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Abstract

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ON LUMINESCENCE STUDIES OF THE ROLE OF IMPURITY SILVER CENTERS IN THE PROCESS OF PHOTOLYSIS OF SILVER HALIDES

A large body of experimental material obtained in the study of the flash properties and the mechanism of luminescence of silver chloride ([1,2]) led to the conclusion that in AgCl impurity centers of a "silver" nature can be traps for both electrons and holes ([2–5]). Of essential importance for substantiating this conclusion were the results of works ([6–10]), in which the nature of the luminescence centers of silver-halide phosphors was elucidated. It turned out that in the formation of the luminescence centers of these compounds, the primary role belongs to formations consisting of one or several Ag atoms ([7]); and it is precisely these centers that are effective hole traps ([2,4]). With respect to their ability to localize free electrons, luminescence studies gave a negative answer ([5]). As was established in ([3,5]), deep electron traps in AgCl are formed by silver particles of precolloidal and colloidal dispersion.

The conclusions drawn on the basis of studying the luminescent properties of a silver-chloride emulsion—that impurity silver centers can be centers for the capture of both electrons and holes—are in good agreement with the concepts being developed in scientific photography ([11,12]). It should be noted, however, that at present there is still no consensus in assessing the contribution made by the indicated silver formations to the localization of free charges during photolysis. Thus, for example, Mott ([13]) and a number of other investigators ([14–16]) develop the viewpoint according to which the photosensitivity center is a trap for an electron. In contrast to these concepts, Mitchell believes ([17]) that photosensitivity centers adsorb silver ions. In works ([11,18,19]) it is indicated that silver formations of atomic-molecular dispersion, arising in emulsions during their preparation, are traps for holes.

Fig. 1. Luminescence spectrum of a silver-chloride emulsion; **1**—before treatment of the emulsion with a potassium dichromate solution; **2**—after treatment with a 0.01% solution of $K_2Cr_2O_7$ for 25 min.; **3**—after subsequent exposure to u.-v. light for 3 sec.

In the present work it is possible to show that luminescence measurements can

Fig. 1. Luminescence spectrum of a silver-chloride emulsion; 1—before treatment of the emulsion with a potassium dichromate solution; 2—after treatment with a 0.01% solution of $K_2Cr_2O_7$ for 25 min.; 3—after subsequent exposure to ultraviolet light for 3 sec.

Figure 1: Fig. 1. Luminescence spectrum of a silver-chloride emulsion; 1—before treatment of the emulsion with a potassium dichromate solution; 2—after treatment with a 0.01% solution of $K_2Cr_2O_7$ for 25 min.; 3—after subsequent exposure to ultraviolet light for 3 sec.

provide additional information on the role of photosensitivity centers and fog centers as traps for electrons or holes. Indeed, if photosensitivity centers are silver particles of atomic-molecular dispersion ([19,20]) and serve as centers for hole capture, then in this case one should expect that the change in the intensity of the luminescence band of an emulsion subjected to different times of second ripening (t_2) should reproduce the course of the change in its photosensitivity (S). On the other hand, if photosensitivity centers belong to those silver centers that are traps for electrons, then

the dependence S–t_2 should correlate with the dependence of the flash properties of these samples on t_2.

A fine-grained silver chloride emulsion was chosen as the object of study ([4,21]). Luminescence measurements were carried out at liquid-nitrogen temperature using an apparatus described earlier ([1,3]). The steady glow of the specimens could be recorded by photoelectric and photographic methods. The luminescence spectra of all emulsion samples were characterized by a single band with $\lambda_{max} = 525$ mμ (Fig. 1, 1). Under the action of long-wavelength light, a flash and quenching of this glow were observed ([4]).

As was already indicated earlier ([5]), the proof of the silver nature of the luminescence centers of the silver chloride emulsion was based, first, on data from the excitation spectra of these objects and, second, on the close analogy of their luminescent properties with those of typical AgCl phosphors ([7,22,23]). In the present work we considered it necessary to carry out a number of additional experiments that would confirm the conclusions drawn about the nature of the luminescence centers with greater reliability. For this purpose, we studied the effect of treating the emulsions with a potassium dichromate solution (0.01%) and of exposing them to ultraviolet light at room temperature on the level of their steady luminescence. It turned out (Fig. 1, 2, 3) that the oxidizing agent decreases, whereas exposure increases, the intensity of the green band. Since under the action of the oxidizing agent destruction of the "silver" centers of atomic-molecular dispersity occurs ([19]), while ultraviolet irradiation is capable of creating them anew, the results presented are good confirmation of the previously advanced ideas concerning the nature of the luminescence centers of the silver chloride emulsion.

Fig. 2. Change in the intensity of the green glow of a silver chloride emulsion as a function of the time of the second ripening

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The second step of the investigations consisted in clarifying the nature of the electron-capture centers of the objects studied. To solve this question, for emulsion samples subjected to different times of second ripening, the destruction spectra of ionized luminescence centers were studied ([2,3,5])*. These experiments showed that, for all objects, in the range from 0.44 to 0.7 μ a monotonic increase of Q toward shorter wavelengths is observed (see ([5]), Fig. 1 B, curve 1). In this case, as was shown in ([5]), optical bleaching of electrons from localization levels is a process of their photoemission from centers of silver of precolloidal dispersity, and these same impurity centers create the deepest traps for electrons.

After the preliminary experiments indicated above had been carried out, the further investigation consisted in establishing the dependence of the photosensitivity (S), fog density (D), glow intensity (I), and the quantities Q_1 and Q_2^{**} on the duration (t_2) of the second ripening of the emulsion. The meaning

* As a measure of the effect in studying the destruction spectrum of ionized luminescence centers, the quantity

$$Q = \frac{\Delta I}{B_\nu \Delta t I_1},$$

was adopted, where ΔI is equal to the difference in flash intensity before (I_1) and after bleaching; B_ν is the magnitude of the "bleaching" luminous flux of frequency ν; Δt is the bleaching time. The determination of Q was carried out according to the procedure indicated in ([3,5]).

** Here Q_1 and Q_2 are the magnitudes of the effect of destruction of ionized luminescence centers when monochromatic light with $\lambda = 0.44\,\mu$ (Q_1) and $\lambda = 46\,\mu$ (Q_2) was used for bleaching.

The comparison of the curves $S - t_2$ and $I - t_2$ has already been discussed above. The meaning of determining the dependence of Q_1 or Q_2 on t_2 is as follows. Since optical bleaching in silver chloride in the region from 0.44 to $0.6\,\mu$ is associated with the effect of photoemission of electrons from silver particles, it is quite clear that the greater the number of these trapping centers, the larger the values of Q_1 and Q_2 will be. Thus, comparison of the values of Q_1 or Q_2 for a specimen with different times of second ripening makes it possible to judge the change in the concentration of precolloidal silver centers in the emulsion as t_2 is increased.

Fig. 3

Figure 3: Fig. 3

It was found that the curve of I versus t_2 (Fig. 2) repeats the course of the curve of S versus t_2 (Fig. 3), and that the change of Q_1 and Q_2 with t_2 corresponds to the change of D with t_2 (Fig. 3). These results make it possible to draw the following conclusions.

1. Fog centers are silver particles of precolloidal dispersity and are electron traps.

2. Comparison of the dependences of I on t_2 and S on t_2 makes it possible to suppose that the photosensitivity centers belong at least in part to "silver" formations of atomic-molecular dispersity and serve as effective hole traps. True, one must here take into account the fact that the drop in the intensity of the luminescence of the emulsion with increasing t_2 may to some extent also result from an increase in the concentration of fog centers in the specimens. In this case, a change in the number of precolloidal silver particles on the surface of AgCl microcrystals will cause attenuation both of the exciting radiation and of the luminescence itself.* But regardless of the corrections that may be introduced by further study of the dependence of I on t_2, it should be specially emphasized that, since atomic-molecular silver centers are hole traps and not electron traps, they cannot increase their size during photolysis by the Gurney–Mott mechanism. For this case we propose the following scheme (p. 130) of the deep photolysis of silver halides.

Fig. 3. Dependence of the value of photosensitivity (S), fog density (D), and the magnitude of the effect of destruction of ionized luminescence centers by monochromatic light with $\lambda = 0.44\,\mu$ (Q_1) and $\lambda = 0.46\,\mu$ (Q_2) on the duration of the second ripening of the silver chloride emulsion.

At the initial stages of photolysis, the increase of a silver particle takes place by the Mitchell mechanism ([17]). However, we believe that, in contrast to Mitchell' s views, according to the indicated scheme the impurity centers already present in the specimens, which arose in the emulsion preparations during their manufacture, begin to grow. The presence of such centers in an unexposed silver chloride emulsion is confirmed by all luminescence measurements. The same primary centers can, first, trap holes and, second, accept silver ions and grow by the Mitchell mechanism into latent-image centers. The manifestation of one or another function of impurity centers at the initial stages of photolysis is of a purely probabilistic character.

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* It is perfectly clear that completely unambiguous conclusions about the role of photosensitivity centers in photographic emulsion can be provided by exper-

iments involving the comprehensive study of the photographic and luminescent properties of a silver chloride emulsion in which the value of S passes through a maximum as t_2 is increased, while the fog density changes insignificantly.

With an increase in the size of the primary center, its ability to localize holes decreases, while its ability to capture electrons increases. After the silver particle reaches a certain critical size, it becomes only a trap for electrons (the latent-image center is only a trap for electrons). From this moment on, further growth of the impurity center proceeds by the Gurney–Mott mechanism.

Thus, it may be thought that in the process of photolysis there exist different mechanisms for increasing the size of silver centers.

In the results presented, attention is drawn to the fact that, when considering the mechanism of deep photolysis of silver halides, electron, hole, and ionic processes must be taken into account.

In papers ([18,19]) a scheme was proposed illustrating the transformation of silver centers in the photographic process. Taking into account the mechanism of formation of a silver particle at different stages of photolysis, this scheme now assumes the following form (see scheme, III).

Scheme

$$\mathrm{Ag} \to \mathrm{Ag}_2 \to \mathrm{Ag}_3 \to \cdots \left\{ \begin{array}{ccc} \mathrm{Ag}_n & \mathrm{Ag}_{n+1} & \mathrm{Ag}_{n+2} \\ \downarrow & \nearrow\searrow & \nearrow\searrow \\ \mathrm{Ag}_{n+1}^{+} & \mathrm{Ag}_{n+2}^{+} & \cdots \end{array} \right\} \cdots \mathrm{Ag}_m \longrightarrow \left\{ \begin{array}{ccc} \mathrm{Ag}_m & \mathrm{Ag}_{m+1} & \mathrm{Ag}_{m+2} \\ \downarrow & \nearrow\searrow & \nearrow\searrow \\ \mathrm{Ag}_m^{-} & \mathrm{Ag}_{m+1}^{-} & \cdots \end{array} \right\} \cdots \mathrm{Ag}_k, \qquad k \gg$$

Atomic-molecular centers. Acceptors of holes. They affect the "speed," photosensitivity; luminescence centers are partly formed from them

(I)

Precolloidal silver particles, developing centers, latent-image centers

(II)

Colloidal silver particles, bleach centers (latent-image reversal, solarization).

(III)

In conclusion, I would like to note that the facts obtained once again emphasize the great possibilities opened up by the previously proposed method ([4,21]) for a combined study of the luminescent and photographic properties of emulsions.

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