

About each sodium atom are six fluorine atoms with distances $\text{Na}-2\text{F}_I=2.31$ A. and $\text{Na}-4\text{F}_{II}=2.36$ A. Each thorium atom is bonded to nine fluorine atoms, the interatomic distances being

$$\text{Th}-3\text{F}_I=2.34 \text{ A.}, \quad \text{Th}-3\text{F}_{II}=2.42 \text{ A.}$$

and $\text{Th}-3\text{F}_{II}=2.35$ A.

The mean distances are

$$\text{Na}-6\text{F}=2.34 \text{ A.} \quad \text{and} \quad \text{Th}-9\text{F}=2.40 \text{ A.}$$

The distances observed in other compounds are (Zachariassen, 1948a):

$$\beta_1\text{-K}_2\text{ThF}_6 \quad \text{Th}-9\text{F}=2.38 \text{ A.}$$

$$\beta_2\text{-Na}_2\text{ThF}_6 \quad \text{Th}-9\text{F}=2.42 \text{ A.} \quad \text{and} \quad \text{Na}-6\text{F}=2.33 \text{ A.}$$

$$\text{NaF} \quad \text{Na}-6\text{F}=2.31 \text{ A.}$$

Clearly the NaTh_2F_9 structure is obtained from that of U_2F_9 by replacing uranium with thorium and by inserting the sodium atoms into octahedral 'holes'.

Attempts to prepare the analogous compound

NaU_2F_9 have been unsuccessful. In the system $\text{NaF}-\text{UF}_4$ there is no phase between UF_4 and NaUF_5 .

I am grateful to Dr Ralph Livingston for the samples of U_2F_9 and of ThF_4 , and to Miss Anne Plettinger for having taken the diffraction patterns.

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Structure of Thin Films of Silver and Silver Iodide on Silver Bromide Substrates*

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The electron-diffraction reflection method has been used to examine thin deposits formed on large single crystals of silver bromide. Silver films were prepared by evaporation and silver iodide was formed by reaction of the silver bromide with dilute solutions of potassium iodide and of a cyanine iodide sensitizing dye. The various orientations and structures of these deposits can be accounted for by assuming that the coating layers are built up by a disordered stacking of close-packed layers on minute octahedral faces of the substrate. Comparison is made with related observations previously reported by others.

Thin films of silver and silver iodide on the surfaces of single crystals of silver bromide have been examined by the reflection technique of electron diffraction. These deposits are of particular interest because of the possibility of their occurrence in photographic processes.

Experimental

Crystals of silver bromide, in the shape of hemispheres 1 cm. or larger in diameter, were grown on an air-cooled platinum finger placed in contact with the surface of the melt. The melt was at roughly 15°C. above the melting-point, and the air velocity was crudely adjusted so that the grown crystal was ready to be raised from the melt in about 2 hr. Usually, more than one individual crystal was formed, but only single-crystal regions were used in the diffraction experiments. Since

cleavage faces cannot be made on silver bromide, flat faces were ground against sandpaper and then polished against filter paper moistened with ordinary photographic fixing solution. The existence of more than one crystal domain could be readily detected at this stage by the appearance of demarcation lines caused by different rates of etching in the various domains. From the electron-diffraction pattern Miller indices were assigned to the face, and, by further grinding and polishing at the appropriate angle to this face, a face having small indices could be formed. Since the (111) face is predominant in the usual precipitates of silver bromide, it is of special interest and was studied more than any others.

Deposits of silver were formed on these substrates by evaporation in the specimen chamber of the electron-diffraction instrument. The silver in the form of a fine wire was weighed and placed on a tantalum strip at

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a distance of 6–8 cm. from the substrate. The pressure in the chamber was of the order of 5×10^{-4} mm. Hg during evaporation. The substrate was kept at room temperature, while the tantalum was heated quickly to a temperature such that the silver was deposited at a rate of roughly one atom layer per second. The weights of some deposits on glass were determined by chemical analysis as a calibration of the evaporation process. Diffraction patterns were readily produced by silver deposits having an average thickness between 4 and 5 Å. These thin deposits disappeared completely after bombardment in the electron beam for about 30 sec. However, only about 10 sec. were required for making a suitable photographic exposure on Eastman Kodak Contrast Lantern-Slide Plates.

Deposits of silver iodide were formed by reaction of the substrate crystals with dilute aqueous solutions of potassium iodide or of a carbocyanine iodide dye, such as may be used to change the spectral sensitivity of a photographic emulsion. The concentrations were of the order of 10 mg.l.⁻¹, and will be stated specifically in the discussion which follows. The reactions were allowed to take place by placing the silver bromide crystals in these solutions at room temperature and allowing them to stand without stirring for about 20 min. The surface was then rinsed with distilled water, dried, and examined in the diffraction instrument.

The diffraction patterns were obtained in the General Electric electron-diffraction instrument at an accelerating potential of about 40 kV., and generally ten or more patterns were recorded for each coating layer or type of reaction.

Structure of silver

The diffraction patterns of thin silver deposits contain both spots and rings superimposed on the pattern of the substrate. Because of the small size of the silver crystallites, both the spots and the rings are rather broad, and the ring intensities quite unlike those in normal X-ray powder patterns. The ring intensities observed correspond to those predicted by Germer & White (1941) for aggregates of about 55 atoms. Fig. 1 shows the pattern obtained when the electron beam was incident in a twofold direction of the substrate on whose (111) face the deposit had been allowed to stand for 16 hr. The sharper spots which are drawn out normal to the shadow edge by refraction are from the substrate. The relative intensities of the spots and rings suggest that there may be roughly equal amounts of silver present in random and in preferred orientations. The diffraction patterns from deposits which had been allowed to stand for 16 hr. before photographing, compared to those taken within a few seconds after deposition, indicated some increase in crystallite size by an increase in resolution of the innermost rings, for which $h^2 + k^2 + l^2$ equals 3 and 4. According to the calculations of Germer & White (1941) on the diffraction effects for small spherical crystallites of atoms in cubic close-

packing, these rings are well resolved for particles containing 379 atoms, whereas they are unresolved for aggregates of 55 atoms. An attempt to determine the crystallite size from microphotometer traces of the rings was not successful because of uncertainty in the base-line position. No change in the sharpness of the spots was observed on allowing the deposit to stand. From the breadth of the spots, a crystallite size of 40 Å. was estimated.

The various preferred orientations of the silver will now be considered. Photographs of a deposit on a cube face with the electron beam incident along a fourfold direction showed a single silver orientation which was identical with that of the substrate. Further experiments showed the diffraction spots on this apparently single orientation to be caused actually by a superposition of spots of several orientations. Most photographs were obtained with electrons incident in a twofold direction of the silver bromide. Under these circumstances, when the deposit was on a (111) face, four separate orientations of the silver were observed, as in Fig. 1.

The four orientations of the silver may be described in Fig. 2 which is a schematic representation of some of the features of Fig. 1. Here, *P* is the point where the undeviated beam registered, *EE* is the shadow edge, and the directions *A* and *B* are parallel to two of the threefold symmetry axes of the substrate crystal. One of the silver orientations is identical with that of the substrate and also has threefold symmetry directions parallel to *A* and *B*. Each of the other three silver orientations may be described by the directions of two of its threefold axes which are parallel to the pairs of directions, *A* and *C*, *C* and *F*, and *B* and *D*. The first two of the orientations just described have patterns of equal intensity, and the last two have patterns of equal but much smaller intensity than the first two. A similar diffraction pattern was observed from a deposit of silver on a thin hexagonal-shaped platelike crystal which had been grown from hydrobromic acid solution.

These orientations are rather like those described by Cochrane (1936) for deposits of nickel or cobalt on a (110) face of a single crystal of copper. Cochrane pointed out that the orientations he observed could be explained as a repeated twinning on (111) faces of the crystals as they grew out from minute octahedral faces of the substrate. A more recent treatment of this type of disorder in the stacking in layer lattices has been given by Wilson (1942).

The two orientations whose threefold directions have been described in Fig. 2 as parallel to *A* and *B* and to *A* and *C* arise from close-packed layers of silver which build out in the *A* direction in the two possible sequences for stacking the three kinds of layers of a face-centered cubic array of atoms. The equality of intensities from the two orientations indicates that either sequence was equally probable at the start. If the two sequences occur in a given crystallite, twinning is said

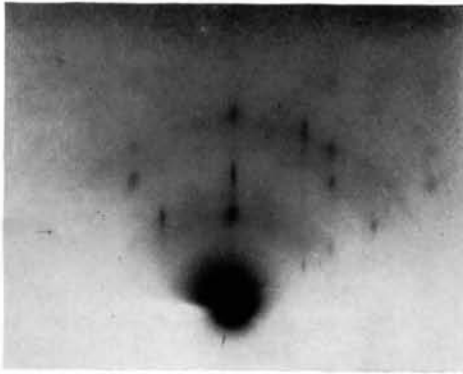


Fig. 1. Silver deposit, $\sim 5 \text{ \AA}$. thick, on a (111) face of silver bromide. Electrons incident along a [110] azimuth.

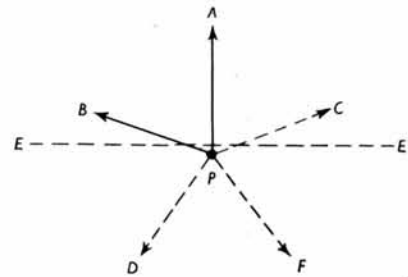


Fig. 2. Schematic representation of directions of three-fold symmetry in photographs of some deposits on a (111) face of silver bromide.

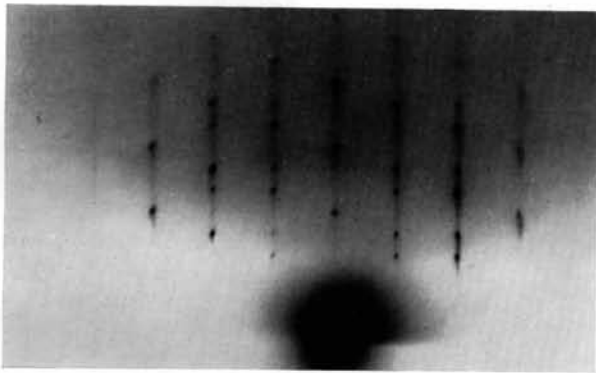


Fig. 3. Two orientations of cubic silver iodide on a (111) face of silver bromide.

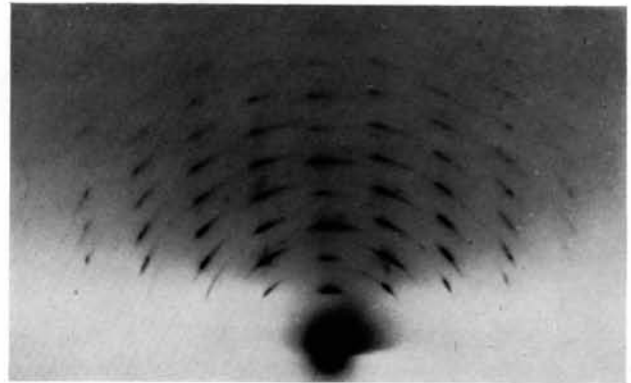


Fig. 4. One prominent orientation of hexagonal silver iodide on a (111) face of silver bromide.

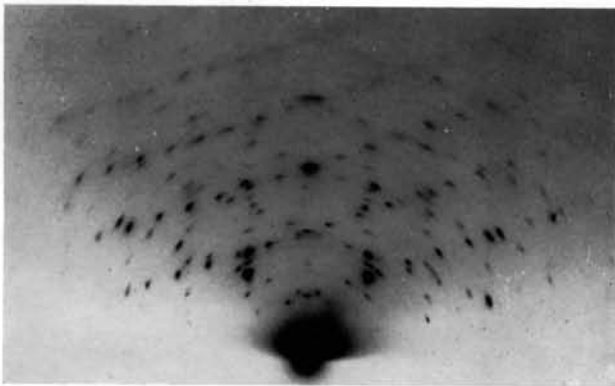


Fig. 5. Five orientations of silver iodide on a (111) face of silver bromide. Three orientations due to the hexagonal structure, and two orientations due to the cubic structure.

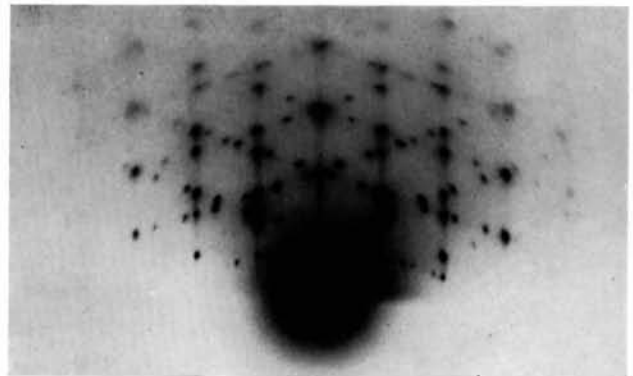


Fig. 6. Four orientations of silver iodide on a (111) face of silver bromide. Two orientations due to the hexagonal structure, and two orientations due to the cubic structure.

to occur. That twinning is probable is supported by the observation of the two orientations, whose threefold directions are parallel to B and D and to C and F , which arise from a twinning of the silver crystallites on those (111) faces which develop normal to B and C . It is observed according to expectation that these latter two orientations produce very much weaker diffraction patterns than the first two.

The existence of multiple orientations of silver in the photograph just described is not inconsistent with the observation of only one orientation in photographs with the electron beam incident in a fourfold direction of the substrate. It may be shown, by using simple transformations of co-ordinates, that all four orientations described in Fig. 2 produce spots on only the one square net observed in photographs where the substrate pattern has a fourfold symmetry.

When rather thick layers of silver (~ 500 Å.) were deposited at about the same rate as the thin layers, the diffraction patterns contained both rings and spots. The intensities in the rings corresponded to those in normal X-ray powder diagrams, and the spots were much sharper than for the thin deposits. The preferred orientations observed were generally the same as those observed for the thin layers, but, in addition, a few extra spots were observed which could not be explained by twinning of the silver on its (111) planes after building on octahedral faces of the substrate. Since no two of the extra spots were related to the same preferred orientation, it was not possible to determine the orientations. It was observed that at least two other orientations existed such that [110] and [311] directions in the silver were normal to the octahedral face of the substrate. None of the patterns from thick or thin deposits showed streaks which might indicate the development of particular faces on the deposits.

Structures of silver iodide

The films of silver iodide which are formed by reaction of silver bromide crystals with dilute aqueous solutions of potassium iodide or of a carbocyanine iodide dye have been observed to have either the hexagonal wurtzite-type structure or the cubic zinblende-type structure. In some instances, weak powder rings of the hexagonal structure were observed in addition to the spots due to the oriented layer.

Most photographs were obtained with the electron beam incident in a twofold direction of the substrate. In this orientation, the differences between the cubic and hexagonal silver iodide patterns are quite obvious, and identification of the particular structure is very simple. The difference in the two patterns is accentuated by multiple reflections which give the forbidden 001 hexagonal reflection whose spacing is 7.51 Å. In most photographs these multiple reflections cause all the diffraction spots to have equal intensities, whatever the structure factors.

The diffraction patterns resulting from the coatings

formed by reaction of the silver bromide with the dye solution indicated the formation of the hexagonal modification of silver iodide and in some instances some of the cubic modification. On the other hand, the reaction with potassium iodide gave patterns which, in all cases, were due to the cubic modification alone. This is quite contrary to the report of Schwab (1947), who found by X-ray diffraction only the hexagonal modification in oriented coating layers of silver iodide on silver bromide. However, he used a potassium iodide solution which was more concentrated and undoubtedly produced a coating layer which was much thicker than those used in the present experiments. This difference in structures may be a confirmation of the observation of Kolkmeijer & van Hengel (1934) that silver iodide is precipitated from solution in the cubic form if silver ions are in excess, and in the hexagonal form if iodide ions are in excess.

The preferred orientations of a silver iodide layer formed by reaction of an octahedral face of the substrate with potassium iodide solution may be described by the schematic representation in Fig. 2. As has been stated previously, the directions A and B represent the directions of two of the threefold directions of the substrate crystal in the diffraction pattern. When the potassium iodide solution is particularly dilute, 1.4 mg.l.⁻¹ of water, only one orientation of cubic silver iodide results. This orientation is identical with that of the substrate and has two of its threefold directions parallel to A and B . If the concentration is 90 mg.l.⁻¹ of water, two orientations of cubic silver iodide result. One orientation is identical with that of the substrate, but the other has two of its threefold axes parallel to A and C . The spots on the photograph generally show considerable streaking in the A direction. Such a photograph is shown in Fig. 3. In some photographs, both spots and streaks occurred at those points where $h - 2k + l = 6n$, and streaks alone occurred at the other positions. The two orientations of the cubic silver iodide and streaking in the threefold direction of reflections for which $h - 2k + l = 2m \neq 6n$ is in agreement with the predictions from the theory of Wilson (1942), which explained the X-ray diffraction patterns from cobalt, reported by Edwards & Lipson (1942) as caused by a disorder in stacking of close-packed layers of the crystals. The existence of this stacking disorder only for the reaction in the more concentrated potassium iodide solution is quite reasonable.

When the silver bromide crystal was put in a solution of 20 mg. of carbocyanine iodide in water (20 mg.l.⁻¹), a silver iodide coating was formed which had several orientations, and on some occasions both cubic and hexagonal crystals grew simultaneously. The hexagonal axes of the silver iodide crystals had the three possible orientations along the directions A , B , or C of Fig. 2. The orientations along B and C usually gave equally strong patterns, but these were generally weaker than that given by the orientation along A . Fig. 4 shows

a pattern from a hexagonal silver iodide deposit in which the only reflections of high intensity are those whose crystallites have their hexagonal axes in the direction *A*, normal to the shadow edge.

Often two cubic patterns appear whose orientations are the same as have just been discussed for the reaction with potassium iodide. Fig. 5 shows a photograph of the two cubic orientations and three hexagonal. Fig. 6 shows a photograph of the two cubic orientations, and only those two hexagonal orientations whose axes are along the *B* and *C* direction of Fig. 2. Wherever spots corresponding to the cubic structure exist, they have streaks passing through them. The origin of these various orientations of cubic and hexagonal silver iodide may be explained in terms of a type of stacking disorder in which layers stack along the normal to the octahedral face of the substrate in the direction *A* in Fig. 2, and along the threefold direction *B* or *C* which may develop in the resultant structure.

Since it was thought possible that the initial stages in the growth of these layers might determine the final result, some experiments were performed in which growth was started in one solution, then continued in a different one. The growth at a particular time was found to depend upon the character of solution rather than upon the seeds which had been formed. The potassium iodide solution caused only the cubic modification to grow, whereas the dye iodide solution caused both hexagonal and cubic growth.

Similar effects were observed when other faces of the silver bromide were used. To account for the orientations observed, it must be assumed that minute octahedral faces exist in the substrate on which the close-packed silver iodide layers could build.

Lattice parameters

In many photographs, diffraction spots from both the substrate crystal and the coating layer were present, and measurements of relative lattice parameters were obtained. These measurements were complicated by lack of sharp spots in the photographs. In the measurements of thin coatings of silver, the spots were broad because of the small size of the crystallites. Moreover, spots were generally neither small nor radially symmetric, owing to refraction effects or to slight misalignments of crystallites about the preferred orientations. In addition to these factors, there may be some error caused by the failure of the diffraction maxima to satisfy exactly the Laue conditions.

The unit-cell constants of silver and silver iodide are given by Wyckoff (1935). When corrected from kX. to Ångström units, the cube edge length of silver is 4.085 Å., and of silver iodide is 6.486 Å. The hexagonal modification of silver iodide has values $c_0 = 7.509$ Å. and $a_0 = 4.589$ Å. The cube edge of silver bromide is 5.775 Å. (Wing, private communication). All the lattice parameters were measured relative to this value for the

substrate. Under these circumstances, the following lattice constants were found:

for silver, $a_0 = 4.10 \pm 0.02$ Å.;

for cubic silver iodide,

$$a_0 = 6.49 \pm 0.02 \text{ Å.};$$

for hexagonal silver iodide,

$$c_0 = 7.53 \pm 0.02 \text{ Å.} \quad \text{and} \quad a_0 = 4.59 \pm 0.02 \text{ Å.}$$

The errors indicated are the average deviations from the mean of several readings from different diffraction records. Within these errors, the values agree with those given by Wyckoff for the pure bulk materials.

Discussion

Some differences in the results of the present study from those of other workers who have studied similar deposits by the electron-diffraction technique deserve comment. Thin films of face-centered cubic metals which Quarrell (1937) prepared on cellulose by sublimation, electrodeposition, chemical deposition, and chemical displacement showed extra rings due to the hexagonal close-packing of the first deposited layers. Studying deposits of various thicknesses, he inferred that the hexagonal close-packing always exists in thin deposits and that transition from hexagonal to cubic close-packing occurs as deposition proceeds. The very thin silver deposits on silver bromide observed in the present study gave no diffraction spots due to hexagonal silver. Of course, the twinning on the (111) face of the cubic silver does introduce layers in the structure which follow the hexagonal stacking sequence, but the number of such sequences is apparently relatively small.

The streaking through the diffraction spots of cubic silver iodide, which is observed in Figs. 5 and 6, and especially in Fig. 3, resembles that shown by Cochrane (1936) in diffraction patterns from deposits of nickel on a single crystal of copper. He attributes the streaks to the layers involved in the twinning phenomenon. But the detailed theory of Wilson (1942) predicts that streaking will occur only for certain classes of reflections, not for all reflections as observed here and by Cochrane. Such reflections as those lying on the central vertical row in Fig. 3, for example, should not be streaked. It appears that the streaks are caused primarily by refraction, since all the streaks are noticeably stronger on the side of the spots near the shadow edge. No streaks were observed in the diffraction patterns of hexagonal silver iodide.

Cochrane's measurement of lattice constants showed that coatings of nickel and cobalt on copper maintained the same atomic spacing as the substrate until the coatings reached thicknesses of about 100 Å. Oriented silver coatings on copper which were not twinned had the usual silver-lattice constant. The present observations show no deviation of lattice constant of the oriented crystallites of silver from that of the bulk material at only 5 Å. thickness. The very poor fit of

the silver structure to the copper or silver bromide substrates compared with the fit of nickel and cobalt to copper may permit the silver to retain its own spacing.

Deposits of silver condensed *in vacuo* on rocksalt cleavage faces at about 200° C. have been examined by Goche & Wilman (1939). It was found that the deposits were twinned on (111) faces, but on heating at 500° C. the films were converted entirely to the single orientation parallel to the substrate. Apparently all of the diffraction spots which appeared with the electrons incident in the [110] direction could be accounted for, as in their Fig. 2 (a), by a twinning on the four (111) faces of the silver crystallites. In the present experiments; there is, in addition to a twinning on the (111) faces of the crystal growing parallel to the substrate, a twinning on the (111) faces of the twins thus formed. Further, it is clear that the amount of twinning on the various (111) faces is not at all the same because of a preferred development of certain faces. This may be illustrated by reference to Figs. 1 and 2. The directions *A* and *B* are each normal to a (111) face of the silver crystallites growing parallel to the substrate. That there is much more growth of twins on the face normal to *A* than on the face normal to *B* is indicated by the much stronger spots corresponding to the *AC* orientation than to the *BD* orientation. The *CF* orientation is due to a twinning on the face normal to *C* which is a (111) face on the twin on the face normal to *A*. The equality of intensities of reflections due to *BD* and *CF* orientations indicates that there is just as much growth of twins, under the conditions of these experiments, on the (111) face normal to *B* as there is on the (111) face normal to *C*.

Further experiments by Wilman (1940), treating twinned silver deposits on rocksalt with halogen vapors, give additional evidence for the extra diffraction spots being caused by twinning alone and not by crystal surfaces parallel to octahedral planes, since the extra spots remain even after attack of the silver by the halogen. The silver halides formed had the normal structures, although the chloride crystals were often, and the cubic iodide crystals always, twinned on (111) planes. By comparison with graphite as a standard, lattice-parameter measurements were made of the

silver at various stages of attack and of the silver halides, and in all cases were in agreement with the X-ray values for the massive forms.

It has been suggested by Dankov (1939) that the almost identical distances between neighboring silver atoms in the diagonal directions of the cube faces of the silver structure and between neighboring silver and bromide ions in the directions of the cube edges of the silver bromide structure may permit the easy growth of silver in certain orientations on silver bromide, and that this may be of importance in the peculiar photographic sensitivity of silver bromide. However, none of the suggested orientations was observed under the conditions of the present experiments.*

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* Experiments undertaken since submitting this manuscript show that silver produced in silver bromide by irradiation with a mercury-vapor lamp gives precisely the electron-diffraction pattern to be expected for joining of (110) planes of the two crystals rotated at 90° with respect to one another. In this case, the periodicities of the atoms in the two crystals are identical at the boundary. On the other hand, the surface deposits of silver on silver bromide apparently depend upon terraces or troughs for aligning the rows of atoms parallel to those of the substrate.