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The Conductivity of Silver Bromide in the Presence of Bromine

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It was shown that silver bromide crystals, additively colored in bromine fumes, acquire hole conductivity, the magnitude of which is proportional to the square root of the partial pressure of halogen in the gas and rises with increase in temperature according to an exponential law. The magnitude of the hole conductivity in AgBr even for low pressures of bromine is comparable in value with the ionic conductivity of these crystals. In additive coloration, V_1 centers are formed. These are complex, consisting of a single vacant cation site with a hole localized on it. The thermal dissociation energy of V_1 centers in AgBr is estimated to be 0.3 ev. F -centers are not formed in silver bromide on account of lack of vacant anion sites in its structure. Neither atoms nor molecules of bromine dissolve and diffuse in the AgBr lattice.

1. INTRODUCTION

IN recent years, a large number of studies have been published concerned with clarification of the nature of the structural defects in the silver halides. On the basis of theoretical calculations¹ and experimental results²⁻⁵ it has been established that in these crystals, Frenkel-type structural defects are formed. Seitz⁶ and Mitchell⁷, however, supposed that Schottky defects can exist as well in small concentrations. Such an interpretation was occasioned by the need to explain the mechanism of formation of the latent photographic image, and also the mode of development of silver dendrites in single crystals of AgBr in the process of electrolysis⁸. It was also assumed that sensitizers, such as Ag_2S , aid in the formation of vacant anion sites in the crystal lattice. Hypotheses have also been expressed on the diffusion of anion vacancies pairwise with cation vacancies. Such groups do not have to reveal themselves in measurements of electrical conductivity and of transference numbers, despite the motion of anions. Such a hypothesis, however, is refuted by experimental data on self-diffusion, measured by means of radioactive tracers⁹⁻¹¹. In particular, according to the data of Murina and his co-workers^{10,11}, the transference

numbers for bromine ions in AgBr do not exceed 5.2×10^{-4} -- a value falling within the range of experimental errors*.

In subsequent works, Mitchell abandoned his initial point of view. Together with Hedges¹¹ he established that the internal latent image in silver bromide is formed on internal surfaces associated with the polyhedral structure of monocrystals, connected with the development of dislocations (where boundaries mesh) or mosaic blocks, owing to deformation under the influence of mechanical forces or temperature variations. Prolonged annealing of pure monocrystals near the melting point and slow cooling improved their structure, and in such specimens no latent image developed inside the crystal.

Meikliar and Putseiko¹¹ consider that it is unnecessary to hypothesize Schottky defects for the formation of F -centers in silver halides. As is known, on exposure of a crystal to ultraviolet light, electrons and holes arise. The latter are considered by the authors as neutral halogen atoms on lattice sites. It is assumed that in the process of photolysis, bromine atoms can pass into inter-

* Regrettably, these investigations were carried out on polycrystals. They should be repeated on monocrystals of a high degree of purity, annealed at high temperatures for elimination of their polyhedral structure.

stitial positrons, diffuse in the crystal lattice and leave it. Thus, vacant anion sites are formed, having deeper levels of electron localization than interstitial silver ions and, consequently, there emerge all conditions necessary for the existence of *F*-centers. These same color centers can, in the opinion of these authors, appear also as a result of thermal decomposition of the salt. In support of this point of view, the absorption spectra of AgBr and of AgCl crystals after transillumination or heating are cited. In both cases, new absorption bands were discovered with maxima* at 430-440 $m\mu$ in AgBr and at 370-380 $m\mu$ in AgCl. These bands are identified with the *F*-centers in the alkali halide salts on the basis that their position, to a first approximation, conforms to Mollwo's empirical formula $\nu d^2 = \text{const.}$

Such a basis for the possibility of *F*-centers in silver halide salts seems inadequate to us. In fact, the photolysis of AgBr, not bromine atoms, but holes, are formed. The latter, in combination with vacant cation sites, can produce *V*-centers. A portion of the holes, migrating in the crystal, can reach the surface where they are localized (see below). Such motion is realized by an electronic mechanism without the transfer of the very atoms or ions of bromine in the crystal lattice. In the thermal decomposition of AgBr, bromine molecules likewise are formed only on the surfaces of the crystal.

The presence in the crystals of *V*-centers and of holes determines, according to the conditions of equilibrium, the occurrence of halogen atoms and molecules adsorbed on outer facets and along boundaries of contact of mosaic grains (if a specimen has a developed polyhedral substructure). Therefore, it is fully natural to expect the appearance of bands peculiar to halogen molecules in the absorption spectra of such crystals¹⁵. In fact, the additional bands observed by Meiklier and Putseiko in crystals of AgBr and AgCl fully correspond both in their shape and in the position of their maximum to the absorption spectrum characteristic of bromine or chlorine¹⁶. That band with maximum at 420 $m\mu$ was detected also by Mollwo¹⁷ on the long wavelength edge of the *V* band in KBr, additively colored in an atmosphere of bromine.

In connection with the questions raised here, it seemed of interest to us to study the process of additive coloration of AgBr in bromine fumes as a function of temperature of the crystal and of

* That band with maximum at 430 $m\mu$ was found by Golub and Kirillov¹⁴ in the absorption spectrum of a photochemically colored film of bromo-gelatin emulsion.

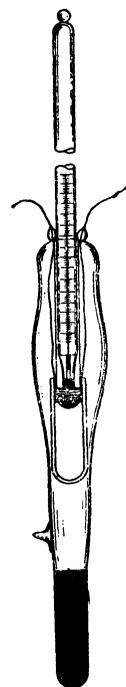


FIG. 1

partial pressure of halogen. Checking the change of conductivity of the crystal during its coloration, we had an opportunity to determine whether atoms or molecules of bromine can dissolve and diffuse in the silver bromide lattice, or whether this process is connected with the formation of *V*-centers and holes, the spatial migration of which is not related to the diffusion of halogen atoms. In the first case, the electrical conductivity of the crystals would remain unchanged, but in the second, it would vary in proportion to the concentration of holes. Studies of the equilibria in the process of additive coloration permit us to ascertain the structure of the *V*-centers which are formed and the energy of their thermal dissociation.

II. EXPERIMENTAL METHODS

The additive coloration of monocrystals of silver bromide was carried out in a glass ampoule, which is shown schematically in Fig. 1. The monocrystal (in the form of a cylinder) was located in the upper half of the ampoule. Electrodes of sheet platinum were fastened on its end faces through a fine coating of graphite. Inside the ampoule, there was an extension to the level of the crystal for a thermometer, by means of which the temperature of the specimen was measured. Liquid bromine, previously purified by the method of Honigschmidt and Zintl¹⁸, was situated in the

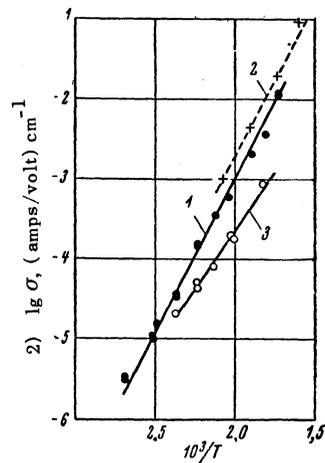
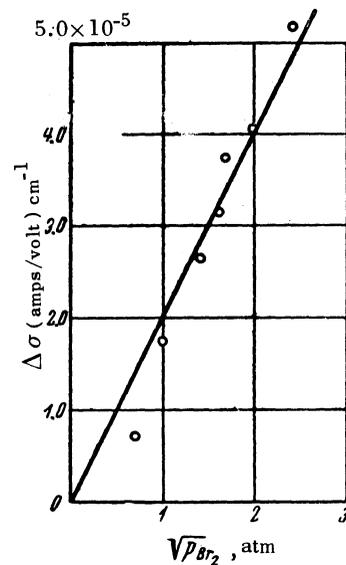


FIG. 2

lower portion of the ampoule. For removal of traces of moisture from the bromine, molten calcium bromide was used. After filling with bromine, the lower portion of the ampoule was cooled with dry ice, evacuated on a diffusion pump to 10^{-5} mm Hg and disconnected. Then the ampoule was placed in a two-stage furnace with two independent windings of nichrome wire. The upper and lower halves of the furnace were separated by a thermally insulated band. Such an apparatus design permitted the investigation of the conductivity of crystals at various temperatures and pressures of bromine. Thermostatting was done to an accuracy of $\pm 0.5^\circ$. The lower portion of the ampoule with the liquid bromine was located in a hole in a massive aluminum block for the elimination of a temperature gradient along the height of the furnace. The partial pressure of bromine in the gaseous phase was determined according to the temperature of its saturated fumes. The measurements of the electrical conductivity of the crystals were carried out on alternating current from an audio-frequency generator at 1000 cycles with a bridge circuit using an alternating current amplifier for small voltages.

III. RESULTS OF THE EXPERIMENTS

At the beginning of each series of measurements, the crystal was treated in bromine fumes at a pressure of 2 atms and temperature 300° C, in order to eliminate possible products of photolysis. After this, the bromine was frozen out during the simultaneous heating of the specimen. The electrical conductivity of silver bromide was determined in the interval from 100 to 300° . The results of these measurements are plotted in Fig. 2 (curve 1). They can be presented in the form of

FIG. 3. Isotherm for 150° C

an equation

$$\sigma = 1.02 \times 10^5 \exp(-18200/RT) \Omega^{-1} \text{cm}^{-1}. \quad (1)$$

The electrical conductivity has the same temperature coefficient as in the work of Koch and Wagner¹⁹ (curve 2 in Fig. 2), but a somewhat smaller factor before the exponential. Measurements of the resistivity of AgBr were then carried out at a fixed temperature with different pressures of bromine fumes. In contact with halogen fumes, the electrical conductivity of silver bromide increases both with rising temperature and with increasing partial pressure of halogen. Additional conductivity $\Delta\sigma$ is related to the migration of holes which are formed in the crystal during additive coloration.

The quantity $\Delta\sigma$ is calculated from the difference between the electrical conductivity of the crystal in the presence of bromine and without it (after freezing out). In the calculations it was assumed that in the overall electrical conductivity, the portion which comes from the ionic component remains unchanged in the presence of holes. Strictly speaking, this assumption is rather arbitrary, inasmuch as in the process of additive coloration, as will be shown below, a reduction in the equilibrium concentration of interstitial silver ions takes place. Besides that, a portion of the vacant sites are associated with holes in the form of electro-neutral complexes, motionless in an electric field. Thus, a certain number of structural defects does not participate in the transfer of electrical charge. At high temperatures and small partial pressures of halogen, however, the concentration of V -centers and holes is small,

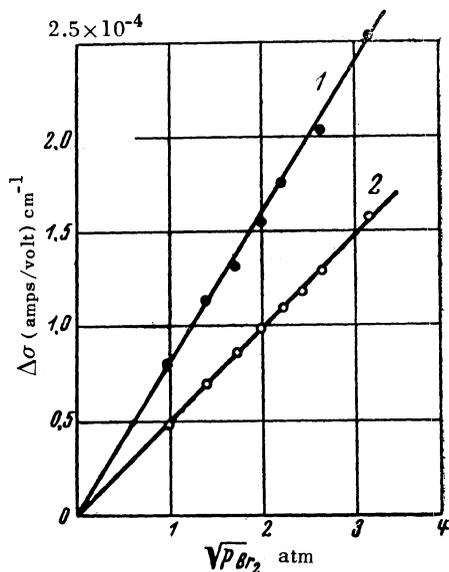


FIG. 4. 1-Isotherm for 196° C, 2-Isotherm for 175°.

and therefore they vary the equilibrium concentration of the structural defects in the crystal only insignificantly.

The process of additive coloration of AgBr in bromine fumes is completely reversible, as was established by us in specially arranged experiments.

At high temperatures, equilibrium is attained rapidly, approximately at the same speed with which bromine fumes enter or leave the atmosphere which surrounds the crystal. Therefore, quenching the crystal by rapid cooling fails to retain the V -centers.

In Figs. 3-5 the dependence of the change in hole-conductivity of silver bromide on the pressure of bromine is given, for four isotherms. In the coordinates chosen, the zero value of $\Delta\sigma$ corresponds to the conductivity of pure AgBr at the given temperature in the absence of bromine.

The results of the experiments are presented in Fig. 2 (curve 3) and can be described in the form of an equation as a function of the pressure of the halogen fumes and of the temperature.

$$\Delta\sigma = 1.82 \cdot 10^2 \sqrt{p_{Br_2}} \exp(-13520/RT) \Omega^{-1} \cdot \text{cm}^{-1} \text{ atm}^{1/2} \quad (2)$$

The relative change of the hole-conductivity in comparison with the ionic is given by the relation

$$\frac{\Delta\sigma}{\sigma} = 1.78 \cdot 10^{-3} \sqrt{p_{Br_2}} \exp(4680/RT) \quad (3)$$

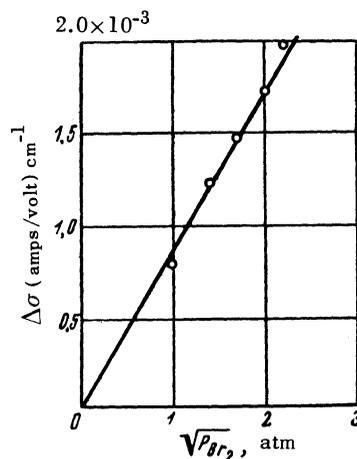
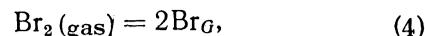


FIG. 5. Isotherm for 273° C

As is seen from Eq. (3), the relative conductivity is lowered with increase in temperature of the crystals. At room temperature (25°) the hole conductivity becomes equal to the ionic already at a bromine pressure of ~ 40 mm Hg.

IV. DISCUSSION OF THE RESULTS

Upon heating silver bromide in a bromine atmosphere, holes are formed in the crystals. Omitting the intermediate steps of the process (dissociation of bromine molecules into atoms and their adsorption on the faces of a crystal), one can write down this reaction in the form of an equation¹⁵



from which it follows that

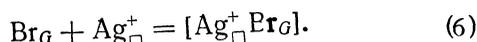
$$C_{Br_G} = \sqrt{K_1} \sqrt{p_{Br_2}} \quad (5)$$

where C_{Br_G} is the equilibrium concentration of holes in the crystal, and K_1 is the equilibrium constant of the reaction (4).

The process of hole formation in a crystal during additive coloration (if we consider it in equilibrium with molecular bromine) is bimolecular. Therefore, the equilibrium concentration of holes under isothermal conditions varies in proportion to the square root of the partial pressure of bromine in the fumes [Eq. (5)]. The established relation (5) is confirmed by the experiments on the variation of the hole conductivity of AgBr ($\Delta\sigma$) as a function of bromine pressure (Figs. (3-5)).

Positive holes and vacant cation sites inside the crystal interact with one another with the

creation of V_1 -centers*

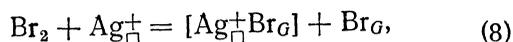


Their equilibrium concentration is determined by the equation

$$C_{\text{Ag}_{\square}^+ \text{Br}_G} = K_2 \cdot C_{\text{Ag}_{\square}^+} \cdot C_{\text{Br}_G}. \quad (7)$$

Here $\text{Ag}_{\square}^+ \text{Br}_G$ denotes a V_1 -center in the form of an associated complex of a vacant cation site (Ag_{\square}^+) and a hole (Br_G), and K_2 is the equilibrium constant of the reaction (6).

The process of the formation of V_1 -centers (6) is likewise bimolecular, but opposite in direction to the process of hole formation (4). Taking into consideration the reversibility of both reactions and combining Eqs. (4) and (6), we find



whence we obtain

$$C_{[\text{Ag}_{\square}^+ \text{Br}_G]} = K_3 p_{\text{Br}_2} C_{\text{Ag}_{\square}^+} / C_{\text{Br}_G}, \quad (9)$$

where $K_3 = K_1 K_2$.

Thus, in the final result, it turns out that the equilibrium concentration of V_1 -centers varies proportionally to the pressure of bromine molecules. An analogous result as obtained by Mollwo¹⁷ in the study of processes of additive coloration of KBr and KI in vapors of the corresponding halogens. Using the law of mass action, the author arrived at the incorrect conclusion that color centers are halogen molecules, dissolved in the crystal lattice. For this reason, Seitz supposed that in additive coloring V_2 -centers are formed, which consist of a pair of holes associated with two vacant cation sites. These authors, however, did not take into account that structural defects of the crystal also take part in the process, and that along with V_1 -centers free holes arise. The equilibrium concentration of holes unassociated, under given thermodynamic conditions, in the form of V_1 -centers, likewise varies as a function of the partial pressure of bromine. Consequently, additive coloration cannot be compared with the ordinary process of solution.

Combining Eqs. (5) and (9), we find

$$C_{[\text{Ag}_{\square}^+ \text{Br}_G]} = K_4 \sqrt{p_{\text{Br}_2}} C_{\text{Ag}_{\square}^+}. \quad (10)$$

In this equation $K_4 = K_3 / \sqrt{K_1}$ or $K_4 \sqrt{p_{\text{Br}_2}} = K_2 \times C_{\text{Br}_G}$.

Consequently, the equilibrium concentration of V_1 -centers varies proportionally to the product of the concentrations of the holes and of the vacant cation sites (for $T = \text{const}$) not connected under the given conditions with associated complexes.

Although the equilibrium concentration of V_1 centers rises with the pressure of bromine, nevertheless, the number of these centers cannot increase indefinitely. With an increase of holes, the concentration of cation vacancies decreases accordingly and so also does the possibility of formation of new V_1 -centers. Furthermore, the engendering of holes in the lattice is attended with a loss from it of an equivalent number of mobile cations (interstitial silver ions), the concentration of which is determined by the characteristics of the crystal and depends only on its temperature. In the very process of additive coloration, new structural defects evidently do not arise, insofar as the energy of thermal dissociation of V_1 -centers is considerably less than the work of transferring cations from lattice sites to interstitial positions.

The value of the activation energy [in Eq. (2)] for hole conductivity (0.586 eV) is not the heat effect of additive coloration, in the same way as also the corresponding values of energy computed by Mollwo from the variation of the equilibrium concentration of V_1 -centers as a function of temperature. As follows from Eq. (8), for the calculation of the heat of formation of V_1 -centers, one should also take into account the corresponding changes in the concentrations of cation vacancies and of holes, insofar as their activities are not equal to unity.

The hole conductivity of silver bromide $\Delta\sigma$ can be represented in the form of an equation

$$\Delta\sigma = en_v \bar{\alpha} v, \quad (11)$$

where e is the elementary charge, n_v is the concentration of V_1 -centers, α is the degree of their thermal dissociation and v the mobility of the holes. In this equation $n_v \bar{\alpha}$ corresponds to the equilibrium concentration of holes. For an estimate of the value of the thermal dissociation energy of V_1 -centers, one can assume that the

* Here, as also later on, a V_1 -center is considered as an associated complex of a single cation vacancy in the lattice with a hole localized on it. According to their properties and the position of the band in the absorption spectrum of a crystal, V_1 -centers correspond to the V_2 -centers in Seitz's terminology²⁰.

mobility of the holes is independent of their concentration and does not vary with temperature (within narrow limits), and that the equilibrium concentration of V_1 -centers, at a constant pressure of bromine, rises with temperature in proportion to the concentration of vacant cation sites ($n_{Ag\Box}^+$). According to Koch and Wagner

$$n_{Ag\Box}^+ = 29 \exp(-20\,000/2RT). \quad (12)$$

Combining Eqs. (2), (11) and (12) and supposing that the process of dissociation of V_1 -centers has a bimolecular mechanism, we find $\alpha \approx \exp(-7040/2RT)$. Consequently, to a first approximation, the energy of thermal dissociation of V_1 -centers $\xi = 0.3$ ev*.

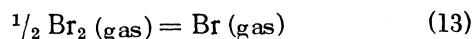
It is interesting to compare this value with the thermal dissociation energy of V_1 -centers in alkali halide crystals. According to the observations of Mollwo¹¹, the mobility of color centers in KBr and KI decreases with an increase in their concentration. As the author himself also noted, however, these changes in mobility are merely apparent. They are determined by the degree of dissociation of the color centers. V_1 -centers themselves are not accelerated in an electric field since they have no net charge. We have used the experimental data of Mollwo, who measured the apparent mobility of V_1 -centers with their concentration fixed as a function of temperature and found their thermal dissociation energy equal to ~ 0.3 ev for KBr and ~ 0.34 ev for KI. As was to be expected, the energy of thermal dissociation of V_1 -centers is considerably less than the energy of the optical transition in the maximum of the V_1 band (for KBr $\lambda_m = 267$ m μ or 4.64 ev). In the first case, a spatial separation of the holes from the cation vacancies occurs, while in the second, electrons make transitions from the fundamental band to levels of V_1 -centers. The mechanisms of these processes are entirely different, but the final results are identical.

The formation and disappearance of holes during additive coloration always takes place only on boundary surfaces of the crystal. Holes can arise only during the presence of halogen atoms on the surface. While holes are being drawn out of the crystal, surface anions behave as traps for holes. Thereupon, they themselves are converted to atoms.

* This value should be made more precise by independent determinations of the equilibrium concentrations of V_1 -centers and of holes at various temperatures.

The conditions necessary for the additive coloration of crystals are determined to a considerable degree by the extent of dissociation of the halogen and also by the concentration and mobility of interstitial cations. Taking into account the reversibility of the process, we can examine the additive coloration as a function of the concentration of halogen atoms.

We worked out the equation for the free energy of the process of dissociation of bromine



according to the data of Lewis and Randall²¹, and found

$$\Delta F_7^0 = 21\,570 - 12.0 T. \quad (14)$$

Combining Eqs. (4) and (13), we find for the reaction* $Br (\text{gas}) = Br_G$, the equilibrium concentration of holes

$$C_{BrG} = \frac{V\bar{K}_1}{V\bar{K}_5} p_{Br}, \quad (15)$$

where K_5 is the equilibrium constant of the reaction (13). Taking into account Eq. (2), we find

$$\begin{aligned} \Delta\sigma &= eC_{BrG}\bar{v} \quad (16) \\ &= 1.65 \times 10^{-4} \cdot p_{Br} \exp(8050/RT). \end{aligned}$$

If, as earlier, the mobility \bar{v} is taken as a fixed quantity, then the energy of formation of holes in contact with bromine atoms comes out to ~ 0.35 ev.

In the formation of V_1 -centers and holes, neither molecules nor atoms of halogen are dissolved in the crystal lattice. In reality, a stoichiometric excess of halogen, which can be detected by chemical analysis, arises as a result of a stoichiometric deficiency of metal atoms coming from the removal of electrons from the lattice upon introduction of holes with the attendant removal of a corresponding number of interstitial cations. The experiments of Uchida and Nakai²², who demonstrated the possibility of obtaining V_1 -centers in KI and NaI by an electro-chemical method, by the introduction of holes into the crystal from a pointed anode similarly to the way F -centers can be treated by the introduction of electrons into the crystal from the cathode, can serve as a direct corroboration of this.

* The process of hole-formation becomes monomolecular, if it is considered in equilibrium with atomic bromine.

Both optical measurements and the study of the conductivity of AgBr furnish us a basis to deny the possibility of the formation of F -centers in AgBr. Evidently, in these crystals, which have mobile holes in their makeup, V_1 - and F -centers cannot simultaneously exist with the same absorption spectrum as adsorbed bromine molecules.

V. THE MECHANISM OF ADDITIVE COLORATION OF AgBr IN A BROMINE ATMOSPHERE

In the analysis of the mechanism of additive coloration we proceed from the formation in the crystal of structural defects of Frenkel type. This initial postulate is fully substantiated for the silver halides. If such a crystal is introduced into a halogen atmosphere, then the latter will be adsorbed on the facets and internal surfaces of the specimen in the form of molecules and atoms. The concentration of the latter, obviously, will depend on the partial pressure of the halogen molecules and the degree of their dissociation at the assigned temperature.

Halide ions, situated on the surface layers of the crystalline lattice, are able to give up their valence electrons to the adsorbed atoms. The probability of such an exchange is increased with the concentration of these atoms, wherewith holes arise in the crystal. They possess high mobility and therefore are able to migrate into the lattice with great speed. Such motion is restrained by the negative charge which develops on the surface. Inside the crystal, near its surface layers a considerable potential gradient arises which depends on the concentration and mobility of the holes. Under the influence of this field, interstitial cations drift to the surface, where they are joined to anions of halide and form new lattice planes. Their motion reduces the gradient of potential in the crystal and removes the charge on the surface. The crystal remains electrically neutral. The rate of additive coloration is determined by the concentration and mobility of the interstitial ions--the slowest step of additive coloration. Holes and vacant cation sites have opposite effective charges and therefore can recombine with the formation of V_1 -centers, which, in their turn, exist in equilibrium with "free" holes. The motion of holes into the crystal lattice is possible only when mobile cations are present in its structure. Therefore, their maximum concentration is controlled by the presence of interstitial cations in the structure of the crystal.

Holes cannot only arise, but also disappear at the surface of a crystal. With reduction of the concentration of halogen atoms in the adsorbed

layer, conditions are established favorable for the localization of holes by halide ions on the surface. Under these conditions, halogen atoms are formed which can leave the crystal. The surface acquires a positive charge, due to a stoichiometric excess of cations. The flow of holes to the surface establishes a gradient of potential inside the crystal directed from the surface into the volume. Under the influence of this field, cations travel into the lattice. Inasmuch as additive coloration is a reversible process, the original properties are restored upon bleaching.

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