structure shown in Fig. 3 superimposed on it in broken lines. Fig. 6 shows the final structure.

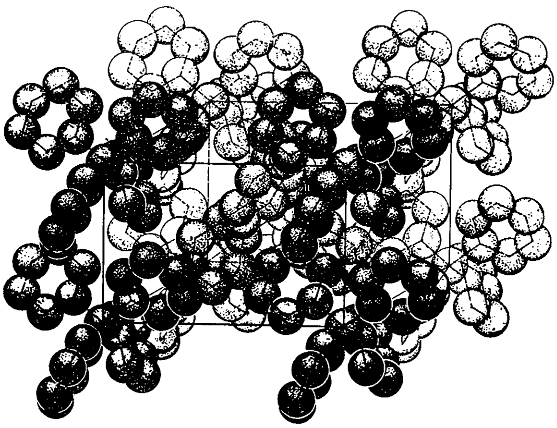

Fig. 6. A three-dimensional model of the tetraphenylmethane structure.

Discussion of the structure

The positions of the atoms are given in Table 2. The atom no. 0 is the central carbon atom and the other atoms are numbered about the six-membered ring.

Fig. 6 was drawn to scale from the data of Tables 1 and 2. Table 2 was used to calculate the interatomic distances, showing that the tetrahedral bonds on the central carbon atom are 1·47 A. while the bonds in the rings are 1·39 A. Fig. 6 indicates the presence of much void space which may account for the low density (1·173 g.cm.$^{-3}$) of this compound, and Fig. 5 indicates that the void space follows planes in the (110) direction in coincidence with the developed planes of the habit of needle crystals.

Table 2. *Atomic coordinates*

Atom number	*x*	*y*	*z*
0	0	0	0
1	0·112	−0·016	0·119
2	0·104	−0·079	0·311
3	0·207	−0·093	0·423
4	0·223	0·034	0·037
5	0·327	0·020	0·149
6	0·319	−0·043	0·341

We are appreciative of a grant from the University of Utah Research Fund for carrying out this project. We are indebted to Dr W. J. Horton for preparation of the crystals and to A. Morrey Bailey for assistance in making certain of the drawings.

References

Binnie, W. P. & Robertson, J. M. (1949). *Acta Cryst.* **2**, 116.
Buerger, J. M. & Klein, G. E. (1946). *J. Appl. Phys.* **17**, 285.
George, H. W. (1926). *Proc. Roy. Soc.* A, **113**, 585.
Patterson, A. L. & Tunnell, G. (1942). *Amer. Min.* **27**, 655.
Robertson, J. M. (1943*a*). *J. Sci. Instrum.* **20**, 169.
Robertson, J. M. (1943*b*). *Nature, Lond.*, **152**, 411.

Acta Cryst. (1950). **3**, 219

Structure and Growth Mechanism of Photolytic Silver in Silver Bromide*

By Chester R. Berry and Robert L. Griffith

Research Laboratories, Eastman Kodak Company, Rochester 4, N.Y., U.S.A.

(*Received* 3 *October* 1949)

An investigation has been made by X-ray and electron diffraction of single crystals of pure silver bromide during the process of photolytic decomposition induced by irradiating the crystals with ultraviolet light. The orientation of the silver determined from the X-ray diffraction patterns is quite different from the orientations determined from the electron diffraction patterns. This corresponds to differences in the silver orientations in the body and near the surface of the silver bromide crystals. Two different mechanisms of silver separation in these two regions of the crystals, one based on the motion of cations, and the other on the aggregation of *F*-centers, appear to account for the silver orientations observed.

Introduction

These investigations were initiated to determine whether there is any preferred orientation of the silver produced by photodecomposition of silver bromide.† Dankov (1939) has suggested that the peculiar photosensitivity of silver bromide may be due to the almost exact correspondence of the length of the face diagonal of the silver unit cell with the cube edge of silver bromide. This would enable the silver to grow on the silver bromide in certain orientations with nearly perfect correspondence of atomic periodicities at the boundary. The two conditions which preserve this correspondence are growth of (100) faces together, one rotated 45° to the other, and growth of (110) faces together, one rotated 90° to the other.

---

* Communication No. 1291 from the Kodak Research Laboratories.

† By microscopic examination, Trivelli & Sheppard (1925) recognized the 'vectorial decomposition' of silver bromide. Photomicrographs shown in their paper appear to agree with present observations.

In a previous paper (Berry, 1949), it was shown that when silver is deposited on a (111) face of silver bromide by vacuum sublimation, growth begins with the symmetry directions of the silver parallel to the corresponding directions of the silver bromide (hereafter called 'parallel orientation'). Surface cracks or terraces along [110] directions are probably effective in aligning the silver, in this case.

Kooy & Burgers (1948) have found that single crystals of silver chloride produce oriented silver when they are irradiated by ultra-violet light, but the orientation had not been determined at that time.

Experimental

The crystals of silver bromide were grown in the form of thin trigonal plates by slow evaporation of a saturated solution of silver bromide in hydrobromic acid. For X-ray diffraction study, crystals about three- or four-tenths of a millimeter in the largest dimension and a tenth of a millimeter or less in thickness were selected and mounted in a Weissenberg camera to rotate about a [110] direction (parallel to an edge of the crystal). Rotation and zero-level Weissenberg patterns were obtained by using filtered copper X-radiation. The crystals used in the electron-diffraction study were about ten times as large as those used in the X-ray study. They were mounted in the electron-diffraction instrument so as to obtain a reflection-type pattern from a large (111) face, with the electrons incident in a [110] direction in that face.

A 4 W. General Electric Steri-lamp, giving considerable visible as well as ultra-violet radiation, was used to irradiate the crystals, which were placed a few inches away. Diffraction patterns were obtained before and after various intervals of irradiation.

Orientations observed by electron diffraction

With the electron beam incident in a [110] direction in the silver bromide, an electron-diffraction pattern of silver would be observed for either of the orientations suggested by Dankov or for the parallel orientation. Before ultra-violet irradiation, no silver was detected even after electron bombardment for several times the normal exposure. With one crystal, silver was found after 8 min. of irradiation. The pattern of the silver was precisely that to be expected for a growth of (110) faces together, the (110) face of silver bromide being one of those at 35° rather than at 90° to the (111) surface. After 16 min. of irradiation, the silver pattern was considerably more pronounced. The diffraction pattern at this stage is shown in Fig. 1. The weaker, sharp spots lying at the corners of a square net are caused by the silver, and the stronger, elongated spots are from the silver bromide.*

After irradiation of the crystal for a total of 45 min., parts of the silver bromide and adhering silver began to break up and gave, in addition to the pattern of Fig. 1, some rings due to randomly oriented crystallites. Further irradiation caused these rings to increase in intensity.

A final diffraction pattern, obtained after about 8 hr. total exposure, showed a wealth of superimposed diffraction patterns. There were the ring patterns from randomly oriented silver and silver bromide, and the spot patterns of silver bromide, of silver growing on a (110) silver bromide face at 35° to the surface, of silver growing on a (110) silver bromide face normal to the surface, and of silver growing on a (100) face of silver bromide. However, no evidence was found of the parallel silver orientation.

A second silver bromide crystal was examined, but no silver reflections were found in the diffraction pattern until after about 2½ hr. of irradiation. At this point, the silver pattern was similar to that shown in Fig. 1. After almost 4 hr. of irradiation, there was observed an additional silver pattern produced by the growth of silver on a (110) face of silver bromide, which was at 90° to the surface. The experiments with this crystal were concluded at this stage.

Orientation observed by X-ray diffraction

The X-ray diffraction photographs of crystals which had received sufficient ultra-violet exposure contained a pattern of silver with preferred orientation, the degree of which, as judged from the length of the maxima on the photographs, was somewhat less than that observed by electron diffraction. In this case, the preferred orientation was the parallel orientation. There was no evidence on any of the patterns of silver oriented in any of the ways found in the electron-diffraction experiments, although if a sufficient amount of silver had been present in these orientations to produce a detectable pattern, it would have been easily recognized. Figs. 2 and 3 are the Weissenberg patterns of the same crystal before and after 3 hr. of ultra-violet irradiation.

Further experimental investigations

It was of interest to determine how great an effect the X-ray beam would have in producing silver in the crystals, since two of the crystals studied by X-ray diffraction showed a faint trace of the oriented silver pattern before exposure to ultra-violet light. The intensity of this pattern was greatly increased by exposure to ultra-violet for 1–3 hr. This was accompanied by some fragmentation and misalignment of the silver bromide. In another instance, a crystal was cut into two pieces, neither of which showed any detectable silver on a Weissenberg pattern taken with a long exposure. One fragment was then exposed to ultra-violet light for 1 hr., after which a Weissenberg photograph was obtained showing a weak pattern of

---

* A few sharp silver reflections, which are not part of the square-net pattern, may be seen at larger angles. These are caused by the same silver–silver bromide orientation, but with the structures joined at a different (110) silver bromide interface.

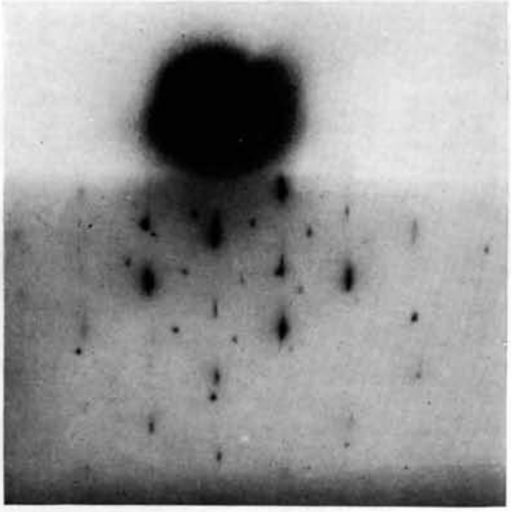

Fig. 1. Electron-diffraction pattern of exposed silver bromide. Reflection from (111) face with electrons incident in [110] direction.

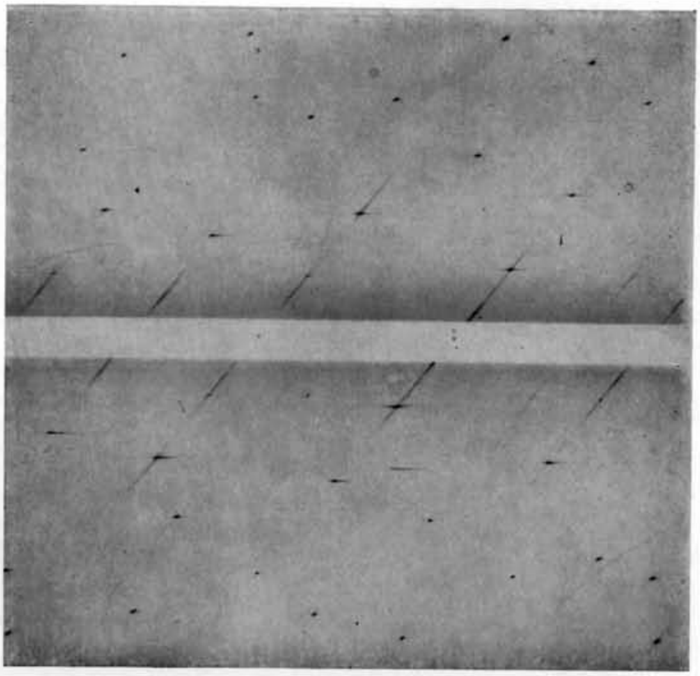

Fig. 2. Zero-level Weissenberg photograph of unexposed silver bromide. Rotation about [110] axis.

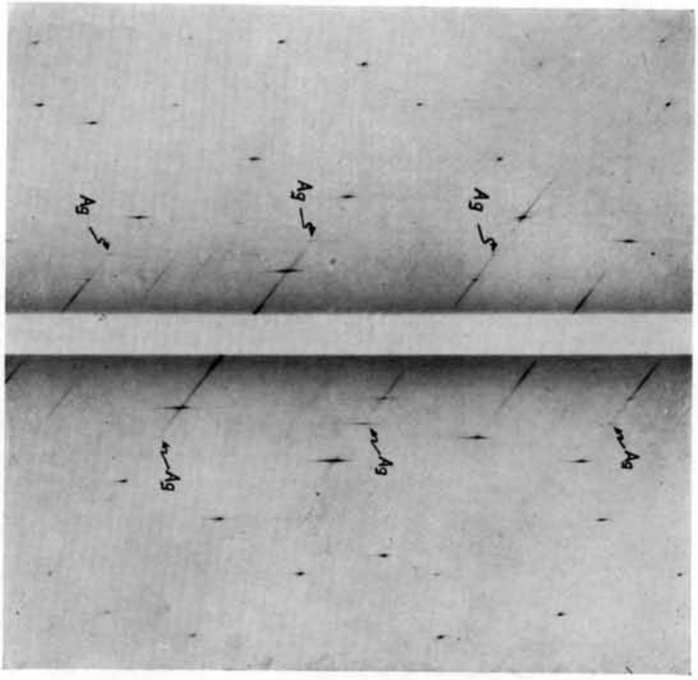

Fig. 3. Zero-level Weissenberg photograph of exposed silver bromide. Rotation about [110] axis.

oriented silver. The second fragment was given twice the X-ray exposure required to record a diffraction pattern, after which no trace of silver could be found on the Weissenberg photograph. This fragment was then exposed to ultra-violet radiation for 1 hr. and a Weissenberg pattern was obtained which showed a weak pattern of silver. This seemed to indicate that most of the silver was the result of the ultra-violet exposure. The fact that, in the case of the first two crystals examined, a faint pattern of silver was observed before ultra-violet exposure may be attributed to the variable sensitivity of the various crystals and to the fact that all of these crystals had been handled in room light.

To assure the fact that the crystals used for the X-ray and electron-diffraction experiments were similar, two crystals were examined, first by electron diffraction and then by X-ray diffraction. After ultra-violet irradiation, the electron-diffraction patterns showed silver growing with a (110) face parallel to a (110) face of the underlying silver bromide. When these crystals were then examined by X-ray diffraction, the pattern of silver in the parallel orientation was found. Reexamination with electrons failed to yield a pattern of silver. Apparently, the surface of the crystals had been altered either by handling or by the action of the X-ray beam. The former seems more likely, since at one stage in the procedure after the initial electron-diffraction study, the crystals were dipped in acetone to dissolve the cement used in mounting them.

Mechanisms of silver separation

Two different mechanisms must be required for the production of the two distinct types of orientation of the silver near the surface and in the body of the silver bromide crystal. Mitchell (1949) has discussed two mechanisms for the formation of silver in a silver bromide crystal. One mechanism depends upon the existence of vacant anion sites. These sites may trap electrons to become F-centers. Then, the F-centers may move in the presence of other vacant anion sites by tunneling of the electrons through the potential barrier, and F-center aggregates may form in lines or planes until the aggregate collapses to the metal lattice. This scheme is proposed by Mitchell to account for the sensitizing action of silver sulfide by introduction of F-centers into the grains of an emulsion.

The second mechanism depends upon the existence of cracks or dislocations in the crystal. In this case, no vacant anion sites or F-centers are necessary and the scheme of cation motion proposed by Gurney & Mott (1938) and revised by Berg (1943) is possible.

These two mechanisms appear to account for the two different types of silver orientation observed by diffraction. The correspondence of the internal orientation of silver observed by X-rays with the orientation of silver observed on depositing the silver on an external surface is a hint that the internal silver may be formed at internal cracks, crevices, or dislocations. Further, Mitchell contends that there are very few Schottky defects inside a relatively pure crystal at room temperature, so the mechanism of F-center aggregation hardly seems possible. Cracks and dislocations probably exist and extend in [110] directions just as in the bubble models of a metal described by Bragg & Nye (1947). Direct evidence for the tendency of dislocation to occur in this direction is obtained from the experiments of Nye (1948) on stressed silver chloride crystals. In every case which he observed, glide directions occurred along [110] lines. The silver atoms form threads along these directions by a process of trapping of electrons and neutralization of these trapped electrons by mobile silver ions in these regions. For lack of constraints in such a region, the silver atoms may close-pack, which causes a [110] direction to develop along this line in the metal structure. Crossing of such threads would give a two-dimensional base on which the silver may build, with its symmetry directions parallel to the corresponding symmetry directions of the silver bromide. The presence of a considerable amount of randomly oriented silver may be due either to nuclei of silver crystals starting to grow in random orientations or to the disorientation caused by distortion during the growth.

On the other hand, the near-surface orientations of silver apparently do not depend upon cracks or dislocations for their growth. The proximity of the surface through which bromine may escape permits replacement of bromide ions with vacant sites and electrons, so that the mechanism of silver separation involving F-center aggregation may operate. Since the mobility of bromine within a crystal is probably due to electron transfer from a bromide ion to a bromine atom (Berg, 1943), no such vacant sites are created except at the surface. In the silver bromide structure, rows containing only bromide ions occur along [110] directions. These rows may be replaced by electrons (aggregated F-centers) which may be combined with nearby silver ions to start the growth of metallic silver in the observed orientations. The difference in the silver threads formed in this case and in the case of internally separated silver must be that the silver atoms are constrained not to close-pack along these lines now, but to preserve the separation of silver atoms in the [100] direction of metallic silver. This may occur here in the more rigid structure, where this is the periodicity of neighboring ions, but it may not occur at a crack. When two crossed or parallel threads have been formed in a (100) or (110) plane of the silver bromide, they may act as a two-dimensional net from which three-dimensional growth may proceed. It is assumed that this process will not operate if the two [110] directions establish a (111) plane because a good fit of silver on silver bromide would not be obtained.

These two mechanisms appear to account for the two different types of orientation of silver. It is assumed that most of the silver formed in these crystals is in the interior at dislocations or internal cracks where only the mechanism involving cation motion can be operative, thus giving only the parallel orientation of silver as observed by X-rays. The electron-diffraction method detects only the silver very near the surface. Since by this method only the orientations suggested by Dankov are observed, one must assume that, although both the mechanism based on cation motion and the mechanism of F-center aggregation may be possible at the surface, the latter is favored. This seems to be explained by the calculations of Simpson (1949) which show that the electron trap associated with a vacant anion site is of greater depth than the trap associated with an interstitial positive ion in silver bromide.

References

BERG, W. F. (1943). *Trans. Faraday Soc.* **39**, 115.

BERRY, C. R. (1949). *Acta Cryst.* **2**, 393.

BRAGG, W. L. & NYE, J. F. (1947). *Proc. Roy. Soc.* A, **190**, 474.

DANKOV, P. D. (1939). *C.R. Acad. Sci. U.R.S.S.* **24**, 773.

GURNEY, R. W. & MOTT, N. F. (1938). *Proc. Roy. Soc.* A, **164**, 151.

KOOY, J. N. & BURGERS, W. G. (1948). *Rec. Trav. Chim. Pays-Bas*, **67**, 21.

MITCHELL, J. W. (1949). *Phil. Mag.* (7), **40**, 249.

NYE, J. F. (1948). *Nature, Lond.*, **162**, 299.

SIMPSON, J. H. (1949). *Proc. Roy. Soc.* A, **197**, 269.

TRIVELLI, A. P. H. & SHEPPARD, S. E. (1925). *J. Phys. Chem.* **29**, 1568.

Acta Cryst. (1950). **3**, 222

The Structures of the *n*-Propylammonium Halides at Room Temperature*

BY MURRAY VERNON KING† AND WILLIAM N. LIPSCOMB

School of Chemistry, University of Minnesota, Minneapolis 14, *Minnesota, U.S.A.*

(*Received* 30 *September* 1949)

Structures are found for n-propylammonium chloride, bromide and iodide with space group D_{4h}^7–$P4/nmm$, with two molecules of $C_3H_7NH_3X$ per unit cell. These structures are related to the structure of tetragonal PbO, with the n-propylammonium ion replacing Pb, and the halide ion replacing O. The cations extend along the fourfold axes; hence they must either rotate or show orientational disorder. Study of the structure factors shows that the cation in the chloride crystal shows configurational isomerism, and an electron-density projection of the chloride crystal shows that a model of the crystal showing free rotation of the cation fits the X-ray data slightly better than a model showing simple orientational disorder. An electron-density projection of the bromide crystal also shows no preferred orientations of the cation, within the limits of error of the determination.

Introduction

Determinations of the structures of n-propylammonium chloride, bromide and iodide have been reported by Hendricks (1928*a*). These structures were related to the cesium chloride structure by the substitution of the n-propylammonium ion for the cesium ion. The unit cell reported was tetragonal, with the cations extended along fourfold axes with the NH_3^+ ends all pointing in the same direction. According to Pauling (1930), the cations must be considered zigzag in shape, and therefore must rotate if the tetragonal symmetry is to be preserved. However, a structure of this same type was reported for methylammonium chloride by Hendricks (1928*b*), but was subsequently disproved by Hughes & Lipscomb (1946), who established a structure in which the NH_3^+ ends of the cations pointed alternately in opposite directions. The present work was undertaken to find whether the n-propylammonium halides also have this type of structure, rather than the structure reported by Hendricks.

Another reason for undertaking this research was to investigate the nature of the rotating group by X-ray diffraction studies. The groups might rotate essentially without hindrance, or might rotate in a potential field, according to the model of the hindered rotator proposed by Pauling (1930), or might show orientational disorder without continuous rotation, according to the model proposed by Frenkel (1935). The n-propylammonium halides were thought to afford a fairly favorable case for the study of the rotating group, since the rotating carbon and nitrogen atoms have appreciable scattering power for X-rays, whereas in many crystals, only hydrogen atoms rotate.

Preparation and physical properties of crystals

Crystals of n-propylammonium chloride, bromide and iodide were prepared by recrystallization from organic solvents by cooling hot, nearly saturated solutions to room temperature and letting the solutions stand for 2 days. For the chloride, chloroform was used as the solvent; for the bromide, n-butyl acetate was used; and

---

* This paper is in part material from a thesis submitted by M. V. King to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the Ph.D. degree.

† Present address: Department of Physics, The Pennsylvania State College, State College, Penna., U.S.A.