Nucleation of Hole Traps in Silver Halide Crystals*

L. CORDONE, S. L. FORNILI, AND S. MICCIANCIO
Istituto di Fisica dell'Università and Gruppi Nazionali Struttura della Materia of the Consiglio Nazionale delle Ricerche, Palermo, Italy

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Experimental results are presented concerning the growth curves of the previously found long-lived (or even permanent) photoinduced conductivity in doped AgBr crystals. These results yield for the first time, direct evidence for the kinetics, as well as for the mechanism of the trapping of photoliberated holes, which is the counterpart of the primary photographic process and renders it possible. The effect itself can be used as a novel technique for the investigation of some many-body effects, or for making special devices.

I. INTRODUCTION

PREVIOUS work at this laboratory has shown the possibility of establishing, by a *transient* illumination, a long-lived, or even *permanent*, concentration of conduction electrons in silver halide crystals.[1] As predicted long ago by Mitchell, this is possible when the crystal contains trapping centers for the photoliberated holes that do not act as recombination centers,[2–4] *and* when the temperature is low enough to decrease sufficiently the mobility of the interstitial silver ions. In fact, in these conditions, once the electron traps in the crystal are filled, the photoliberated electrons will remain in the conduction band, since they can neither recombine with holes nor take part in the photographic process. This provides a straightforward explanation[1,4] for the effect of "secondary photocurrents" in silver halides (that is, a long-lived photoinduced conductivity), found long ago at Gottingen.[5,6]

In the present work we report experimental results on the growth, upon illumination, of a conductivity of this type in doped AgBr crystals, and we point out how they yield direct evidence for the kinetics, as well as for the mechanism of the photoliberated hole trapping. We also point out their relevant implications. We shall continue to call this type of photoconductivity "secondary," as opposed to the "primary" photoconductivity that is due to those carriers undergoing immediate recombination when illumination is turned off.[6]

II. EXPERIMENTAL

Conductivity measurements were made with a 260-AP Boonton Q meter at a frequency of 1 MHz, using a capacitor arrangement in a resonating LC circuit. At this high frequency, and (as in the present case) with relatively low electron concentrations, space-charge and electrode effects become irrelevant.[1,7] The circuit resonance frequency was kept constant by adjusting the instrument's internal capacitance value to compensate for dielectric-constant changes. The instrument was modified so as to allow chart recording of the Q-value changes. Aquadag electrodes were painted on the specimen, since it was known from previous work[1] that this does not alter the results in the present conditions, while it does enhance sensitivity. During, or prior to, the experiment the sample (typically, a cylinder about 7 mm in diameter and 3.5 mm in height) could be irradiated at low temperature in a direction orthogonal to the applied ac field, by means of a filtered Philips SP-1000 lamp and a quartz light pipe about 3 mm in diameter in series with a light condenser. Radiation at a weakly absorbed wavelength was selected, in order to obtain volume effects only, since the more strongly absorbed lines present in the unfiltered Hg radiation also cause "surface" effects. Up to about 2×10^{15} photons/sec of approximatively 545-nm wavelength could reach the lateral surface of the sample. In the present experiments, however, the intensity was kept at a much lower level. The choice of the 545-nm radiation was dictated by the fact that, in these conditions, the primary photoconductivity was irrelevant compared with the integrated buildup of the secondary photoconductivity. It was further realized that the use of "safe" light (Na lamps) can alter the results, because, on one hand, it gives rise to some photoconductivity, while, on the other hand, it can free the trapped holes, which can then recombine with electrons from the conduction band. To avoid these complications, the crystals were kept in the dark except for the desired exposure. Samples were carefully cut from large crystals, prepared by the Mitchell technique.[8] They were gently ground to the desired dimensions, etched in a KCN solution, soaked in redistilled water, and dried. Finally, they were annealed in the appropriate atmosphere.

III. RESULTS AND DISCUSSION

It was found that AgBr samples containing Cd^{++} in molar concentrations of 10^{-5}–10^{-4}, grown and annealed

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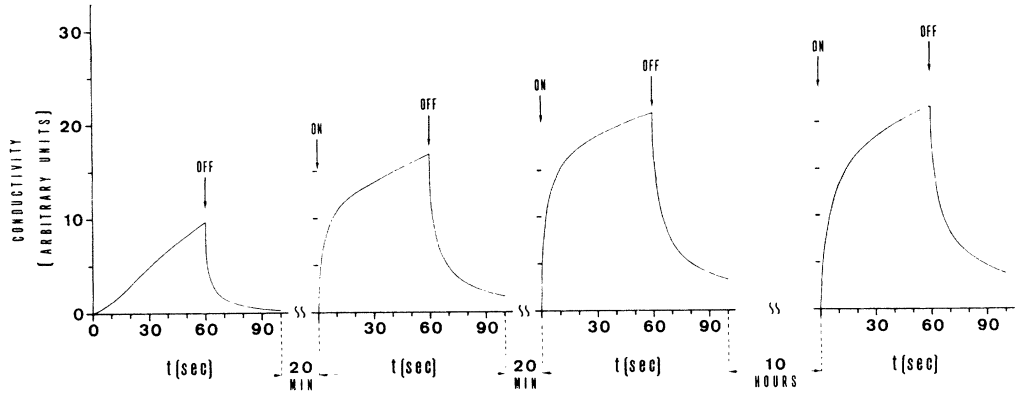

FIG. 1. Electronic conductivity versus irradiation (or storage) time in a doped AgBr single crystal, irradiated throughout its volume, showing effectiveness of hole trapping in increasing the available number of hole traps. The temperature is 77°K and the light intensity is about 2×10^{13} photons (545 nm)/sec. The electron concentration corresponding to the maximum value of conductivity shown in the figure is of the order of $10^{10}/cm^3$, as calculated using the mobility value of D. C. Burnham, F. C. Brown, and R. S. Knox, Phys. Rev. **119**, 1560 (1960). The experimental and theoretical points of the "rise" curves 2–4 coincide within plotting accuracy (see text).

in an inert atmosphere and having undergone no other treatment, present, upon illumination with 545-nm radiation at 77°K, a long-lived conductivity that decays (at that temperature) within seconds, minutes, or hours—the lifetime being dependent upon the radiation dose and wavelength. Superposed on this, a permanent component of conductivity was found, upon irradiation for a sufficient number of seconds, in samples that had been annealed either in oxygen or in an atmosphere containing even small traces of oxygen ($\sim10^{-3}M$). This result was also obtained in Ref. 1, and is in full agreement with what Mitchell had predicted long ago.[4] This part of the conductivity has been observed to remain unchanged over weeks at 77°K.[1] Also, it depends very markedly upon the radiation wavelength. For example, when using the 436-nm line (which is much more intensely absorbed, although at 77°K it does not give rise to a true surface effect), it is much stronger. The reasons for this behavior will become evident in the following.

In the present series of experiments, we have used AgBr:Cd^{++} (10^{-5}–$10^{-4}M$) crystals annealed, either in a truly inert atmosphere (nitrogen) or in oxygen, and kept in the dark. The effects that we want to discuss were qualitatively unprejudiced by the presence of a truly permanent component of the photoinduced conductivity. Furthermore, that component was negligible in the present experiments.

Typical photocurrent growth and decay curves are shown in Fig. 1 for the case of a AgBr:Cd^{++} ($10^{-5}M$) sample annealed in an atmosphere of nitrogen that contained about $10^{-4}M$ of oxygen and irradiated with about 2×10^{13} photons/sec (545 nm). From the results condensed in the figure, we conclude that:

(1) Under prolonged irradiation (up to $\frac{1}{2}$ h) the slope of the photocurrent growth curves tends to a smaller (constant) value, which is well different from zero. This evidences the continuous creation of additional hole traps.[9,10] The creation of these additional traps hardly may be ascribed to a direct effect of illumination. Therefore, it very strongly suggests the operation of a mechanism of the type proposed by Mitchell.[2–4] In this mechanism, a combination of electronic and ionic processes stabilizes the hole trapping and creates, at the same time, new trapping sites. In fact, the temporary trapping of a hole at a halogen ion occupying a defective position is stabilized by the expulsion of a silver ion from a nearby site to an interstitial position. This leads to the formation of a halogen X_2^- molecular ion, which, at the same time, constitutes a new trap, so that halogen molecules are eventually formed.[2,3] This mechanism evidently also creates new silver-ion vacancies. In the case of volume effects, it can more easily start at sites near impurity ions such as copper[11,12] or[4] O^{--}, compensating, e.g., for Cd^{++}, but it may also start at positive-ion vacancies in favorable sites, such as dislocation kink sites, under prolonged and sufficiently intense irradiation capable of establishing the necessary concentration of holes. It is of interest to note that the impurity concentration will be higher in the proximity of dislocations,[13–17] and that an excess of positive-ion vacancies is introduced when doping with doubly charged positive ions. It is also of interest to note that the operation of this mechanism is expected to produce a reciprocity failure at low intensities, much as in the case of the

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TABLE I. Values of the constants in Eqs. (1) and (2) corresponding to curves 2–4 in Fig. 1.

	n_0	a	b	c
Curve 2	10.8	10.4	0.27	0.11
Curve 3	16.0	15.6	0.27	0.10
Curve 4	15.2	14.5	0.18	0.12

trapping of electrons and the related formation and growth of the photographic silver specks.[2,3]

(2) The first of the growth curves in Fig. 1 shows that hole traps are not initially present in the crystal in massive concentrations. Their nucleation needs an "incubation" period under illumination. This requirement is even better evidenced when using lower illumination levels. This behavior parallels a "reciprocity failure," which we have, in fact, found in this case, similar to that occurring in the case of nucleation of the primary "photographic image."[2,3]

(3) Reillumination immediately after dark decay at 77°K leads to a remarkably higher *initial* rate of growth of conductivity upon illumination. If reillumination is preceded by dark storage, this "memory" effect is less conspicuous or even canceled, depending upon the storage time and temperature. Upon storage for a short time at 300°K, all the "memory" is lost and the conditions are restored that give rise to the first curve in Fig. 1. Even storage at 77°K, however, has some effect, as indicated by the last curve in Fig. 1.

We believe that this "memory" must be due to the permanence of disorder caused in the lattice by the only ionic processes occurring upon illumination, that is, those involved in the hole trapping. These changes remain in spite of the annihilation of the electrons and holes originally photoliberated. In terms of the Mitchell mechanism of hole trapping, this is just what one expects. In fact, following the conductivity decay—that is, following the electron-hole recombination—the interstitial silver ions corresponding to the annihilated electron-hole pairs will be expected (on the basis of a reversal of the mechanism) to jump back to their original sites, thus restoring the geometrical lattice order. However, this complete restoration of order will not occur rapidly at low temperature. Therefore, upon reillumination, a quicker operation of the Mitchell mechanism (that is, a quicker attainment of the previous conductivity value) will be expected.

One should also note that at 77°K a fraction of the initially photoliberated electrons will not take part in the conduction, since they will be trapped at traps deeper than 77°K.[18,19] This fraction will not necessarily recombine with holes when the conductivity decays at 77°K. A corresponding number of holes may thus escape annihilation. Now, if the trapping of these holes has occurred by a mechanism of the Mitchell type, this may preserve in the crystal a disorder that will favor the further trapping of holes upon reillumination, as compared with that possible during the first illumination. Nevertheless, one should note from the figure that the memory effect concerns conductivity levels that increase at each decay reillumination cycle. This shows that the memory is not merely due to the (constant) number of electrons that might remain in the electron traps. This conclusion is also in agreement with the already mentioned dependence of the conductivity lifetime upon radiation doses, which suggests that higher doses result in higher stability of the hole traps and of the lattice disorder associated with them.

Within the framework of the model just discussed, one expects (as is experimentally observed) that the memory effect will be destroyed by sufficiently long dark storage, capable of allowing the eventual annihilation of all electrons and holes, as well as the complete restoration of the ordered lattice. (Depending upon storage time and temperature, this eventual annihilation can take place either directly or through the formation and further spontaneous bleaching of metallic silver specks.)

The model also predicts that the number of hole traps is not constant in the crystal, since, as we have already seen, when the trapping proceeds new vacancies are created by the expulsion of silver ions to interstitial positions. These additional vacancies provide (up to a certain point) further sites at which the holes can be trapped.

This nucleation and growth of hole traps indeed accounts for our experimental observations. In fact, as long as one has a concentration-independent electron mobility, growth curves 2–4 in Fig. 1 should obey, in our model, a kinetics of the type

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

where n is the number of photoinduced conduction electrons, n_0 is 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 b measures the time constant for filling the traps at the given illumination level. b is assumed to be the same for both types of traps.

Upon integration Eq. (1) gives

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

where $a = n_0 - c/b$. Indeed, the agreement between the experimental points and those obtained by a computer least-squares fit for a law of the type of Eq. (2) is so good that the two sets of points are not distinguishable in the figure. For curves 2, 3, and 4 in Fig. 1, the n_0 values are in the ratio 1:1.5:1.4, respectively, as one

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can see from Table I, which gives the values of the constants in Eqs. (1) and (2).

IV. CONCLUSIONS

In conclusion, the present results provide direct supporting evidence for both the Mitchell mechanism and the related kinetics of the trapping of photoliberated holes. The end result of this mechanism is the buildup of halogen molecules by means of the alternate condensation of photoliberated holes and of positive-ion vacancies, created by the expulsion of positive ions to interstitial positions. These halogen molecules, in the present case of volume effect, remain within the crystal.[20] They constitute the counterpart of the metallic silver specks obtainable by volume irradiation at room temperature by the (complementary) alternate condensation of photoliberated electrons and mobile silver ions.

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In addition, the present results provide a new technique for the study of several types of many-body interactions (e.g., phonon-plasmon interaction, etc.) as a function of the number of conduction electrons in the dark. This new technique appears particularly promising because it allows the number of conduction electrons to be varied in *one and the same sample* at *constant temperature* (that is, in one well-defined dynamical situation of the crystal). The possibility of using the above results to make new devices should also be noted. In particular, one might hope that the permanent photoconductivity here discussed could be "erased" by infrared illumination. Work is in progress also in this direction.

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Computer Simulation of the Lattice Dynamics of Solids*

J. M. DICKEY
Brookhaven National Laboratory, Upton, New York 11973

AND

ARTHUR PASKIN
Queens College of The City University of New York, Flushing, New York
and
Brookhaven National Laboratory, Upton, New York 11973

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Neutron-diffraction data on dispersion curves for the rare-gas solids has emphasized the need for an anharmonic treatment of lattice dynamics. The molecular-dynamic technique is a powerful way of examining the temperature and volume dependence of phonon properties, since anharmonicity is treated without approximation. Using a Lennard-Jones potential, classical calculations have been made, at different temperatures and volumes, of average phonon properties such as pressure and energy, correlations in velocity and position, frequency distribution of normal modes, and phonon-dispersion curves. The volume dependence of the frequency was used to test the Gruneisen approximation. The magnitude of fluctuations in temperature and in the various correlations were compared with theory. These calculations predict relatively large shifts in frequency at constant volume as the temperature is raised in the regime where the classical approximation is valid.

I. INTRODUCTION

NEUTRON-DIFFRACTION measurements have recently[1,2] yielded phonon-dispersion curves for rare-gas solids at different temperatures, with the volume held constant, as well as at different densities. High-precision measurements of this type may ultimately provide critical tests of empirical pair potentials, anharmonic effects and the possible need for 3-body potentials.[3] The ability to measure phonon frequencies at constant volume over a wide range of temperatures generates a need for an exact treatment of anharmonicity. As measurements are made at arbitrary densities anharmonic frequency shifts, as a function of lattice spacing, are required to make meaningful comparison of experimental data with theoretical calculations. Further, recent interest in the phonon properties of extremely thin films and surface effects demands a

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