

concerning an upper limit for the quadrupole interaction at the iron nucleus.

Concerning the chemical shifts, there is no evidence of any temperature dependence. The values of the chemical shift however, do seem to be consistently greater at the a sites than the value at the d sites. Noting that H_{eff} is greater at the a sites than at the d sites, one might speculate on a possible correlation between chemical shift and the saturation value of H_{eff} . If an appreciable part of the chemical shift is due to an isotope shift, as has been suggested by Kistner and Sunyar,⁴ such a correlation may arise since the

isotope shift should certainly be influenced by changes in the value of s wave functions at the nucleus and it is possible that H_{eff} will also be influenced by these changes.

ACKNOWLEDGMENTS

The authors would like to thank M. Schieber of the department of electronics, the Weizmann Institute, for preparing the garnets, E. Sunyar of Brookhaven National Laboratory for information concerning electronic circuits, E. Segal for help in constructing the apparatus, and A. Mustachi for help in chemical problems.

PHYSICAL REVIEW

VOLUME 122, NUMBER 3

MAY 1, 1961

Photoconductivity and Trapping in Silver Chloride Crystals*

ALBERT M. GORDON†

Laboratory of Atomic and Solid State Physics and Department of Engineering Physics, Cornell University, Ithaca, New York

(Received December 15, 1960)

Photoconductivity and trapping were investigated in pure, cuprous-chloride-doped, nickel-chloride-doped, and darkened silver chloride crystals. The photoconductivity was measured primarily at 88°K. The initial photoresponse increases with rising absorption constant, peaks at wavelengths for which the absorption constant is 3 to 5 cm⁻¹, and falls rapidly to 1/20 to 1/10 of the peak value at wavelengths at which the absorption constant is 50 to 100 cm⁻¹. This decrease in photoresponse at short wavelengths is explained in terms of trapping and recombination through centers in a surface region. The effect of irradiation and the filling of traps was investigated. Values of the schubweg for electrons in the bulk material were obtained from these experiments. The cuprous-chloride-doped samples had a long-wavelength tail on the photoresponse curve corresponding to the long-wavelength tail observed in the optical absorption. The photoconductivity does not show any peaks in the infrared. There was, however, a photoresponse with a threshold at approximately

10 000 Å in samples irradiated at 88°K and a peak for those irradiated at room temperature. This response was attributed to photoemission from free silver introduced unavoidably during the preparation of the samples. The warming of samples irradiated at 88°K to fill traps produced no measurable thermoluminescence. Electrical warming curves (measurement of current as a function of time during warming) disclosed a number of trapping levels. All samples except the nickel-chloride-doped sample showed peaks at 115°, 140°, and 180°K related to activation energies of approximately 0.20, 0.28, and 0.45 eV. The nickel-chloride-doped sample showed only peaks at 115° and 180°K. The cuprous-chloride-doped samples and the darkened pure sample showed a peak at 160°K corresponding to a thermal activation energy of approximately 0.36 eV. On some samples another peak was visible at 240°K with a thermal activation energy of approximately 0.62 eV. Possible interpretations for these various peaks are discussed.

I. INTRODUCTION

PHOTOCONDUCTIVITY in silver chloride crystals at low temperatures is a well-known phenomenon. Early measurements by Lehfeldt¹ and Hecht² showed that photoconductivity could be produced by the absorption of light in the region of the fundamental absorption edge. The results could be interpreted by attributing a finite range to the electrons. Later photoconductivity measurements^{3,4} showed that the contri-

bution of hole motion at temperatures below 200°K is insignificant in comparison with that of electron motion. These observations also indicated that the schubweg (range per unit field) was not constant over the entire crystal but had different values depending on whether the electron traveled in the surface region or in the bulk. The schubweg in the surface region was either smaller or larger than in the bulk region depending upon the sample preparation.

The existence of such a surface layer is of wider interest since it may give a clue to the unsuccessful attempts in this laboratory to observe photoconductivity in the alkali halides during irradiation in the region of fundamental absorption.⁵ A comparison of the optical absorption spectra for the alkali⁶ and the silver⁷ halides demonstrates a striking difference in

* Submitted as partial fulfillment of the requirements for the degree of Doctor of Philosophy at Cornell University, Ithaca, New York, 1961. This work was in part supported by a research grant from the Eastman Kodak Company, Rochester, New York.

† Present address: Department of Physiology, University College, London, England.

¹ W. Lehfeldt, Nachr. Akad. Wiss. Göttingen, Fachgruppe 2, 171 (1935).

² K. Hecht, Z. Physik, **77**, 234 (1932).

³ R. Van Heyningen and F. C. Brown, Phys. Rev. **111**, 462 (1958) and R. Van Heyningen, thesis, University of Illinois, Urbana, Illinois (1957).

⁴ A. E. Michel, thesis, Cornell University, Ithaca, New York, 1960 and Phys. Rev. (to be published).

⁵ J. W. Taylor and P. L. Hartman, Phys. Rev. **113**, 1421 (1959).

⁶ J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959).

⁷ Y. Okamoto, Nachr. Akad. Wiss. Göttingen, Math-physik Kl IIa, **14**, 275 (1956).

absorption constant in the wavelength region where the band to band transition (creation of free electron-hole pairs) makes a significant contribution to the absorption. Because of the exciton peak in the alkali halides, the absorption constant is near 10^5 cm^{-1} in this wavelength region. In the silver halides, the absorption constant is much lower in the wavelength region to the long-wavelength side of the exciton peak in which the absorption is best explained in terms of a parity-forbidden band to band transition from the silver $4d^{10}$ valence band to a $4d^9 5s$ conduction band.⁸ Thus, free electron-hole pairs can be produced by absorption of light in the region of fundamental absorption in the bulk in the silver halides but only in a very narrow surface layer for the alkali halides. A highly disturbed layer with a high density of traps or recombination centers could prevent the detection of a photocurrent. In addition, a high absorption constant would imply a high free-charge density with the resulting increased probability of free-carrier recombination. Thus it was felt that a detailed knowledge of the wavelength dependence of the photoresponse in silver chloride crystals containing various amounts and kinds of impurities might shed light on this problem.

Trapping of electrons and holes is of primary importance in determining the range of these carriers. Both the drift mobility and lifetime depend strongly on trapping. The range of electrons in silver chloride is quite sensitive to the crystal treatment⁹ and to the additions of impurities, in particular of nickel⁴ and oxygen.^{3,4} It was thought that a study of the occurrence, and of the activation energies of the trapping levels as a function of crystal composition and treatment might prove valuable in the understanding of the trapping mechanism in the pure material.

Activation energies of trapping levels in silver chloride have been investigated by means of optical activation,¹⁰ thermoluminescence,¹¹ and electrical warming curve measurements.^{3,10,12,13} In the first method the positions of peaks in the photoresponse for wavelengths outside the fundamental absorption region are measured at a temperature at which charges created by prior illumination have been trapped. The latter two types of measurements are performed by observing the luminescence and electrical currents generated during the warming of the crystal from the low temperature at which the charges were freed and trapped. A combination of these three measurements with various samples could prove useful in determining more exactly the nature of the trapping centers.

II. THEORETICAL CONSIDERATIONS

Photoconductivity

If upon the absorption of a quantum of light, an electron is excited into the conduction band, leaving a hole in the valence band, conceivably the electron and hole will be free to move. If, at time $t=0$, N_0 free electrons (or holes) are created, the number of electrons (or holes), N , that are still free after a time t is given by

$$N = N_0 e^{-t/\tau}. \quad (1)$$

τ is defined as the lifetime of the electron (or hole). The schubweg, w_0 , i.e., the range per unit electric field, is $w_0 = \mu\tau$, where μ is the drift mobility. The range, w , is given by $w = w_0 E$, where E is the electric field strength. Equation (1) can then be rewritten in terms of w and x , the distance from the point of release of the N_0 carriers, in the direction of the field,

$$N = N_0 e^{-x/w}. \quad (2)$$

If I_0 electrons are released per second and drift an average distance \bar{x} in the direction of the electric field, a current

$$I = I_0 e \bar{x} / l \quad (3)$$

will flow in the outside circuit, where l is the separation between the electrodes and e is the electronic charge. In order to obtain the photocurrent that can be expected from this model, one must calculate the average drift distance, \bar{x} . This can be done for different field geometries in terms of the absorption constant K for the wavelength of illumination, the electron range w , and some geometrical factors of the crystal. I_0 depends on the light intensity F_0 , the reflectivity R , the quantum efficiency η , for the production of electron-hole pairs, the absorption constant K , and the thickness of the crystal d .

$$I_0 = \eta(1-R)F_0(1-e^{-Kd}). \quad (4)$$

The two geometries to be considered are illustrated in the block diagram of Fig. 1. In case I, the illumination

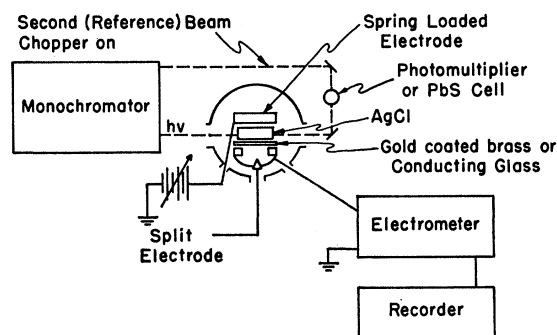


FIG. 1. Block diagram of the apparatus. The sample is shown in position for measurement of optical absorption and illumination perpendicular to the field direction (case I). For illumination parallel to the field direction (case II), the cryostat is rotated through 90 deg so that the illumination passes through the split electrode.

⁸ W. Martienssen (private communication).

⁹ J. R. Haynes, Rev. Sci. Instr. **19**, 51 (1949).

¹⁰ M. A. Gilileo, Phys. Rev. **91**, 534 (1953).

¹¹ A. R. Moore, thesis, Cornell University, Ithaca, New York, 1949 (unpublished).

¹² A. M. Goodman, thesis, Princeton University, Princeton, New Jersey, 1957 (unpublished).

¹³ B. B. Snively, thesis, Princeton University, Princeton, New Jersey, 1959 (unpublished).

is perpendicular to the applied field direction. In case II, the illumination is parallel to the applied field direction through a transparent electrode. This geometry is obtained from the picture in Fig. 1 by rotating the cryostat through 90°. In both cases, the electrodes are formed by parallel plates.

For case I, using the formula of Hecht² for \bar{x} , with the assumptions of a uniform field, no hole motion, no charge injection, a constant electron range for the whole material, the current is

$$I = e\eta F_0(1-R)(1-e^{-Kd})(1-e^{-l/2w})w/l, \quad (5)$$

where the light is incident midway between the two electrodes. The equation is the same for the reverse field direction.

In case II, one must consider separately two possible field directions. Under the same assumptions as before, Van Heyningen³ has shown that for forward bias, i.e., with the transparent electrode as the cathode, the current is given by

$$I_f = e\eta F_0(1-R) \frac{w}{l} \left[1 - \frac{e^{-Kl}}{1-Kw} + \frac{Kwe^{-l/2w}}{1-Kw} \right], \quad (6)$$

and for the reverse bias (transparent electrode is the anode) by

$$I_r = e\eta F_0(1-R) \frac{w}{l} \left[\frac{1}{1+Kw} + \frac{Kw}{1+Kw} \exp\{-(K+1/w)l\} - e^{-Kl} \right]. \quad (7)$$

Trapping

Electrons or holes trapped at localized centers in the crystal can be released optically or thermally. The activation energies for the two processes may differ.¹⁴ In thermal activation the two states, between which the electron or hole makes the transition, are equilibrium states, while in optical activation, the state to which the electron or hole is excited may not necessarily be an equilibrium state. Only the trapping and release of electrons will be discussed in the following analysis although the analysis will be general enough to include holes, too.

Optical activation generally will produce peaks in the photocurrent as a function of wavelength for illumination with light of wavelength outside the region of fundamental absorption. However, this photocurrent will only be detectable if the rate of release of the electrons and the range are large enough. The optical activation energy is given by the wavelength at which the peak occurs.

Thermal activation energies may be measured by warming the crystal from a low temperature at which

electrons have been generated and then trapped. If definite trapping levels are present, the electrical conductivity and luminescence (if it is connected with free carriers) will show peaks as a function of time (temperature). The temperature of these peaks can be correlated to the thermal activation energy of the trapping levels. In both of these measurements, the rate of release of electrons from the traps and the range of electrons or the luminescent efficiency must be large enough to enable detection. The reason for the peaks in the luminescence or conductivity can be seen easily if the assumption is made that the current or luminescence is proportional to the rate of release of free carriers from the traps. This rate is proportional to the probability for release and the number of trapped carriers. The probability of release increases while the number of trapped carriers decreases with increasing temperature. Thus a peak will result.

Randall and Wilkins¹⁵ have derived an expression for the thermoluminescence as a function of temperature during warming. Under the assumption of a single trapping level, no retrapping, constant luminescent efficiency over the temperature range in question, and a small number of electrons in the conduction band compared to the density of states, the thermoluminescence as a function of temperature will be

$$F = Cn_0s e^{-U/kT} \exp\left[-\int_0^T \frac{s}{\beta} e^{-U/kT} dT\right], \quad (8)$$

where C is a constant involving the luminescent efficiency, n_0 the density of trapped charges, U the thermal activation energy, s the frequency factor appearing in the excitation probability of the trapped electron, β the rate of warming, and T the absolute temperature. Similarly, the same equation can be derived for the current. The only difference occurs in the constant C , which now involves the range of the electrons rather than the luminescent efficiency.

Solving Eq. (8) for the maximum, under the assumptions that ds/dT and dC/dT are zero over the temperature region in question, gives the condition

$$s = \beta \frac{U}{kT^{*2}} \exp(U/kT^*), \quad (9)$$

where T^* is the temperature at the maximum. For $s \sim 10^{10} \text{ sec}^{-1}$ and β a few degrees per minute, U is approximately $25kT^*$. The experimental curves can be compared with the theoretical Eq. (8) and the values of U and s calculated approximately. Since s in Eq. (9) depends so strongly on the selected value of U , the activation energies can be calculated much more accurately than the frequency factors.

¹⁴ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940).

¹⁵ J. T. Randall and M. H. F. Wilkins, *Proc. Roy. Soc. (London)* **A184**, 347 (1945).

III. EXPERIMENTAL PROCEDURES AND APPARATUS

The apparatus consisted basically of a cryostat, a monochromator, and an electrometer. (See Fig. 1.) The monochromator was a Cary model 14 recording spectrophotometer.¹⁶ The light source was the standard tungsten lamp provided with this instrument. Stray light was very low since the monochromator of this unit has two dispersing elements. With the slit width used normally (0.3 mm), the band width was approximately 10 Å. In addition to serving as a monochromator, the instrument could be used in its usual manner to measure the optical absorption of the sample. When used as a monochromator, the chopper was turned off and all the light was allowed to pass through the sample. The monochromator had a wavelength scanning mechanism with a wide variety of speeds, from $\frac{1}{2}$ Å/sec to 100 Å/sec. The wavelength calibration was checked and corrected using a mercury line source. The wavelength calibration was reproducible to $\frac{1}{2}$ Å. Spectral intensity curves for this source and monochromator are available in the literature.¹⁰ The present instrument was checked at 9000 Å with a Kipp thermopile, and the intensity was found to agree with the published value within the accuracy of the measurement. Other points were checked relative to this value and the shape of the spectral intensity curve found to agree with the published data except for several small peaks which were attributed by the manufacturer to the optical system. These peaks were outside the range of interest for the photoconductivity experiments. The published data were used in all cases to calculate the measured photoresponse (I/F_0) as a function of wavelength.

The cryostat was mounted in the cell compartment of the spectrophotometer, fitting tightly into a special cover built for this compartment. This assured reproducible alignment in the light beam. The cryostat was a helium cryostat with two concentric reservoirs. The sample holder was mounted on the bottom of the inner reservoir and shielded thermally with a copper can which fastened onto the outer reservoir. The sample holder consisted of two gold-plated brass electrodes fastened to a $\frac{1}{32}$ -in. thick piece of Teflon. One electrode was split in the center to allow illumination through the electrode. The other electrode was attached by way of a thin copper strip which applied enough pressure to hold the sample in place. Electrical contacts to the sample holder were made by a thermocouple attached to the spring loaded electrode and by a 3-mil copper wire connected through a high-impedance vacuum lead-in to the split electrode. Three quartz windows were mounted on the outer wall of the cryostat to provide a light path through the crystal for absorption measurements and also for photoconductivity measurements of both cases I and II. 3-mil diameter copper-constantan thermocouples were used to monitor the

temperature of the sample. Actually the temperature of the spring loaded electrode was monitored, but the temperature thus determined was checked against the true sample temperature using a piece of silver chloride in which a thermocouple had been imbedded. The agreement was within 1°K at 88°K and within 5°K during warming of the sample. The temperatures were recorded on a chart recorder.

The photocurrents and warming currents were determined with a Cary model 31 vibrating reed electrometer¹⁷ measuring the voltage drop across one of the high value resistors built into the pick-up head. The smallest detectable current with the existing noise level was 5×10^{-16} amp. The output was recorded on a chart recorder.

In cooling the sample to 88°K, much care was taken to keep the cooling rate below 30°K per hr. Several observers^{3,4} have referred to the effect of thermal strains on the electrical properties of silver chloride which prompted this precaution. The natural cooling rate of the evacuated cryostat with liquid nitrogen in the outer reservoir alone was slow enough to provide the needed rate. Because of the long time (20 hr) required to reach the desired temperature, an automatic transfer system was designed to keep the nitrogen level in the reservoirs constant overnight.

The luminescence was investigated using the 1P28 photomultiplier in its place in the spectrophotometer or an E.M.I. photomultiplier, type 6097S, which looked at the sample through a hole bored in the side of the cell compartment. The geometry for the E.M.I. photomultiplier was the better one. The photocathode intercepted a solid angle of approximately 0.2 sterad at the sample. With only 600 v applied to the photomultiplier for low dark current, it was estimated that a luminescent intensity of 2×10^6 quanta/sec could be detected.

Great care was taken in the sample preparation to prevent excessive straining or contamination of the crystals. The silver chloride crystals were obtained from the Research Laboratories of the Eastman Kodak Company.¹⁸ The preparation procedures were quite similar to those described elsewhere in the literature.⁴ Samples were cut from the boules using a chrome plated model makers saw in a miter box in which the crystals were held with beeswax. The samples were then polished on ground glass plates. The plates were ground to various degrees of roughness using grinding compounds of different mesh sizes. For the coarse polish, ammonium hydroxide was used to lubricate the plates. For the finer polish, distilled water was used. Polishing was concluded when the samples had all surfaces flat and relatively free from scratches when viewed using the reflection of the filament of a red safe light. Before

¹⁶ Cary model 14 recording spectrophotometer, Applied Physics Corporation, Pasadena, California.

¹⁷ Cary model 31 vibrating reed electrometer, Applied Physics Corporation, Pasadena, California.

¹⁸ The author wishes to thank Dr. F. Urbach and Dr. F. Moser for providing these crystals.

annealing, the samples were etched for one minute in concentrated HCl, rinsed in distilled water, and dried carefully. The samples were annealed for 10 hr at 420°C. For the annealing, the samples were placed on a quartz slide which had been dusted with fine quartz powder to prevent sticking. After annealing, they were cooled slowly (20°C/hr). All annealing was done in an atmosphere of helium.

Aquadag electrodes were painted on the sample to provide good electrical contact. The samples were in size about 1 cm×1 cm×3 mm. The electrodes were painted on the two largest faces. Dag was painted on one face only for the crystal which was to be illuminated through the electrode.

The sample preparation was done under red safe light conditions. The red filters used with flashlights also employed had an optical density greater than 5.4 between 5600 and 2000 Å except for a narrow transmission band from 3800 to 4500 Å where the optical density decreased to 4.0. The red safe lights had no measurable output below 4800 Å as determined with the Cary model 14 spectrophotometer. Though these absorption values are high, this still permits traces of active light to reach the crystal during the long time necessary for the preparation.

IV. RESULTS AND DISCUSSION

The various silver chloride samples studied can be classified as follows: pure; grown in vacuum; doped with cuprous chloride or nickel chloride; pure, darkened at room temperature; and doped with cuprous chloride, darkened at room temperature.

Photoconductivity

In measuring the photoresponse of the samples, the wavelength of the illuminating light was scanned through the region of interest at 2.5 Å/sec with a

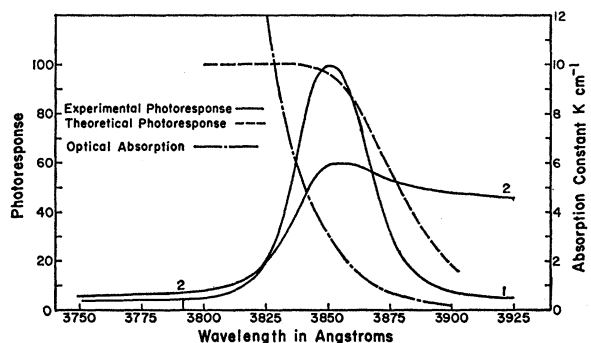


FIG. 2. Wavelength dependence of the photoresponse for pure, vacuum-grown AgCl (curve 1) and cuprous-chloride-doped AgCl, 20 ppm, (curve 2), case I geometry, 100 v, electrode separations 3.6 and 3.5 mm, respectively, and crystal width 1.1 cm. For the photoresponse, $100 = 3.3 \times 10^{-22}$ coul/quanta. Temperature 88°K. The optical absorption data is that of Van Heyningen.³ The theoretical photoresponse for a single-region model is plotted also.

constant voltage applied to the crystal. The scanning was both from long to short wavelength and vice versa. There was a hysteresis in the response due to the response time of the recorder producing a 5 Å shift in the peak position from the one type scan to the other. The values shown in the figures of this paper are averages of the forward and backward sweep, each normalized to 100 and divided by the number of quanta per second at each wavelength, and renormalized to a value of 100 at the peak. There was evidence of some polarization since the current decreased by about 5% between the initial and the second scan. However, the shape of the photoresponse versus wavelength curve for one direction scanning was well reproducible in most cases. The cases for which this was not true will be discussed in detail later. The schubwegs were calculated from the currents during the initial sweep, before any significant polarization could occur.

The photoresponse at 88°K for a pure, vacuum grown sample can be seen in Fig. 2 for case I geometry. For comparison the optical absorption constant at 88°K is also reproduced. The absorption data are a combination of those of Van Heyningen³ and Okamoto⁷ adjusted for the temperature difference. As can be seen, the photoresponse has a peak where the optical absorption constant is about 3 cm^{-1} and falls off at shorter wavelengths, i.e., at higher absorption constant, to a value of about 1/20 of the peak value. The theoretical curve calculated from Eq. (5) is also plotted in Fig. 2. Obviously some mechanism not considered in the derivation of Eq. (5) is decreasing the short wavelength photoresponse from the expected value. This result was reproducible for the three pure samples studied and agreed in the general peaked appearance with some of the measurements of others.^{3,10,19}

This behavior can be explained qualitatively and also, as will be shown later, quantitatively, by assuming the existence of a layer near the surface with a very short free electron lifetime. This short lifetime may be caused by recombination or by trapping. Such a surface layer with electronic properties different from those of the bulk material had been postulated earlier by Van Heyningen³ and by Michel⁴ in order to explain their experimental findings.

To check the importance of bimolecular (free carrier) recombination, the dependence of the photocurrent on light intensity was investigated at three wavelengths, one on either side of the peak and one at the peak. In all cases the photocurrent was linearly dependent on the light intensity over the range of 10^8 to 10^{10} quanta/sec. This was also true for measurements taken on all other samples. This implies that if one can consider all the free carriers to be generated by the light, bimolecular recombination does not play an important role in this decrease of the photoresponse at short wavelengths.

¹⁹ D. A. Wiegand, thesis, Cornell University, Ithaca, New York, 1956 and Phys. Rev. **113**, 52, (1959).

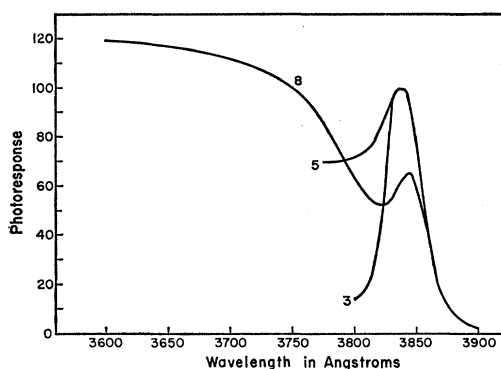


FIG. 3. Wavelength dependence of the photoresponse for pure, vacuum-grown AgCl, 50 v, case II geometry, forward bias, electrode separation 2.6 mm. Sweeps number 3, 5, and 8 through this region are shown. For sweep 3, $100 = 1.3 \times 10^{-22}$ coul/quanta. For sweeps 5 and 8, $100 = 0.31 \times 10^{-22}$ coul/quanta. Temperature 88°K.

A square root dependence of current on light intensity would be expected if bimolecular recombination were the limiting factor.²⁰ If recombination is of importance, it must be by way of recombination centers.

To determine the role of trapping, a pure sample was irradiated with 5×10^{13} quanta at 3850 Å while the field was applied, in an attempt to fill traps. However, even after this illumination, the short wavelength response had not built up significantly; but the results were ambiguous due to a large electronic polarization having been produced, which could be shown to exist by the observation of reverse currents upon subsequent illumination with no field applied.

It was felt that experiments with the illumination through the electrode might shed light on this problem. With geometry I, the electrons remain approximately a fixed distance from the surface during their drift in the electric field. With geometry II, for forward bias, the electrons are pulled away from the surface into the interior of the crystal. The initial sweep from 3900 to 3800 Å for this geometry produced the same type of photoresponse as for case I, i.e., a sharp peak. With repeated sweeps, however, the short wavelength photoresponse began to build up. (See Fig. 3.) Apparently the traps were being filled up, increasing the electron ranges in the surface region. (There was little change in the response for the reverse bias photoresponse.) The slight dip in the response for sweep number 8 can be attributed to the preferential filling of traps in a very narrow layer immediately at the surface within a wider low lifetime region. The preferential filling is a direct consequence of the very strong absorption for shorter wavelengths. The difference between the buildup of the short wavelength response in case I and case II can be explained by recombination. In fact, recombination is less important in case II because the electrons and holes are separated from one another by the electric

field. In case I the electrons move through the region of release of the carriers and the chances for recombination are enhanced reducing the possibilities of filling traps and in general reducing the importance of traps in limiting the electron range.

To investigate further the role of recombination, the photoresponse of samples doped with cuprous chloride was studied using geometry I. These samples contained approximately 1, 10, and 20 ppm by weight of cuprous chloride. The cuprous ion is believed to act as a hole trap²¹ since it increases the photolytic sensitivity at room temperature, i.e., prevents the recombination of the electron and hole. Thus one would expect that the addition of Cu^+ will reduce the importance of the recombination process in the short-wavelength photoresponse, and thus enhance the role of the traps. Indeed, experiments bear this out. Figure 2 shows the initial response of a 20-ppm doped sample. Compared to the pure, vacuum grown sample, there was no significant increase in the short-wavelength photoresponse. Upon further illumination, however, with less than 10^{13} quanta of 3850 Å, the short-wavelength response built up greatly as shown in Fig. 4 for a sample doped with approximately 1 ppm. It actually exceeds that near the peak of the initial response indicating a range greater in the surface than in the bulk. The dip in the curve can be explained in the same manner as the similar dip shown in Fig. 3.

Since trapping and recombination in a surface region seem to be important in limiting the photoresponse, the photoresponse was calculated assuming a surface region with a low lifetime. Comparing the peak in Fig. 2 to the short wavelength value, it can be seen that the ratio between the range in the surface and in the bulk is approximately 1/20. Thus to a first approximation, the

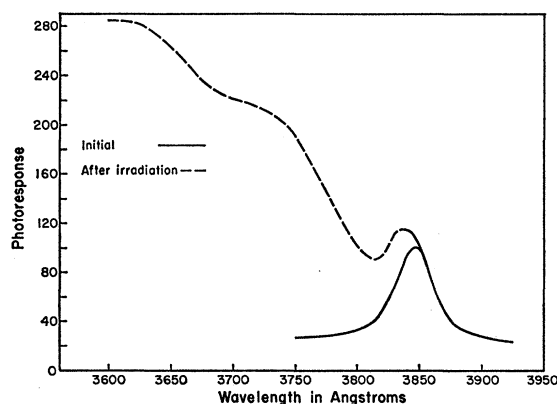


FIG. 4. Wavelength dependence of the photoresponse of cuprous-chloride-doped AgCl, 1 ppm, for the sample initially and after irradiation, case I geometry, electrode separation 4.3 mm, sample width 1.1 cm. Initial voltage 100 volts, final applied voltage 300 volts, but modified by polarization. $100 = 0.64 \times 10^{-22}$ coul/quanta. Temperature 88°K.

²⁰ Richard H. Bube, *Photoconductivity of Solids* (John Wiley & Sons, Inc., New York, 1960), p. 63.

²¹ F. Moser, N. R. Nail, and F. Urbach, *J. Phys. Chem. Solids* **9**, 217 (1959).

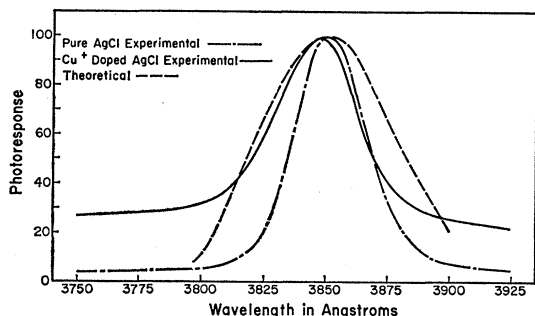


FIG. 5. Wavelength dependence of the photoresponse of cuprous-chloride-doped AgCl, 1 ppm, and pure, vacuum-grown AgCl, case I geometry, compared to the theoretical response assuming no contribution from a surface region of thickness (d_1) 5×10^{-2} cm, 100 v, electrode separation 4.3 and 3.6 mm, respectively, widths 1.1 cm. 100 for the cuprous-chloride-doped sample $= 0.64 \times 10^{-22}$ coul/quanta. 100 for the pure AgCl $= 3.3 \times 10^{-22}$ coul/quanta. Temperature 88°K.

photocurrent is due only to light absorbed in the bulk. With this approximation, Eq. (5) has to be multiplied by a factor $\exp(-Kd_1)$, where d_1 is the thickness of the disturbed surface region. This function is compared to the experimental curves for the pure and the 1 ppm cuprous doped samples in Fig. 5 using the absorption constant values referred to earlier and $d_1 = 5 \times 10^{-2}$ cm. For the theoretical curve, $\eta(1-R)$ is assumed constant. The experimental curve for the cuprous-chloride-doped sample has been renormalized to bring the peak value to 100. As can be seen, the agreement between the experimental and theoretical curves is much better on the short wavelength side for the cuprous-chloride-doped sample than for the pure sample.

The conclusions that can be drawn from this series of experiments are that the short-wavelength photoresponse is limited mainly by trapping in a surface region; recombination through centers plays a minor role in the initial decreased response but plays a major role with further illumination, delaying the filling of traps; and the cuprous ion acts as a hole trap at 88°K as well as at room temperature, counteracting recombination.

The cuprous-chloride-doped AgCl samples showed a long-wavelength tail on the photoresponse curve corresponding to the long-wavelength tail on the optical absorption curve. (See Fig. 6.) There is much uncertainty in the measurement of the optical absorption in the long-wavelength region because of an uncertainty in the baseline so that it is difficult to correlate photocurrent and absorption. The photoresponse in these samples was lower than that in the pure samples by about a factor of two. This can be attributed to a decrease in the range by photolytic silver introduced during the sample preparation. A cuprous-chloride-doped sample intentionally darkened at room temperature to an optical density of 0.04 at the colloidal silver peak (5700 Å), for a 1.1-cm thick sample, showed a further reduction in the photoresponse at 88°K to

approximately $\frac{1}{2}$ of that of the pure sample. This optical density was just above the detection limit of the present equipment. This decrease is ascribed to either traps introduced by strains accompanying the photolytic silver formation, or to trapping at the photolytic silver specks. Purposeful mechanical straining decreased the lifetime of the pure sample since the photoresponse of a pure crystal which had not been annealed and was cooled rapidly was about 30% lower than the response of the same sample after repolishing, annealing, and slow cooling.

The silver chloride sample doped with approximately 1-ppm nickel chloride showed, for case I geometry, the same type of peak at 88°K as the pure, vacuum grown samples except that the response was lower by a factor of 200.

Schubwegs for electrons can be calculated from the measured photoresponses using Eq. (5). The values of $\eta(1-R)$ and F_0 are taken from the published values of Van Heyningen³ and Gilleo,¹⁰ respectively. A value of

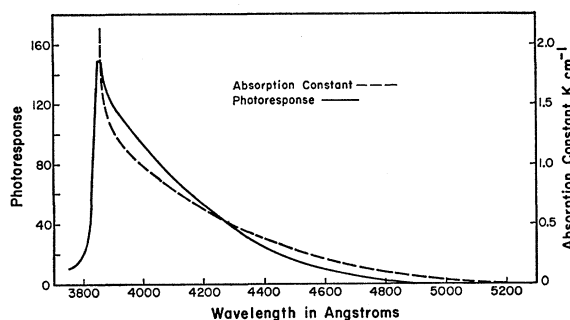


FIG. 6. Wavelength dependence of the photoresponse of cuprous-chloride-doped AgCl, 20 ppm, compared to the optical absorption measured for the same sample, case I geometry, electrode separation 3.5 mm, width 1.1 cm, 100 v, temperature 88°K.

$5 \times 10^{-6} \text{ cm}^2/\text{v}$ is obtained for the schubweg in pure, vacuum-grown AgCl and of $2.6 \times 10^{-8} \text{ cm}^2/\text{v}$ in the nickel-chloride-doped sample. The calculated lifetimes for a mobility of $300 \text{ cm}^2/\text{v-sec}$ ²² are $1.7 \times 10^{-8} \text{ sec}$ and $8.7 \times 10^{-11} \text{ sec}$, respectively. If the values of $\eta(1-R)$ and F_0 used are correct, the calculated schubwegs are accurate to approximately 30%. These values agree reasonably well with other published values for the range and lifetime.^{3,4}

Trapping

Attempts to measure at 88°K the optical activation energy for release of trapped electrons did not succeed due to the existence of a long-wavelength tail on the photoresponse with a threshold at 1.1 to 1.2 eV. This response at 9000 to 10 000 Å was not visible in the samples before illumination at 88°K with approximately 10^{14} quanta of 3850 Å. It has been observed before²³ and

²² F. C. Brown and F. Dart, Phys. Rev. **108**, 281 (1957).

²³ W. C. Caldwell, thesis, Cornell University, Ithaca, New York, 1948 (unpublished).

is attributed to photoemission from colloidal or atomic free silver. The shape of this photoresponse versus wavelength curve compared favorably with the similar curve taken for silver chloride darkened intentionally at room temperature. The only difference was the lack of the colloidal silver peak which appeared in the intentionally darkened samples. This colloidal or atomic free silver must have been formed during preparation of the samples at room temperature and not by the illumination at low temperature. The lack of initial detection can be attributed to a short initial range which was increased during the illumination and trap filling at 88°K. No photoresponse was seen in the region from 1 to 2 μ in any sample.

No thermoluminescence was detected in any of the samples with the photomultiplier used which peaks in the blue-green. The geometry was not ideal for a measurement of this type but an upper limit can be placed on the amount of luminescent light that could have been

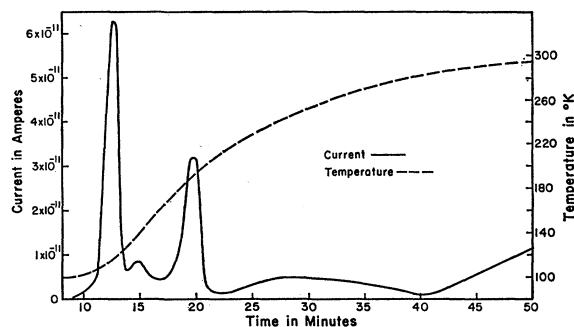


FIG. 7. Electrical warming curve for pure vacuum-grown AgCl, current and temperature vs time during warming from the low temperature at which charges have been trapped. Electronic polarization field is used. The peaks at approximately 117°, 138°, 190°, and 250°K are visible.

emitted and not detected. This was 2×10^6 quanta/sec. Thermoluminescence has been seen in powdered silver chloride with peaks at 85° and 240°K.¹¹ These peaks may take on more significance if the luminescence is associated with the trapping of free holes.¹⁹

Observation of electrical warming curves provided information about thermal activation energies of trapped carriers. In these measurements charges were trapped in the crystal by illumination with 10^{14} quanta of 3850 Å radiation while a voltage of 100 to 200 v was applied to the sample at 88°K. The voltage was then removed, the samples warmed from this temperature and the current measured as a function of time. The electric field was provided by the electronic polarization field which existed after the irradiation mentioned above. This avoided the large noise which was present when the measurements were attempted using externally applied fields. Figure 7 shows a typical electrical warming curve. Both current and temperature are plotted versus warming time. Experimentally there were some difficulties; occasionally the current would

reverse in direction from that expected from the direction of the polarization field. This effect could not be explained easily. In most cases, the current was in the expected direction when a large peak was observed.

Peaks were observed for the pure, vacuum grown samples and the cuprous-chloride-doped samples at 115°, 140°, and 180°K. (These temperatures are used to represent peaks seen in the temperature region close to the temperatures quoted. The actual peak temperature depends on the warming rate.) The nickel-chloride-doped sample had peaks at 115° and 180°K. The cuprous-chloride-doped sample and the darkened pure sample had an additional peak at 160°K which gave the 180°K peak a doublet appearance. In all samples, the 115°K peak was quite distinct. The 140°K peak was much smaller and hard to distinguish from the tail of the 115°K peak. The 180°K peak in the nickel-chloride-doped sample was much larger in relation to the 115°K peak than in any of the other samples. In some samples another small peak was observed near 240°K. It may have been present in all samples since it was difficult to detect. The rapid increase of the ionic conductivity with temperature may have obscured it. Since the peak at 115°K occurs just as the temperature of the sample is starting to rise, it was felt that a better determination could be made by cooling the sample to a lower temperature. A pure, vacuum-grown sample was cooled to 48°K, traps filled by irradiation, then the sample warmed. The same peaks at 115°, 140°, and 180°K were visible with the suggestion of a peak at 240°K. The peaks at 140° and 180°K in silver chloride have been reported in the literature.^{3,10,12,13} The other peaks have not been reported previously.

Estimates of the thermal activation energy can be made by attempting to fit the theoretical warming curve to the experimental curve. Figure 8 shows such a fit for the 115°K peak. The agreement is as good as can be expected considering the assumptions made in deriving the theoretical expression. The values of U and s which gave the best fit where $U=0.20$ eV and $s=5.2 \times 10^6$ sec⁻¹. The 180°K peak was treated in the same manner with the resulting values of $U=0.45$ eV and

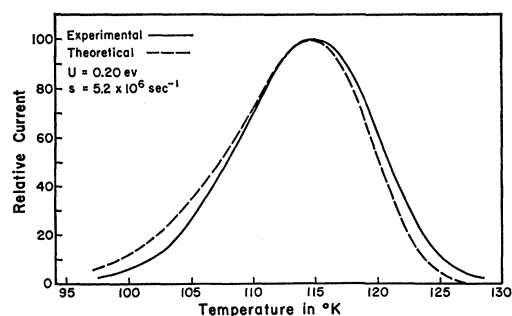


FIG. 8. 115°K peak in the electrical warming curve of pure, vacuum-grown AgCl, current versus temperature, experimental curve compared to the theoretical curve using $s=5.2 \times 10^6$ sec⁻¹ and $U=0.20$ eV.

$s = 2.4 \times 10^{10} \text{ sec}^{-1}$. With the thermal activation energies determined approximately for these two peaks, the activation energies for the other peaks could be estimated. These two peaks were chosen because they both were isolated and quite distinct. The values for the approximate activation energies are 115°K—0.20 eV, 140°K—0.28 eV, 160°K—0.36 eV, 180°K—0.45 eV, and 240°K—0.62 eV.

The 160°K peak is probably associated with electron trapping at or in the region near colloidal silver because of the presence of this peak in the samples which were darkened intentionally and in those samples which probably were darkened unintentionally (the cuprous ion increases the sensitivity of volume photolysis²¹). The trapping level associated with the 115°K peak gives rise to multiple trapping in the samples at 88°K because of the low thermal activation energy. This may be the trapping level responsible for the decreased short-wavelength response because it has such a low activation energy and was so prominent in all samples. A rather shallow trap would be necessary to allow limitation of the short-wavelength response with the role of recombination discussed above. As was proposed by Van Heyningen,³ the 180°K peak may be largely responsible for the determination of the bulk range in silver chloride at 88°K if the relative sizes of the 115° and 180°K peaks in the nickel-chloride-doped sample have significance. The 240°K peak may be associated with hole trapping because of the coincidence of the temperature of this peak and the peak observed in the thermoluminescence.¹¹ This association can be made if the trapping of a free hole is responsible for the luminescence as proposed by Wiegand.¹⁹ Holes may be mobile at these temperatures⁴ so that they could give rise to this peak in the conductivity. If this interpretation is correct, it would imply that holes are trapped in quite deep traps at 88°K. Verification of the proposed

interpretation of these peaks and identification of trapping sites must await further experimentation.

V. CONCLUSIONS

A study of the wavelength dependence of the photo-response in various types of silver chloride crystals for both case I and case II geometry, showed that it was a strongly peaked function. The increase at long wavelengths followed the rising absorption constant. The decrease at shorter wavelengths, higher absorption constant, was shown to be primarily due to trapping in a disturbed surface layer, a few tenths of a millimeter thick. Recombination through centers played a minor role in this decrease, but played a major role in preventing filling of traps with further irradiation.

Trapping levels giving electrical warming curve peaks near 115° and 180°K were observed in all samples. Another peak at 140°K was observed in all samples except the nickel-chloride-doped silver chloride. A peak at 240°K was observed in some samples and may be connected with a hole-trapping center. Another peak near 160°K was observed in those samples which had been darkened at room temperature and was attributed to the trapping of electrons at or in the region near colloidal silver.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Professor P. L. Hartman for his guidance and assistance during the course of this work. For the counsel and advice of Professor H. S. Sack, the author is grateful. The author is greatly obliged to Mrs. C. W. Peterson and Dr. W. Martienssen, Dr. A. Michel, and Dr. H. Mahr for their interesting discussions and assistance. The author received N.S.F. Summer Fellowships during two summers.