direction of the maximum growth of deposited zinc represented by G_1, in the present case. Moreover, the small letters a_1, b_1, c_2,....., i_4, j_4, k_4, in Fig. 12 mark respectively the prominent atomic planes of small glancing angles, which were found by calculation to give rise to the Laue spots on the photographic film, just at the positions of the spots represented by the same letters in Fig. 6, Plate I, when the incident X-ray beam was made to strike the specimen perpendicularly to its stem, taking the direction parallel to the arrow X.[1] As may be seen from Fig. 12,

1. The following correspondence was found to exist between the Laue spots in Fig. 6, Plate I and the indices of the atomic planes of these two crystals :—

a_1, $03\bar{3}1$; b_1, $01\bar{1}0$ & $01\bar{1}2$; c_1, $12\bar{3}0$; d_1, $11\bar{2}0$, e_1, $21\bar{3}0$; f_1, $1\bar{1}01$; g_1, $10\bar{1}0$; h_1, $30\bar{3}1$;

the specimen with which Fig. 6, Plate I was obtained, can be concluded to be of a crystalline configuration essentially the same with that corresponding to Fig. 4, Plate I: i. e., the specimen giving rise to Fig. 6, Plate I, is found to be mostly, if not entirely, composed of two crystals of zinc having one of their $(2\bar{1}\bar{1}0)$ planes in common, and the direction normal to this common plane is parallel to the direction of the maximum growth of deposited zinc.

With regard to a few metals, it was previously found in our laboratory that the common axis of the micro-crystals in electro-deposited specimens, does not always coincide with the direction of their maximum growth.[1] The angle between these two directions indicated by the general notations F and G in the present case, was confirmed to be able to take a finite set of values besides O°. Nevertheless, according to the experimental results obtained by Yamamori[2] and others[3] with various specimens of electro-deposited lead, the aforesaid two directions F and G are noticed always to be crystallographic equivalent, even when the parallelism between them is violated. A similar geometrical relation as stated above, has also been seen with the electro-deposited zinc in the present experiment, each one of these two directions F and G in the electro-deposited zinc coinciding with one of the normals to $(2\bar{1}\bar{1}0)$ planes of its micro-crystals. Thus we may infer that the crystalline configuration of the electro-deposited zinc, is of the same category with that of electro-deposited lead, in connection with the geometrical relation between the direction of the common axis of the micro-crystals and the direction of the maximum growth of the specimens.

(ii) Cadmium

(a) Specimen A: Next the writers investigated the crystalline

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i_1, $\underline{20\bar{2}\bar{1}}$; j_1, $\underline{3\bar{1}\bar{2}\bar{1}}$ & $3\bar{2}\bar{1}2$; k_1, $2\bar{1}\bar{1}1$; a_2, $\underline{\bar{2}111}$; b_2, $20\bar{2}1$; c_2, $30\bar{3}1$; d_2, $\underline{\bar{1}101}$; e_2, $\underline{\bar{3}301}$ & $10\bar{1}0$; f_2, $21\bar{3}0$; g_2, $11\bar{2}0$; h_2, $12\bar{3}1$; i_2, $12\bar{3}0$; j_2, $01\bar{1}0$ & $\underline{0\bar{1}1\bar{2}}$; k_2, 0331 & $\underline{01\bar{1}1}$; a_3, $\underline{\bar{1}3\bar{2}0}$; b_3, $\underline{11\bar{2}2}$; c_3, $\bar{1}2\bar{1}0$ & $\underline{11\bar{2}3}$; d_3, $1\bar{1}00$; e_3, $\underline{10\bar{1}1}$; f_3, $2\bar{3}10$; g_3, $\underline{10\bar{1}2}$; h_3, $\bar{4}311$; i_3, $\bar{3}301$; j_3, $\bar{2}201$; k_3, $\underline{4\bar{2}\bar{2}3}$; l_3, $\underline{2\bar{1}\bar{1}1}$; a_4, $\bar{2}111$; b_4, $\bar{2}112$; c_4, $\underline{3\bar{2}\bar{1}2}$; d_4, $\bar{4}223$; e_4, $10\bar{1}\bar{1}$; f_4, $\underline{\bar{1}\bar{1}00}$; g_4, $\underline{\bar{1}\bar{1}01}$; h_4, $\bar{1}2\bar{1}0$; i_4, $\underline{\bar{1}3\bar{2}0}$; j_4, $\underline{\bar{1}4\bar{3}0}$; k_4, $\underline{\bar{1}3\bar{2}1}$;

It must be frankly accepted, that only the very diffuse Laue spot marked by g_4, is found to take a position where no reflected beam from any prominent atomic plane of these two crystals of zinc, strikes the photographic film. Consequently, it may be thought probable that this spot is given rise to by the crystallite immersed between two crystals above stated. But for the present, we have attributed this spot to the reflection of $\bar{1}\bar{1}01$ plane, notwithstanding it deviates considerably (about 6°) from the theoretical position of the spot produced by the aforesaid atomic plane.

1. H. Hirata & Y. Tanaka: These Momoirs, **15**, 9 (1932) and **17**, 144 (1934).
2. S. Yamamori & S. Yoshimoto: These Memoirs, **21**, 75 (1938).
3. H. Hirata, Y. Tanaka & H. Komatsubara: Bull. Chem. Soc., Japan, **10**, 391 (1935).

configuration of electro-deposited cadmium, by the same procedure as in the case of zinc above described. Some diffraction patterns thus obtained with Specimen A of the electro-deposited cadmium, are reproduced in Figs. 13 and 14, Plate II. Not only the patterns here reproduced, but all those given rise to by the specimens belonging to this category, were found always to consist of a number of short radiating bands, similarly to those shown in Figs. 13 and 14, Plate II. Thus it is clear beyond question that all the specimens designated as Specimen A, are equally of some incomplete fibrous-like structure, in which the micro-crystals rotate within a certain angle.

To make the crystalline configuration of Specimen A more precisely clear, a calculation similar to the previous one was carried out in connection with Figs. 13 and 14, Plate II. As the consequence of this calculation, it became evident that the former figure, Fig. 13, was produced by the micro-crystals of cadmium rotated within an angle 19° in the clockwise sense, from their initial orientation represented in Fig. 7[1] with reference to the direction of the incident X-ray beam X_3, around their common axis F. The fair agreement between the theoretical positions of the prominent radiating bands corresponding to the aforesaid configuration and the observed ones reproduced from Fig. 13, Plate II, may be seen in the annexed figure, Fig. 15. It is noticed in Fig. 15, that the direction of the common axis F deduced from Fig. 13, Plate II, coincides with the direction of the maximum growth of the electrolytic deposition G, similarly to the case of Fig. 4, Plate I.

With regard to the latter figure, Fig. 14, the crystalline configuration corresponding to it, was confirmed to be essentially the same as that of the specimen of electro-deposited zinc giving rise to Fig. 6, Plate I: i. e., Fig. 14, Plate II was given rise to by the rotations of two sets of the micro-crystals situated with reference to each other and to the direction of the incident X-ray beam X as shown in Fig. 12, around their common axis F, which coincide with the normal to one of $(2\bar{1}\bar{1}0)$ planes. One of these two sets of the micro-crystals of cadmium were found to rotate within an angle 19° in the clockwise

1. Strictly speaking, the stereographic projections of the crystals of zinc given in Figs. 7 and 12, are of course as they stand, not applicable to those of cadmium. But the crystal lattices formed by the aforesaid two kinds of metals having already been known to be of the same type and of nearly equal axial ratio, these projections which dealt with the former are referred to here again in considerations concerning the latter.

sense, from their initial orientation represented by the white circles in Fig. 12. While the angle of rotation of the other set of the microcrystals corresponding to the black circles, was estimated to amount to 19° ahd 1° in the clockwise and counter-clockwise senses respectively. By the aforesaid rotations of these two sets of microcrystals, the atomic planes represented by the white and black circles in Fig. 12, were respectively deemed to produce the intensity maxima of the diffracted X-rays at the positions on the photographic film shown in Figs. 16a and 16b; the prominent radiating bands should consequently be expected to appear taking the positions designated by the curves in Fig. 17, which were obtained by combining Figs. 16a and 16b. As may be seen in Fig. 17, the theoretical positions of radiating bands thus obtained, would agree quite well with the observed ones reproduced from Fig. 14, Plate II, if the direction of the maximum growth of deposited cadmium on the photographic film is assumed to be parallel to the direction of the arrow G in the theoretical curves. Here, it must specially be mentioned that this direction G in Fig. 17, which makes an angle of 60° with the direction of the common axis F normal to one of the $(2\bar{1}\bar{1}0)$ planes, is also seen to coincide with the normal to another $(2\bar{1}\bar{1}0)$ plane marked G_2 in Fig. 12, where the indices of

Fig. 15

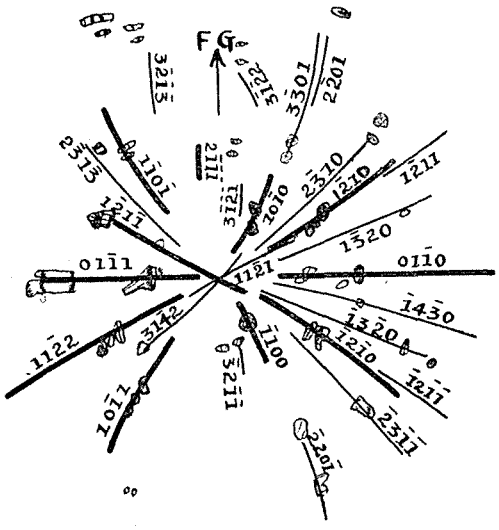
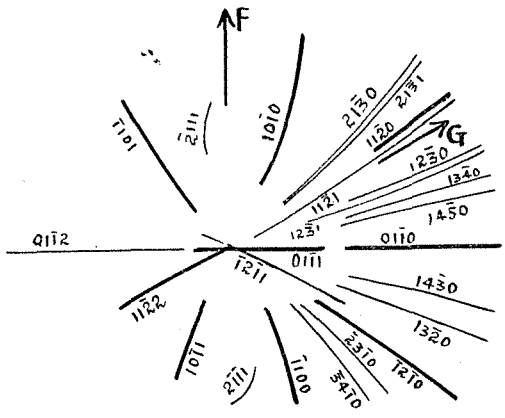
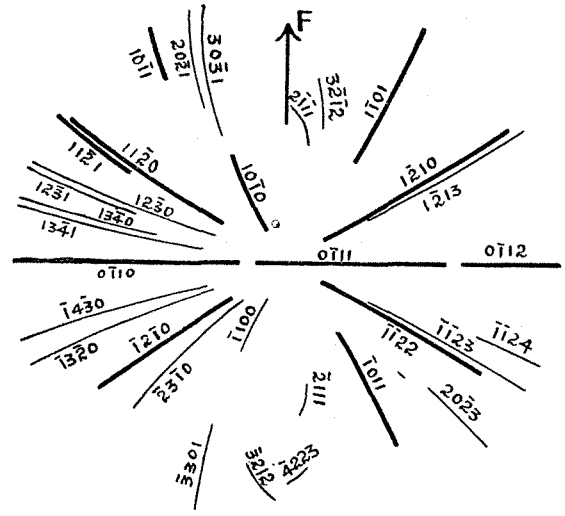


Fig. 16a



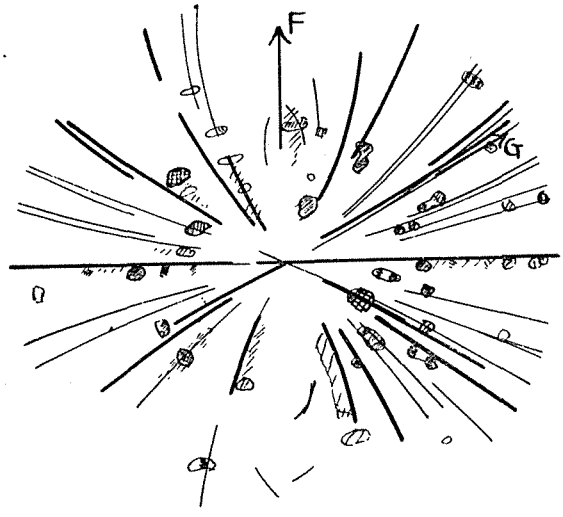
these two atomic planes perpendicular to the directions F and G are respectively designated $2\bar{1}\bar{1}0$ and $\bar{1}\bar{1}20$. The facts adduced above, lead us to conclude that the specimen giving rise to Fig. 14, Plate II, is composed of two sets of micro-crystals of cadmium having one of their $(2\bar{1}\bar{1}0)$ planes in common, and the normal to another $(2\bar{1}\bar{1}0)$ plane inclined by an angle of 60° to the aforesaid common axis parallel to the direction of the maximum growth of deposited cadmium.

Fig. 16b



From the conclusions which have already been drawn with regard to Specimen A, it can be inferred that the electrolytic specimens of cadmium are of a similar crystalline configuration to those of zinc referred in the preceding article. i. e., the direction of the common axis in the electro-deposited cadmium does not always coincide with the direction of its maximum growth; but in any case, these two directions are situated normal to some one of the atomic planes $(2\bar{1}\bar{1}0)$.

Fig. 17



(b) Specimen B: Fig. 18, Plate II is the diffraction figure obtained with a fragment of Specimen B of the electro-deposited cadmium, by

setting the axis of the acicular perpendicular to the incident X-ray beam. Not only Fig. 18, Plate II here reproduced, but all the diffraction patterns given rise to by the specimens of this category were found to be essentially the same, each one of them consisting of a complicated assemblage of radiating bands. Nevertheless, these diffraction patterns differed slightly from one another in the elongation of their radiating bands, but no systematic relation could be found between them. Thus we may conclude that each fragment of Specimen B of electro-deposited cadmium, is made up of an irregular aggregation of many fibrous-like structures.

Conclusion

The arguments which have hitherto been advanced in connection with the crystalline configurations of electrolytic zinc and cadmium, lead us to the following conclusions :—

(1) Some of the specimens of these two metals are composed mostly of a few crystals of considerable size ; but the others are of an incomplete fibrous-like structure in which the micro-crystals of zinc or cadmium rotate within a certain angle around the direction normal to their common plane. In either case, the crystals forming the specimens were so arranged that each of them has one of its $(2\bar{1}\bar{1}0)$ planes in common.

(2) The normal either to the aforesaid common plane or to another $(2\bar{1}\bar{1}0)$ plane inclined by an angle of 60° to this common plane of the crystals, coincides with the direction of the maximum growth of these electrolytically deposited specimens.

From the statements above mentioned, it may be inferred that the lateral faces $(2\bar{1}\bar{1}0)$ of the hexagonal prism of the second order of zinc and cadmium crystals, have a distinctive physical nature. Furthermore, these statements seem to elucidate the reason why the branchlets of the electrolytic specimens of zinc and cadmium make an angle of 60° with each other.

In conclusion, the writers wish to express their sincere thanks to Professor Denzo Uno for his constructive suggestions and the interest he has taken in this investigation. Their thanks are also due to Dr. Hisaji Komatsubara of the Imperial Mint, who kindly supplied all the specimens required, and to Mr. Toshio Yawata for his continual aid during the progress of the experiment.

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Plate I

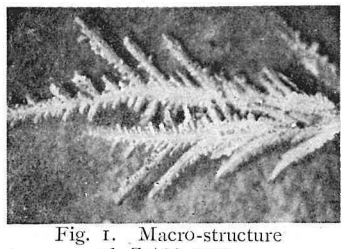

Fig. 1. Macro-structure of *Zn*(A) ×19

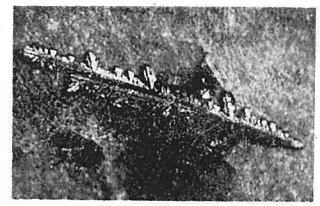

Fig. 2. Macro-structure of *Cd*(A) ×19

Fig. 3. Macro-structure of *Cd*(B) ×15

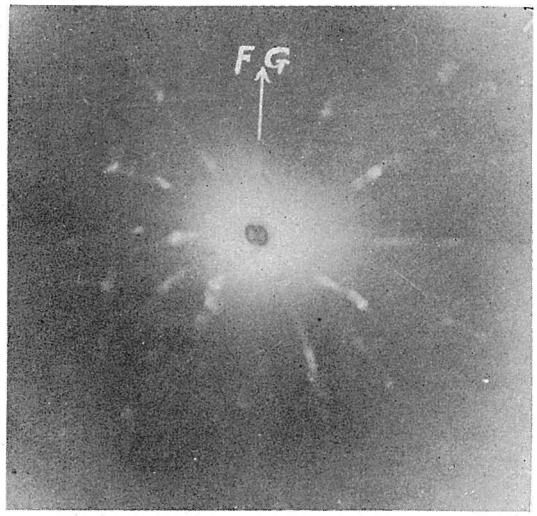

Fig. 4. *Zn*(A)

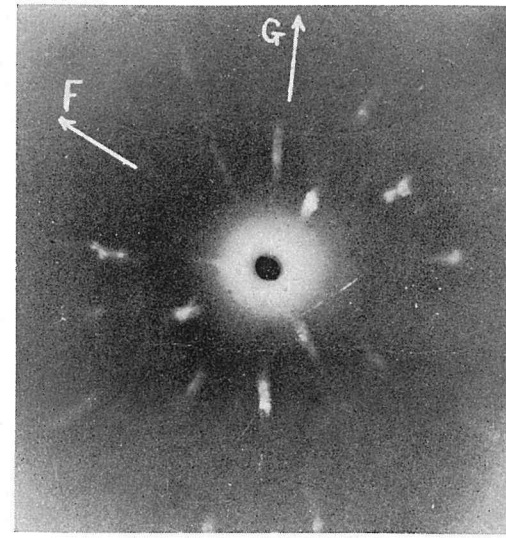

Fig. 5. *Zn*(A)

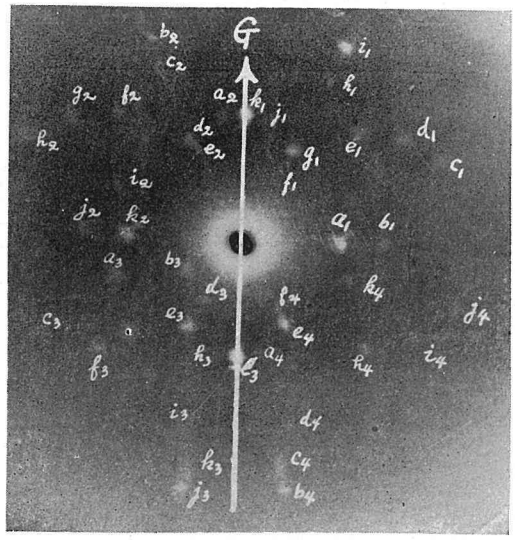

Fig. 6. *Zn*(A)

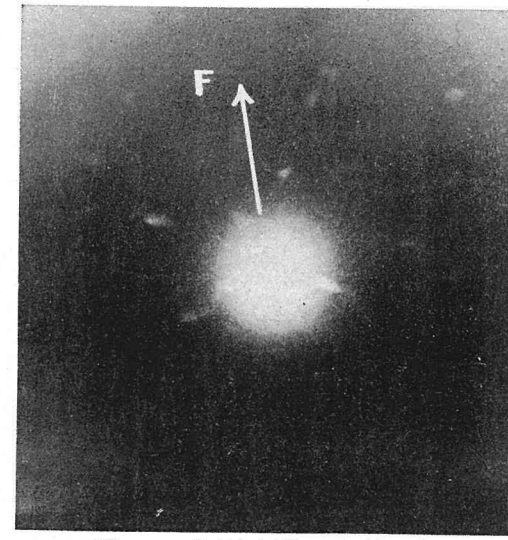

Fig. 10. *Zn*(A) (oblique incidence)

Plate II

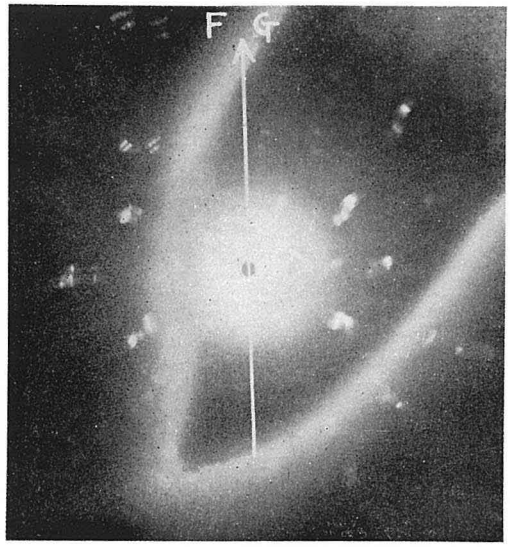

Fig. 13. *Cd*(A)

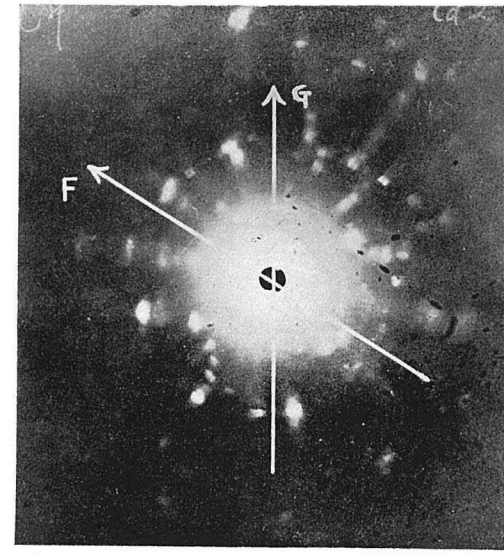

Fig. 14. *Cd*(A)

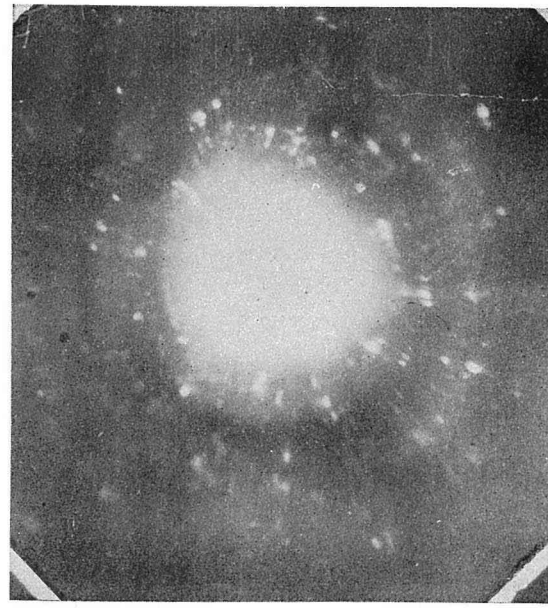

Fig. 18. *Cd*(B)