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ON THE ELECTROPHOTOGRAPHIC ISOOPAQUE OF AgCl SINGLE CRYSTALS

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1. Earlier, one of us ([1,2]) discovered and investigated the photoelectret state in AgCl single crystals cooled to the temperature of liquid nitrogen. The existence of a photoelectret state in AgCl opened the possibility of investigating the form of the isoopaque of the depolarization process of the photoelectret ([3]), and thereby the quasi-stationarity of electronic processes in AgCl ([4]). As was shown in ([3]), the right branch of the depolarization isoopaque is caused by the non-stationarity of the concentration of free carriers, and the light intensity $I = I^*$ corresponding to the beginning of the right branch satisfies the relation

$$I^* \simeq \frac{\beta}{s} M. \tag{1}$$

Here M is the concentration of local levels responsible for the formation of the photoelectret state, and β and s are the interaction cross sections of the local level with the carrier and the photon, respectively. It follows directly from (1) that, with an increase in the concentration of levels M in the crystal or with an increase in the parameter β/s of these levels, the point $I = I^*$ shifts to the right, i.e., into the region of higher values of the light intensity. According to ([1,2]), the photoelectret state in AgCl single crystals is caused by the capture of electrons by levels of colloidal silver. Since the concentration of colloidal-silver particles in AgCl can vary within wide limits when the crystal is illuminated in its own absorption band, it is of interest to investigate the form of the depolarization isoopaque for AgCl single crystals with different concentrations of colloidal silver. This, in turn, would make it possible to verify relation (1) and to estimate the value of the parameter β/s for levels of colloidal silver in AgCl. The proposed investigation is also of general interest, since the formation of the latent photographic and latent electrophotographic image in silver halide compounds is due to the same levels of colloidal silver. As will be shown below, the results obtained do in fact make it possible, in addition to the electron-ion mechanism of Mott and Gurney, to propose a new possible mechanism for deviations from the reciprocity law for photochemical processes.

2. Plastically deformed AgCl crystals in the form of foil 0.25 mm thick were investigated. The specimens were preliminarily annealed for 6 hr at a temperature of 400°. The concentration of colloidal silver was changed by successive exposure of the specimen to the "white" light of an SVDSh-250 lamp. After this, on an SF-4 instrument, the spectral absorption curves were recorded by the differential method at room temperature. As a result, the absorption ΔD of the specimen under investigation was measured relative to an unexposed control specimen in the region 460–1000 mµ. The photoelectret state was produced by photopolarizing the crystal at the temperature of liquid nitrogen. The crystal was polarized for 2 min in a field of 3 kV/cm under monochromatic illumination (λ 365 mµ). For 2 min the photoelectret was kept in the dark with the plates short-circuited, after which ···

its depolarization was carried out by illumination with green light of various intensities. (A ZS-2 filter and a saturated $CuSO_4$ solution were used, cutting off the infrared region of the radiation of the SVDSh-250.)

The light intensity I during depolarization was varied by neutral light filters and was measured with a standard thermopile.

Table 1

Crystal illumination number	Concentration of colloidal silver M, 10^{10} cm^{-3}	Particle diameter 2ρ, mμ	$\Delta\sigma$, 10^{-11} coul/cm^2	ΔM, 10^9 cm^{-3}	γ
I	1.2	33	8.4	2.1	0.17
II	1.95	38	9.4	2.35	0.12
III	3.2	43	10	2.5	0.08
VI	6.3	43	13.6	3.4	0.05

By integrating the depolarization current with respect to time, the released charge was measured, and dependences of the photoelectret charge on the depolarization time t, corresponding to different light intensities I, were constructed. From the family of curves obtained, the isoopaque was determined, i.e., the dependence $\lg(It)$ on $\lg I$, corresponding to one and the same value of the charge σ.

The calculation of the concentration M and radius ρ of the colloidal silver particles in AgCl was carried out by a method previously proposed by P. V. Meiklyar (^{5}). The calculation was based on the formulas of M. V. Savostyanova (^{6}) and on the optical constants of Ag and AgCl borrowed from (^{7}). In comparing the theoretical absorption curves of the Ag—AgCl system with the experimental ones, the distribution of the colloidal particles by size was neglected. Table 1 gives the calculated values of the concentration M and diameter 2ρ of the colloidal particles for four successive illuminations of the specimen. In accordance with the results obtained earlier by P. V. Meiklyar (^{5}), as the illumination time of the specimen is increased there is an increase both in the concentration and

Fig. 1. Depolarization isoopaques of a single crystal of AgCl.
$\sigma_1 = 0.2 \cdot 10^{-11}$ coul/cm^2, $\sigma_2 = 0.4 \cdot 10^{-11}$ coul/cm^2, $\sigma_3 = 0.6 \cdot 10^{-11}$ coul/cm^2.
1 unit $I = 2.95 \cdot 10^{10}$ quanta/cm$^2 \cdot$ sec. The designations of curves I—IV
correspond to Table 1.

Figure 1: Fig. 1. Depolarization isoopaques of a single crystal of AgCl. $\sigma_1 = 0.2 \cdot 10^{-11}$ coul/cm^2, $\sigma_2 = 0.4 \cdot 10^{-11}$ coul/cm^2, $\sigma_3 = 0.6 \cdot 10^{-11}$ coul/cm^2. 1 unit $I = 2.95 \cdot 10^{10}$ quanta/cm$^2 \cdot$ sec. The designations of curves I—IV correspond to Table 1.

in the diameter of the silver particles. In this case, according to (^{5}), the growth of silver particles is characterized by deviation from reciprocity: for one and the same value of the energy It, the particle diameter is the smaller, the higher the light intensity I. In (^{5}) the conclusion is drawn that this factor may additionally account for deviations from reciprocity in the formation of a latent photographic image in a silver halide crystal.

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Finally, it should be borne in mind that, according to (1), the shift of the point $I = I^*$ to the right may be caused both by an increase in the concentration of silver particles and by an increase in their diameter. The increase of s with the illumination time of the crystal is clearly evident from the displacement of the maximum of the absorption curve of the illuminated crystal into the long-wavelength region of the spectrum, which, according to (^{5,6,8}), also indicates an effect of coarsening of the colloids. If it is assumed that the increase of s and β during illumination of the crystal occurs at the same rate (it will be shown below that this is in fact the case), then the expected effect is entirely due to the growth of the measured concentration of silver particles. In any case, this circumstance should always be taken into account when investigating the displacement of the right branch of an electrophotographic isoopaque due to an increase in the concentration of local levels.

3. Figure 1 presents four isoopacs of depolarization of AgCl, corresponding to the four values of the concentration of colloidal silver M indicated in Table 1. All four isoopacs were taken for three values of the charge σ. It is seen from Fig. 1 that all the isoopacs have a right-hand branch bending upward; moreover, in accordance with (1), the beginning of this branch, $I = I^*$, shifts to the right upon successive illumination of the specimen. In accordance with (3, 4), the results obtained indicate non-quasistationary excitation of AgCl in the region $I > I^*$. Figure 2 shows the dependence of $I = I^*$ on the concentration of colloidal silver M for three values of the charge σ. This dependence was obtained directly from the isoopacs of Fig. 1. In accordance with (1), the dependence found of $I = I^*$ on M may be

Figure 2 plot

Figure 2: Figure 2 plot

Figure 3 plot

Figure 3: Figure 3 plot

regarded as linear; hence, in turn, it follows that in the process of growth of the silver particles the parameter β/s does not change appreciably. Figure 3 illustrates the effect of thermal dispersal of the colloids. Isoopac 1 was taken 2 hours after illumination of the crystal, and isoopac 2 after 120 hours. If it is assumed that in this case as well the parameter β/s remains constant, then the observed shift to the left of the point $I = I^*$ is due to a decrease in the concentration of colloidal silver as a result of thermal dispersal.

Fig. 2. Dependence of $I = I^*$ on the concentration of colloidal silver M. Values $\sigma_1, \sigma_2, \sigma_3$, see Fig. 1.

From comparison of (1) with the experimental data of Fig. 2 we found that the value of the parameter β/s lies within the limits 10–20 $\text{cm} \cdot \text{sec}^{-1}$. Using this value, we estimated the magnitude of the electron-capture cross section by a colloidal center, s_{el}, assuming

$$\beta = s_{\text{el}} v_T$$

($v_T = 6.8 \cdot 10^6$ cm/sec at $T = 120^\circ\text{K}$) and $s = 1.2 \cdot 10^{-11}\ \text{cm}^2$. The interaction cross section of a colloidal center with a photon, s, was calculated from the mean value of the radius of a colloidal particle ($\rho \approx 20$ mμ). Thus, for $\beta/s = 15$ it turned out that

$$s_{\text{el}} \approx 3 \cdot 10^{-17}\ \text{cm}^2.$$

This value of s_{el} is more than an order of magnitude smaller than the cross section of a neutral silver atom,

$$s_{\text{Ag}} \approx 6.5 \cdot 10^{-16}\ \text{cm}^2$$

($\rho_{\text{Ag}} = 1.44$ Å).

Fig. 3. Isoopacs of depolarization of AgCl, taken: **1** –after 2 hours and **2** – after 5 days after illumination of the crystal

Starting from the values of the concentration of colloidal silver M given in Table 1, an estimate was made of the degree of filling of silver levels γ during the formation of the photoelectret state in AgCl. The degree of filling

$$\gamma = \Delta M / M$$

was calculated under the assumption of a uniform distribution of charge over the volume of the crystal (ΔM is the number of electrons captured per unit volume by the levels of colloidal silver). The value ΔM was calculated from the formula

$$\Delta M = \frac{\Delta\sigma}{1.6 \cdot 10^{-19}} \frac{1}{h},$$

where $\Delta\sigma$ is the charge density of the photoelectret in coulombs per square centimeter, and $h = 0.025$ cm is the thickness of the crystal. Since the quantity M has the meaning of the increase in the concentration of colloidal silver upon illumination of the crystal, the value $\Delta\sigma$ was determined as the difference between the charges of illuminated and unilluminated (control) specimens. Measurement of $\Delta\sigma$ was carried out by depolarizing the photoelectret with green light of maximum intensity and integrating the discharge current over the entire depolarization time. The results obtained—

are presented in Table 1. Although the values of γ measured for AgCl are large in comparison with the values of γ determined for other crystals (^{9}) (in our case $\gamma_{\text{cr}} \approx 0.1$), the results obtained are in good agreement with the literature data ($^{10-12}$), according to which an individual latent-image center cannot capture more than one electron.

Finally, it should be borne in mind that our estimate of the values of the concentration of colloidal silver M is only approximate, since it depends strongly on the choice of the optical constants of Ag and AgCl. For example, if one uses the values of the radius of the colloidal particles according to P. V. Meiklyar (^{5}), then the corresponding values of the concentration M increase almost threefold. However, this can only decrease both the value of γ and the electron-capture cross section s_{el}, and does not affect the form of the electrophotographic isoopac and the conclusions drawn above concerning the mechanism of deviations from reciprocity for the photoeffect from AgCl.

4. The results obtained in the present work for AgCl single crystals confirm the mechanism proposed earlier (^{3}) for deviations from reciprocity in the formation of a latent electrophotographic image in the region of high light intensities. It is easy to see, however, that these same results make it possible to explain the deviations from reciprocity that were observed by P. V. Meiklyar in studying the growth of colloidal silver particles as a function of the exposure time t and the illuminance I (^{5}). Indeed, at high light intensities, when $I > I^* = \frac{\beta}{s} M$, there is a nonstationary regime of excitation of the crystal, caused by the fact that the probability of emission of an electron from the level of a colloidal center into the conduction band is much greater than the probability of capture of an electron by this center. Under these conditions the growth of colloidal particles will be slowed.

Conversely, if the light intensity is small, $I < I^* = \frac{\beta}{s} M$, then electron capture predominates over emission, and for the same values of the energy It the particles will prove to be larger. Thus, the proposed mechanism makes it possible to explain this effect within the framework of the Mott and Gurney theory, without resorting to special assumptions. Since, as indicated in (5), the dispersity of colloidal silver appreciably affects the measured value of the optical density, the mechanism considered above may be an additional cause of deviations from reciprocity in photochemical processes in silver halide salts. In any case, the analogy between latent photographic and latent electrophotographic images in silver halide compounds appears deeper than had previously been supposed.

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Note: Figure translations are in progress. See original paper for figures.