# Arrangement of the Micro-crystals of Silver Bromide Electro-deposited on the Anode Silver Plate

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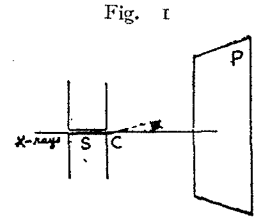
**Abstract**

X-ray studies on substances electro-deposited on the electrode in the solution of an electrolyte have been carried out mainly on the micro-crystals of metals deposited on the cathode. In the present experiment the writer examined the micro-crystals of silver bromide electro-deposited on the anode silver plate in a water solution of potassium bromide.

## 1. Preparation of Specimens

As the solution of an electrolyte the following two kinds were mainly used: the one a water solution of potassium bromide of 1/10 normal concentration which was acidified by adding a small quantity of hydrobromic acid to neutralize the caustic potash produced in the solution by the electrolysis; and the other a water solution of potassium bromide having the same concentration as the above but alkalized from the beginning by the addition of a small quantity of caustic potash. In the following report the former is called A solution and the latter B solution. Silver bromide was electro-deposited on the anode silver plate in a bath of each of these solutions. Specimen C in Fig. 1 was illuminated by the K radiations of copper falling obliquely to its surface with an angle of $\alpha$, and the X-ray diffraction pattern was impressed on the photographic plate P standing perpendicularly to the incident X-ray beam.

Fig. 1




## 2. Silver Bromide Crystals Electro-deposited in the A solution

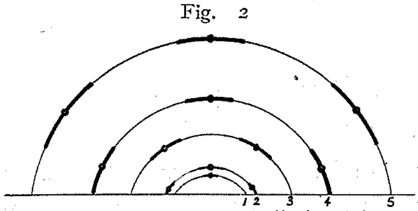
Fig. 1 in Plate I shows the X-ray diffraction pattern obtained by making $\alpha=15^\circ$, with the micro-crystals of silver bromide electro-deposited on the anode silver plate in the A solution, when the electrolysis was continued for ten minutes at the temperature of 18° C, and with the current density of 12 milli-amperes per square centimetre of the anode surface. The silver plate used in the present case had been annealed before it was employed as the anode; so that the micro-crystals of silver in the plate are considered to be arranged at random. The diffraction pattern obtained in this case is composed of ordinary Debye-Scherrer rings and no trace of a fibrous arrangement of the micro-crystals of silver bromide is detected. As the same pattern was always obtained, whatever the orientation of the silver plate for the incident X-rays might be, it is concluded that the orientation of the micro-crystals of silver bromide is at random in this case, parallel with the random orientation of the micro-crystals of the anode silver plate.

Next, Figs. 2 and 3 in Plate I are the X-ray diffraction patterns obtained with the silver bromide electro-deposited on the rolled silver plate, under the same conditions as above mentioned, when the direction of the incident X-rays is respectively perpendicular to the direction of the rolling and along it at the angle $\alpha$ of $15^\circ$. Fig. 2 in Plate I shows the fibrous arrangement of the micro-crystals of silver bromide, but Fig. 3 in Plate I scarcely shows it. These facts indicate that the axis of the fibrous arrangement of the micro-crystals of silver bromide in this case is parallel to the direction of the rolling.

Before determining the fibrous axis, care must be taken that the rings reflected by the atomic planes with indices of all odd numbers scarcely appear, though it goes without saying that the rings reflected by the atomic planes with indices of mixed even and odd numbers are entirely eliminated, as the crystal structure of silver bromide is cubic of the rock-salt type.

The writer used the crystallographic globe[1] devised by Prof. U. Yoshida to determine the fibrous axis; and it is discovered that the micro-crystals of silver bromide have the limited fibrous arrangement in which their cubic faces (001) are nearly parallel to the surface of the silver plate and the fibrous axis is in the direction perpendicular to the dodecahedral face, i. e. [110] and it is parallel to the rolling direction. In Fig. 2 the circular dots represent the positions of the reflected X-ray beam in the case of perfect fibrous arrangement when the K$\alpha$ radia-

Fig. 2




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

tion of copper strikes the specimen perpendicularly to the fibrous axis [110] at the angle $\alpha$ of $15°$; the circular arcs drawn in thick line represent the diffraction pattern as it actually appeared in Fig. 2 in Plate I and the semicircles drawn in thin line are the ordinary Debye-Scherrer rings. The pattern impressed by the $K\beta$ radiation of copper is omitted in the figure. As will be seen in Fig. 2, the agreement between the observation and the calculation is fairly satisfactory. Here it must be noted that the two circular arcs at both ends of (200) ring in Fig. 2 appeared weak and the central circular arc on the same ring in Fig. 2 appeared very strong in the diffraction photograph and that the arcs on (220) ring appeared stronger in intensity than those on the other rings in the diffraction photograph. These facts are in conformity with the view that the orientations of the microcrystals of silver bromide are mostly concentrated to such an ideal one that their cubic face is parallel to the surface of the silver plate by making the normal to a dodecahedral face parallel to the rolling direction along the surface of the silver plate.

The same diffraction pattern as above was also obtained with the specimen electro-deposited in the bath of neutral water solution of potassium bromide or hydrobromic acid.

The micro-crystals of the rolled silver plate arrange in an imperfect fibrous manner having the direction [112] as the fibrous axis parallel to the rolling direction and by setting the dodecahedral face (110) almost parallel to the surface of the silver plate.[1] Thus it is natural to suppose that the micro-crystals of the silver bromide eloctro-deposited on the anode rolled silver plate in acidified or neutral potassium bromide solution or hydrobromic acid solution, assume the cubic form and that their cube-faces lie parallel to the dodecahedral faces of the micro-crystals of silver, which are mostly parallel to the rolled surface of the silver plate; and moreover that the [110] axis of the micro-crystals of silver bromide takes the same direction as the fibrous axis of the silver crystals in the silver plate, which is parallel to the rolling direction of the plate.

### 3. Silver Bromide Crystals Electro-deposited in the B Solution

The diffraction pattern reproduced in Fig. 4 of Plate I was obtained by sending the K radiations of copper to the silver bromide

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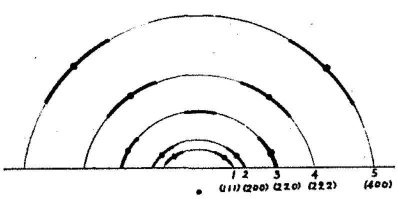
1. R. Glocker: Zeits. f. Phys., **31**, 386 (1925).

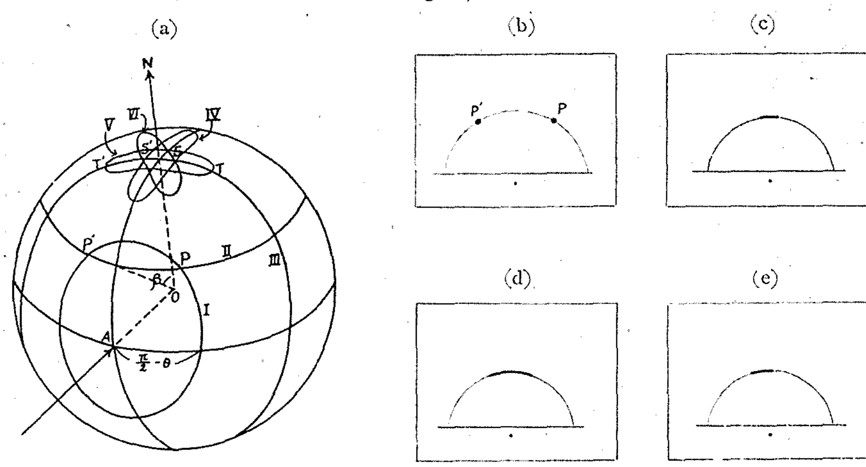
crystals electro-deposited on the surface of an annealed silver plate in the bath of B solution under the conditions mentioned before. This pattern shows an evident fibrous arrangement of the micro-crystals of silver bromide. As the same diffraction pattern was always obtained, whatever the orientation of the silver plate might be, when the angle $\alpha$ was kept constant at $15^\circ$, it is concluded that the fibrous axis is perpendicular to the surface of the silver plate. It was discovered by the aid of the crystallographic globe that the fibrous axis was in the direction of the normal to the dodecahedral face, that is [110], and was perpendicular to the surface of the silver plate. The circular dots in Fig. 3 show the positions of the diffracted $K\alpha$ radiation of copper which are calculated by assuming that the fibrous arrangement is perfect by taking the fiber-axis as discovered above at the angle $\alpha$ of $15^\circ$, and the circular arcs drawn in thick line represent the diffracted spots actually observed on the photograph. The agreement between the observation and the calculation is fairly satisfactory except on the diffraction ring from the atomic plane (220), where a strong diffraction actually occurred, at its middle, at a position not expected from the calculation. This discrepancy seems to be due to some scattering of the fibrous axis within a certain range and this point will be discussed later.

Fig. 3



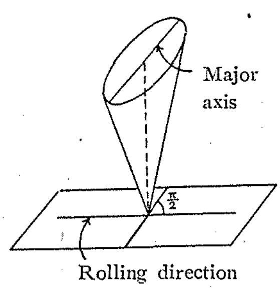

Next, the arrangement of the micro-crystals of silver bromide electro-deposited on the surface of a rolled silver plate was investigated. The silver bromide was electro-deposited on the rolled silver plate under exactly the same conditions described above. The K radiations of copper was sent to the surface of the specimen perpendicularly to and along the rolling direction respectively in Figs. 5 and 6 in Plate II, by making the angle $\alpha$ equal to $22^\circ$ in both cases. The reason why we have made the angle $\alpha$ equal to $22^\circ$ will be revealed afterwards. As the mean positions of the diffraction arcs of these figures coincide with those of Fig. 4 in Plate I, it is understood that the fibrous axis of the micro-crystals of silver bromide is [110] and it stands perpendicular to the surface of the silver plate as in the case of Fig. 4, Plate I. However, on minute inspection, it was observed that the length of the central arc of (220) ring in Fig. 5 in Plate II is shorter than that in Fig. 6 in Plate II. In order to investigate this point, let us construct a sphere of unit radius taking as its center the point O where the specimen is located, in the manner shown in Fig. 4 (a). The K$\alpha$ radiation of copper proceeds in the direction AO, and the direction of the fibrous axis of the micro-crystals of silver bromide is represented by

Fig. 4




ON. If the glancing angle of the K$\alpha$ radiation of copper to a certain atomic plane of the crystal of silver bromide which is just situated to be able to reflect the radiation is $\theta$, then the direction of the normal to the atomic plane which is able to reflect the radiation generates a circular cone having a semi-vertical angle of $\frac{\pi}{2}-\theta$, whose vertex and central axis are O and OA respectively. The intersection of this cone with the unit sphere is represented by the circle I in Fig. 4 (a), which we call the reflecting circle. If in the fibrous arrangement the normal to the same atomic plane makes an angle $\beta$ with ON, the normal also generates a circular cone whose vertex is O, central axis is ON and semi-vertical angle is $\beta$. The intersection of this cone with the unit sphere is shown by the circle II in Fig. 4 (a). If the circles I and II intersect at the points P and P', then two diffraction spots ought to appear on the photograph in the manner shown by the points P and P' in Fig. 4 (b). In the present case ON intersects the reflecting circle III of the atomic plane (220), because the angle $\alpha$ is made to be $22^{\circ}$ which is equal to the glancing angle of the atomic plane (220) of the crystal of silver bromide for the K$\alpha$ radiation of copper to make it reflect from the plane. Thus a diffraction spot ought to appear on the centre of the (220) ring in Fig. 3. But actually this point appears as a circular arc of a certain length in Figs. 5 and 6 in Plate II. This seems to be due to the fact that the fibrous axis is scattered within a certain range around the direction ON in Fig. 4 (a). If the boundary of this range intersects the reflecting circle III in a narrow range as SS′ in Fig. 4 (a), the length of the central arc of the (220) ring becomes short as shown in Fig. 4 (c) or Fig. 5 in Plate II. On the other hand, if that boundary intersects the reflecting circle III in a wider range as TT′ in Fig. 4 (a), the length of the arc of the (220) ring becomes longer as shown in Fig. 4 (d) or Fig. 6 in Plate II. Considering these facts it seems natural to conclude that the form of the boundary of the scattering of the fibrous axis is not a circular cone, but roughly an elliptic cone having ON as its central axis and a right section of the ellipse with its major axis in the direction perpendicular to the rolling direction as shown in Fig. 5. Accordingly the intersection of such boundary with the unit sphere becomes the curve IV or V respectively as shown in Fig. 4 (a) when the X-rays come in the direction perpendicular to or along the rolling direction at the angle $\alpha$ of $22^\circ$. If this supposition is correct, such intersection becomes the curve VI in Fig. 4 (a) when the X-rays strike the specimen obliquely to the rolling direction at the angle $\alpha$ of $22^\circ$. When the angle $\alpha$ is less than $22^\circ$, for example $15^\circ$, the curve VI intersects the circle III at biassed points, as ON no longer intersects the circle III. Then the central arc of the (220) ring in the diffraction pattern is displaced to one side as shown in Fig. 4 (e). The writer confirmed this point by taking a photograph as shown in Fig. 7 in Plate II under such a condition. Thus it seems to be legitimate to consider that the micro-crysals of silver bromide electro-deposited on the surface of a rolled silver plate in alkalized potassium bromide solution assume the form of dodecahedron and that their dodecahedral faces lie nearly parallel to the surface of the silver plate with some range of the scattering of their orientation as above mentioned. Moreover, as the arrangement of the micro-crystals of silver in a rolled silver plate is such as previously stated, it follows that the dodecahedral faces of the micro-crystals of silver bromide are arranged parallel to the dodecahedral faces of the micro-crystals of silver on the surface of the rolled silver plate, by leaving the orientation of other crystallographic directions to chance.

Fig. 5



Thus the arrangement of the micro-crystals of silver bromide electro-deposited on the surface of the anode silver plate is largely affected by the manner of the arrangement of the micro-crystals of silver on the surface of the anode silver plate. This fact resembles the fact that the arrangement of the micro-crystals of a metal electro-deposited on the surface of the cathode is affected by the manner of micro-crystals of the cathode metal.[1]

## 4. Other Properties

The writer also examined the influence of the electric current density through the bath, the concentration and the temperature of the solution upon the grain size and the manner of arrangement of the micro-crystals of silver bromide. For this purpose the diffraction patterns were taken entirely in the same manner as before; and it was found that the weaker the electric current, the more concentrate the solution and the higher the temperature, the greater the grain, and that the manner of the arrangement of the micro-crystals did not suffer any noticeable effect from these circumstances. These facts are similar to the case of metal crystals electro-deposited on the surface of a metallic cathode.[2]

Besides these facts, it is observed that the grain size of the micro-crystals becomes gradually greater with increase of the duration of electrolysis. Moreover the writer carried out the electrolysis by setting the anode silver plate in two different orientations, one in vertical and the other in horizontal orientation; but no difference in the manner of the arrangement of the micro-crystals was detected between these two cases. This shows that gravity has almost no effect upon the manner of the arrangement of the micro-crystals of silver bromide.

In conclusion, the writer wishes to express his sincere gratitude to Prof. U. Yoshida for giving him invaluable suggestions on the present investigation.

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1. W. A. Wood: Proc. Phys. Soc., **43**, 138 (1931).
2. A. Glazunov: Zeits. f. Phys. Chem., A, **167**, 399 (1933).

## Plate I

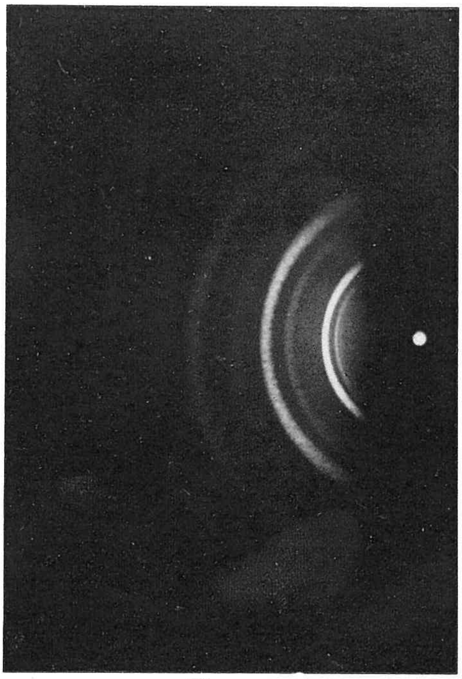

Fig. 1

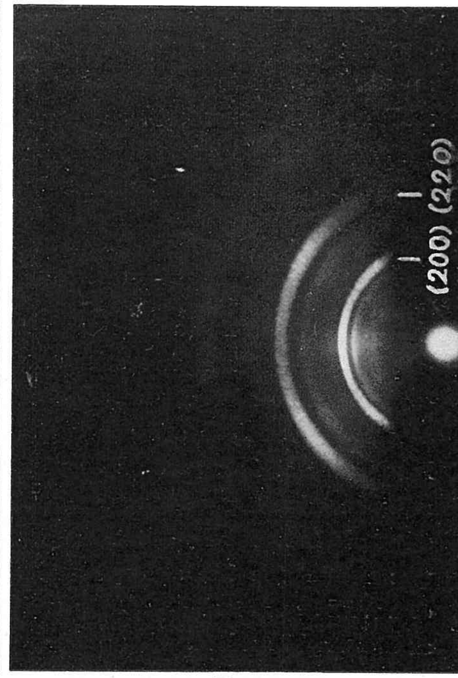


Fig. 2

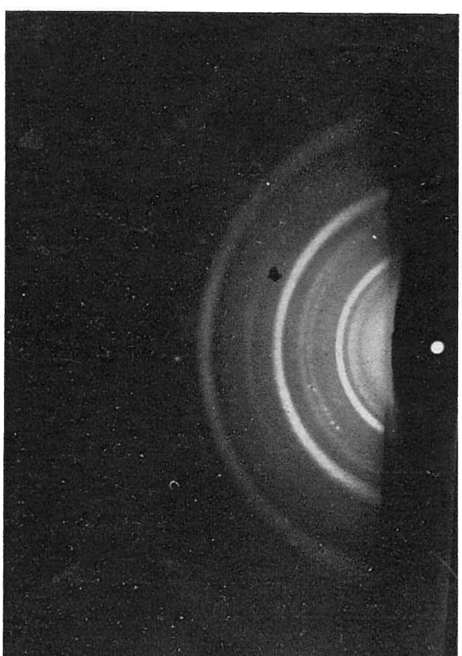

Fig. 3

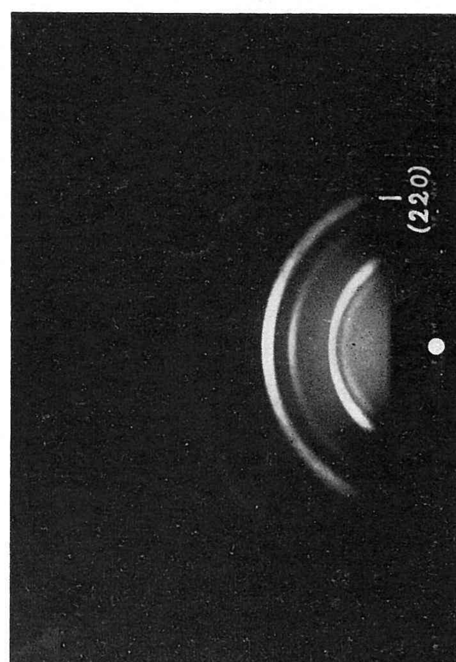


Fig. 4

## Plate II

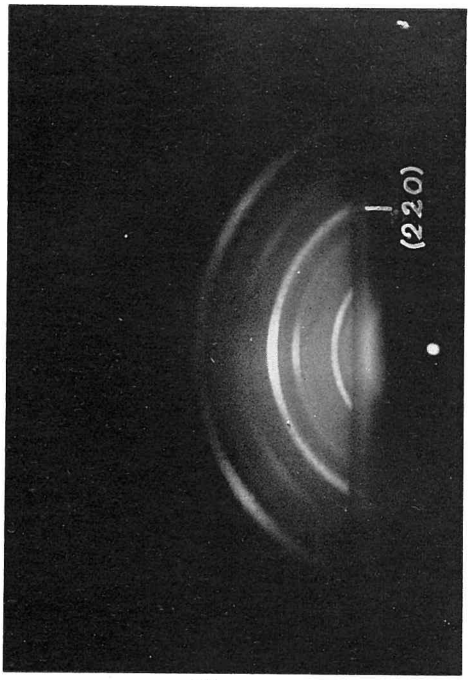


Fig. 5

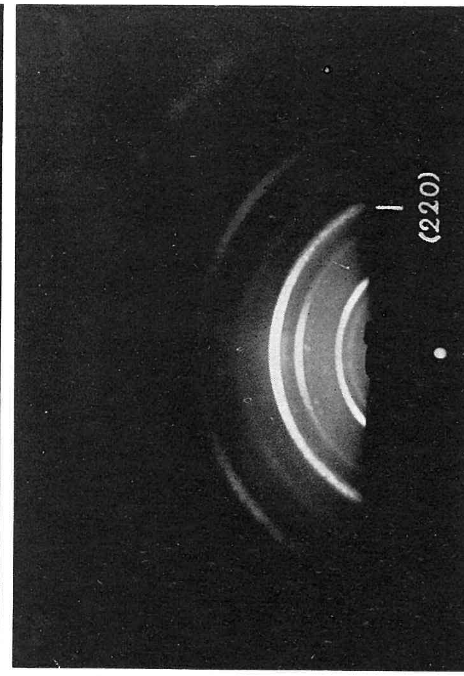


Fig. 6

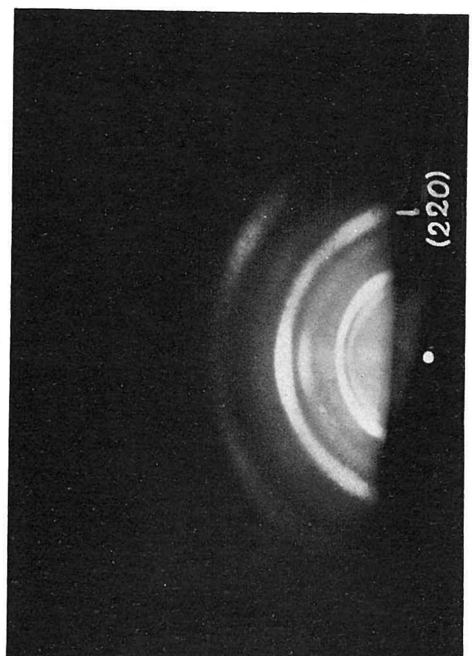


Fig. 7