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Dark Conductivity of Silver Bromide Crystals

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The conductivity of large silver halide crystals in weak fields is shown to be electronic. In stronger fields the ions start moving through the defects and over the surface, and this is accompanied by a growth of dendrites. When the crystals are exposed to light, their conductivity first rises and then falls. The result of the exposure depends on the medium in which the crystal is located.

IT is customary to assume that the dark conductivity of most ionic crystals, including that of silver halide crystals, is ionic. This conclusion is based principally on experiments by Tubandt,[1] who showed that at higher temperatures specimens made of compressed powders of many salts obeyed the Faraday electrolysis law.

Tubandt's determination of the transport numbers has shown that the conductivity of all three silver halides is caused by the positive silver ions. Application of the Frenkel defect theory to these crystals has led to the conclusion that in addition to the interstitial silver ions the vacant sites of these ions also affect the conductivity. The Frenkel defect formation hypothesis was confirmed by many experiments,[2] and at the present time there is no doubt that no defects are formed in silver halides by the Schottky mechanism, with the exception of the single case when the crystal temperature is close to the melting point. Experiments[3] with the diffusion of radioactive bromine and silver in crystals have shown that the diffusion coefficient of the silver ions is considerably higher than that of the bromine ions, while bromine atoms diffuse with relative ease. Incidentally, pressed powders were used in the experiments on the diffusion of radioactive isotopes, as in the Tubandt experiment.

It was further shown[4] that the conductivity of pressed powders at temperatures below 80-100°C is proportional to the surface area of the crystals. This last dependence indicates that at room temperatures the conductivity of pressed powders, with which many investigators perform their experiments, is determined by the motion of the ions over the surface. Room-temperature investigation of the conductivity of silver halide monocrystals is reported only in Ref. 5, and its results make it clear that at room temperature the dark conductivity of large silver halide monocrystals is electronic. At room temperature the surface conductivity of the silver halide crystals is thus determined by the silver ions, while only electrons move deep within the crystal.

It is known from the Kirillov and Levi[6] experiments that the dark conductivity changes after the crystal has been exposed to light, and it was shown in that investigation that the observed change in conductivity is reversible. The electrons that were fixed at local levels during the crystal exposure become thermally free after the conclusion of the exposure. Barshchevskii[7] observed an increase in photoconductivity during the exposure of the crystal.

Investigation of silver halide crystal conductivity is made difficult by the formation of so-called dendrites, i.e., silver filaments that grow from the cathode to the anode and short circuit the crystal. At the same time, investigation of the dendrite formation process is of importance in the explanation of the conductivity mechanism. The structure of dendrites was studied in reference 8.

This article reports the results of an investigation of the dark conductivity and of the electrolysis of silver halide crystals, and also the effect of exposure on these processes.

EXPERIMENTAL PROCEDURE

Specimens were prepared by pouring fused salt between two glass plates followed by prolonged annealing, as described by Meikliar.[9] Added pads of suitable thickness were placed between the plates to obtain thick crystals. During the experiment the crystals were uncovered by stripping one or both glass plates. To check whether the Faraday electrolysis law is obeyed, a setup similar to that described in Ref. 5 was assembled. A silver bromide crystal, several tenths of a millimeter thick, was placed over a silver plate, serving as the anode. A glass tube, into which a solution of potassium nitrate was poured, was pressed against the upper surface of the crystal through a rubber washer. A platinum plate serving as a cathode was placed in the solution. The circuit was energized and the amount of electricity passing through the crystal was measured with a coulomb meter, consisting of a platinum crucible containing a solution of silver nitrate and a silver plate immersed in this solution. The crucible acted as the cathode, and the silver plate as the anode. The electrolysis current was several microamperes; each experiment lasted as much as several days. Whenever a silver filament grew in the crystal during the time of the experiment the current increased sharply and the experiment was discarded as a failure. The weights gained by the coulomb-meter crucible and lost by the anodes of the coulomb meter and the crystal were measured by a precision balance accurate to 5×10^{-5} grams. It was impossible to determine the weight gained by the cathode immersed in the potassium nitrate solution, for the silver was deposited on this cathode as thin filaments which broke easily.

We also made observations on the growth of the dendrites. For this purpose graphite electrodes were coated over the crystal which was placed on the flat surface of a small electric furnace. A potential difference on the order of several tens of volts was applied to the electrodes to raise the crystal temperature, and the growth of dendrites was examined with the aid of a microscope, occasional microphotographs being taken. The same setup was used to heat the exposed crystal. In the latter case graphite, or metal (platinum, copper, cadmium or silver) electrodes were used. The metal electrodes were deposited on the crystal either by evaporation or by cathode spattering.

The effect of crystal exposure on the value of its dark conductivity was then investigated. The exposure was made in air, in vacuum, or in various gas atmospheres. For this purpose the crystal was placed in an evacuated container, the upper portion of which had a flange with a quartz plate inserted. As required, the exposure was made either without evacuation, or after evacuation followed by additional admission of some gas. The source of light was a PRK-4 mercury tube with a set of light filters to separate the spectral lines. The thermal conductivity was measured without removing the crystal from the container. For this purpose, leads passing through the lower portion of the glass container were pressed against the graphite electrodes of the crystal. These conductors were used to connect the crystal alternately to a mirror galvanometer and to the power source.

In some cases the photoconductivity was measured simultaneously with the dark conductivity. In such a case the source of light was also a mercury tube with light filters. Sometimes the crystals were exposed while immersed in a solution of caustic potassium of varying concentration. When convenient, the absorption spectrum of the crystals was measured simultaneously, using a dual monochromator made by the experimental machine shop of the Leningrad State University Physics Institute.

RESULTS OF MEASUREMENTS

The table gives the results of measurements made to verify the applicability of the Faraday law. It can be seen here that at a relatively low potential difference (less than 4 volts) the weight lost by the crystal anode is noticeably less than that lost by the coulomb-meter anode and that gained by the coulomb-meter crucible, while at high potential differences the corresponding quantities are of the same order of magnitude. This means that if the fields inside the crystal are weak its conductivity is purely or predominantly electronic, becoming ionic in strong fields. The ionic conductivity produced by the increase in the field is accompanied by a growth of silver filaments at places where the crystal is inhomogeneous. The more perfect the crystal, i.e., the smaller the number of defects in which ions can move and form metallic filaments, the higher the potential difference at which the conductivity becomes ionic.

Figures 1 and 2 show microphotographs of a silver filament growing on the surface of the crystal from the cathode. Examination under the microscope shows how the filament grows. Measurements have shown that at a temperature of 100°C and an electric field intensity of 50v/cm the filament grows at an approximate rate of $10^{-3} - 10^{-2}$ mm/sec. Reversing the electric field causes the length of the filaments at the electrode (which now becomes an anode) to diminish until it vanishes completely. At the same time filaments begin to grow from the second electrode (now the cathode). Treating such a crystal with its silver filaments in a hydrogen sulfide atmosphere forms silver sulfide on the surface of the crystal with the exception of the places that are directly adjacent to the filaments. This can be seen from Fig. 3. The growth of silver filaments during electrolysis of silver halide crystals was reported in Ref. 8. However, this work was previously unknown to us and our observations were made independently. Heating an exposed crystal in an electric field causes resorption of the photolytic silver near the anode. Figure 4 is a photograph of a crystal uniformly exposed over the entire surface and shows such brightening at the anode. Figure 5 shows a crystal first dusted with silver. When an alternating electric field is applied, the brightening forms at both electrodes, although at a slower rate. We observed this brightening only with graphite and platinum electrodes. When the crystal was

TABLE

Results of Electrolysis Experiments

Weight, milligrams	First Experiment with Crystal			Second Experiment with the Same Crystal		
	Before Experiment	After Experiment	Difference	Before Experiment	After Experiment	Difference
Crystal No. 1	potential — 2 volts			potential — 30 volts		
Coulomb-meter crucible	6465,40	6467,60	+2,20	6465,40	6466,50	+1,10
Coulomb-meter anode	2115,80	2113,55	—2,25	2113,55	2112,50	—1,05
Crystal anode	3571,70	3571,70	0,00	3570,00	3568,90	—1,10
Crystal No. 2	potential — 2 volts			potential — 20 volts		
Coulomb-meter crucible	6346,80	6349,50	+2,70	6346,40	6347,60	+1,20
Coulomb-meter anode	2227,95	2225,10	—2,85	2222,90	2221,80	—1,10
Crystal anode	3423,70	3423,60	—0,10	3422,85	3421,80	—1,05

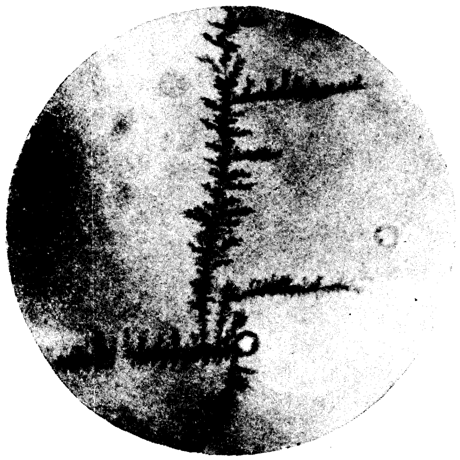

FIG. 1. Microphotograph of silver filament growing from the cathode in the electrolysis of silver bromide. Magnification 40 x, field intensity 60 v/cm, temperature 100-150.°

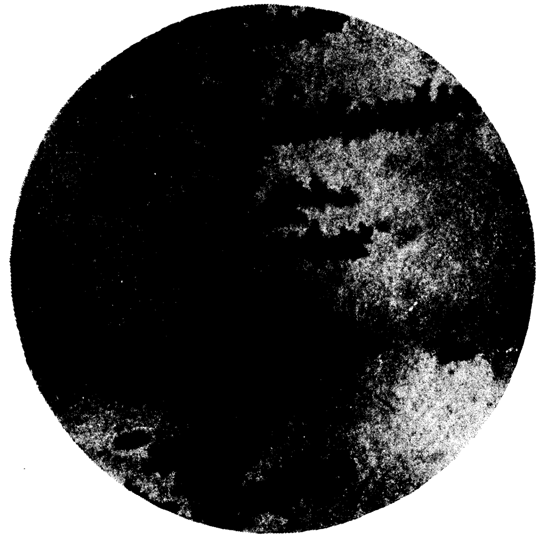

FIG. 2. Microphotograph of portion of the silver filament shown in Fig. 1; magnification 160 x.

coated with silver or copper electrodes, no bright areas were observed near the anode and the flow of current caused a gradual breakdown of the anode itself.

Figure 6 shows the increments of the optical density of the exposed crystal before and after this brightening.

We learned recently that thermal resorption of the photolytic silver near the anode is reported also in Ref. 10. However, in that investigation the experiments were with silver bromide crystals to which silver sulfide was added, and we consider this phenomenon to occur only with such mixed crystals. Our experiments, performed independently, were carried out with silver bromide crystals without any admixtures.

We next investigated the effect of the exposure on the value of the dark conductivity. We observed there that the separation of the photolytic silver depends to a large extent on the nature of the medium in which the crystal is placed during

FIG. 3. Microphotograph of a portion of a crystal with a silver filament, treated in hydrogen sulfide; magnification 400 x.

FIG. 4. Regression of photolitic silver in the electric field at the anode. Potential difference 70 v, interelectrode distance 25 mm, experiment temperature 210.°

FIG. 5. Regression of silver dusted on the surface of the crystal at the anode, under the same conditions as in Fig. 4.

the exposure. Experiments show that the photolytic silver is separated most intensely when the crystal is exposed in a hydrogen sulfide stmosphere or in a vacuum. Exposure in a hydrogen or an oxygen atmosphere produces approximately the same results as in air. This is illustrated by Fig. 7, which shows the increments of the optical density of the various portions of the same crystal exposed in different gaseous media.

The photochemical sensitivity of the crystals increases noticeably also when the crystals are immersed in a solution of potassium hydroxide; as the concentration of the potassium hydroxide increases, the photochemical sensitivity first rises, and then stays constant as the concentration reaches approximately 5%. This is illustrated by Fig. 8, showing the increments of the optical density of crystals exposed in air and in 5% potassium hydroxide.

The effect of crystal exposure on the value of its dark conductivity is quite complicated in character. With respect to this, crystals can be divided into two types: 1) those with high dark resistivity and low photoconductivity and 2) those with low dark resistivity and high photoconductivity.

Exposed crystals of the first type exhibit a gradual and irreversible decrease in the dark conductivity and their photoconductivity at first increases somewhat and then also decreases. This is seen from the curves of Fig. 9. When crystals of the second type are exposed, an increase is observed in the dark conductivity and in the photoconductivity followed, starting with a certain exposure time, by a decrease in both (Fig. 10). If the crystal exposure is stopped at a time when its conductivity is on the rise, both the dark conductivity and the photoconductivity return after a certain time to their initial values, i.e., to the values before the start of the exposure; this is in agreement with the data obtained by Kirillov and Levi.[6] But if the exposure is interrupted while the conductivity decreases, the latter does not return to its initial value; the changes occurring in the crystal in this case appear to be irreversible.

In certain cases the variation of crystal photoconductivity with exposure time is even more complicated and passes through several minima and maxima. However, spectral measurements of the crystal light absorption have shown in all cases that the photoconductivity vs. exposure time curve has a minimum corresponding to light absorption in the spectral interval 400-460 millimicrons, and, conversely, the maximum of this curve corresponds to a lower absorption of light in the above region of the spectrum. Further experiments have shown that the first group of crystals, characterized by low photoconductivity, has a noticeably higher photochemical sensitivity than the second group of crystals with the higher photoconductivity. This is illustrated by Fig. 11, which shows incremental optical density curves of crystals of the first (curve a) and second type (curve b) exposed under

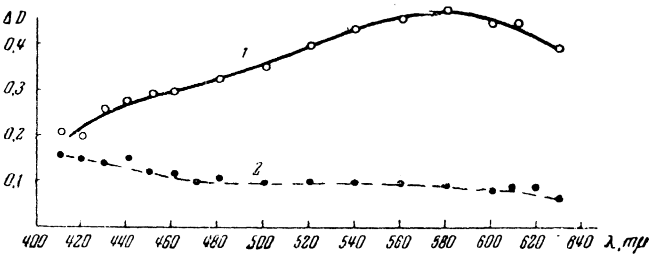

FIG. 6. Curves showing increments of crystal optical density: 1 — after exposure, 2 — after exposure and anode brightening.

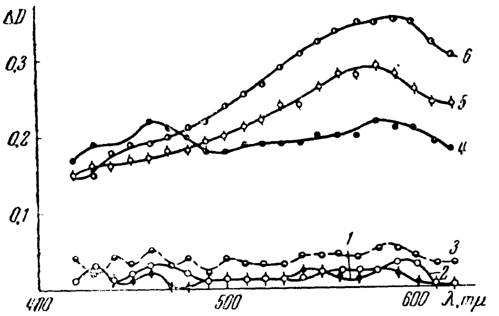

FIG. 7. Curves showing increment of optical density after exposing the crystal for 30 minutes with a mercury-arc lamp in: 1 — oxygen, 2 — hydrogen, 3 — air, 4 — vacuum. Also curves obtained by exposing the crystal: 5 — ten minutes in hydrogen sulfide, 6 — three minutes in potassium hydroxide.

identical conditions. Measurements of the absorption spectra of these crystals have shown that in the 400-460 millimicron spectral region the crystals of the first group have a noticeably higher absorption than those of the second type. This is illustrated in Fig. 12, where curves refer to crystals of the first and second type respectively. Both curves were obtained by comparison with a crystal having an average photoconductivity.

DISCUSSION OF RESULTS

It follws from the data given that the dark conductivity of large silver halide crystals is electronic. The conductivity becomes ionic when the electric field in the crystal is increased, because of the motion of the ions over the defects of the crystal, in which the field reduces the activation energy for the motion of the ions. Such a hypothesis is corroborated by the fact that silver dendrites grow out of the defects as the electric field is increased. The silver ions move over the surface of the crystal. When an electric field is superposed these ions move to the cathode where they absorb electrons and turn into atoms. This is how silver filaments grow at the cathode. Subsequent silver ions reach the sharp point of the filament, where they are discharged and the filament continues to grow. When the field direction is reversed the filament decomposes. Apparently, the silver ions become thermally separated from the positively charged filament (anode). During the growth of the filament, the crystal surface in the direct vicinity of the filaments becomes poor in silver ions, and therefore no silver sulfide is formed in the vicinity of the filaments when such a crystal is developed in hydrogen vapor. The thermal decomposition of particles of metallic silver near the anodes can be explained by the fact that the decomposition starts with the separation of electrons, which migrate to the anode, followed by thermal decomposition of the positively-charged silver particles, as can be seen from the absorption curves on Fig. 6. The silver ions formed move away to the cathode. If the anode is made of graphite or platinum, no new ions arrive to replace the silver ions that move to the cathode. But if the anode is made of another metal, the ions of this metal come to replace the silver ion, and the anode itself becomes decomposed rather than the metal particles. Such a hypothesis concerning the mechanism of the thermal decomposition of silver particles is in agreement with the data by Kazantsev and Meikliar[11] on the regression of the centers of the latent photographic image. The relationship between the dark conductivity and the photoconductivity of the crystal, described above, can be explained in the following manner. Since a relatively large light absorption is observed in the case of crystals of the first type, which have a low photoconductivity in the 400-460 millimicron spectral region (Fig. 12), i.e., in the region where light is absorbed by the F-centers[12], we must assume that the concentration of such centers is relatively high in these crystals. The light absorption in such crystals has an exciton character,[13] and no thermal electrons are liberated

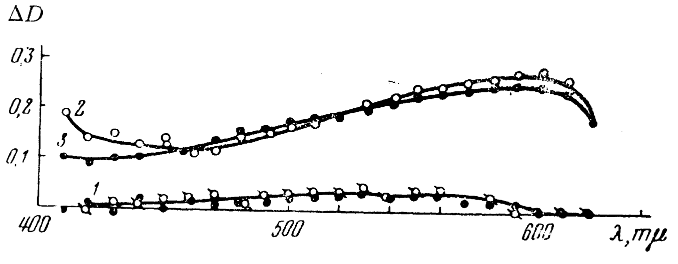

FIG. 8. Increment of optical density of crystal after exposure of 10 minutes in air (1), 10 minutes in 5% potassium hydroxide solution (2) and 5 minutes in potassium hydroxide solution (3).

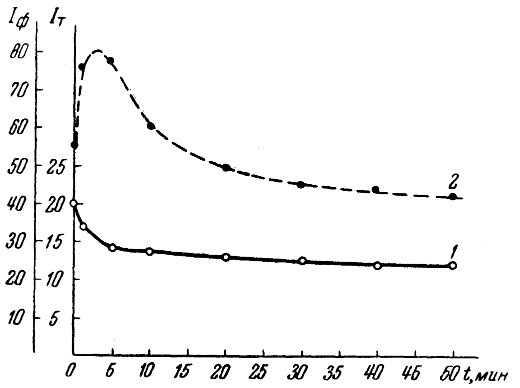

FIG. 9. Dark conductivity (1) and photoconductivity (2) vs. exposure time for a crystal with high dark resistivity ($R = 2.5 \times 10^9$ ohm) and low photoconductivity ($I_{ph}/I_d = 3$).

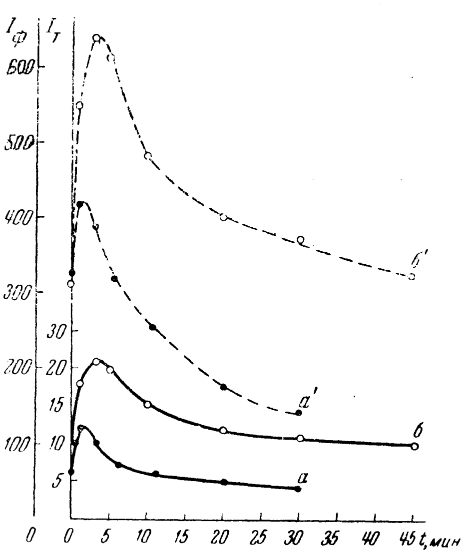

FIG. 10. Dependence of exposure time on dark conductivity (a,b) and on photoconductivity (a′,b′) for two crystals with low dark resistivity ($R = 4 \times 10^8$ and 2×10^8 ohms) and high photoconductivity ($I_{ph}/I_d = 52$ and 35).

from the F-centers. This is why the dark conductivity of such crystals is low and is determined only by the silver ions moving along the surface. When such crystals are exposed the electrons liberated by the light are captured by the silver ions and the conductivity of the crystals decreases monotonically.

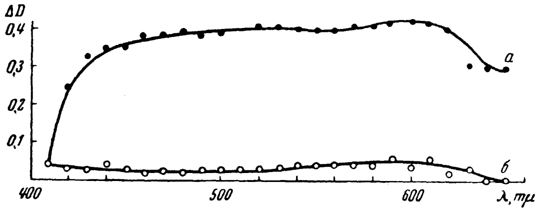

FIG. 11. Curves showing increments of optical density of crystals exposed under identical conditions: a— first type, b— second type.

The crystals of the second type, which have a high photoconductivity, are characterized by low absorption of light in the 400-460 millimicron region (Fig. 12), and consequently, by a low F-center concentration. Here the electrons can be thermally liberated from the F-centers at the start of the exposure and the increase in the number of F-centers during exposure first causes an increase in the dark conductivity. As the exposure time is increased the concentration of the F-centers becomes greater, the absorption of light assumes an exciton character, and this leads to a reduction in the dark conductivity and in the photoconductivity. This agrees with the data on the determination of the photochemical sensitivity of crystals. Crystals of the first type contain more F-centers than those of the second type, and accordingly their photochemical sensitivity is noticeably higher (see Fig. 11).

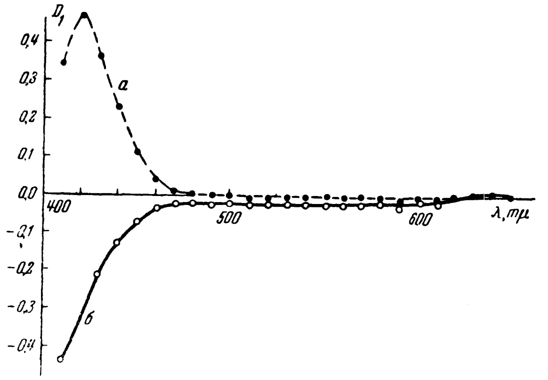

FIG. 12. Comparison of optical density of crystals of the first (a) and second (b) types with that of a crystal having an average photoconductivity ($D_1 = \ln I_0/I_1$).

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175