

breakdown occurs between the first- and second-zone sheets of the Fermi surface.

We would like to express our appreciation to Professor L. M. Falicov for many interesting and stimulating discussions.

*Work supported in part by the Army Research Office (Durham), the Alfred P. Sloan Foundation, and the Advanced Research Projects Agency.

†ARO Research Assistant.

‡Alfred P. Sloan Research Fellow.

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$$\mathcal{Q} = (4\pi^2 e / ch) F = 9.55 \times 10^{-9} \times F.$$

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PERMANENT PHOTOINDUCED CONDUCTIVITY IN SILVER HALIDE CRYSTALS

L. Cordone and M. U. Palma*

Istituto di Fisica dell'Università di Palermo, Palermo, Italy, and Gruppo di Palermo del Gruppo Nazionale Struttura della Materia del Consiglio Nazionale delle Ricerche, Palermo, Italy

(Received 25 October 1965)

In this Letter we report preliminary results which, in agreement with Mitchell's theory of photographic processes, show that it is possible to build up in a controllable way a finite and permanent concentration of electrons in the conduction band of silver halide crystals at low temperatures.

In order to have photoelectrons available to take part in the primary photographic process, a photoelectron-hole recombination must be avoided.¹ As Mitchell has emphasized, this can be obtained if (i) there exist in the crystal suitable traps for holes and (ii) following the hole capture, the same centers do not act as traps for electrons (otherwise they would simply act as recombination centers).

It follows immediately that if there exist conditions under which the two above requirements are satisfied and if furthermore the electrons are not allowed to take part in the primary photographic process, it may be possible in

principle to build up a permanent concentration of mobile electrons in the conduction band of silver halide crystals.

Previous work at this Laboratory²⁻⁵ has led us to investigate the role of positive-ion vacancies in the trapping of photoliberated holes. In order to control the number of vacancies in AgBr, we have used a doping with Cd⁺⁺ ions. Preliminary experiments showed remarkable electric losses at 10 Gc/sec in these crystals, as a result of illumination in the region of fundamental absorption and quick freezing at 77°K. These losses were permanent at 77°K; however, they annealed out by increasing the temperature above certain values.

To ascertain the nature of these losses, we have performed more extensive experiments at different frequencies. The main features of our results on AgBr: Cd⁺⁺ single crystals are the following:

(1) When the temperature is raised, the photo-

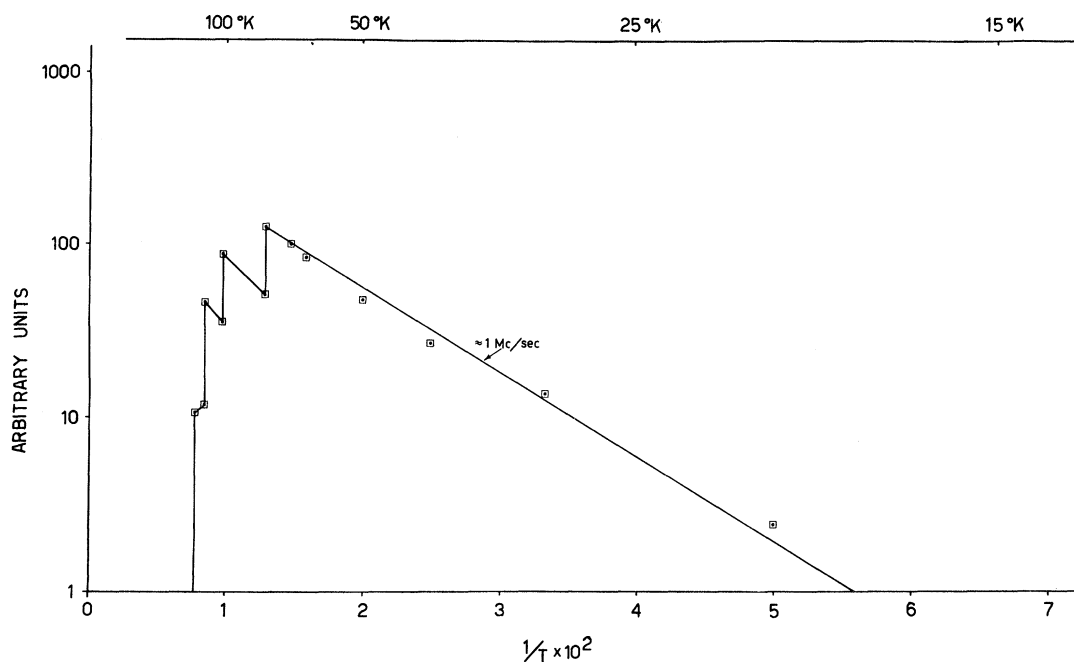


FIG. 1. Photoinduced electric conductivity (measured in the dark) versus temperature, in a $\text{AgBr}:\text{Cd}^{++}$ (10^{-4} mole) crystal, after irradiation at 77°K with unfiltered Hg radiation. The crystal had previously been slightly irradiated at room temperature and quickly frozen at 77°K and it exhibited a very similar behavior. In both cases, no change in conductivity has been observed by storage over weeks at temperatures well below those at which the decays occur. Data were taken at increasing temperature. The decays are irreversible while the lower temperature part is reversible. Reillumination at 77°K after the decays restores the conductivity (which in the present case is shown in arbitrary units and was measured at 1 Mc/sec with a Boonton 260-Ap Q meter).

induced losses increase first and then decay in several steps (occurring at different temperatures).

(2) The general behavior of the losses versus temperature is frequency independent in the range 50 cps to 10 Gc/sec.

(3) Losses may be obtained not only by irradiation at room temperature and freezing at 77°K , but also by direct irradiation at 77°K , i.e., at a temperature at which ionic processes are not likely. Figure 1 refers to this latter case.

(4) At microwave frequencies a cavity technique was used, while a condenser arrangement was used in the other cases. With this latter arrangement the results (see, e.g., Figs. 1 and 2) do not depend on whether, e.g., Aquadag electrodes have been painted on the specimen, or the latter has been insulated from the condenser plates by the use of a thin Mylar film.

From results (2) and (3) we conclude that the losses are due to electronic conduction. This means that the above-mentioned Mitchell's conditions (i) and (ii) are fulfilled and that un-

der our conditions, as expected, the photoelectrons cannot be used up in the photographic process.

At 77°K , due to the unavailability of numerous deep traps in the crystal, these electrons may largely remain in the conduction band. At much lower temperatures, however, they will be trapped at the shallow traps present in the crystals.⁶ Shallow traps are present even in high-purity crystals, due to silver ions at interstitial positions or at special sites, such as jogs of dislocations (see Ref. 1; see also Seitz⁷ for the Seitz-Mott concept of incipient vacancy).

In a wide range of low temperatures, therefore, the number of conduction electrons will increase reversibly with the temperature, until the temperature(s) are reached at which a recombination of electrons with holes of a particular type of trap will be possible and will irreversibly lower the number of conduction electrons and therefore the conductivity. A behavior of this type is shown in Fig. 1.

Concerning the several decays of the conduc-

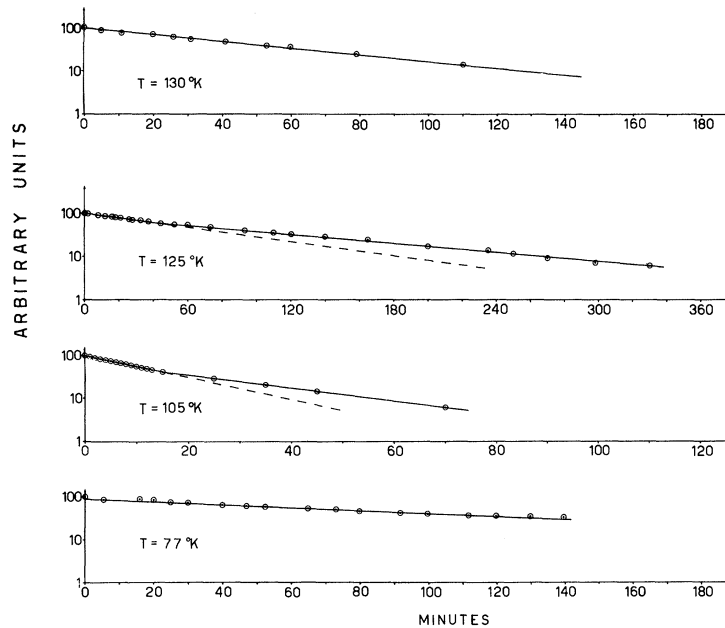


FIG. 2. Partial decays of the photoinduced conductivity of the crystal of Fig. 1. For each fixed temperature, there is plotted versus time the percentage of electrons which remain, of those which are allowed to recombine with holes in that particular decay. (Each decay was measured after those occurring at a lower temperature had been practically brought to an end.)

tivity shown in Fig. 1 and their positions in the temperature scale, each partial decay may be expected to depend exponentially upon the time, at fixed temperature. This is in fact observed, as Fig. 2 shows.

In conclusion, we believe that the present results provide supporting evidence for the hypotheses and predictions put forward by Mitchell concerning the trapping of photoliberated holes and, in particular, that the "secondary photocurrents" found at Göttingen in the early '30's were due to a similar effect, controlled by an unrecognized doping with oxygen.^{8,9}

In this connection, it is of interest to note that while very pure crystals annealed on quartz in an inert atmosphere do not exhibit this effect, Fornili and Micciancio of this Laboratory have found that silver chloride or bromide crystals annealed in air or on MgO exhibit effects qualitatively similar to those here reported. A comparison for the different dopings of the entity and positions (in the temperature scale) of the partial decays of the conductivity is under way at this Laboratory.

We are indebted to Professor J. W. Mitchell who has contributed in a determinant way dur-

ing the early stages of the present work, with invaluable discussions, correspondence, and supply of single crystals. Further crystals prepared by the technique described by Mitchell were kindly supplied by Professor T. Garofano. His cooperation and comments and those of Dr. S. Fornili and Mr. S. Micciancio are also gratefully acknowledged. Grants from the Consiglio Nazionale delle Ricerche and general support from the Comitato Regionale Ricerche Nucleari are also gratefully acknowledged.

*Also at Sezione Siciliana, Istituto Nazionale di Fisica Nucleare, Palermo, Italy.

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MINIMUM-ENERGY CONFIGURATION OF Li^+ IN KCl †

G. J. Dienes

Brookhaven National Laboratory, Upton, New York

and

R. D. Hatcher

Queens College, University of the City of New York, Queens, New York

and

R. Smoluchowski

Princeton University, Princeton, New Jersey

and

W. Wilson

Queens College, University of the City of New York, Queens, New York

(Received 27 October 1965)

Dielectric and electrocaloric measurements have shown that a dipole moment is associated with monatomic impurities in alkali halides.^{1,2} Specifically, Li^+ dissolved in KCl shows a dipole moment of about 2.5 Debye² caused by translational alignment of the Li^+ ions in a cubic direction. These experiments imply that the position of minimum energy for the Li^+ ion is off the ideal lattice site, i.e., the Li^+ is stable in an asymmetrical position and thus forms a dipole with several equivalent equilibrium orientations. Preliminary calculations by Matthew³ indicated that the stable position for Li^+ may be off the lattice site, although this conclusion could not be made with certainty from his calculation. Matthew's calculation was done with only one variable parameter for the nearest-neighbor positions, and the various energy terms were calculated only very approximately.

The purpose of this note is to describe some calculations for various configurations of substitutional Li^+ in KCl , employing the method of Hatcher and Dienes,⁴ which uses machine calculations to evaluate the electrostatic, polarization, dipole-dipole, and repulsive energies, as a function of the displacement of ions from their lattice positions. In the present calculation up to five variable distortion parameters were used. The physical constants used in

the Li^+ in KCl calculation are radii $r_{\text{K}^+} = 1.463 \text{ \AA}$, $r_{\text{Cl}^-} = 1.585 \text{ \AA}$, $r_{\text{Li}^+} = 0.816 \text{ \AA}$; polarizabilities $\alpha_{\text{K}^+} = 1.20 \times 10^{-24} \text{ cm}^3$, $\alpha_{\text{Cl}^-} = 2.96 \times 10^{-24} \text{ cm}^3$, $\alpha_{\text{Li}^+} = 0.029 \times 10^{-24} \text{ cm}^3$; and lattice spacing 3.147 \AA ; and the Born-Mayer constants for the various repulsive interactions were taken from the work of Tosi and Fumi.⁵

In the first calculation the stability of Li^+ substituted for a K^+ on a K^+ site was investigated in the rigid lattice, i.e., all ions but the Li^+ were held fixed while the Li^+ ion was given a small displacement in the $\langle 100 \rangle$ direction. The stability criterion is analytically given by a determinant W as described in the appendix of Ref. 4. A positive value of W is required for stability. In this particularly simple case W consists of one term, namely, the second derivative $\partial^2 E / \partial p^2$, where E is the energy of the system (Coulomb, polarization, and repulsive terms) and p is the displacement parameter assigned to Li^+ . W in this calculation turned out to be negative and, therefore, the lattice-site position for Li^+ is not a minimum with respect to displacement of the Li^+ in the $\langle 100 \rangle$ direction. A similar calculation for K^+ itself on its own lattice site gave a positive value for W (a strong minimum) showing that these calculations are consistent. A similar calculation for Na^+ substituted for K^+ (with $r_{\text{Na}^+} = 1.170 \text{ \AA}$, $\alpha_{\text{Na}^+} = 0.255 \times 10^{-24} \text{ cm}^3$) gave