Infrared-Induced Dispersal of Hole Traps in AgBr†

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Infrared radiation has been found to cause a redistribution of the clusters of traps for valence-band holes in doped silver-halide crystals. This new effect was found by monitoring the concentration of trapped holes by the equivalent concentration of free electrons in the conduction band. Reciprocity failure was also found at low irradiation levels. In addition to their relevance to solid state physics, these new effects extend the analogies between normal and complementary photographic images.

Previous work at this Laboratory has shown that the growth of photographic silver specks within the volume of silver-halide crystals is paralleled by the condensation of holes together with Ag^+ vacancies.[1,2] This condensation occurs at suitable sites in the crystal and gives rise to clusters which constitute the complementary photographic image.[1,2]

The condensation of holes and vacancies may, under suitable conditions, fail to be paralleled by the primary photographic condensation of electrons and Ag^+ ions. This is the case when the temperature is low enough to decrease sufficiently the mobility of interstitial silver ions.[1,3] In this case, the optically freed electrons build up a conductivity which can be long lasting or even permanent in the dark.[1,2]

In experiments at this Laboratory, up to about 10^{12} electrons/cm^3 have been obtained in the conduction band of suitably doped silver-halide single crystals.[1,2] At these low concentrations the electron effective mass and mobility are safely assumed to be constant. Therefore, the growth of electronic conductivity under irradiation provides relevant information concerning the nucleation and growth of hole traps.[2] Hopefully, further relevant information could be obtained by investigating the behavior of the complementary image under infrared (IR) irradiation, i.e., under conditions which have long been known to give rise to the classical Herschel and Debot effects which (see, e.g., Mitchell[3]) concern a redistribution, caused by IR irradiation, of the silver nuclei (constituting the latent image) between the surface and volume of silver-halide grains.

In the present work, we have used conductivity techniques to detect and study the occurrence of an effect of IR radiation upon the complementary image clusters. This effect is indeed of the Herschel-Debot type. This, together with a reciprocity failure for the formation of complementary image clusters upon irradiation in the visible, extends the analogies between normal and complementary photographic images.

The techniques for irradiation and for conductivity measurements have been described in Ref. 2. The 545-nm wavelength line from a high-pressure mercury source was selected as described in Ref. 2. The IR source was a Model 8c Leuci 250-W near-IR lamp.

(A) Irradiation with visible light only.—Curves *A*, *B*, and *C* in Fig. 1 represent typical photoconductivity growth curves[2] at 77°K for doped AgBr crystals. Doping, dimensions, annealings, and irradiation conditions of specimens are as discussed in Ref. 2.

Curve *A* in Fig. 1 is typically the growth curve that is obtained using a virgin specimen or one which has been stored in the dark at room temperature.[2] It appears evident that the majority of the hole traps are created during illumination and that their nucleation needs an incubation peri-

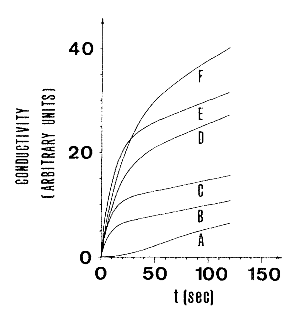

FIG. 1. Photoconductivity growth curves (arbitrary units) of a doped AgBr crystal at 77°K. Curve *A* refers either to a virgin specimen or to one which has been stored in the dark at room temperature. Curves *B*, *C*, *D*, *E*, and *F* refer to successive reilluminations of the specimen following 20 min of storage at 77°K to allow decay. IR irradiation preceeded the *D* and *F* growths. Note that a small amount of permanent conductivity is left after a decay. Each successive growth is referred to this conductivity level.

od. This incubation period is evidenced even better at lower light intensities, at which reciprocity failure is very evident. As an example, a reduction by a factor 10 in the light intensity, requires an increase by a factor 90 in the exposure time (i.e., an increase by a factor 9 in the overall dose) to reach the same conductivity level.

Curves B and C are obtained upon two successive reilluminations each following 20 min of dark storage at 77°K to allow decay. A detailed discussion of curves of the types A, B, and C in Fig. 1 may be found in Ref. 2. Nevertheless, it is useful to stress here that (i) following the first irradiation and decay the slope of the photocurrent growth curves saturates rapidly, and remains nearly constant at the light intensity levels used, also under prolonged irradiation (e.g., up to $\frac{1}{2}$ h); (ii) this slope saturation value remains nearly constant, also in subsequent decay and reirradiation experiments, provided that the samples are kept in the dark at low temperature and that this storage does not last much more than $\frac{1}{2}$-1 h; (iii) at variance with the growth curves, the different decays do not obey a simple kinetics, with one (or few) decay time. For this reason the growth-curve parameters are obtained on a quantitative basis and the effects of different treatments upon the rapidity of decay are described in a qualitative fashion.

(B) Effects of IR radiation.—In Fig. 2 are shown the results of experiments in which the crystal was illuminated with IR light during the conductivity decay. One sees that the onset of a steady IR irradiation causes a sharp transient

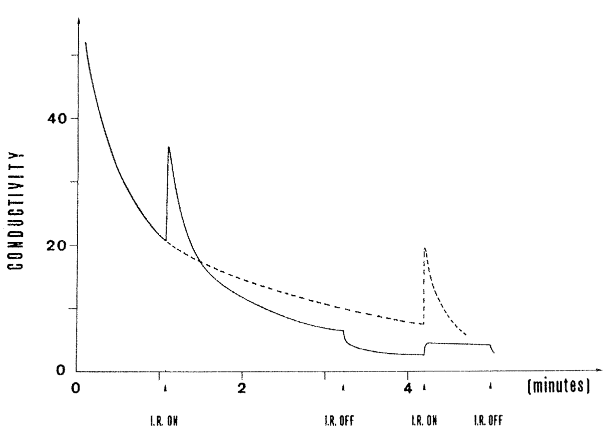

FIG. 2. Effects of IR irradiation on a doped AgBr crystal previously irradiated with visible light (545 nm) at 77°K (solid line). The dashed line was drawn on the basis of other experiments and it shows qualitatively the effect of the *first* IR irradiation when it occurs at a later time. Conductivity in arbitrary units.

increase of conductivity. On the other hand, if the first irradiation occurs during decay, the transient increase of conductivity is followed by an acceleration of the decay. Subsequent IR irradiations, occurring when the decay has been completed, have the sole effect of increasing the conductivity level at a new value which remains constant as long as the IR irradiation continues. This effect is not found if the crystal has not been previously irradiated with visible light while kept at low temperature.

Irradiation with IR also affects the "memory"[2] of the crystals, as seen by subsequent irradiation with 545-nm light. In Fig. 1, IR irradiation has been used between the conductivity growth experiments relative to curves C and D and those relative to curves E and F. The effects upon the "memory" are evident and they will be discussed in more detail in what follows.

(C) Discussion and data analysis.—As previously pointed out[2] the growth of the secondary photoconductivity, following the start of nucleation of hole traps, obeys the rate equation

$$dn/dt = (1/\tau)(n_0 + ct - n), \tag{1}$$

where n measures the number of photoliberated electrons, n_0 measures the number of hole traps present in the crystal at the beginning of each particular irradiation, c measures the rate at which new traps are created, and τ measures the time constant for filling the hole traps at the given illumination level. Upon integration Eq. (1) gives

$$n = a(1 - e^{-t/\tau}) + ct, \tag{2}$$

where $a = n_0 - c\tau$. The n_0, τ, and c values relative to the different experiments were obtained by computer least-squares fits of Eq. (2) to experimental points. The fitting was so satisfactory that, e.g., in Fig. 1, theoretical and experimental points coincide within drawing accuracy.

Information on the number, nucleation, and rearrangements of hole traps are contained in the above parameters. The effects of IR radiation on the hole traps are evidenced and measured by the changes caused in these parameters.

In Fig. 3 we report the parameter values of a set of six successive visible light irradiations, each followed by a dark decay of conductivity, as discussed in Ref. 2. It appears evident from the figure that all parameters tend to behave asymptotically under these conditions.

In Fig. 4 we report a similar set of values, relative to curves B, C, D, E, and F shown in

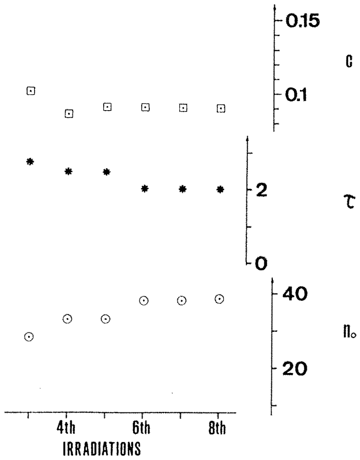

FIG. 3. Typical behavior of the parameters c, τ, and n_0 for a set of six successive growth curves (not shown in figure) each followed by a dark decay of conductivity. Parameter τ is expressed in seconds, while the orders of magnitude of the units for the remaining two parameters are, for n_0, $\approx 10^9$ cm^{-3}, and for c, $\approx 10^9$ cm^{-3} sec^{-1}.

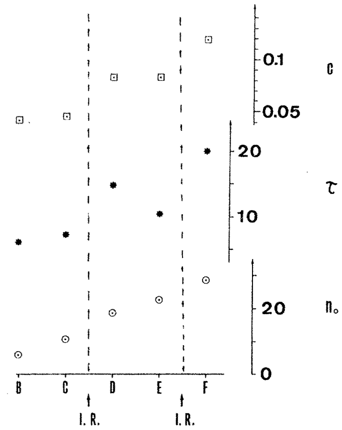

FIG. 4. Behavior of the parameters c, τ, and n_0 for the set of five growth curves B, C, D, E, and F of Fig. 1 (same units as in Fig. 3). The specimen was not that of the case of Fig. 3, but is behaved in a similar way except for the difference in the actual values of the parameters. In the present case the specimen was IR irradiated twice (i.e., prior to the D and F growths).

Fig. 1. At variance with the case of Fig. 3, the specimen was IR irradiated prior to the D and F growths. The change in the asymptotic behavior of the n_0, τ, and c values, which was already evident from Fig. 1, is here illustrated quantitatively.

This effect of IR irradiation is very well interpreted in terms of a dispersal of the complementary image centers. Such a dispersal is expected to increase the lattice disorder and thus to increase the number of centers capable of trapping holes and to stabilize this trapping by a further ionic step of the type discussed in Ref. 2. This will correspond, therefore, to an increase of both the n_0 and c values. The increase in the τ value is also explained in terms of the mentioned dispersal. In fact, in this case, the "initially present traps" will need a longer time to stabilize the trapping by a process of the type discussed in Ref. 2.

The above model is consistent with results shown in Fig. 2. In fact, the untrapping of carriers operated by the IR, evident from the figure, is the first step for the redistribution of the complementary image clusters and it is also consistent with the increased electron-hole annihilation rate.

In conclusion, these effects of IR may be considered (apart from the different techniques by which they are revealed) as the Herschel-Debot effects as seen from the point of view of the complementary photographic image.

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