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Abstract

Full Text

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ON THE ELECTRONIC MECHANISM OF DEVIATIONS FROM THE RECIPROCITY LAW IN SILVER HALIDE CRYSTALS

(Presented by Academician A. V. Shubnikov on May 6, 1963)

The discovery and study of the photoelectret state in AgCl single crystals (^{1,2}), as well as the investigation of the shape of isopleths of polarization or depolarization for AgCl (^{3}), make it possible to propose an electronic mechanism for deviations from the photochemical reciprocity law in AgHal crystals, consistent with one of the theories proposed earlier (^{4}).

1. Numerous experimental works have been devoted to testing the fulfillment of the reciprocity law for AgHal and to studying deviations from this law over a wide range of light-intensity values; their results are summarized in a detailed review by A. L. Kartuzhanskii (^{5}). In Fig. 1 we give a series of isopleths borrowed from the work of A. L. Kartuzhanskii and P. V. Meiklyar (^{6}).

Fig. 1. Isopleths of the photographic process corresponding to different temperatures (after A. L. Kartuzhanskii and P. V. Meiklyar (^{6}))

Usually three characteristic regions are distinguished on an isopleth (points t_0 and t_n in Fig. 1). The regions $t > t_0$ and $t_\mathrm{n} < t < t_0$ are characterized by deviations from reciprocity, whereas for sufficiently short exposure times $t \le t_\mathrm{n}$ the reciprocity law is fulfilled. The data of work (^{6}), shown in Fig. 1, indicate that as the temperature is lowered the points $t = t_0$ and $t = t_\mathrm{n}$ shift to the right. The values of the light intensity I corresponding to the points $t = t_0$ and $t = t_\mathrm{n}$, respectively, decrease as the temperature is lowered (^{7}).

2. According to Mott and Gurney (^{8}), deviations from reciprocity at high light intensities ($t_\mathrm{n} < t < t_0$) are due to the two-stage mechanism of formation of the latent image in AgHal and to the large inertia of the ionic stage compared with the electronic one. In the region $t > t_0$ (low light

> intensities), deviations from reciprocity are associated with thermal activation of trapped electrons. According to P. V. Meiklyar (^{4}), deviations from reciprocity in AgHal for $t < t_0$ are due to a purely electronic mechanism. Thus, in (^{9}) it was shown that for AgCl and AgBr, as the light intensity is increased, a transition occurs from monomolecular to bimolecular recombination and, correspondingly, from a linear to a sublinear lux-ampere characteristic. In accordance with this, at high light intensities the filling of local levels by electrons becomes less effective.

If one adheres to this latter point of view, then a common mechanism must underlie deviations from reciprocity both for photochemical processes in AgHal and for the electrophotographic process in a broad class of crystals. The investigation of the photoelectret state in AgCl (^{1,2}) and of the depolarization isopleths of AgCl (^{3}) confirms this assumption to a considerable extent.

In (^{10}) a general equation was obtained for the isopaque of polarization or depolarization of the photoelectret:

$$\frac{dH}{dI} = \frac{1}{In} \int_0^H \left[n - I \frac{dn}{dI} \right] dH. \tag{1}$$

Here $H = It$ is the exposure, n is the concentration of free carriers, and I is the light intensity chosen, in constructing the isopaque, as the independent variable. It follows in particular from (1) that if the lux-ampere characteristic of the crystal is linear ($n = cI$), then the reciprocity law is fulfilled, $dH/dI = 0$; if, however, the lux-ampere characteristic is sublinear ($n = cI^\alpha,\ \alpha < 1$), then deviations from reciprocity occur, $dH/dI > 0$. We investigated the experimental isopaques of depolarization of the photoelectret from AgCl (^{3}). Figure 2 presents isopaques obtained upon depolarization of the photoelectret in two spectral regions: in the band of colloidal centers, $\lambda = 500\text{–}600$ mμ (curve 1), and for $\lambda = 405$ mμ (curve 2). At sufficiently high light intensities, both isopaques exhibit deviations from reciprocity. Separate measurements showed that, in accordance with (1), the upward bend of the isopaque occurs in that interval of values of I where, for AgCl, the linear segment of the corresponding lux-ampere characteristic changes into a sublinear one. According to E. A. Kirillov and I. Z. Levi (^{11}), as well as a number of other works (for example, (^{12})), the short-wavelength absorption maximum $\lambda = 405$ mμ in AgCl is due to silver centers of noncolloidal type. The results of investigations by K. V. Chibisov (^{13}) allow one to suppose that these centers are close in their nature to latent-image centers in AgCl. In any case, it may be asserted that both upon excitation of AgCl in the colloid band and upon excitation in the band with maximum $\lambda = 405$ mμ, the depolarization isopaques show, at high light intensities, deviations from reciprocity. These deviations are due to the transition from monomolecular recombination to bimolecular recombination, i.e., to a purely electronic mechanism. Thus the results obtained by us may serve as additional confirmation of the electronic mechanism of deviations from reciprocity, which

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

underlies the theory proposed earlier (^{4}).

Fig. 2. Isopaques of depolarization of the photoelectret from AgCl.
1—$\lambda = 500$—600 mμ, 2—$\lambda = 405$ mμ

Fig. 3. Scheme of energy levels for AgCl

3. A consecutive consideration of recombination processes in AgHal on the basis of Rose' s phenomenological theory (^{14}, ^{15}) leads to the construction of a theoretical isopaque for photochemical processes that coincides in form with the experimental isopaque (^{6}) and exhibits the same character of temperature dependence. Let us consider the recombination conditions for the scheme of energy levels shown in Fig. 3. Here n and P are, respectively, the concentrations of electrons in the conduction band and holes in the valence band. The densities of the ground states for electrons and holes are denoted respectively by n_{t1} and n_p. As applied to an AgHal crystal, n_{t1} denotes the density of levels of colloidal silver, forming a continuous distribution. According to studies of the red boundary of the effect

Herschel, these levels are located at a depth of the order of 1 eV. Along with this, in AgHal crystals there is a continuous distribution of shallow traps. The results of studies of thermally stimulated currents in AgCl $^{(18)}$ show that in this crystal there exists a continuous distribution of traps in the energy band from 0.03 to 0.55 eV. The results of studies of AgCl luminescence $^{(19)}$ also testify to this. In Fig. 3 the width of the energy band in which the shallow traps are uniformly distributed with density n_u is denoted by u_0, and the density of shallow traps filled with electrons is denoted by n_{t2}. In the dark the Fermi level is located in the interval between the shallow traps and the colloidal centers.

At low light intensities I (weak excitation) the Fermi level is located at a large distance $u > u_0$ from the bottom of the conduction band and, consequently,

$$n \ll n_{t2} \ll n_{t1}; \qquad n_p \approx n_{t1}; \qquad n = \frac{I}{v s_n n_{t1}}. \tag{2}$$

Under these conditions the lux-ampere characteristic is linear, and, according to (1), the reciprocity law is fulfilled (v is the thermal velocity of the electron, s_n is the electron capture cross section). Naturally, thermal activation of captured electrons into the conduction band will lead to additional deviations from reciprocity. Thus, conditions (2) correspond to the right branch of the isoopacity curve shown in Fig. 1 ($t > t_0$).

With increasing light intensity I, the Fermi level shifts toward the conduction band and the energy difference $u - u_0$ decreases, which leads to an increase in the concentration of electrons in shallow traps n_{t2}. In (14) it was shown that the condition $n_{t2} \approx n_{t1}$ corresponds to the onset of the transition of the monomolecular recombination mechanism to the bimolecular one and, accordingly, to the transition of the linear region of the lux-ampere characteristic to a sublinear one,

$$n \ll n_{t2} \approx n_{t1}, \qquad n_p \approx 2n_{t2}, \qquad n \approx I^{1/2} \left(\frac{N_c}{2vs_n n_u kT} \right)^{1/2} e^{-u_0/kT}. \tag{3}$$

Here N_c is the density of states in the conduction band, determined from the relation $n = N_c e^{-u/kT}$. Thus, in the region $t < t_0$ conditions (3) are fulfilled, the lux-ampere characteristic is sublinear and, in accordance with (1), the isoopacity curve bends upward (the beginning of the left branch of the isoopacity curve shown in Fig. 1). It can be shown that the light intensity I_0 corresponding to the point $t = t_0$ of the isoopacity curve is determined by the expression

$$I_0 = 2\frac{N_c v s_n}{n_u kT} e^{-u_0/kT} n_{t1}^2. \tag{4}$$

As follows from (4), when the temperature of the crystal is lowered, the point $I = I_0$ shifts toward lower values of the light intensity (and, correspondingly, the point $t = t_0$ shifts toward larger values of the exposure time), which agrees with the experimental data (see Fig. 1).

At sufficiently large values of the light intensity, the conditions of strong excitation $n \approx P \gg n_t, n_p$ may be fulfilled. In this case, according to (15), the lux-ampere characteristic of the crystal again becomes linear and, in accordance with (1), the reciprocity law is fulfilled:

$$n \approx P \gg n_{t1},\, n_{t2},\, n_p$$

$$n \approx P \approx I\tau = I\frac{1}{v\left(\dfrac{s_n s_p}{s_n + s_p}\right) N_g}. \tag{5}$$

Here s_n and s_p are, respectively, the capture cross sections of the electron and the hole, and N_g is the total concentration of ground states. It is natural to assume that

the validity of the law of reciprocity in the region $t \ll t_{\mathrm{n}}$ and, correspondingly, at sufficiently high light intensities $I \gg I_{\mathrm{n}}$, is connected with fulfillment of the conditions of strong excitation (5). From the condition $n \simeq n_{t2}$ one can estimate the value $I = I_\mathrm{n}$

$$
\begin{aligned}
I_\mathrm{n} &\simeq \frac{1}{\tau} n_u kT e^{-(u-u_0)/kT}, && u > u_0,\\
I_\mathrm{n} &\simeq \frac{1}{\tau} n_u kT, && u \ll u_0.
\end{aligned}
\tag{6}
$$

Here τ is the lifetime determined from expression (5). In accordance with (6), when the temperature is lowered the point $I = I_\mathrm{n}$, just like the point $I = I_0$, shifts toward lower values of the light intensity, which, as was indicated above, is observed experimentally.

The electronic mechanism considered above for deviations from the photochemical law of reciprocity, connected with a change in the recombination conditions in an AgHal crystal, in no way excludes the possibility of realization of a two-stage mechanism of the Mott and Gurney type. For us it is essential only to emphasize that even the electronic stage alone of this process is characterized by nonreciprocity and displays the same character of deviations from reciprocity and the same temperature dependence of these deviations as does the entire process as a whole.

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