

# Photoconductivity of Silver Chloride Crystals Under Pulsed X-Ray Irradiation\*

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The photoconductivity produced by irradiation with 0.2- $\mu$ sec x-ray pulses was studied in AgCl as a function of temperature (80–280°K), x-ray intensity and penetration, field strength, and crystal preparation, in order to obtain information about lifetimes and mobilities of electrons and holes. The measurements of electron lifetimes ( $\sim 1$   $\mu$ sec) and mobilities in air-grown crystals are in agreement with those reported in the literature. The photoconductive response can be described by assuming deep electron traps throughout the volume of the crystal and possibly a disturbed surface layer. No hole motion is observed below 250°K; above that temperature the schubweg per unit field is estimated at  $5 \times 10^{-8}$  cm<sup>2</sup>/v. The electron lifetime in crystals

grown and annealed in He is much smaller than in the air-grown samples. Assuming the same mobility in both samples the lifetime at 80°K is  $3 \times 10^{-9}$  sec. At higher temperatures the pulses show long tails, and between 200° and 280°K the saturation time varies exponentially with  $1/T$ . It is assumed that shallow traps exist ( $\sim 0.08$  eV) in a thin surface region which otherwise has a long electron lifetime as compared with the bulk of the crystal. Measurements on crystals doped with 20 ppm Cu<sup>+</sup> indicate that the Cu<sup>+</sup> ions do not act as effective electron traps. On the other hand, the presence of 1 ppm Ni ions reduces the lifetime at 80°K to less than  $3 \times 10^{-11}$  sec, indicating a capture cross section of the Ni ion larger than 300 (Å)<sup>2</sup>.

## I. INTRODUCTION

LIFETIMES and mobilities of electrons and holes in the silver halides play an important role in the formation of the photographic latent image<sup>1</sup> and they have been the subject of a number of studies. In this laboratory Wiegand<sup>2</sup> measured the decay time of the photocurrent and luminescence of AgCl in the steady state, i.e., after the crystal had been illuminated for some time. Recent pulse experiments were made by Brown<sup>3</sup> using particles for the excitation, and by Brown<sup>4,5</sup> and Van Heyningen and Brown<sup>6</sup> using pulses of light. In the present investigation also, use is made of a pulse method, but with x rays for excitation. Similar to  $\beta$ -ray excitation, the electron-hole pair production in the case of x rays occurs by secondary processes; however the x-ray method gives more flexibility in the choice of energy, pulse width, penetration depths, etc., than does the particle method. Several samples of each type, with the exception of the Ni-doped crystal, often cut from different boules, were measured and many experimental runs were repeated. In general, there were variations from one specimen to the other. The data presented in this paper are selected examples illustrating the general behavior of the different type of materials. For more complete data and

other details reference is made to the original thesis.<sup>7</sup> Special attention was given to the problem of hole motion, because of the controversial nature of this question.

## II. EXPERIMENTAL PROCEDURE

Electrodes, one of which is transparent to x rays, are placed on opposite faces of a platelike crystal. An electric field is produced in the crystal by a voltage applied to the series combination of a resistor and the crystal. A short pulse of x rays incident on one surface of the crystal produces charge carriers near that surface which are then displaced by the electric field. This displacement of carriers induces a charge on the electrodes and the resulting voltage pulse is amplified and displayed on an oscilloscope. The time constant is made large compared to the duration of the photoconductive transient so that the circuit acts as an integrator. The duration of the electric field determines whether electrons or holes are pulled through the crystal.

If the x-ray pulse is infinitesimally short and if the crystal contains traps or recombination centers distributed uniformly through the volume of the crystal, the induced voltage pulse is given by<sup>3</sup>

$$v(t) = \frac{n_0 e \tau}{C t_D} \begin{cases} (1 - e^{-t/\tau}), & t < t_D \\ (1 - e^{-t_D/\tau}), & t > t_D \end{cases} \quad (1)$$

where  $\tau$  is the lifetime, i.e., the mean time an electron spends in the conduction band before being trapped;  $t_D$  the transit time;  $n_0$  the total number of carriers produced by one pulse;  $C$  the capacity of the crystal plus stray capacity; and  $e$  the electronic charge.

In the actual experiments the excitation is not instantaneous but is approximately a rectangular pulse

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<sup>1</sup> J. W. Mitchell, Repts. Progr. in Phys. **20**, 433 (1957).

<sup>2</sup> D. A. Wiegand, thesis, Cornell University, Ithaca, New York, 1956 (unpublished); Phys. Rev. **113**, 52 (1959).

<sup>3</sup> F. C. Brown, Phys. Rev. **97**, 355 (1955).

<sup>4</sup> F. C. Brown and F. E. Dart, Phys. Rev. **108**, 281 (1957).

<sup>5</sup> F. C. Brown, J. Phys. Chem. Solids **4**, 206 (1958).

<sup>6</sup> R. Van Heyningen, thesis, University of Illinois, Urbana, Illinois 1958 (unpublished); R. Van Heyningen and F. C. Brown, Phys. Rev. **111**, 462 (1958).

<sup>7</sup> A. Michel, thesis, Cornell University, Ithaca, New York, 1960 (unpublished).

of duration  $t_1$ . The induced voltage is then given by<sup>8</sup>

$$v(t) = \frac{n_0 e \tau}{C t_D} \begin{cases} -\frac{\tau}{t_1} (1 - e^{-t/\tau}), & 0 < t < t_1 \\ 1 - \frac{\tau}{t_1} (e^{t_1/\tau} - 1) e^{-t/\tau}, & t_1 < t < t_D \\ 1 - \frac{\tau}{t_1} \left[ e^{-(t-t_1)/\tau} + \left( \frac{t-t_D}{\tau} - 1 \right) e^{-t_D/\tau} \right], & t_D < t < t_D + t_1 \\ 1 - e^{-t_D/\tau}, & t > t_D + t_1 \end{cases} \quad (2)$$

These formulas are valid only if the carriers are produced in a layer small compared to the schubweg. Such is the case for the forward polarity (i.e., the field pulls electrons through the crystal) response of the air-grown crystals. Since the x rays penetrate a small but finite distance into the crystal and the schubweg of the holes is extremely short, the reverse polarity response is determined primarily by electrons returning to the irradiated electrode and consequently its time dependence is not described by Eq. (2).

A block diagram of the apparatus is shown in Fig. 1. In order to minimize polarization effects resulting from "dark" currents,<sup>5</sup> a pulsed electric field of approximately 2 msec duration is used. It is produced by a General Radio 1217A pulse generator followed by an amplifier. The maximum available voltage is 3 kv. The x-ray pulse is obtained by applying a 500 v, 0.2  $\mu$ sec pulse to the grid of a specially constructed x-ray tube. This tube is a modification of one used by previous investigators<sup>2,8</sup> and was originally designed and constructed by R. Rosa and T. Castner.<sup>9</sup> For most of the experiments radiation from a copper target was used. The maximum intensity was approximately  $1.3 \times 10^{-3}$  ergs/pulse.

In the detection of the signal pulse, which is of the order of millivolts, in the presence of the much larger field pulse, use is made of the fact that the duration of the signal pulse is much shorter than the field pulse. The time constant of the series resistor and the crystal plus stray capacitance is such that the circuit is integrating to the fast signal pulse but differentiating to the field pulse. In spite of the strong differentiation, sufficient feed through of the front edge of the field pulse exists to block the high-gain amplifier and a relay is used to gate the input to the amplifier. A cathode follower separates the relay from the crystal. The detection circuit is mounted directly on the cryostat

in an effort to minimize the stray capacitance. The relative timing of various events is illustrated in Fig. 2.

The sample holder is a spring-loaded piston device with a light spring tension to minimize mechanical stress on the crystal. Contact with the irradiated electrode is made by a flat annulus with a 1.1-cm-diam aperture; the other contact is a disk. Both are gold-plated to prevent contamination.

The design of the cryostat is similar to that of a helium cryostat, i.e., it has an outer liquid nitrogen reservoir to act as a heat shield. The temperature of the sample must be changed very slowly to prevent thermal strain.<sup>3</sup> A slow cooling rate, 20°/hr, is achieved by adding liquid nitrogen only to the outer reservoir and adjusting the power to a heater in the inner reservoir. The temperature is measured by means of two 3-mil copper-constantan thermocouples, one of which is bolted to the cover of the sample chamber and the other imbedded in the polystyrene piston of the sample holder. The temperature is monitored on a dual channel recorder. The cryostat is evacuated to a pressure of less than  $5 \times 10^{-3}$  mm Hg. The x rays enter the cryostat through a  $\frac{1}{2}$  mil Mylar window which is made opaque by an evaporated Al layer.

### III. SAMPLE PREPARATION

The silver chloride samples can be classified into four types: (1) crystals grown and annealed in the presence of air, (2) those grown and annealed in a helium atmosphere, (3) crystals doped with 20 ppm Cu<sup>+</sup> ions, and (4) crystals doped with 1 ppm Ni ions. The doped crystals were also grown and annealed in an inert atmosphere. The material is of high purity; the concentration of heavy metal impurities, except for iron and those intentionally added, is below the limit of spectrochemical detection.

The samples are slabs 2.5–4 mm thick and slightly larger in area than the circular aperture (1.1 cm diam) of the ring electrode. They were cut with a chromium-plated X-Acto saw from larger sections received from

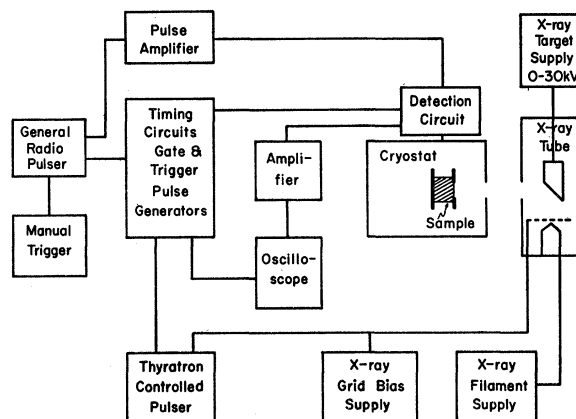


FIG. 1. Block diagram of the apparatus.

<sup>8</sup> M. S. Werman, thesis, Cornell University, Ithaca, New York, 1957 (unpublished); Office of Naval Research technical report (unpublished).

<sup>9</sup> R. J. Rosa, Senior Project Report, Department of Engineering Physics, Cornell University, Ithaca, New York, 1953 (unpublished).

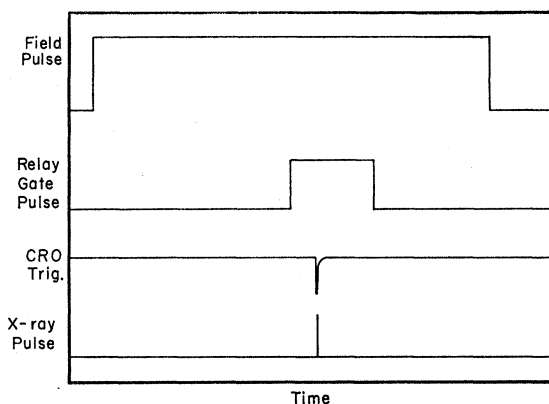


FIG. 2. Relative timing of various pulses.

the Eastman Kodak Company.<sup>10</sup> For this operation the crystals were waxed in a Lucite miter box. The saw blade was occasionally lubricated with a few drops of xylene to prevent clogging of the teeth with beeswax and to wash out the particle of silver chloride.

The surfaces of the crystals were polished on ground glass plates of various coarseness. An etching solution of  $\text{NH}_4\text{OH}$  was used with the coarse plates while distilled water served as a lubricant for the finer polishing. When viewed between crossed Polaroids, a profuse strain pattern was observed which appeared to be confined to the surface region. Some of the samples were lapped on a flannel cloth saturated with an etching solution of 50% *n*-butylamine and 50% ethyl alcohol. The lapping procedure removed the fine scratches and rendered the crystals more transparent; also the strained region at the surface was greatly diminished.

After the surface preparation the samples were thoroughly washed in distilled water (also alcohol if the lapping operation was employed) and were subsequently handled only with glass forceps. They were then etched for 1 min in concentrated hydrochloric acid and again rinsed in distilled water. They were annealed in a quartz system with either an air or helium atmosphere. The temperature of the furnace was controlled by a "Symplotrol" which was programmed to raise the temperature from room temperature to  $420^\circ\text{C}$  in 10 hr. The temperature was held at  $420^\circ\text{C}$  for about 6 hr and then lowered to room temperature at a rate of less than  $20^\circ\text{C}$  per hr.

Electrodes were applied in one of two ways. The first consisted of applying aquadag directly to the crystal surfaces. In the second method, the surface of the crystal was first coated with a solution of polystyrene in xylene which, when dried, formed a polystyrene blocking layer about  $\frac{1}{2}$  mil thick; on top of this layer, aquadag was applied. The aquadag layers were a few tenths of a mil thick and their resistances measured across the crystal surface, were of the order

<sup>10</sup> The author wishes to thank Dr. F. Urbach and Dr. F. Moser of the Eastman Kodak Research Laboratory for providing these crystals.

of 5000 ohms. Aquadag was selected for this layer rather than a metallic coating because of its transparency to x rays (approximately 98% at 2 Å) and ease of application. The samples were single crystals or a composite of a few large crystals.

#### IV. RESULTS AND DISCUSSION

Since the different types of samples behave quite differently, the results for each type are discussed separately. Before presenting the detailed results, however, some remarks concerning the penetration of the x rays into the sample are necessary.

Radiation from a copper target operated at voltages used in these experiments is composed of both characteristic and continuous components. The absorption length of the characteristic radiation is approximately  $10^{-3}$  cm. For the highest target potential used in this study (30 kv) the most penetrating component has an absorption length of 0.022 cm, which is about 6 to 8%

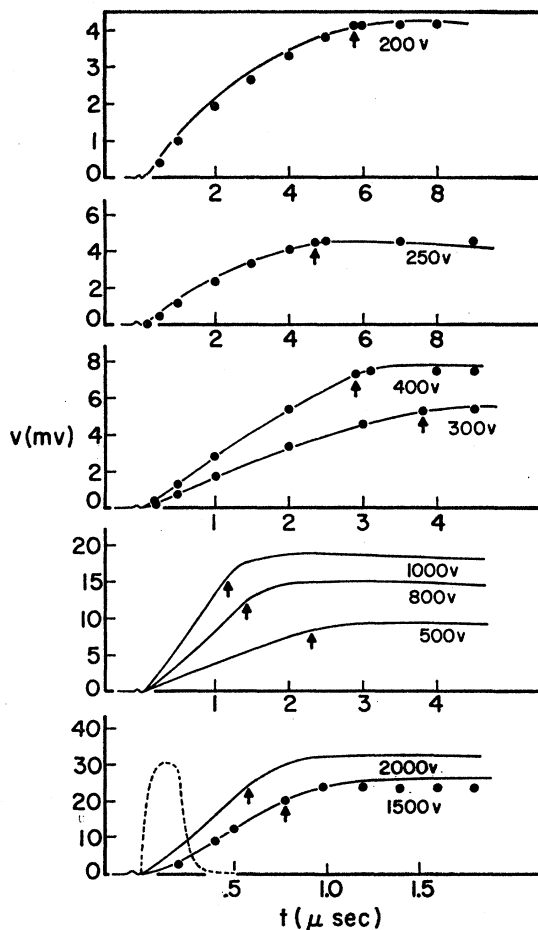


FIG. 3. Oscilloscope traces; air-grown sample. The arrows indicate the transit time. The circles are values calculated from Eq. (2) (see text). The dotted curve is an image of the x-ray pulse.

of the crystal thickness.<sup>11</sup> However, the amount of energy appearing in this portion of the spectrum is a relatively small fraction of the total x-ray energy.

### (a) Air-Grown Crystals

The lifetime of electrons in crystals grown in the presence of oxygen is several orders of magnitude greater than in crystals grown in vacuum or in inert atmosphere.<sup>12</sup> In general, the air-grown crystals have electron lifetimes of a few microseconds, so that the electrons can be displaced distances of the order of the crystal thickness with low fields. Consequently, the interpretation of the data is more straightforward than when the carriers are trapped very close to the irradiated surface. The forward polarity (electrons pulled away from the irradiated electrode into the crystal) and reverse polarity responses will be discussed separately. However, it should be mentioned here that the schubweg of the holes is very small compared to that of the electrons and, consequently, the contribution to the forward polarity pulse resulting from holes returning to the irradiated electrode is very small.

#### Forward Polarity Pulses

If a simple trapping model is applicable to these crystals,<sup>5</sup> the pulse shape is described by Eq. (2). A set of oscilloscope traces is reproduced in Fig. 3. Also shown is an x-ray pulse as observed with a scintillating crystal and a photomultiplier. The voltage across the sample is specified with each trace and the temperature is 215°K. These curves were traced from projected images of the 35-mm photographs of the scope pictures. The small "wiggles" at the beginning of each pulse result from a pickup signal from the x-ray pulsing equipment, and aid in determining the starting point of the pulse.

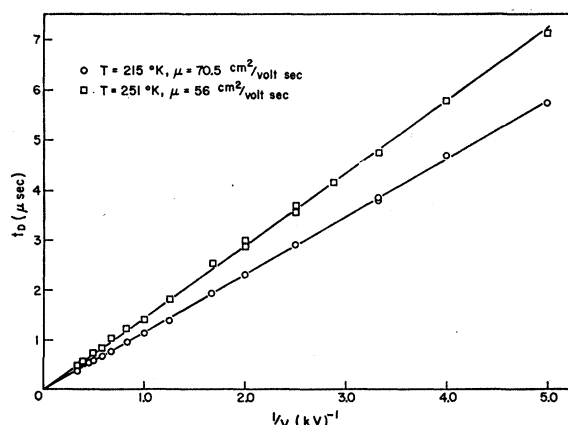


Fig. 4. Transit time  $t_D$  vs  $1/V$ ; air-grown sample.

<sup>11</sup> The absorption was calculated from the mass absorption coefficient of Ag and Cl given in the *Handbook of Chemistry and Physics*, 33rd Ed.

<sup>12</sup> F. C. Brown and F. Seitz, *Photographic Sensitivity*, Maruzen Company, Ltd., Tokyo (1958), Vol. 2, p. 19.

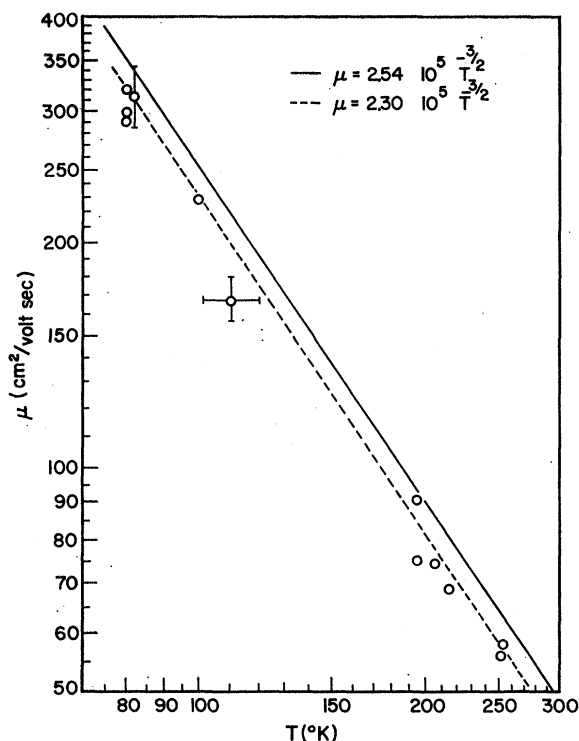


Fig. 5. Electron mobility vs  $T$ ; air-grown sample.

The mobility  $\mu$  can be calculated from the transit time  $t_D$  which is related to the applied voltage  $V$  by

$$t_D = D^2 / \mu V, \quad (3)$$

where  $D$  is the crystal thickness. If the lifetime is sufficiently long, then at time  $t_D$  charges begin collecting at the electrode and a change in slope is observed. A small arrow under each curve marks  $t_D$ . In Fig. 4,  $t_D$  is plotted vs  $1/V$  for 215° and 251°K. Straight lines are obtained, from which mobilities of 70.5 and 56 cm<sup>2</sup>/v sec for the two temperatures are calculated. In Fig. 5 the mobility is plotted vs temperature. The relative errors are estimated at about 5% at the higher temperatures and 10% at the lower temperatures. The absolute accuracy, limited by the voltage, time and temperature calibrations, and the measurement of the crystal thickness, is approximately 10%. Errors are marked for two of the points for which a greater uncertainty exists. The dashed curve in Fig. 5 fits the data reasonably well and represents the equation  $\mu = 2.3 \times 10^5 T^{-3/2}$ . The data of Haynes and Shockley<sup>13</sup> and of Brown<sup>4</sup> are represented by the solid curve ( $\mu = 2.54 \times 10^5 T^{-3/2}$ ). The difference between the two curves is well within the above-mentioned errors.

The  $T^{-3/2}$  dependence is characteristic of scattering by acoustical lattice vibrations. However, in the Hall mobility experiments of Kobayashi and Brown<sup>14</sup> it was

<sup>13</sup> J. Haynes and W. Shockley, *Phys. Rev.* **82**, 935 (1951).

<sup>14</sup> K. Kobayashi and F. C. Brown, *Phys. Rev.* **113**, 507 (1959).

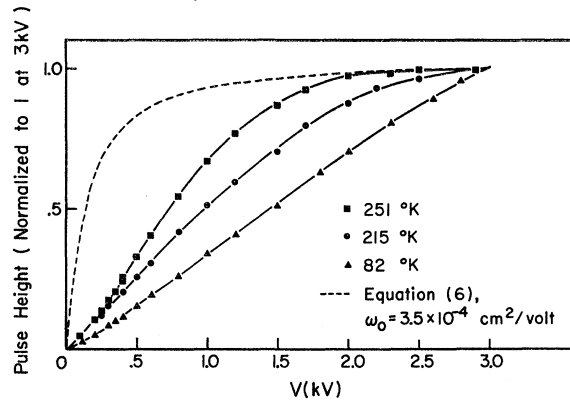


FIG. 6. Pulse height vs voltage; effect of temperature; air-grown sample.

found that at temperatures above 80°K electrons are scattered predominantly by optical mode phonons and the mobility should be characterized by a  $(e^{-\theta/T})$  dependence. The data of Fig. 5 are not sufficiently accurate to determine if this is the case and, in addition, the drift mobility in parts of the temperature range may be influenced by temporary trapping.

The lifetime  $\tau$  can be measured directly from the pulse shape at low fields. By choosing three equally spaced points,  $t_a$ ,  $t_b$ , and  $t_c$ , in the time interval  $t_1 \leq t \leq t_D$  and measuring the corresponding voltages,  $v_a$ ,  $v_b$ , and  $v_c$ , the lifetime can be calculated from the relation

$$(v_c - v_b)/(v_b - v_a) = e^{-(t_b - t_a)/\tau}; \quad t_c - t_b = t_b - t_a. \quad (4)$$

A list of values of  $\tau$  for some of the pulses of Fig. 4 is given in Table I. There is considerable variation in the value of the lifetime determined in this way. The error is larger at higher than at lower voltages. There seems to be a tendency for  $\tau$  to increase with voltage up to about 300 v. Since the transit time is long at the lower voltages, it is possible that the shape of the pulse becomes slightly altered because of the finite time constant of the integrating circuit. A reasonable average of the lifetime for this sample is about 5  $\mu$ sec.

The measurements of lifetimes at various temperatures are summarized in Table II. The lifetime decreases by a factor of 5 or 10 when the temperature is decreased from 200° to 80°K. The lifetime is given by the equation

$$\tau = 1/(N\sigma u), \quad (5)$$

where  $N$  is the trap density,  $\sigma$  the cross section, and  $u$  the average electron velocity. Since the drift velocity is small compared to the thermal velocity for the fields used in this study,  $u$  is proportional to the square root of the temperature. The increase in  $u$  causes  $\tau$  to drop only by a factor of 1.5 for the above temperature change. Consequently, either the density of effective traps or their cross section must increase as the temperature is decreased. Also, there is a tendency for the lifetime, at least at low temperature, to decrease with each successive experiment. Either the introduction of strains

TABLE I. Electron lifetimes calculated from pulse shapes (215°K).

Voltage (kv)	$t_b - t_a$ ( $\mu$ sec)	$\tau$ ( $\mu$ sec)	Voltage (kv)	$t_b - t_a$ ( $\mu$ sec)	$\tau$ ( $\mu$ sec)
200	2.0	4.3	300	1.375	5.06
200	2.25	3.8	300	1.0	5.69
250	1.75	4.8	300	1.375	5.12
250	1.75	4.3	300	1.5	4.55
300	1.5	5.7	400	1.0	5.65
300	1.25	5.1	400	1.025	4.7

from handling and cooling or the effects of exposure could be responsible; however, reannealing of the sample did not restore the lifetime to its original value.

The dependence of the pulse height on the applied voltage gives a measure of the schubweg per unit field ( $w_0$ ). Since, in the simple trapping model  $w_0 = \mu\tau$ , it provides an independent check of the values of the mobility and lifetime determined in the foregoing. The pulse height is given by Eq. (2) for  $t \geq t_D + t_1$  which, upon rewriting, becomes

$$v_s = AV \left[ 1 - \exp\left(-\frac{D^2}{w_0 V}\right) \right], \quad (6)$$

where  $A$  is a constant independent of  $V$ . Figure 6 shows a plot of the pulse height vs voltage.

Taking  $w_0 = 3.5 \times 10^{-4}$  cm<sup>2</sup>/v as obtained from the values of  $\tau$  and  $\mu$  given earlier, and choosing  $A$  so as to fit the point at 2.5 kv, the dotted curve is calculated. The discrepancy is evident. The experimental curve can be fitted by choosing a value of  $w_0$  10 times smaller which is clearly incompatible with the values for  $\mu$  and  $\tau$ . That these values are correct can also be seen from a more careful study of the pulse shapes. By using these values for  $\mu$  and  $\tau$  and 0.22 sec for  $t_1$ , one can calculate the pulse shape from Eq. (2). The results of such calculations are indicated by circles in some of the traces in Fig. 3; for each curve  $n_0$  was adjusted for coincidence at  $t = t_D$ . The agreement between calculated and observed values is good. The slight discrepancy at the two lowest voltages, 200 and 250 v, is in accord with the variation of the lifetime shown in Table I. The continuing rise of the pulse after  $t = t_D + t_1$  is, in part, a consequence of the fact that the x-ray pulse is not square but has a finite tail. However, for some of the pulses of Fig. 3 the "overshoot" is longer than this tail. The effect is most evident in the 800- and 1000-v pulses where the rise continues for nearly 1  $\mu$ sec after  $t_D$ , while the shape of the x-ray pulses indicates that the saturation should occur in 0.5  $\mu$ sec after  $t_D$ , as indeed it does at the highest voltages. The explanation is possibly related to the existence of a small number of shallow traps near the illuminated surface, which retain electrons for a short period of time and then release them into the conduction band, thus giving rise to a delayed arrival at the back electrode.

Since the pulse shapes agree reasonably well with

TABLE II. Temperature variation of electron lifetime for sample -5.

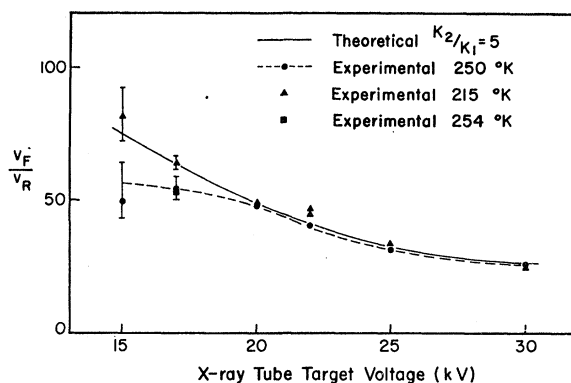
$T$ (°K)	Run No.	( $\mu$ sec)	$T$ (°K)	Run No.	( $\mu$ sec)
80	9	1.5	194	11	3.5
80	11	0.75	205	10	6.0
82	17	0.5	215	17	5.0
100	9	1.0	251	17	5.5
120	9	1.2	254	21	5.3

Eq. (2) it is believed that throughout the volume of the crystal the simple trapping model applies and that the anomalous  $PH$ - $V$  curve is related to some effects in the surface region. In such a "two-region" model the pulse height depends on the number of electrons produced in the surface region that enter the second region, as well as on the schubweg in the second region. The effect of the first region on the transit time and pulse shape is negligible if it is very thin compared to the crystal thickness and if the schubweg in the second region is large. The number of electrons reaching the second region decreases as the lifetime in the first region decreases and increases as the voltage is increased. The shortening of the lifetime may be due to recombination in the illuminated region or to trapping by defects present in the surface layer. Since the shape of the observed  $PH$  vs  $V$  curve is not very sensitive to the x-ray intensity or the penetration depth (target voltage and material), the first cause seems less probable. The strong temperature dependence illustrated in Fig. 6 (the schubweg, and thus the theoretical curve does not vary much with temperature) can be explained by either mechanism. The latter mechanism, however, accounts for the long tail in the pulses at higher temperatures which, as mentioned earlier, may be the result of delayed reemission from the traps in the surface region. The defects are possibly introduced during the surface preparation of the samples. The results of Van Heyningen<sup>6</sup> concerning the influence of the surface treatment on the  $PH$ - $V$  curves are in agreement with this interpretation.

A quantity of interest is the average ionization energy, i.e., the ratio of the total energy in the x-ray pulse to the total number of electrons excited into the conduction band. If one assumes that for the highest voltage essentially all of the electrons produced are pulled through the entire crystal, inducing a voltage  $v_s$ , then the average ionization energy  $\epsilon$  is given by

$$\epsilon = Ie/Cv_s, \quad (7)$$

where  $I$  is the total x-ray energy striking the crystal. The values for  $\epsilon$  lie between 17 and 31 eV and are high compared with 7.5 eV as determined from nuclear-counter-type experiments.<sup>3</sup> An ionization energy of 7.5 eV is also consistent with studies of photographic emulsions exposed to x rays. The ionization energies determined in this investigation thus indicate that not all of the electrons produced are collected at the

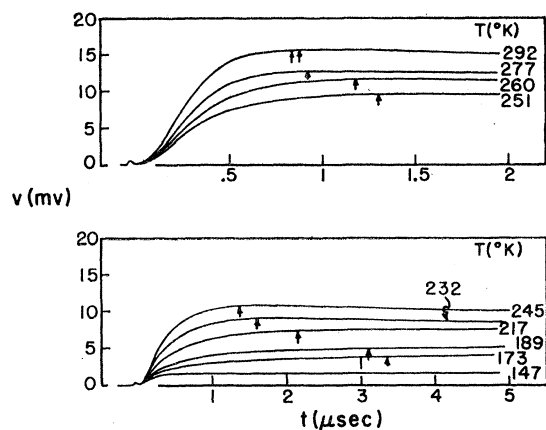
FIG. 7. Ratio of forward to reverse pulse heights ( $v_F/v_R$ ) vs x-ray tube target voltage.

opposite electrode, which is consistent with the idea that the  $PH$ - $V$  curve anomalies result from recombination or trapping in a surface layer.

#### Reverse Polarity Pulses

It was stated earlier that the displacement of holes was much smaller than that of the electrons. The time dependence of the reverse pulses is consistent with this statement. However, the intensity dependence of the reverse pulse height provides conclusive evidence that electrons play the dominant role. At a constant target voltage the pulse height varies linearly with intensity. At high target voltage, 25 kV, the pulse height is much larger, about 2.5 times in one sample, while at 15 kV, it is much smaller, about one-half, than for the same intensity at 20 kV. This behavior is in sharp contrast to the behavior of the forward pulses where points for all target voltages fall on the same line. Since the pulse height depends not only on the number of electrons but also on the distance they travel before reaching the irradiated electrode, the more penetrating radiation should indeed give rise to larger reverse pulses.

A quantitative analysis given elsewhere<sup>7</sup> permits the calculation of the ratio of forward to reverse pulse heights, assuming that only electrons are mobile, and that the field is high enough so that all electrons reach the electrode. The results depend on a factor  $K_2/K_1$ , which is the ratio of the free carrier production by the characteristic radiation to that by the continuum. In Fig. 7 the ratio of pulse heights is plotted as a function of target voltage for 215° and 251°K, together with the theoretical curve calculated with a value of 5 for  $K_2/K_1$ , which is well within the wide range of values indicated in the literature. The agreement is good except for the points for 15 and 17 kV at 251°K. Though these points are less accurate because of very small pulse heights, they are definitely below the theoretical curve, indicating that reverse pulses are larger than foreseen by the theory. If this is a result of hole motion, then at 15 kV, about 0.1 mV (or 25% of the pulse height) is the result of the holes, and this contribution should not

FIG. 8. Oscilloscope traces, He-grown sample,  $v = 500$  v.

change with target voltage. Since the pulse is about 1.2 mv at 30 kv, the part due to holes becomes less important and is within the experimental error. At 215°K the holes are frozen in and all the points fall on the theoretical curve. The schubweg for holes can be calculated from the formula

$$w = CD\epsilon v / eI, \quad (8)$$

where  $v$  is the induced voltage due to holes, 0.1 mv, and the other symbols are the same as used earlier. Taking  $\epsilon = 25$  ev as determined from the forward polarity response and an intensity  $I$  of  $1.2 \times 10^{-4}$  ergs/pulse,  $w$  becomes  $0.915 \times 10^{-3}$  cm, and the schubweg per unit field is  $w_0 = 1.3 \times 10^{-7}$  cm<sup>2</sup>/v. If an ionization energy of 7.5 ev is used,  $w_0 = 3.9 \times 10^{-8}$  cm<sup>2</sup>/v. These values are rather small, but not unreasonable, and account for the difficulty of observing hole motion at temperatures below 250°K.

### (b) Helium-Grown Crystals

Crystals grown and annealed in an inert atmosphere (He) have a much shorter lifetime and show a much more complex behavior than do air-grown crystals. In particular, there are marked variations as the temperature is changed.

At low temperature ( $\sim 100^\circ\text{K}$ ) the results agree with experiments by other authors. The motion of holes is believed to be negligible compared to that of the electrons since the variation of the reverse polarity pulse heights with target voltage is similar to that obtained with the air-grown crystals.

The forward polarity pulse saturates very quickly, indicating a short electron lifetime. At low voltages the saturation time increases, but determination of the lifetime is impossible. Measurements of the mobility lack precision and are subject to doubt because of possible temporary trapping effects.<sup>3</sup> Estimates yield values for  $\mu$  of the order of 200 to 300 cm<sup>2</sup>/sec, which is consistent with the results for the air-grown material. The schubweg can be determined from the pulse height

TABLE III. The schubweg per unit field of electrons in the He-grown crystals.

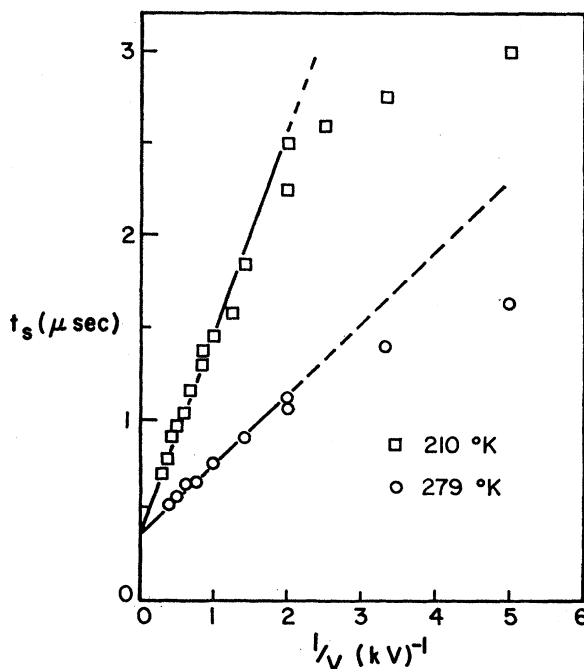
Sample No.	$T$ (°K)	$w_0$ (cm <sup>2</sup> /v)	
		$\epsilon = 25$ ev	$\epsilon = 7.5$ ev
1	100	$1.9 \times 10^{-6}$	$6.3 \times 10^{-7}$
1	100	$2.7 \times 10^{-6}$	$9.0 \times 10^{-7}$
2	106	$2.3 \times 10^{-6}$	$7.7 \times 10^{-7}$
3	80	$3.8 \times 10^{-6}$	$12.7 \times 10^{-7}$
3	80	$3.9 \times 10^{-6}$	$13.0 \times 10^{-7}$
10	82	$2.5 \times 10^{-6}$	$8.3 \times 10^{-7}$

and the average ionization energy. In Table III values of  $w_0$  are listed for  $\epsilon = 25$  ev and  $\epsilon = 7.5$  ev. The calculations with  $\epsilon = 25$  ev are in better agreement with the results of Van Heyningen,<sup>6</sup> who found  $w_0$  to be in the range of  $10^{-6}$  to  $4 \times 10^{-6}$  cm<sup>2</sup>/v.

The pulse height increases linearly with the field and no saturation is detected. This behavior is in agreement with the small schubweg listed in Table III. The slopes of the lines are proportional to the x-ray intensities.

At high temperatures (170°–280°K) the pulse height increases significantly with temperature. Some of the pulse shapes for a potential of 500 v are reproduced in Fig. 8. At temperatures below 150°K the pulses have a rise time comparable to the x-ray pulse width, but at higher temperatures a long tail begins to appear (see, for example, the 173°K pulse). At still higher temperatures the saturation time again becomes short.

The dependence of  $t_s$  on temperature and voltage suggests a model in which electrons are trapped in shallow traps and reemitted as they drift through the

FIG. 9. Saturation time ( $t_s$ ) vs  $1/V$ ; He-grown sample.

crystal. The saturation time  $t_s$  is then

$$t_s = N(\tau_1 + \tau_2) + t_1, \quad (9)$$

where  $\tau_1$  is the average time an electron spends in the conduction band before being captured by a shallow trap,  $\tau_2$  the average time spent in each trap, and  $N$  the number of times the electron is trapped in its transit through the crystal.  $N$  is determined by the ratio of the total distance  $d$  traveled to the product of the drift velocity and  $\tau_1$ , or

$$t_s = (dD/\mu V \tau_1)(\tau_1 + \tau_2) + t_1, \quad (10)$$

The observed dependence of  $t_s$  on voltage, Fig. 9, is in accord with this formula at high field intensities. The deviation at lower voltages can be regarded as a sign that the schubweg has become comparable to, or smaller than,  $d$ . Since  $\tau_2$  decreases with increasing temperature more rapidly than  $\mu$ , the slope of the lines will also decrease as the temperature is raised, as is indeed observed. From Fig. 9 it can also be seen that the intercept,  $V = \infty$ , is  $\sim 0.3 \mu\text{sec}$ , which, if the tail of the x-ray pulse is included in the value of  $t_1$ , is in agreement with Eq. (10). Finally, it must be pointed out that the distance  $d$  is not the crystal thickness. Assuming normal values for the mobility, the saturation time for high fields would have to be much longer than is actually observed, if the electrons were to reach the back electrode. Thus, one is again led to a "two-region" model, as in the case of the air-grown crystals. The essential difference is in the properties of the second region, which has a very long lifetime in air-grown crystals but a short one in helium-annealed samples. In addition, it seems that at least in the first region

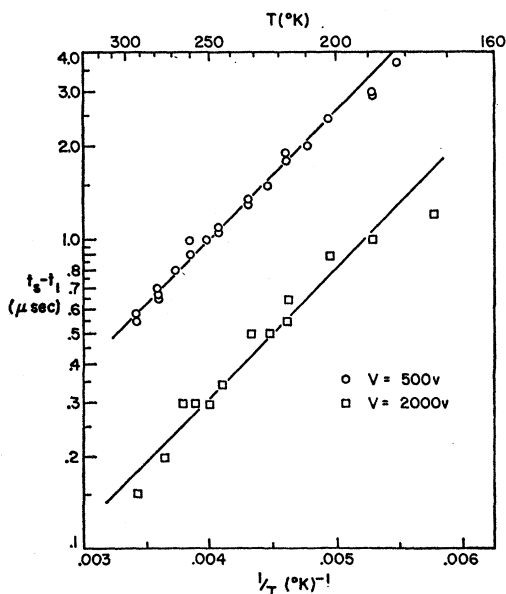


FIG. 10. Saturation time minus x-ray pulse width ( $t_s - t_1$ ) vs  $1/T$ .

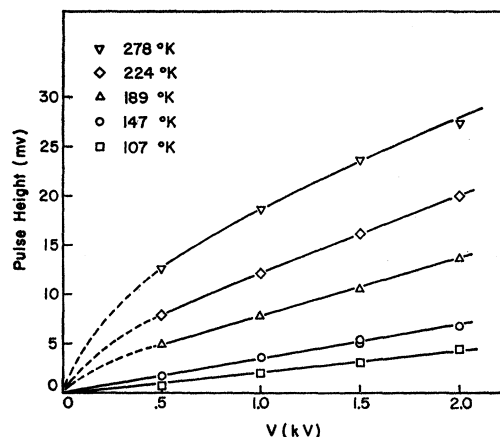


FIG. 11. Pulse height vs voltage; He-grown sample.

(near the surface) shallow traps are present in the helium-annealed specimens.

In the temperature range where the temporary trapping contributes markedly to the saturation time,  $\tau_2$  will be greater than  $\tau_1$ . If all traps lie at the same level, with an energy  $U$  below the conduction band, then

$$1/\tau_2 = s e^{-U/kT}, \quad (11)$$

where  $s$  is the attempt frequency. Assuming  $\mu = \mu_0 T^{-3/2}$  and  $s = s_0 T^{3/2}$ , one obtains

$$t_s = \frac{dDT^{-3/2}}{\mu_0 s_0 V \tau_1} e^{U/kT} + t_1. \quad (12)$$

If  $t_1$  is given by Eq. (5) and  $N$  and  $\sigma$  are temperature independent, then  $\tau_1$  is proportional to  $T^{-3/2}$  through the thermal velocity and consequently  $t_s - t_1$  should depend exponentially on  $1/T$ . In Fig. 10 the values of  $t_s - t_1$ , where  $t_1$  is taken as  $0.3 \mu\text{sec}$ , are plotted on a logarithmic scale vs  $1/T$ . For the 500-v data a straight line is obtained from which an activation energy of 0.081 eV is calculated. The data for the higher voltage 2000 v show more scatter, but the activation energy is consistent with a value of about 0.08 eV. Electrical glow experiments show a large release of trapped charge in the range of  $35^\circ\text{K}$  which is attributed to a trapping level of 0.08 eV.<sup>6</sup> It is also interesting to note that the structure of this glow peak is particularly variable with the individual crystal. Van Heyningen<sup>6</sup> suggests that singly charged impurity atoms may provide such levels.

An upper limit may be placed on  $d$  in the following way. At  $280^\circ\text{K}$   $t_s$  is approximately  $0.8 \mu\text{sec}$ . By substituting this value into Eq. (10) and using  $t_1 = 0.3 \mu\text{sec}$  to include the tail of the x-ray pulse, and  $\mu = 55 \text{ cm}^2/\text{v sec}$ , then  $d \cdot \tau_2/\tau_1 = 5 \times 10^{-2} \text{ cm}$ . Since at this temperature  $\tau_2 > \tau_1$ ,  $d$  must be less than  $5 \times 10^{-2} \text{ cm}$ .

The cross section of the shallow traps can be calculated if  $d$  is known. With  $\tau_2 = 10^{-7} \text{ sec}$  at  $200^\circ\text{K}$  and  $U = 0.081 \text{ eV}$ , Eq. (11) yields a value of  $10^9 \text{ sec}^{-1}$  for the attempt frequency  $s$ . With this value for  $s$ , and



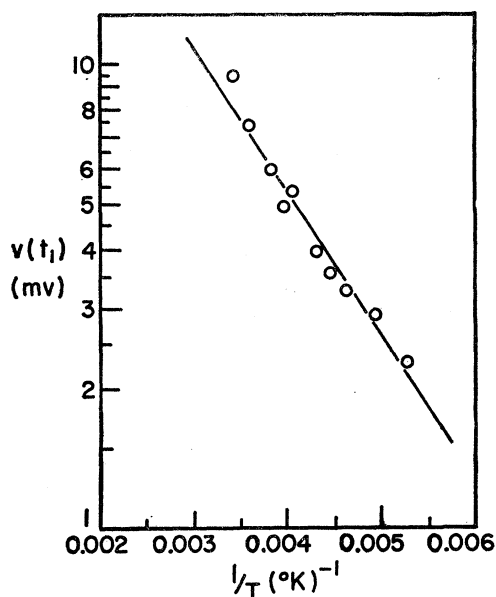


FIG. 12.  $v_{t1}$  vs  $1/T$ , He-grown sample.

taking  $d=10^{-2}$  cm, a cross section  $\sigma$  of  $10^{-16}$  cm $^2$  is obtained by means of a relation derived by Herring,<sup>15</sup> assuming  $m^*=m$ .

The field dependence of the pulse height is given in Fig. 11. At low temperatures the curves are straight lines, while at high temperature the curves have a steeper slope at low than at high fields. This behavior supports the "two-region" model proposed in the foregoing. The first region is assumed to have a long electron lifetime relative to the second region and thus is characterized by a longer electron schubweg. Since the slope of the  $PH$ - $V$  curves is proportional to the schubweg per unit field  $w_0$ , the changing slope in Fig. 11 suggests that at low voltages, where the electrons move mainly in the first region, a large  $w_0$  applies, while at high fields most of the electrons traverse the first region and the further increase in displacement is determined by a smaller  $w_0$  characteristic of the second region. At very low temperatures the "temporary" (shallow) traps of the first region hold electrons for a long time compared with the observation time, thus decreasing the schubweg per unit field in the first region and producing a completely linear  $PH$ - $V$  curve. It is possible that the existence of a longer lifetime region near the surface is caused by the inward diffusion of adsorbed oxygen during the annealing process.

By referring back to Fig. 8, it is seen that the pulse height increases with temperature. According to the "two-region" model, above about 200°K the pulse height should be independent of temperature, since in this temperature range and for moderate voltages the electrons are displaced through the first region, but

penetrate only a small distance into the second region. A close examination of Fig. 8 reveals that the difference between the maximum height and the value at 0.3  $\mu$ sec is 5 mv for all the pulses taken above 200°K. Thus the temperature affects only the induced voltage during the excitation time. The temperature dependence of the induced voltage at the end of the x-ray pulse  $v_{t1}$  is shown in Fig. 12. In the range from 180° to 280°K it is approximately exponential. The activation energy is  $\sim 0.06$  ev, which is remarkably close to the value obtained for the depth of the shallow traps in the surface region. However, there does not seem to be any simple model which relates this activation energy to the trap depth. Possible explanations of the exponential behavior of  $v_{t1}$  are only very speculative. It should be noted, though, that the increase in pulse height with voltage at the higher temperatures also occurs only during the excitation time, which suggests that recombination may be an important factor.

The effect of previous exposure on the pulse heights is also of interest. For instance, in a specific experiment a few pulses were applied during the cooling of the crystal. They give rise to pulse heights about 30% below the values obtained later. The saturation time was about the same. Similar increases in pulse height after the sample was exposed to only a few pulses were observed in other crystals of this type. The effects of previous exposure seem to indicate that, in addition to the shallow traps, there is a small concentration of very deep traps which significantly affects the electron lifetime and which holds electrons for periods of time of the order of hours, even at 250°K. The fact that the pulse height increases after the first set of measurements indicates that approximately 20 pulses supplied sufficient electrons to fill the deeper traps in the long-lifetime region ( $\sim 10^{-2}$  cm thick) near the irradiated electrode. Assuming that the deep traps are uniformly distributed in this region and that all of the electrons produced by the 20 pulses are eventually captured by them, their density is  $\sim 10^{10}$ /cc.

Finally, it is interesting to note that the reverse polarity pulses are of the same magnitude or even slightly larger than those of the air-grown samples. Again, this confirms the idea that in the helium-grown samples the surface region has a relatively long electron lifetime. The variation of the reverse pulse heights with x-ray tube target voltage was similar to that with the air-grown samples, which is the justification for the statement made earlier that the contribution of the hole motion is not significant.

### (c) Crystals with Additions of $\text{Cu}^+$ Ions

The experiment of Moser, Nail, and Urbach on photolytic darkening of AgCl crystals indicate that  $\text{Cu}^+$  ions trap holes rather than electrons.<sup>16</sup> That the

<sup>15</sup> C. Herring, *Fundamental Formulas of Physics*, edited by D. H. Menzel (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1955), p. 630.

<sup>16</sup> F. Moser, R. Nail, F. Urbach, *J. Phys. Chem. Solids* **9**, 217 (1959).

ion does not act as an electron trap is also borne out by the present study. The behavior at low temperatures was very similar to that of the He-grown crystals and the values of the schubweg per unit field of electrons is approximately the same as given in Table III. This result indicates that the  $\text{Cu}^+$  ions do not act as effective electron traps. The reverse polarity response, too, was similar to that of the pure crystals, and, if Moser's interpretation is correct, is further proof that the reverse pulses are a result of electron rather than hole motion.

As in the case of the He-grown crystals, the height of the forward polarity pulses increases with temperature. The increase of the pulse height with temperature is smaller in magnitude than in the case of the He-grown samples but is approximately exponential with temperature for  $T > 200^\circ\text{K}$ . The activation energy is 0.048 eV for  $V = 500$  v, but the increase in the induced voltage does not occur only during the excitation time as with the He-grown crystals. A lower response for the first set of measurements supports the hypothesis of the presence of a small concentration of deep traps, discussed in the previous section.

In contrast with the case of the He-grown crystals, the saturation time for  $T > 180^\circ\text{K}$  does not change with temperature or applied voltage. Also, the curves of the pulse height vs the applied field are linear except at the highest temperatures, where there is a small curvature. Thinking again in terms of the two-region model the results with the  $\text{Cu}^+$ -doped crystal seem to indicate that, in this case, the two regions have comparable, short electron lifetimes, or that there exists only one region with a short lifetime. On the other hand, the number of electrons escaping the region where they are produced still depends on the recombination process in this region and, if this recombination occurs via not too deep traps, the number of conduction electrons will increase with temperature. The differences between the doped and undoped crystals may possibly be the result of the diffusion of adsorbed oxygen into the crystals. In the case of the doped crystals, the adsorbed oxygen may preferentially react with the cuprous ions and thus will not increase the electron lifetime in the region near the surface.

#### (d) Crystals with Addition of Ni Ions

The effect of a very small concentration of Ni ions on the photoconductive response is very striking; the addition of 1 ppm essentially quenches the photoconductivity. At  $80^\circ\text{K}$  no pulses were detected in either the forward or reverse direction with the highest available field and x-ray intensity. By assuming the same average ionization energy as in the air-grown

samples, an upper limit of the schubweg per unit field is  $10^{-8}$  cm<sup>2</sup>/v. If the mobility in these crystals is also the same, i.e.,  $\sim 300$  cm<sup>2</sup>/v sec, the lifetime is less than  $3 \times 10^{-11}$  sec, which implies that the trapping cross section is greater than  $300$  (Å)<sup>2</sup>. At  $160^\circ$  and  $210^\circ\text{K}$ , very small pulses were observed and  $w_0$  was estimated to be of the order of  $5 \times 10^{-8}$  cm<sup>2</sup>/v. At the highest temperature,  $270^\circ\text{K}$ , no response was detected, which may be due to a relaxation of the internal field, since the ionic conductivity of this sample was very high. The luminescence of Ni-doped crystals is also quenched, and thus nickel acts as a "killer" impurity.

### V. CONCLUSIONS

Measurement of the photoconductivity excited by short x-ray pulses provides a suitable method for the study of lifetimes and mobilities of carriers in AgCl. In air-grown and carefully annealed crystals the lifetime of electrons is of the order of a few microseconds, and the mobilities agree with other measurements reported in the literature. The pulse shape is in good agreement with the calculations. A study of the pulse heights as a function of applied field suggests the presence of a thin surface layer which exhibits a short electron lifetime, possibly caused by traps introduced during the surface treatment. Growing and annealing in an inert atmosphere reduces the electron lifetime by several orders of magnitude. Pulses in a temperature range from  $200^\circ$  to  $280^\circ\text{K}$  show long "tails" which indicate trapping and reemission of electrons during transit through a surface layer. The depth of these traps is estimated at 0.08 eV. The addition of  $\text{Cu}^+$  ions does not change essentially the behavior of crystals annealed in an inert atmosphere, except for the trapping phenomena in the surface layer. Thus  $\text{Cu}^+$  ions do not act as effective electron traps. The addition of Ni ions reduces the lifetime at  $80^\circ\text{K}$  to less than  $3 \times 10^{-11}$  sec, corresponding to a very large capture cross section.

The schubweg of holes is negligible compared with that of electrons; in fact no hole motion was detected except above  $250^\circ\text{K}$ . The reverse polarity pulses are explained by electrons returning to the irradiated electrode from the illuminated region which has a finite thickness resulting from the penetration of the x-rays.

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