$$0\leq\beta\leq1:\quad \pi^2E_a^{(2)}(0)=2f(\beta)+\frac{3}{\beta}-\frac{15}{2}+\left(\ln\frac{\beta}{2}\right)^2+\frac{\beta^2-1}{\beta^2}\ln(1-\beta),\tag{D5}$$

$$1\leq\beta\leq2:\quad \pi^2E_a^{(2)}(0)=-2f\left(-\frac{1}{\beta}\right)+(\ln2)^2+\frac{\pi^2}{6}-\frac{3}{2}-\frac{3}{\beta}-2\ln2\ln\beta+\frac{\beta^2-1}{\beta^2}\ln(\beta+1).\tag{D6}$$

ACKNOWLEDGMENTS

We wish, first and foremost, to express our gratitude to Professor David Pines, who has guided and inspired us throughout this calculation. We wish to thank the National Science Foundation for its generous support during the work. One of us (D. L.) wishes to thank the Ford Motor Company Scientific Laboratory and the General Electric Research Laboratory for their kind hospitality and guidance as well as the generous allowance of their digital computing facilities.

PHYSICAL REVIEW VOLUME 111, NUMBER 2 JULY 15, 1958

Transient Photoconductivity in Silver Chloride at Low Temperatures*

R. S. Van Heyningen† and Frederick C. Brown
Department of Physics, University of Illinois, Urbana, Illinois

(Received March 24, 1958)

Primary photoconductivity has been investigated down to 6.5°K in single crystals of pure AgCl using low intensity, monochromatic light pulses and a sensitive electrometer. Results are presented which are in agreement with a theory of the transient response taking into account light absorption and electron trapping. The electron yield per absorbed photon (quantum efficiency) is found to be high, somewhat less than one, in the long-wavelength tail and through the first peak of optical absorption for all crystals and temperatures down to 6.5°K. These results agree with the proposed band scheme if one allows for direct and indirect transitions as discussed in Sec. V. Electron trappping properties are strongly dependent on sample preparation, but certain features are believed characteristic of the silver halides. Whereas the density of deep (0.5 ev) traps may be very low in well-annealed AgCl, a high density of very shallow (<0.1 ev) traps exists in the crystals prepared so far. Prominent electrical glow peaks have been observed at 15°K, 35°K, and 178°K. No evidence for hole mobility has been found and upper limits on possible hole ranges are given.

I. INTRODUCTION

At low temperatures silver chloride is a sensitive photoconductor which has vanishingly small dark conductivity. Primary photocurrents, characterized by a saturation behavior with increasing collection voltage, were observed in crystals of this material by Lehfeldt[1] many years ago. He showed that experiments carried out with a sensitive electrometer and low-intensity flash illumination lend themselves to a relatively simple interpretation in terms of electron range (*Schubweg*) governed by a volume distribution of traps. When range can be determined, it is possible to compute the quantum efficiency defined as the ratio of the number of electron-hole pairs created to the number of photons absorbed.

In order to understand the optical excitation process, it is of importance to know how the quantum efficiency depends on impurity content and temperature in the region of fundamental absorption, which begins in the vicinity of 400 mμ and extends into the far ultraviolet. In particular, one would like to compare the spectral dependence of quantum efficiency with optical absorption over a wide range of absorption coefficients. Whether or not holes as well as electrons contribute to the photoresponse of the silver halides is a problem of considerable interest,[2–5] and certain other results of the earlier work remain unexplained. For example, the striking decrease in photoconductivity that has been observed at temperatures below 50°K[1,6] might be explained either by a drop in quantum efficiency or by a reduced range at low temperatures due to shallow traps. The present experiment extends quantum

---

* Supported in part by the U. S. Air Force.

† Now at Research Laboratories, Eastman Kodak Company. Work performed in partial fulfillment of the requirements for the Ph.D. degree at the University of Illinois.

[1] W. Lehfeldt, Göttingen Nachr. II, 1, 171 (1935).

[2] F. Seitz, Revs. Modern Phys. 23, 328 (1951); *Photographic Sensitivity* edited by S. Fujisawa (Maruzen Company, Ltd., Tokyo, 1956), Vol. 1, p. 10.

[3] F. C. Brown and F. Seitz, in *Photographic Sensitivity* (Maruzen Company, Ltd., Tokyo, 1958), Vol. 2, p. 19.

[4] J. W. Mitchell, in *Chemistry of the Solid State*, edited by W. E. Garner (Butterworths Scientific Publications, London, 1955), p. 321.

[5] L. P. Smith, in *Semiconducting Materials*, edited by K. H. Henisch (Butterworths Scientific Publications, London, 1951), p. 114.

[6] D. A. Wiegand, thesis, Cornell University, Ithaca, New York, 1956 (unpublished).

efficiency and electron range measurements to lower temperatures and shorter wavelengths for various AgCl crystals of high purity and different preparation.[7,8]

It will be shown that the quantum efficiency is high, somewhat less than one, in the long-wavelength tail and through the first peak of optical absorption for all crystals and temperatures down to 6.5°K. On the other hand, electron trapping properties vary greatly. The distribution of traps in the volume and near the surfaces has a strong influence on the photoconductive response.[9,10] Whereas the density of deep traps may be very low in well-annealed AgCl, it is characteristic that these crystals have a relatively high density of very shallow traps. Measurable drift of holes has not been detected under any circumstances.

II. THEORY OF THE EXPERIMENT

A. Transient Photoconductivity

The properties of a high-resistivity photoconductor may be investigated by the study of transient primary photocurrents.[1,9] However, the observation of primary as distinguished from secondary photocurrents is subject to several restrictions.[10–12] Space charge limitations, entrance of charge at the electrodes, and charge multiplication must not occur. These difficulties are avoided in the present experiment by using light pulses of extremely low intensity and by blocking the electrodes with insulating nonphotoconducting layers. For small applied electric fields and quantum efficiencies less than unity, one may reasonably assume that charge multiplication does not occur throughout the range of wavelengths employed.

In the simplest case imagine a single crystal of thickness l placed between plane parallel electrodes and illuminated through the cathode by strongly absorbed light. An electric field, $E=V/l$, is established by a battery of voltage V connected in the external circuit in series with an electrometer for measuring charge. Electrons released into the conduction band by light will be swept into the crystal where they are trapped by a uniform density of deep traps. If n_0 electrons are released at time, $t=0$, the number free after a time t is $n=n_0e^{-t/\tau}$. The mean time for trapping is $\tau=1/(N_t\sigma u)$, where N_t is the trap density, σ the trap cross section, and u the mean thermal velocity of the electrons. The average range or *Schubweg* of the electrons is $w=\mu E\tau$, where μ is the electron mobility. A useful property of the crystal is the range per unit field, $w_0=\mu\tau$. Using $t=x/\mu E$ and the definition of range, the number of electrons which travel a distance x into the crystal and are still free after time t is $n=n_0e^{-x/w}$. The electrometer will record a charge $q=ex/l$ for each electron of charge e which drifts a distance x in the crystal.

The above considerations can be used to derive the net charge flow in the external circuit in the simple case outlined. However, in actual practice the relation between measured charge and the charge released is complicated by the penetration of the light and by the fact that some electrons may be collected at the anode. The intensity of light I at a depth x is related to the incident intensity by $I=I_0e^{-Kx}$, where K is the absorption constant which depends upon wavelength. For light pulses of N_0 total incident photons, the number which actually enter the crystal is reduced by the reflectivity R to $N_0(1-R)$. Within the crystal, in an interval x to $x+dx$, the number of photons actually absorbed is $dN=-KN_0(1-R)e^{-Kx}$. Since we are interested only in those absorptions which lead to the production of free electrons (holes will be considered immobile), the number of electrons dn released in dx is less than the number of photons absorbed by the ratio $dn/dN=\eta$, where η is the quantum efficiency. Hence $dn=K\eta N_0(1-R)e^{-Kx}dx$. Integrating this last expression from 0 to l we get the total number of electrons released within the crystal

$$n=\eta N_0(1-R)(1-e^{-Kl}). \tag{1}$$

The charge which flows in the external circuit can be obtained in analogy with the case of a single electron by defining a saturation factor $\psi=\bar{x}/l$. The quantity $\bar{x}$ is the average electron displacement, equal to the total displacement X of all the electrons divided by n. Upon inserting the value of electronic charge e one arrives at the charge measured by the electrometer.

$$Q=e\eta N_0(1-R)(1-e^{-Kl})\psi. \tag{2}$$

The factor ψ takes into account the mean range of electrons and the finite depth of optical absorption. It can be derived in the case that the illuminated electrode is negative (forward polarity) designated by ψ_f or in the case that the illuminated electrode is positive (reverse polarity) given by ψ_r. The calculations are similar.

To derive ψ_f one evaluates the total displacement X, consisting of two parts: X_1 due to electrons trapped in the crystal volume and X_2 due to electrons collected at the anode. Of the Δn electrons released within the interval x to $x+\Delta x$ a number $d(\Delta n')$ will be trapped within the interval x' to $x'+dx'$:

$$d(\Delta n')=-\frac{\Delta n}{w}\exp\left[-\frac{(x'-x)}{w}\right]dx'; \quad x'>x.$$

Integrating over x' we have the contribution ΔX_1 to X_1 coming from charges released in x to $x+\Delta x$ which are subsequently trapped. The total displacement of

---

[7] Nail, Moser, Goddard, and Urbach. Rev. Sci. Instr. **28**, 275 (1957). We are indebted to Dr. F. Urbach and Dr. F. Hamm for these crystals.

[8] F. C. Brown, J. Phys. Chem. Solids **4**, 206 (1958).

[9] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1948), pp. 80, 117.

[10] A. Rose, RCA Revs. **12**, 363 (1951).

[11] P. J. van Heerden, Phys. Rev. **106**, 468 (1957); **108**, 230 (1957).

[12] S. M. Ryvkin, Doklady Akad. Nauk S.S.S.R. **106**, 250 (1956).

all such electrons is

$$\Delta X_1=\int_x^l (x'-x)d(\Delta n') =w\Delta n\left[1-\frac{l-x+w}{w}\exp\left[-\frac{(l-x)}{w}\right]\right].$$

Similarly, the contribution ΔX_2 to X_2 which comes from the charges released in x to $x+\Delta x$ and are ultimately collected at the anode is

$$\Delta X_2=\Delta n(l-x)\exp\left[-\frac{(l-x)}{w}\right].$$

To obtain $X=X_1+X_2$, replace the Δ's by differentials and integrate over $0\leq x\leq l$. The average displacement $\bar{x}$ is obtained by dividing X by the total number, n, of charges released. The function $\psi_f=\bar{x}/l$ that we originally set out to obtain is then

$$\psi_f=\frac{1}{1-e^{-Kl}}\frac{w}{l}\left[1-\frac{e^{-Kl}}{1-Kw}+\frac{Kw}{1-Kw}e^{-l/w}\right]. \tag{3}$$

If we go to the limit as $K\rightarrow\infty$ which corresponds to all the light being absorbed at $x=0$, we obtain

$$\psi_f=\frac{w}{l}(1-e^{-l/w}), \tag{4}$$

a formula given by Hecht.[13] If the opposite limit, $K=0$, is taken, then

$$\psi_f=\frac{w}{l}\left[1-\frac{w}{l}(1-e^{-l/w})\right], \tag{5}$$

which corresponds to uniform absorption.[9] For complete saturation of the photocurrent, i.e., $w=\infty$, the quantity ψ_f in Eq. (4) approaches unity and for Eq. (5) it approaches one-half.

For the reverse polarity case in which the illuminated surface is at the anode, ψ_r may be calculated by methods similar to those used in calculating ψ_f. The result is

$$\psi_r=\frac{1}{1-e^{-Kl}} \times\frac{w}{l}\left\{\frac{1}{1+Kw}+\frac{Kw}{1+Kw}\exp\left[-\left(K+\frac{1}{w}\right)l\right]-e^{-Kl}\right\}. \tag{6}$$

For uniform absorption, $K=0$, ψ_r approaches the limit for ψ_f, Eq. (5), as is to be expected. As K approaches infinity ψ_r goes to zero. If Kl is very large such that the exponential terms in (6) can be neglected, then

$$\psi_r\simeq\frac{w}{l}\left(\frac{1}{1+Kw}\right). \tag{7}$$

These saturation factors are used in conjunction with Eq. (2) and determine the charge flow in the external circuit for given values of K, l, and w. The range w is proportional to the field E, and if high enough voltages can be applied so that some of the released charge is collected, then theoretical saturation curves can be fitted to the experimental data to determine w. This allows one to compute $\eta(1-R)$ from Eq. (2).

In deriving the expressions for ψ, it has been assumed that only electrons contribute to the photoresponse. This has been found to be the case in all the crystals tested to date. On the basis of this assumption, it is possible to obtain w in low-range crystals by comparing the forward and reverse responses at a fixed wavelength in the absorption edge. The ratio, Q_f/Q_r, from the above expressions, is a complicated function of K and w. However, if the wavelength and voltage are chosen so that both Kl and l/w are large, neglect of exponential terms results in the approximate relation

$$Q_f/Q_r\simeq Kw+1. \tag{8}$$

If K is known, w may be obtained and vice versa. For a crystal in which w is known, acceptable values of absorption coefficients K have been computed in this manner and will be presented in Sec. IV-C.

B. Thermal Release from Traps

It is a characteristic of the AgCl crystals studied that in certain temperature ranges trapped electrons remain trapped for a time long compared to the time of measurement (several seconds). However, at other rather well-defined temperatures thermal release from traps may be observed. This leads one to adopt the point of view that discrete trapping levels exist in the silver halides. The properties of these traps can be obtained from current glow curves of the type observed by Dutton and Maurer.[14]

The traps are first filled by illumination at low temperature, after which the crystal is warmed at a steady rate in the presence of an applied field. Current "glow peaks" are recorded at temperatures corresponding to rapid release from traps. An analysis of the method was first given for the case of thermoluminescence.[15,16] A simple model assumes a trap depth, E, below the conduction band and a frequency factor, s, so that the probability per second for thermal ionization is given by

$$\frac{1}{\tau_g}=se^{-E/kT}. \tag{9}$$

The usual theory[16] gives the shape of the luminescence

---

[13] K. Hecht, Z. Physik **77**, 235 (1932).

[14] D. Dutton and R. Maurer, Phys. Rev. **90**, 126 (1953).

[15] F. Urbach, Wien. Ber. (IIA), **139**, 363 (1930).

[16] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) **A184**, 366 (1945).

versus temperature curve and allows one to determine E from the following formula if s is known:

$$E=kT^*\ln s\left[1+\frac{\ln(kT^{*2}/\beta E)}{\ln s}\right]. \qquad (10)$$

Here β is the rate of warming and T^* the temperature of maximum glow. A single trap depth, E, is assumed and multiple trapping is not taken into account. The above analysis should be applicable to electrical glow curves in the case that the thermally released electrons have a constant mean range w_0E determined by deep traps.

An approximate analysis has been given by Grossweiner[17] which permits E and s to be calculated separately from the shape of the observed current-temperature curve. He finds that they are given in terms of T^* and T', the temperature of the maximum and the temperature at which the increasing current reaches half-maximum, by the following equations:

$$E=1.51kT^*T'/(T^*-T'), \qquad (11)$$

$$s=\beta(E/kT^{*2})e^{E/kT^*}. \qquad (12)$$

It is difficult to determine s with high accuracy by this means because of its strong dependence on the usually small difference, T^*-T'.[17a]

A relation[18] between s and trap cross section σ can be obtained from the principle of detailed balancing. The result shows that a large cross section and a high-frequency factor are compatible. In the present experiment one can estimate σ if the density of traps N_t can be found. The product, $N_t\sigma$, and range, w_0, are related by

$$w_0=\mu\tau=\mu/N_t\sigma u,$$

where μ is the mobility and u the mean thermal velocity. An approximate upper limit on N_t has been found in at least one case in AgCl for the present experiment by filling traps.[1] Still another way to obtain information on trap characteristics is to establish a fixed temperature in the vicinity of a "glow" peak and observe the decay time constant of photoconductive response. Results will be given in Sec. IV which reveal the general features of electron trapping in AgCl.

III. EXPERIMENTAL DETAILS

A. Apparatus

The low temperatures at which the experiments were performed were maintained for long periods of time by a helium cryostat similar in many respects to the one designed by Mapother and Witt.[19] Since AgCl crystals deform easily, they cannot be clamped tightly to assure thermal contact with a cold reservoir. Instead, the crystal was placed in a closed copper chamber connected to the bottom of the helium reservoir in the cryostat. Helium gas admitted to the chamber assured adequate heat exchange between the cold walls and the crystal. Rapid cooling also strains the crystals, so the cooling rate was kept below 10°C per hour. Access to the crystal chamber was through a lead gasket seal.

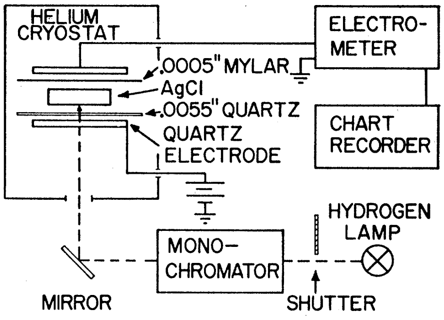

FIG. 1. Block diagram of apparatus. Crystal, blocking layers, and electrodes are optically flat and are in contact. The lower transparent electrode is quartz with a NESA coating of about 2000 ohms/square.

Temperatures were measured with a copper-constantan thermocouple and a carbon resistance thermometer, each calibrated against a standard platinum resistance thermometer. Two electrical leads were brought into the crystal chamber and connected to the electrodes between which the crystal was placed, as shown schematically in Fig. 1. The lower transparent electrode was a 1-mm thick NESA-coated[20] quartz slide which was connected to a highly insulated battery voltage supply. A shielded lead from the upper metallic electrode was connected to the input of a vibrating reed electrometer.[21] The electrodes were blocked with insulating layers to prevent charge from entering or leaving the crystal. A sheet of Mylar plastic 0.5 mil thick served as the blocking layer on the unilluminated side, and the illuminated electrode was blocked with a 5.5-mil thick quartz plate of optical quality.

The electrometer output was connected to a recording potentiometer. On the recorder chart, the integrated charge pulse measured by the electrometer appeared as a step in the trace of the pen. The magnitude of the step could be determined quite accurately by graphically eliminating the effect of drift and averaging out the noise. Careful shielding of insulators and leads resulted in background drift currents as low as 5×10^{-17} ampere. The instruments were calibrated directly in terms of standard charge pulses. When data were taken on thermal release of charge, calibrated high-value resistors were put in parallel across the electrometer input, so that current was measured instead of charge.

Light was obtained from a dc hydrogen Nester lamp

---

[17] L. I. Grossweiner, J. Appl. Phys. **24**, 1306 (1953).

[17a] C. H. Haake, J. Opt. Soc. Am. **47**, 649 (1957).

[18] C. Herring, *Fundamental Formulas of Physics*, edited by D. H. Menzel (Prentice Hall Publications, Inc., New York, 1955), p. 630.

[19] D. E. Mapother and F. E. L. Witt, Rev. Sci. Instr. **26**, 843 (1955).

[20] D. N. Lyon and T. H. Geballe, Rev. Sci. Instr. **21**, 769 (1950).

[21] Model 30, Applied Physics Corporation, Pasadena, California.

TABLE I. Summary of electronic properties for several AgCl crystals at 80°K.

Crystal number	Unit range of electrons, w_0(cm^2/volt)	Upper limit unit range of holes, w_0(cm^2/volt)	Quantum efficiency times reflectivity factor at 340 mμ $\eta(1-R)$
XVIII$_1$	4.0×10^{-5}	...	0.51
H342-196	8×10^{-6}	...	...
C63-6	9.0×10^{-6}	...	0.55
C56-7	4.0×10^{-6}	...	...
XXII$_4$	1.05×10^{-3}	9.0×10^{-9}	0.55
C54-7	1.8×10^{-6}	3.2×10^{-8}	<0.9
XIX$_4$	1.5×10^{-6}	3.5×10^{-8}	<1.0

with a usable output down to less than 220 mμ. A double monochromator[22] with quartz prisms provided light of high spectral purity. The light intensity as a function of wavelength and monochromator slit width was calibrated periodically with a cesium-antimony photocell.[23] With the slit widths used, the spectral bandwidth was usually about 20 A. A rotating-sector disk, driven by a synchronous motor, passed one-tenth second light pulses, one of which could be picked out when desired by a synchronized camera shutter placed in front of the monochromator entrance slit. The level of illumination was kept as low as possible, about 3×10^6 photons per pulse.

B. Sample Preparation

Results will be presented for several different single-crystal specimens of AgCl. The crystals labeled by Roman numerals in Table I were prepared at the University of Illinois by techniques described elsewhere.[8] Others, indicated by the letter C (Bridgman) and by the letter H (Kyropoulos), were grown at the Research Laboratories of the Eastman Kodak Company.[7] Spectrographic analysis of the Kodak crystals showed a few tenths of a part per million by weight total heavy metal impurities. A similar analysis of crystals grown at Illinois indicated less than one part per million total metal impurity. Crystal XIX$_4$ was grown in vacuum and annealed in an inert atmosphere in such a way as to be free from traces of dissolved silver oxide. Other samples, such as XXII$_4$, were grown in air or in the presence of moisture and are believed to contain minute traces of the oxide.

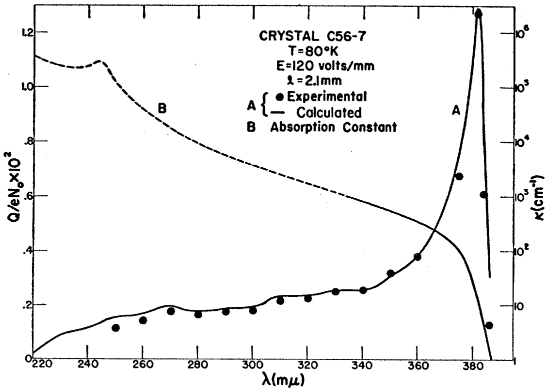

FIG. 2. Wavelength dependence of photoresponse for crystal C56-7 which had a thin defective surface layer. Curve *A* was calculated from theory with proper choice of defective layer thickness and range. Curve *B* is a log plot of absorption constant from Fig. 5 (solid curve) and the data of Tutihasi[27] (dotted curve).

Since the spectral distribution of photoresponse and the photoresponse as a function of applied field depend strongly on the condition of the illuminated surface, great care had to be taken in preparing surfaces that were flat and free from strains. The best results were obtained by the following procedure used in the case of XXII$_4$. First, the crystal was oriented by an analysis of back-reflection x-ray patterns. Etch pits do not form so readily on a (100) surface so samples were cut along these planes with a special carbide-tipped circular saw. A microtome was then used to remove slices from the surface, five microns thick at a time, until approximately one-tenth of a millimeter was removed. The crystal was lightly lapped on a flat glass surface using a 3% solution of potassium cyanide, until the small scratches left by the microtome blade were gone, and the reflected image of the filament of a ruby lamp could not be improved. The image was quite free from distortion.

With the surface to be illuminated upward, the crystal was then placed on fine quartz powder inside an annealing furnace which was programmed to go from room temperature to 400°C in about twenty hours. After several hours at this temperature the programmer was reversed and the crystal brought back down to room temperature at the same rate. Under polarized light no strain patterns were visible after annealing. The crystal was again lightly lapped before testing. Annealing could be carried out either in air or in helium gas. All of the operations described were performed under darkroom red light.

IV. RESULTS

A. Spectral Response and Quantum Efficiency

In a series of preliminary tests on a nonphotoconducting spacer, no measurable response was found which could be ascribed to electron emission from electrodes into vacuum. Initial runs on several AgCl samples indicated that photoconductivity begins coincidently with the fundamental optical absorption edge near 400 mμ. It was ascertained that the experiments could be carried out with small enough light intensity so that the results from 200 to 400 mμ were characteristic and did not depend on space charge, previous illumination to fill traps, or photodiffusion

---

[22] Carl Leiss, Berlin-Steglitz, Germany.

[23] Kindly supplied by Dr. L. Apker at the General Electric Research Laboratories, Schenectady, New York.

effects.[24,25] Red light was not relied upon to release space charge because of the effect of trap filling.

Early results showed that an unexposed crystal slowly cooled to 80°K showed no detectable photoresponse at wavelengths longer than 400 mμ out to 1 μ. However, small enhanced photosensitivity developed in this range of wavelengths after prolonged illumination of a cold crystal within the region of fundamental absorption.[24,26] This type of response, which is undoubtedly due to trapped electrons, will not be dealt with here.

Under proper conditions of low illumination intensity and crystal uniformity, photoresponse in agreement with the theory outlined in Sec. II-A was observed. The change Q was found to depend linearly on the number of incident photons per pulse, N_0. The dependence of Q/eN_0 on collecting voltage was found to fit saturation curves as outlined in the theory and discussed under carrier range in the next section. However, the dependence of response on wavelength, at high values of absorption constant, was found to be strongly affected by surfacing of the crystals. To illustrate this effect, the surface region of crystal C56-7 was intentionally disturbed by rubbing on emery paper. Figure 2 shows the observed spectral response which peaks sharply at the absorption edge. The absorption constant at 80°K is plotted on a logarithmic scale in Fig. 2 for comparison.[27,28] A peaked spectral response of this type has been shown characteristic of surface trapping and recombination processes.[29] For the case of Fig. 2, a saturation function ψ (depends on K) has been calculated for a simple model which assumes a thin surface layer of thickness l_s with a uniform but higher trap density than the interior of the crystal. The solid curve shown in Fig. 2 was obtained from such a theory using the values of $\eta(1-R)$ taken from the results of crystal XXII$_4$. The parameters which best fit the experimental data are thicknesses $l_s=0.008$ cm, $l_v=0.202$ cm and ranges for an applied field of $E=120$ volts/mm, $w_s=1.0\times10^{-3}$ cm and $w_v=4.7\times10^{-3}$ cm. These also fit the dependence of Q/N_0 on E which is concave upwards at low fields.

Figures 3(a) and (b) show data for a carefully surfaced crystal which was free from surface defects of the type described above. From Eq. (2), Sec. II one can compute $\eta(1-R)$ when ψ_f is known. The latter can be obtained by fitting saturation curves of the type shown in Fig. 4. Typical results are given in Fig. 3(b) along with the data of Lehfeldt.[1] The small reverse polarity data shown in Fig. 3(a) were of opposite sign from the forward data but are plotted as shown for the sake of convenience. The reverse response can be explained entirely in terms of electron drift toward the illuminated anode due to penetration of the light.

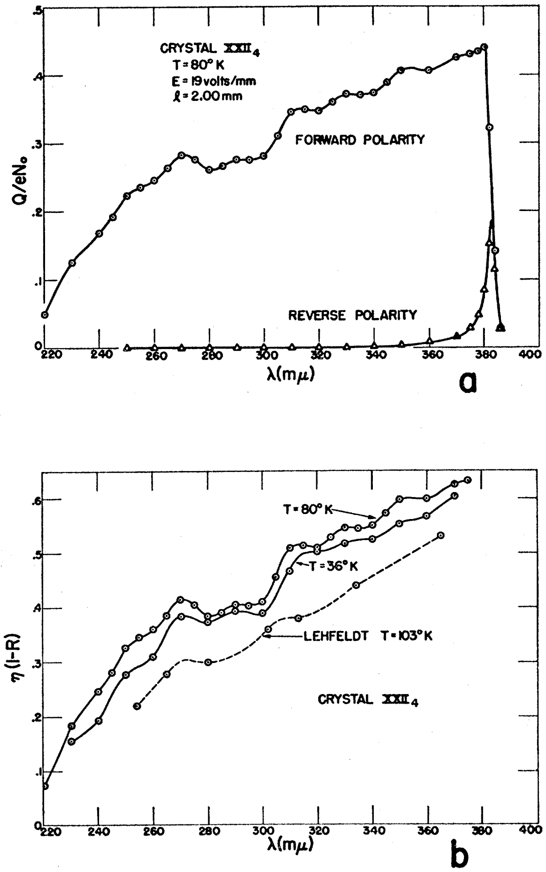

FIG. 3. (a) Wavelength dependence of photoresponse typical of a carefully surfaced crystal. Collecting voltage was constant for these points and was below forward polarity saturation. The reverse polarity data (illuminated electrode positive) were of opposite sign. (b) Quantum efficiency including the effect of reflectivity for crystal XXII$_4$ at temperatures of 80°K and 35°K. The lowest curve shows the data of Lehfeldt[1] at 103°K.

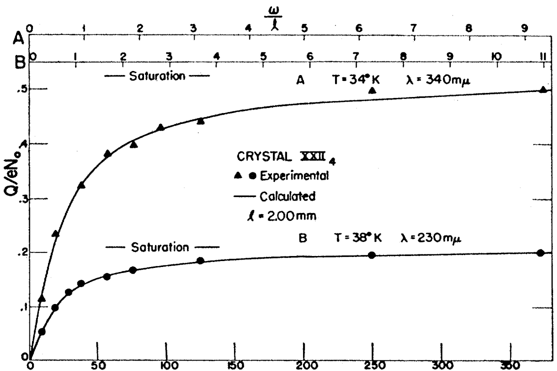

FIG. 4. An example of saturation curves at two different wavelengths and nearly the same temperature. The solid lines are theoretical curves adjusted according to the scales at the top. Unit ranges were slightly different at the two temperatures.

---

[24] A. Goodman, thesis, Princeton University, 1957 (unpublished). We are indebted to Professor George Warfield for an early report of this work.

[25] A. B. Kotliarevsky, J. Exptl. Theoret. Phys. U.S.S.R. **17**, 516 (1947).

[26] M. A. Gilleo, Phys. Rev. **91**, 534 (1953).

[27] S. Tutihasi, Phys. Rev. **105**, 882 (1957).

[28] Y. Okamoto, Göttingen Nachr. II, **14**, 275 (1956).

[29] H. B. DeVore, Phys. Rev. **102**, 86 (1956).

A high quantum efficiency for production of free carriers in the fundamental absorption region and in its long-wavelength tail appears to be a property intrinsic to silver chloride. Moreover, this efficiency is independent of previous illumination or of the filling of traps. As seen in Table I, direct measurements on three different samples yielded essentially the same value of quantum efficiency, and indirect estimates for two other crystals, although subject to more uncertainty, gave roughly the same values. The structure seen in Fig. 3(b) was reproducible from sample to sample and from run to run, indicating the relative accuracy of the points which was of the order of 5%. The absolute values of $\eta(1-R)$, comparing one crystal with another, were subject to an estimated systematic error of about 13%.

With decreasing temperature, the spectral dependence and magnitude of the quantum efficiency remain essentially unchanged throughout the entire spectral region from near the absorption edge (which shifts slightly with temperature) to the short-wavelength side of the optical absorption peak. The spectral dependence of quantum efficiency uncorrected for reflectivity is essentially the same at 35°K as at 80°K. Although the exact value of η was not measured at 6.5°K, a lower limit about an order of magnitude less than the values at higher temperatures was established. From a consideration of the behavior of the photoresponse, particularly with respect to the range of electrons and the energy distribution of traps, it is highly probable that there is no significant change in the magnitude of η from higher temperatures to 6.5°K.

B. Electron Range

Figure 4 shows the saturation behavior of the charge response of crystal $XXII_4$ with increasing applied field at two wavelengths and slightly different temperatures. From curves like these the range w_0 in different crystals may be determined, or if the range is too short for saturation to be observed, the method of Eq. (8) can be used. Alternately range can be calculated from Eq. (2) by assuming a value of $\eta(1-R)$. Table I shows values of unit range at 80°K which vary from $w_0=1.05\times10^{-3}$ cm²/volt (crystal $XXII_4$, air-grown and air-annealed) to $w_0=1.5\times10^{-6}$ cm²/volt (crystal XIX_4, grown in vacuum and annealed in helium).

The range depends on temperature through the mobility[30] and the density of deep traps. Table II gives the unit range at different temperatures for crystal $XXII_4$. At 80°K, 38°K, and 34°K the range was measured directly by saturating the forward polarity charge response. At 15°K and 6.5°K, the range was calculated from unsaturated forward response data, assuming that the quantum efficiency does not change from the measured value at higher temperatures. These results will be discussed further in connection with glow curves presented in Sec. IV-C.

TABLE II. Unit range of electrons in crystal $XXII_4$ at various temperatures.

Temperature °K	Unit range (cm²/volt)
80	1.05×10^{-3}
38	4.7×10^{-4}
34	4.0×10^{-4}
15	1.3×10^{-7}
6.5	3.3×10^{-9}

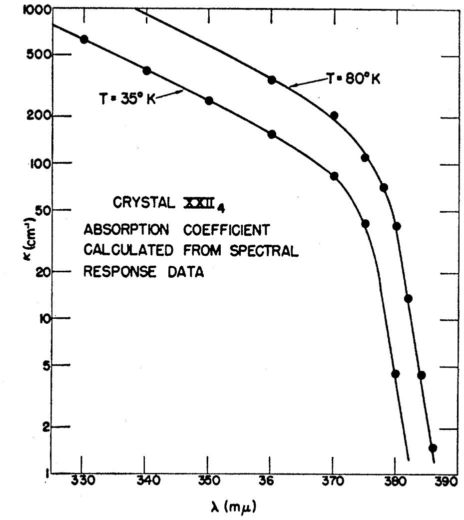

FIG. 5. Absorption constant *versus* wavelength for crystal $XXII_4$, determined from the ratio of forward to reverse photoresponse.

C. Hole Range

As mentioned in connection with Fig. 3(a), the reverse polarity response observed in the vicinity of the absorption edge with illuminated electrode positive can be explained in terms of electron drift only. An upper limit on the range of holes may be obtained by applying a large field in this reverse polarity and illuminating with strongly absorbed light. The contribution of electron motion to the charge response will be small because of the large absorption constant. Assume for the moment that holes are mobile and have short ranges. A short range means that the saturation factor for holes can be approximated by $\psi_f^h \simeq w^h/l$. This can be used in Eq. (2) to determine unit range for holes w_0^h from the observed charge response. At 260 mμ ($K=5\times10^4$ cm⁻¹) and 80°K the field was increased in steps to 10^4 volts/cm. Light intensity was increased from 10^6 to 6.3×10^7 photons per pulse without an observable response in the reverse direction. A charge of 8.7×10^3 electron units could have been distinguished from the noise. The saturated reverse electron response at this short wavelength and light intensity would amount to only 2×10^3 electrons, still below the limit

---

[30] F. C. Brown and F. Dart, Phys. Rev. **108**, 281 (1957).

of detectability. From the value of $\eta(1-R)=0.31$, obtained from the forward electron response of crystal XXII$_4$ [Fig. 3(b)], an upper limit for hole range is $w_0^h<9.0\times10^{-9}$ cm²/volt. The unit range for electrons was $w_0^e=1.05\times10^{-3}$ cm²/volt, which gives $w_0^h/w_0^e<8.6\times10^{-6}$. Estimates of the upper limit of w_0^h for other crystals are given in Table I. It was not necessary to evoke hole motion in any case. In preliminary tests some reverse polarity response was found at short wavelengths, but in each case it arose because of surfaces which were not equipotential or from space charge effects.

It has thus been shown that holes contribute little, if any, to photoconductivity in the various AgCl crystals examined. By making use of this result for a crystal of known electron range, the absorption constant, K, can be determined from Eq. (8) and the more complicated relation it approximates. The results obtained in this way, from the ratio of forward to reverse response, are given in Fig. 5 for crystal XXII$_4$. The accuracy with which these points were determined is of the order of 10%. They cover the range of absorption coefficients between the data for thin films and thick crystals and are independent of reflectivity.

D. Electron Trapping

The electrical glow curve of crystal XXII$_4$ between 9°K and 90°K with previous illumination of 2×10^{10} quanta is given in Fig. 6. Essentially the same peaks were observed for crystals XVIII$_1$, C54-7 and C56-7, except that near 35°K the curve was more complicated in some cases. For example, a shoulder appeared on the low-temperature side of the 36°K peak as well as on the high-temperature side for crystal C56-7. The peak near 75°K was not always present and appeared to be related to strains, introduced into the crystal by rapid temperature changes or mild cold-working.[31]

A large decrease in electron range was observed just below the 35°K and the 15°K glow peaks seen in Fig. 6. Table II shows that for crystal XXII$_4$, w_0 decreased from 4.7×10^{-3} cm²/volt at 38°K to 1.3×10^{-7} cm²/volt on the upper side of the 15°K peak. This decrease is certainly due to electron trapping. Recent experiments on Hall effect[31a] indicate that the Hall mobility of electrons rises to values as high as 5000 cm² volt-sec at low temperature. Using this value of μ, the trapping time at 15°K may be computed to be $\tau=w_0/\mu=2.6\times10^{-11}$ sec. If we take a trapping cross section somewhat larger than geometric, $\sigma=10^{-12}$ cm², and a mean thermal velocity, $u=2.5\times10^6$ cm/sec, the density of 36°K traps, $N_t=1.5\times10^{16}$ cm^{-3}. This is of the order of the total heavy metal impurities (chiefly iron) determined spectrochemically for crystals of similar preparation. As shown by Eq. (10), the thermal trap depth, E, depends upon the temperature of maximum current, T^*, and to a lesser extent upon the frequency factor, s. For a value of s in the vicinity of 10^{10} sec^{-1}, $E\simeq25kT^*$, which says that the 36°K traps have a thermal depth of about 0.08 ev.

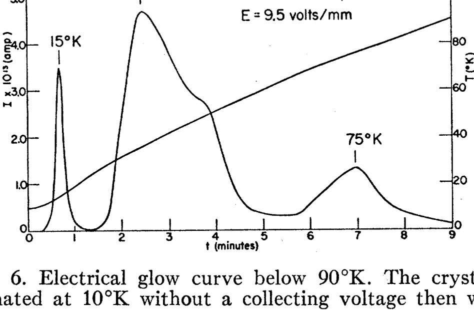

FIG. 6. Electrical glow curve below 90°K. The crystal was illuminated at 10°K without a collecting voltage then warmed with field on, as shown.

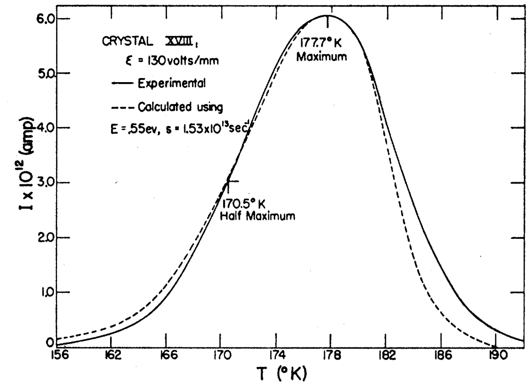

FIG. 7. High-temperature glow peak after previous illumination at 80°K. The dotted curve is from theory for a single-trap model of characteristics shown. The warming rate was about 0.02°K/sec.

Similarly, the glow peak at 15°K corresponds to traps of about 0.03 ev which are responsible for a still further decrease in range below this temperature (see Table II). They must be present in still larger density or have larger cross section than the 36°K traps.

Above 90°K the spectrum of glow peaks was relatively simple. In the case of well-annealed crystals no prominent peaks were observed until temperatures as high as 180°K. (In a few cases an indication of a peak at 130°K was found.) Furthermore, electron range changed only gradually from 80°K to at least 150°K. Thermal release from the deep traps which control electron lifetime in this temperature range are shown in Fig. 7 where current is plotted as a function of temperature. The dashed curve is calculated from the theory of Randall and Wilkins[16] using $E=0.55$ ev and $s=1.5\times10^{13}$ sec^{-1}. These are the values of trap depth and frequency factor one obtains from the observed data using Eqs. (11) and (12). Because of assumptions, such as no multiple trapping and freedom from space charge, the value of s stated above is probably order of magni-

---

[31] F. C. Brown, Phys. Rev. **97**, 355 (1955).

[31a] K. Kobayashi and F. C. Brown (to be published).

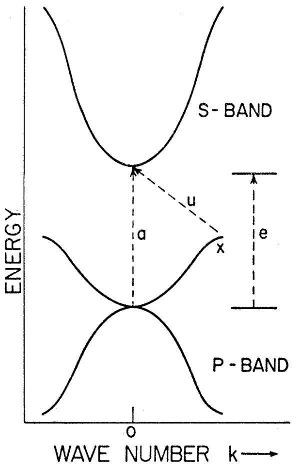

FIG. 8. Schematic diagram of proposed[2] band structure in the reduced zone scheme for the silver halides. This is the case in which the indirect transitions, *u*, have lower energy than the allowed exciton transitions, *e*.

tude correct only. Multiple trapping has the effect of shifting T^* to higher temperatures and was not believed to be as important as space charge effects in the present case. The observation of glow peaks much above 180°K was limited by ionic conductivity.

A frequency factor as high as 1.5×10^{13} sec^{-1} implies a large trapping cross section in the vicinity of 10^{-14} to 10^{-13} cm^2. Independent evidence for a large cross section was obtained from the results of a trap-filling experiment at 80°K. Crystal C63-6 was carefully illuminated by light at the band edge without an applied voltage. This resulted in a marked increase in electron range. Assuming that each photon absorbed in the volume releases one electron which fills a trap, the density of deep traps present before illumination was found to be 2.5×10^{12} cm^{-3}. This corresponds to a trapping cross section of about 10^{-12} cm^2 for the measured range and a mobility of 200 cm^2/volt-sec at 80°K. By comparing ranges, we conclude that the density of the 0.55-ev traps was always relatively low and varied from 2×10^{10} cm^{-3} in crystal XXII$_4$, to 1.5×10^{13} cm^{-3} in crystal XIX$_4$.

V. DISCUSSION

The long-wavelength tail of the optical absorption peak and the existence of photoconductivity in this region for the silver halides may be explained with the aid of a model proposed by Seitz.[2] It is suggested that a plot of energy *versus* wave number for the conduction band is simple in the vicinity of $k=0$ but that the valence band turns strongly upward in at least one crystallographic direction as shown in Fig. 8. Allowed optical transitions occur vertically in such a diagram because of the selection rule, $\Delta k=0$. An allowed or direct transition to an exciton level is indicated by the letter *e* in the figure. Normally forbidden transitions of energy less than the direct transitions occur when the selection rule is relaxed by imperfections.[2,32] These so-called indirect transitions, which leave a conduction electron near the zone center and a hole near the boundary, are represented by the diagonal line, *u*, in Fig. 8.

It seems reasonable to attribute the observed high yield of photoelectrons in AgCl from about 310 mμ to 390 mμ to indirect transitions. Throughout this range the absorption data of Fig. 4 roughly fits the E^2 energy dependence given by theory,[33] with a threshold for indirect transitions in the vicinity of 390 mμ. Quantum efficiency was closely the same in different samples at various temperatures, but it was not unity. A competing nonconducting process, such as excitation of the silver ion from the $4d^{10}$ to $4d^95s$ state[2,34] would explain the discrepancy and perhaps some of the variation with wavelength.

The magnitude of the optical absorption constant at wavelengths shorter than 310 mμ and in the neighborhood of the first absorption peak is indicative of allowed optical transitions, probably to exciton levels. If the exciton level lies below the bottom of the conduction band, the optical transition would not ordinarily lead to photoconductivity. Inasmuch as electron yield was observed at all temperatures in the spectral region of the peak, it appears that the excited state, *e*, on the halogen ion dissociates with high probability into a free electron and hole. It may be that the nonconducting bound state, *e*, goes into a lower energy state with the electron in the conduction band at $k=0$, and the hole in the valence band near the zone boundary. A phonon would be required to conserve wave-number vector, but this might not be a strongly temperature-dependent process.

The observed values of $\eta(1-R)$ do decrease somewhat for wavelengths shorter than 260 mμ. This decrease cannot be entirely accounted for by an increase in reflectivity, as shown by Fig. 9 which compares quantum efficiency, η, and absorption constant.[35] It is thought at the present time that very thin defective surface layers ($\sim10^{-5}$ cm) give rise to trapping and recombination which effects the apparent internal yield in the region of very high absorption. More information is needed about the exact behavior of reflectivity and absorption at low temperature for samples on which internal yield is measured.

---

[32] D. L. Dexter, *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4–6, 1954*, edited by R. G. Breckenridge *et al.* (John Wiley and Sons, Inc., New York, 1956), p. 155.

[33] Bardeen, Blatt, and Hall, *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4–6, 1954*, edited by R. G. Breckenridge *et al.* (John Wiley and Sons, Inc., New York, 1956), p. 146.

[34] J. Krumhansl, *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4–6, 1954*, edited by R. G. Breckenridge *et al.* (John Wiley and Sons, Inc., New York, 1956), p. 450.

[35] Preliminary reflectivity data taken at low temperatures on solid blocks and thin films of AgCl were kindly supplied by Professor P. Hartman. These data indicate an increase in *R* of about 30% at 240 mμ.

In contrast to the behavior of quantum efficiency, electron range varied greatly with sample preparation and with temperature. In all unstrained crystals the range from 35°K to 180°K was controlled by a relatively low density of traps of thermal depth about 0.5 ev. The large cross section and low concentration of these states suggests that they may be due to an excess charge in the lattice, possibly a three or four valent heavy metal ion. Below 35°K the range of electrons in silver chloride decreases sharply due to a high density of shallow traps. At these low temperatures the situation is similar to the alkali halides where electrons have very short trapping times. Silver chloride has a static dielectric constant of 12.3 which tends to explain the existence of shallow trapping states thought at present to be due to substitutional charged impurities.

The fact that holes do not move is in agreement with some of the earlier investigations[1] but in disagreement with others.[5] A possible explanation of the reverse polarity response reported by Smith[5] may be related to electron trapping and luminescence.[6,36] Crystals $XXII_4$ and XIX_4 were illuminated with steady ultraviolet light while cold, and they both showed the characteristic green emission which peaks at 480 mμ.[37,38] Normally this luminescent light would be only weakly absorbed in the crystal. However, previous exposure of a cold crystal will produce an enhanced photosensitivity which lies just in the region of the green emission.[24] Electrons released in the volume by the luminescent light could then give rise to reverse polarity response. Such an effect was not important in the present experiment because of the very low pulsed excitation intensity. That holes do not make an appreciable contribution to the conductivity may be due to a very high density of hole traps in all specimens studied or to a characteristic low hole mobility in ionic crystals of this type.

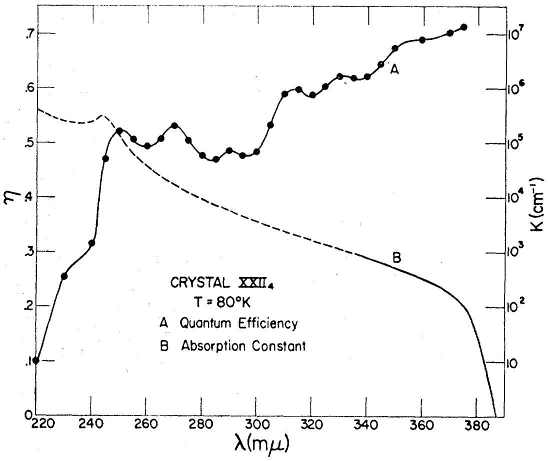

FIG. 9. Curve *A* shows quantum efficiency at 80°K determined from photoresponse and preliminary low-temperature reflectivity data.[35] Curve *B* is a log plot of absorption constant from Fig. 5 and the data of Tutihasi.[27]

ACKNOWLEDGMENTS

The authors would like to express their appreciation to Professors R. Maurer and F. Seitz for helpful discussions. They are greatly obliged to Dr. F. Urbach, F. Moser, and F. Hamm of Eastman Kodak Laboratories. The help of Dr. S. M. Dodds, Pittsburgh Plate Glass Company and Mr. F. E. L. Witt is gratefully acknowledged. One of the authors, R. S. Van H., received the aid of a fellowship provided by The Haloid Company.

---

[36] Farnell, Burton, and Hallama, Phil. Mag. **41**, 157, 545 (1950).

[37] P. G. Aline, Phys. Rev. **105**, 406 (1957).

[38] The excitation spectrum of the total luminescence transmitted by the crystal was studied. It is produced by a wide range of wavelengths and probably also occurs under particle bombardment. The results are in agreement with the conclusion that the green luminescence arises due to transport and trapping of charge carriers.[6]