

first become available, Herman⁸ showed that such a calculation, even with the adjustment of the various force constants, could not account for the observations. It has now been shown by Herman¹¹ that by including the interaction between rather distant neighbors, say fifth or sixth, the theory can be adjusted to give the observed dispersion relations. As a result, sufficiently many parameters are available so that it is possible to fit a variety of measured results in a way that would not be possible if only nearest and next-nearest neighbors were important in lattice vibrations.

The necessity for including a force between distant neighbors seems to indicate that there is some mechanism in germanium giving rise to a long-range force. One such mechanism, a quadrupole distortion of the valence

¹¹ F. Herman (private communication).

electron gas, has been postulated by Lax¹² but as yet calculations attempting to fit theory to experiment have not been made. It is hoped that by the inclusion in the calculation of some model for the long-range force, the theory will be able to explain the experimental results with only a few parameters.

ACKNOWLEDGMENTS

We wish to thank Dr. F. Herman of the RCA Laboratories, Princeton, New Jersey for kindly supplying us with the germanium crystals, and for many discussions concerning the theoretical aspects of the above work. We also wish to thank Dr. P. Keinle who assisted with a few of the measurements.

¹² M. Lax, *Phys. Rev. Letters* **1**, 131 (1958).

Low-Temperature Luminescence and Photoconductivity of AgCl*

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The magnitudes and the decay processes of the luminescence and the photoconductivity of AgCl have been simultaneously investigated between 4°K and 210°K. The decrease of the luminescence intensity with increasing temperature can be attributed to a competing recombination process, not accompanied by visible radiation, and having a thermal activation energy of $E=0.05$ ev. The decay times are not monotonic functions of temperature, but show maxima. These maxima can be explained in terms of a model in which energy is transported from the site of absorption to the luminescence center by mobile holes and electrons. Delay in this transport is caused by hole and electron trapping, and temperature dependence of the delay determines the temperature dependence of the decay times. Decay curves calculated on the basis of this model are in qualitative agreement with the observed data. The relative magnitudes of the luminescence and photocurrent decay times and the dependence of the decay and rise times on annealing indicate that if the major portion of the photoconductivity is due to electron motion, then luminescence occurs when holes are captured. It is suggested that this recombination occurs at silver ion vacancies.

I. INTRODUCTION

THE production of excited states of solids, such as conduction band electrons, by the absorption of light quanta may be thought of as the first step in a cyclic process whereby energy is absorbed, stored for a time, and then emitted either as photons or phonons. This paper is concerned with the electronic processes associated with the latter two steps in this cycle, i.e., storage and emission. The investigation was limited to low temperatures so that changes in the crystal due to the photographic process can be considered negligible.

It is possible to distinguish between two types of cycles. In one case energy transport is possible so that the sites of the absorption process and of the return to

the ground state are not necessarily the same. In the second case transport is not possible so that the whole cycle of absorption, storage, and emission takes place in localized centers such as the luminescence center considered by Seitz.¹ In many materials it seems reasonable that both cycles may occur simultaneously. However, it is also apparent that under particular experimental conditions one or the other of the two types of cycles may be predominant as, for example, in the case of impurity activated luminescence.

In AgCl both the luminescence and the photoconductivity are excited by wavelengths in the tail of the fundamental absorption band, thus suggesting that luminescence and photoconductivity are part of the same cycle, a charge transport cycle. While the results of other experiments also suggest this relationship between the luminescence and photoconductivity,

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¹ F. Seitz, *Trans. Faraday Soc.* **35**, 74 (1939).

Moore² concluded that luminescence does not occur when photoelectrons are captured. One of the objectives of this investigation has been to re-examine the question of whether or not the luminescence process involves transport.

In photoconductors the dissipation of energy by luminescence must be intimately connected with the photoconductive properties if charge transport is necessary for luminescence. One means of determining if this charge transport is necessary is by simultaneous measurements of luminescence and photoconductivity and such measurements have been made as a function of several parameters.

Energy may be considered to be stored in conduction band electrons, in valence band holes, in trapping states associated with electrons and holes, and in metastable states associated with the luminescence center. From information of the lifetimes and capture times of these states, deductions may be made as to the type of centers involved and also whether or not the same centers are associated with the luminescence and with the capture of electrons and holes. Measurements by Waldner³ indicate that the luminescence and photoconductivity decay times, and so the probabilities for capture and emission, are of the same order of magnitude at 77°K. In addition, Waldner and Wood⁴ found the rise of both quantities with the start of the excitation to be dependent on conditions immediately preceding the excitation in a qualitatively similar fashion. However, the time constants for the rises were not the same. These results suggest that the luminescence and the photoconductivity may be related to the same cycle but not in a simple fashion. Therefore, more extensive measurements were made of the transient characteristics of the luminescence and photocurrent.

It is known that annealing under various conditions can be used as a method of altering the recombination and trapping states in semiconductors and insulators. Waldner, for instance, found that in AgCl the luminescence decay times could be changed appreciably by annealing. Measurements have therefore also been made of the decay and rise properties as a function of annealing conditions.

II. EXPERIMENTAL PROCEDURE

Apparatus

Only the more important features of the experimental portions of this work are described here. Several parts of the equipment are treated by Waldner³ and a more thorough description appears in the author's thesis.⁵

² A. Moore, thesis, Cornell University, Ithaca, New York, 1949 (unpublished).

³ M. Waldner (to be published); M. Waldner, thesis, Cornell University, Ithaca, New York, 1954 (unpublished).

⁴ R. Wood, thesis, Cornell University, Ithaca, New York, 1953 (unpublished).

⁵ D. A. Wiegand, thesis, Cornell University, Ithaca, New York, 1956 (unpublished).

Measurements were made between 4° and 210°K with the sample mounted in a vacuum cryostat of the type described by Duerig and Mador.⁶ The sample was held in place by spring-loaded contacts and was surrounded by a shield at the temperature of the sample. Temperature measurements were made with a gold-cobalt/silver-gold thermocouple embedded in the sample adjacent to the irradiated portion. The thermocouple was calibrated for each low-temperature run by fitting a calibration curve obtained from the Bureau of Standards to the measured helium and nitrogen points. While the temperatures given at the nitrogen and helium points are accurate to within a few degrees, intermediate temperatures which were obtained by allowing the cryostat to warm from nitrogen or helium temperatures are not as meaningful since temperature differences as high as 10° were observed between different portions of the sample.

In the majority of cases excitation was by monochromatic light obtained from an AH6 high pressure mercury lamp and a Bausch and Lomb quartz monochromator. The luminescence intensity was measured by a photomultiplier tube, precautions having been taken to eliminate the exciting radiation by the use of filters and advantageous geometry. The photocurrent was determined by applying an ac or dc voltage source in series with the sample and a resistor and by recording the voltage across this resistor. Alternately, by the use of an ac bridge both conductivity and capacitance changes under irradiation were measured. For decay measurements the excitation was interrupted either by a rotating or by a solenoid shutter of the types described by Waldner.³ The pulse length is roughly 2 milliseconds, the pulse rate is 120 per second for the rotating shutter, and the time constant which determines the time response of the whole system is 5 μ sec for the rotating shutter and 50 μ sec for the solenoid shutter. For the rise measurements the excitation was turned on by the solenoid shutter. In some cases the initial portion of the decay curves were found by Waldner³ to be very close to the system decay characteristic. To study this portion of the decay pulsed x-ray excitation was used.⁷ The x-ray tube contains a grid so that the current is controlled as in a conventional triode. Rise and decay times of 0.3 microsecond and variable pulse lengths can be obtained with this apparatus.

Samples

Measurements were made on crystals of AgCl grown at Cornell, at the Kodak Research Laboratories, and at the Harshaw Chemical Company.⁸ Both the Cornell and the Kodak materials were grown in a Stockbarger

⁶ W. H. Duerig and I. L. Mador, *Rev. Sci. Instr.* **23**, 421 (1952).

⁷ The author is indebted to R. Rosa and R. Castner for the construction, and to Professor L. P. Parrat for his guidance in the design and use of the x-ray apparatus.

⁸ The author is indebted to Dr. F. Urbach of the Kodak Research Laboratories and Mr. Glen Slack of Cornell University for making AgCl available.

furnace by the Bridgman method. However, while the Cornell crystals were grown in a platinum crucible in air, the Kodak crystals were grown in a Pyrex or quartz container in an atmosphere of dry nitrogen. Nitrogen which had been first passed through liquid chlorine was bubbled through the molten Kodak material to remove oxide and then dry nitrogen alone was passed through to remove dissolved chlorine.⁹

While the purities of the Cornell and Harshaw materials are unknown, the following results of a spectrographic analysis were supplied by Kodak: traces of iron, lead, magnesium, and silicon were found. The iron concentration is given as about 2×10^{-7} , the lead as 10^{-7} , and the others as less. Tests for aluminum, cadmium, copper, manganese, nickel, tin, and zinc were negative.

Two different geometries were used: bars $0.2 \times 0.2 \times 2.0$ cm and circular wafers 0.025 cm thick and 1 cm in diameter. Both types were cut to rough dimensions with a jeweler's saw. The bar-like samples were then worked to the final dimensions on a ground glass plate with a sodium thiosulfate solution (30%), while wafers were machined to final dimensions on a lathe. The samples were then etched with ammonium hydroxide or hydrochloric acid and thoroughly rinsed in distilled water.

Electrodes were put on opposite 0.2×2.0 cm faces of the bar samples and on the flat sides of the wafers. Both evaporated gold and painted graphite electrodes were used. The bar samples were irradiated in a direction perpendicular to the applied electrical field direction, while the wafer samples were irradiated through one electrode and in the field direction. Since measurements failed to detect any differences between these two geometries, it seems reasonable to assume that the observed photoconductivity is a volume rather than a surface effect.

III. EXPERIMENTAL RESULTS

Only the green-blue luminescence band characteristic of AgCl was studied and the emission spectrum is similar to that reported by other investigators.¹⁰ Under some conditions a red and yellow luminescence was also observed but was not studied in detail. The photoconductivity reported in this investigation is of the so-called secondary type and the dependence on the exciting wavelength is similar to that reported by others,¹¹ with a maximum at about 3800 Å at 77°K.¹²

⁹ Nail, Moser, Goddard, and Urbach, *Rev. Sci. Instr.* **28**, 275 (1957).

¹⁰ Farnell, Burton, and Hallama, *Phil. Mag.* **41**, 157 (1950); Farnell, Burton, and Hallama, *Phil. Mag.* **41**, 545 (1950).

¹¹ W. Caldwell, thesis, Cornell University, Ithaca, New York, 1948 (unpublished).

¹² A review of the physical properties of the silver halides is given by F. Seitz [*Revs. Modern Phys.* **23**, 328 (1951)], and a review of some more recent experiments is given by Wiegand.⁵

Temperature Dependence

In Fig. 1 the magnitudes of the luminescence and the ac photocurrent are given as a function of temperature for a bar-type sample of Kodak AgCl. A similar temperature dependence of luminescence was obtained for Cornell material, and earlier Wood⁴ found that the photoconductivity of a wafer-type sample of Cornell material depends on temperature in the same fashion.

The decrease of the luminescence with increasing temperature suggests a thermally activated competing nonradiative recombination process. Following others¹³ the probability per unit time for a luminescent transition can be taken as a constant d , independent of temperature, and the probability per unit time of a competing nonradiative process as $b_0 \exp(-E/kT)$. The luminescence efficiency is then given by

$$\frac{L}{L_0} = \frac{d}{d + b_0 \exp(-E/kT)} = \frac{1}{1 + (b_0/d) \exp(-E/kT)}, \quad (1)$$

where L is the luminescence at the temperature T , and L_0 is the luminescence at $T=0$. In Fig. 2 the luminescence data of Fig. 1 are replotted as $(L_0/L - 1)$ vs $1/T$. For L_0 the value at $T=4^\circ\text{K}$ is taken. It is seen that Eq. (1) is followed and that an energy $E=0.05$ eV and a value of the ratio $b_0/d=2 \times 10^5$ are obtained. The same energy but a slightly smaller value of the ratio b_0/d were obtained from Cornell material for exciting wavelengths of 3160 Å and 3650 Å. The deviation from a straight line at low temperatures is probably not significant since the curve in this region is very sensitive to the value chosen for L_0 . The break in the curve at the higher temperature is unexplained.

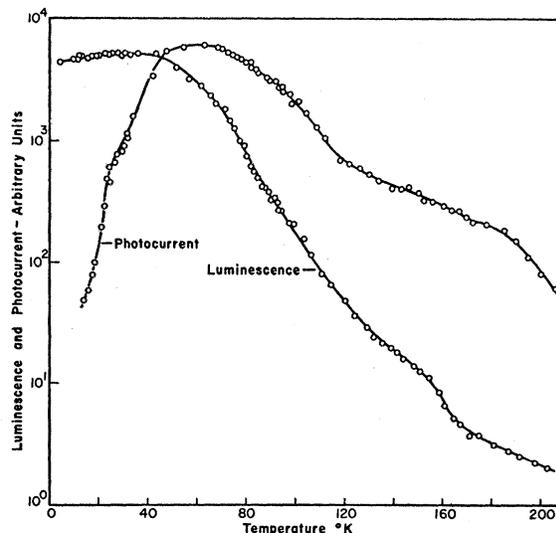


Fig. 1. Luminescence and photocurrent vs temperature. The exciting wavelength is 3650 Å and the frequency of the applied field is 2000 cps.

¹³ G. Garlick, *Luminescent Materials* (Oxford University Press, Oxford, 1949), p. 6.

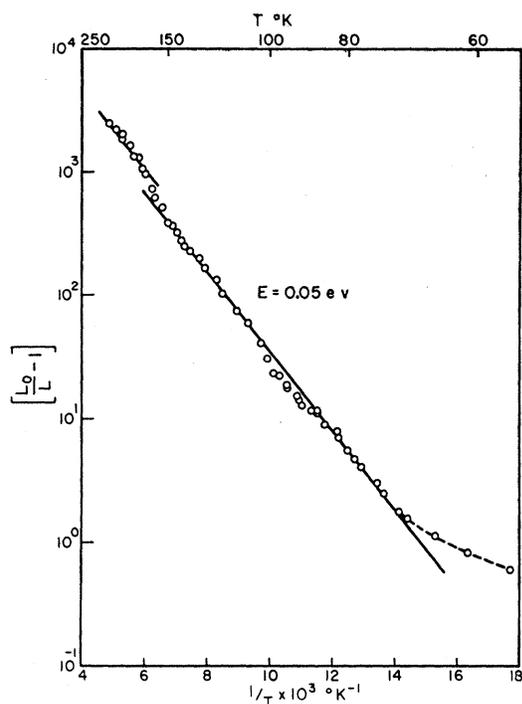


FIG. 2. Luminescent data of Fig. 1 replotted as $[L_0/L - 1]$ vs $1/T$, where L_0 and L are the luminescence at $T = 4^\circ\text{K}$ and at the temperature T , respectively. From the slope an energy of 0.05 eV is obtained and from the intercept a value of $b_0/d = 2 \times 10^5$.

If b_0 is taken as the order of magnitude of the lattice vibrational frequency of 10^{13} per second and if d is taken as roughly the transition probability for an allowed optical transition or 10^8 per second, a ratio $b_0/d = 10^5$ is obtained in agreement with the observed value. A similar functional dependence of the luminescence on temperature was found by Farnell *et al.*¹⁰ for a mixed precipitate of AgBr and 4 mole per cent AgI above 20°K , and by Kane¹⁴ for AgCl above 77°K . However, in both cases the constants of Eq. (1) were quite different from those found in this work. It is believed that Kane used Harshaw AgCl.

The photoconductivity of Fig. 1 is replotted vs $1/T$ in Fig. 3. The best fit of a straight line to the data between 14° and 50°K yields an activation energy of 0.01 eV. Wood⁴ first obtained this value for a wafer sample of Cornell AgCl. Lehfeltd¹⁵ found the same general temperature dependence of the photocurrent; however, the activation energy which can be calculated from his curve is much larger than that given above. Lehfeltd measured dc conductivity so that the difference may be due to space charge effects. This exponential increase of the photocurrent with increasing temperature in the low-temperature range suggests that a thermal activation process is necessary to create conduction electrons from excited states. However, the

¹⁴ E. Kane (private communication).

¹⁵ W. Lehfeltd, *Nachr. Ges. Wiss. Göttingen* 1, 171 (1935), Fachgruppe II.

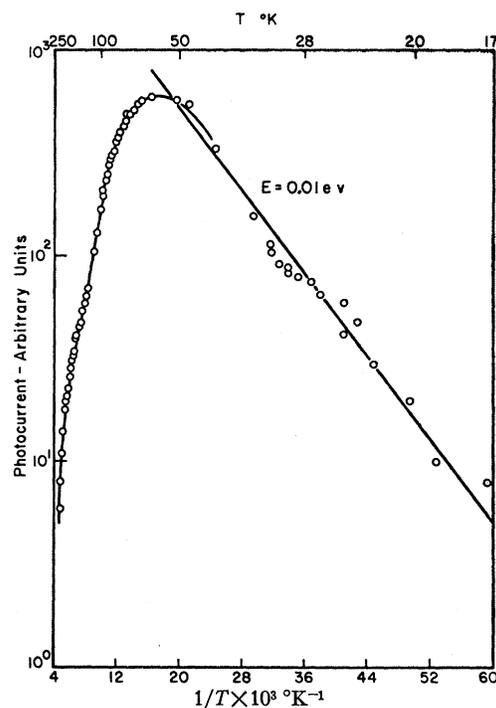


FIG. 3. Photocurrent data of Fig. 1 replotted vs $1/T$. From the slope an energy of 0.01 eV is obtained.

secondary photoconductivity is also directly proportional to the mobility and lifetime of the carriers, and further may depend on space charge effects which can effect the internal field. Therefore an interpretation of the data of Fig. 3 requires additional information and a discussion is deferred to a later section.

The photocurrent curve of Fig. 1 indicates structure between 20° and 30°K . This structure also appears in Wood's⁴ data. At a later date and with the use of an ac bridge a small maximum in the photoexcited conductivity of this sample was observed at roughly 23°K . However, when the data is plotted as in Fig. 3 an average slope gives the same activation energy as that obtained from Fig. 3. This difference between the data of Fig. 1 and the latter observations may be due to changes in the sample, since it received considerable irradiation at higher temperatures between the two sets of measurements. Indications of structure also appear in the photocurrent curve of Fig. 1 above 80°K and a maximum has been observed at roughly 180°K . Additional structure between 80° and 180°K was found to be frequency dependent and is probably associated with a dispersion phenomena to be considered separately.¹⁶

All of the above photocurrent data were obtained by using continuous excitation. Measurements were also made of the current pulses between 70° and 240°K excited by light pulses of a few microseconds duration. The pulses were applied every $1/120$ second and the

¹⁶ D. A. Wiegand and H. S. Sack (to be published).

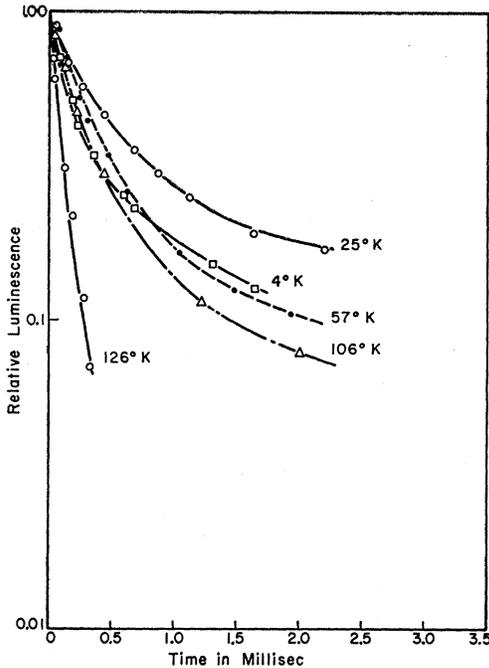


FIG. 4. Typical luminescent decay curves for several temperatures. Fractional luminescence vs. time after removal of excitation. $\lambda_{ex} = 3650 \text{ \AA}$.

electric field was reversed for each pulse to minimize space-charge effects. Maxima in the magnitude of the current pulses were observed by this method at roughly 80° and 200°K .

In Fig. 4 typical luminescence decay curves are given at several temperatures for Kodak silver chloride. The decay curves are not exponential, nor do they seem to be made up of exponential sections. In contrast to this the ac photocurrent decay curves, of which examples are given in Fig. 5, are either exponential or are composed of exponential sections for all temperatures. A comparison of the decay curves of the two figures will also reveal that the photocurrent decays are much slower than the luminescence decays over the whole temperature range examined. This difference in the functional form and the time of decay of the luminescent and photocurrent curves was also found for Harshaw and annealed Cornell AgCl at 77°K . In addition, the luminescence decay times for AgCl from the three sources are similar at 77°K as are the photocurrent decay times. In Fig. 6 the luminescence and photocurrent decay times are given as a function of temperature. Since the decay does not always follow an exponential law the definition of a "decay time" is somewhat arbitrary. For the present purpose the decay time is taken as the time required for the measured quantity to decrease to $1/e$ of the initial value. While the photocurrent decay time is much larger than the luminescence decay time, the general nature of the temperature dependence of the two decay times are the

same above 30°K . Because of lack of sensitivity the photocurrent decay could not be recorded below this temperature.

Although the time constant for the luminescence decay of unannealed Cornell material at 77°K was found to be smaller by roughly a factor of 10 than shown in Fig. 6, the temperature dependence of the decay times and the form of the decay curves are similar to those of Figs. 4 and 6. While the photocurrent decays of unannealed Cornell AgCl were not investigated as a function of temperature, Waldner³ found the decay times in most cases at 77°K to be much smaller than those for the Kodak material and of the same order of magnitude as the luminescence decay time of the unannealed material. In some cases the initial portions of the photocurrent decay curve for unannealed material were not greatly different from the system decay. However, by the use of the pulsed x-ray source, current decay times of roughly one to three μsec were observed. Luminescence decay times after x-ray excitation were approximately the same as after ultraviolet excitation.

It should also be noted that in the case of the unannealed Cornell AgCl Waldner found two photocurrent decay times with time constants of the order of a few microseconds and milliseconds, respectively. While for some regions of a given sample he obtained photocurrent decay curves having a "fast" and a "slow" component with the above time constants, on other regions of the same samples he obtained only the slow

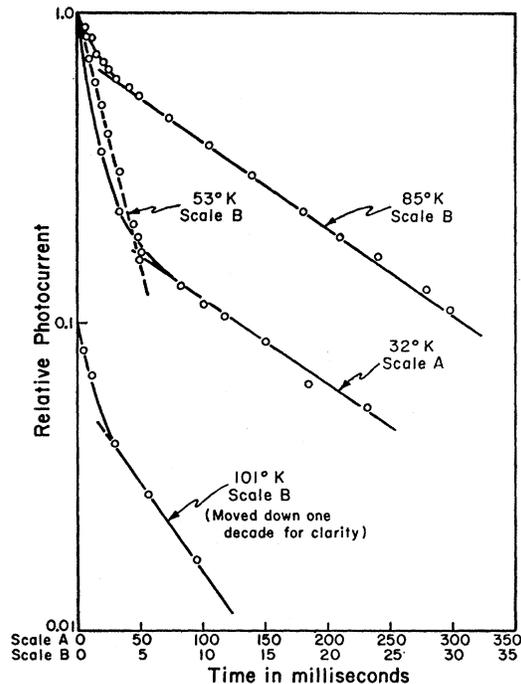


FIG. 5. Typical photocurrent decay curves for several temperatures. Fractional photocurrent vs. time after removal of excitation. $\lambda_{ex} = 3650 \text{ \AA}$ and $f = 10^3 \text{ cps}$.

or fast part. The decay was, however, more generally composed predominantly of the fast part. The luminescence decay did not exhibit a variation for different regions of one sample. This photocurrent data indicates that the samples were not homogeneous and results of this sort were not found for Kodak or Harshaw AgCl. The results for annealed Cornell AgCl are given below.

The decay curves were also found to depend on the intensity and wavelength of the exciting radiation and, in the case of the photocurrent, the magnitude and frequency of the applied voltage. While the decays are not very sensitive to intensity, the decay times in all cases decreased with increasing intensity of excitation, thus suggesting that the recombination probability increases with the density of mobile charges. The wavelength dependence is as might be expected since there is a change in effective intensity because the absorption constant is a function of wavelength. The dependence of the photocurrent on voltage and frequency is complicated by polarization and by a dispersion in the dielectric properties.¹⁶ However, the photocurrent decay curves are fairly insensitive to both the frequency and the voltage. The dependence of the luminescent and photocurrent decay on all of the above parameters is further complicated by the fact that the decay curves can generally be broken up into two or more sections which depend on the parameters in different ways.¹⁷

Dependence of Decay Properties on Annealing

To further study the dependence of the decay times on annealing conditions, wafer-type samples of Cornell

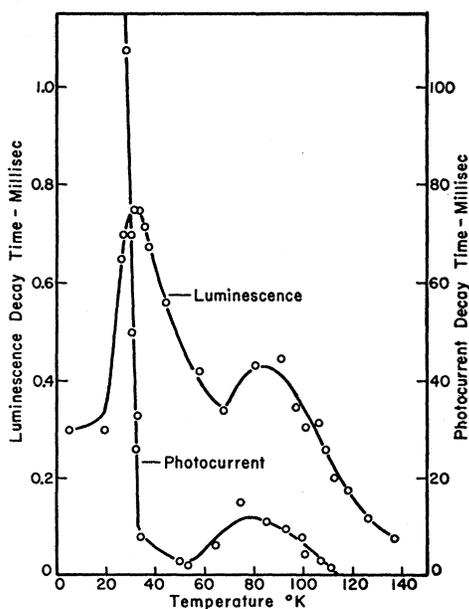


FIG. 6. Luminescence and photocurrent decay times vs temperature. $\lambda_{\text{ex}} = 3650 \text{ \AA}$ and $f = 10^8 \text{ cps}$.

¹⁷ A more complete discussion of this is given in the author's thesis.⁵

material were annealed either in vacuum or in a chlorine atmosphere at 400°C for roughly 8 hours and cooled at the rate of 33°C per hour.¹⁸ During the annealing process, the sample rested on a polished quartz shelf in a quartz tube in such a way as to be shielded from visible and ultraviolet radiation. A pressure of 10^{-5} mm of mercury was maintained during vacuum annealing by a mercury diffusion pump with a cold trap, and a continuous flow of commercial chlorine gas was maintained for annealing in a chlorine atmosphere.

Decay curves, as a function of annealing conditions, were taken only at 77°K . After annealing Cornell AgCl in vacuum, the luminescence and photocurrent decay times were found to be larger and similar to those for the Kodak and Harshaw materials. Since Waldner³ found the photocurrent and luminescence decay times generally to be of the same magnitude before annealing, these results indicate a larger change in the photocurrent than the luminescence decay time. Although the photocurrent decay after annealing was found in one case to be a function of position on the sample as observed by Waldner for the unannealed material, the photocurrent decay time was always much larger than the luminescence decay time.

Immediately after annealing in a chlorine atmosphere the luminescence decay was composed of an initial fast portion which was not always significantly different from the system decay curve, and a slower component. However, this state was not stable. The initial portion of the luminescence decay curve changed with time after chlorine annealing and approached that found after vacuum annealing. While the photocurrent decay was not observed immediately after chlorine annealing, it was found to be the same as after vacuum annealing at a time when the luminescence decay was the same as after vacuum annealing. These observations suggest that the photocurrent decay changed with time after annealing in a chlorine atmosphere.

Qualitative measurements failed to indicate any large change in the luminescence emission spectrum as a result of vacuum annealing. After chlorine annealing a yellow color of luminescence was observed in addition to the green-blue band, and the intensity of this yellow luminescence decreased with time after annealing.

Luminescence vs Wavelength

If the luminescence process occurs in isolated centers, such as that considered by Seitz,¹ there should be an absorption band for exciting the luminescence corresponding to an optical transition between two discrete energy levels. However, attempts to find such an absorption band at liquid nitrogen temperature have failed. The luminescence was observed as a function of exciting wavelength between 4000 \AA and 2700 \AA for equal numbers of incident quanta per second. While the

¹⁸ The author is indebted to Mr. Glen Slack for making the annealing furnace available.

luminescent efficiency is low at 4000 Å, it was found to rise abruptly at roughly 3600 Å and to remain constant for further decreases in wavelength to 2700 Å. Because the manufacturer's calibration curve of phototube current *vs* incident wavelength was used in determining the exciting intensity, this data can only be taken as approximate. However, similar results were obtained by using two different types of phototubes to measure the incident intensity. More recently Colwell and Sack¹⁹ have found that both the photocurrent and the luminescence increase abruptly at the onset of the fundamental absorption band, and that the luminescence does not decrease appreciably down to 2600 Å. These results indicate that there is no absorption band for luminescent excitation separate from the fundamental absorption band and thus that luminescence and photocurrent are excited by whatever process is responsible for the fundamental absorption band.

Rise Measurements

Measurements have also been made of the rise of the luminescence and photocurrent. Waldner³ and Wood⁴ found that at 77°K the rise of the luminescence and photocurrent in unannealed Cornell AgCl is dependent on the history of the sample immediately preceding the start of irradiation. If the rise curves were investigated by turning the irradiation on immediately following a prior irradiation, the rise times were not significantly different from the system rise time which was of the order of 50 μsec in this case. However, if several minutes were allowed to elapse between irradiations, or if the sample was irradiated with infrared, or warmed to room temperature and recooled, the rise times were found to be much larger and to vary from 0.1 sec to 1.0 minute. In almost all cases the photocurrent rise was slower than the luminescence rise.

After annealing in vacuum the luminescence rise was faster than the system rise time for all conditions of measurements described above, while after annealing in a chlorine atmosphere the rise was similar to that before annealing. The photocurrent rise, in contrast, was found to be roughly independent of annealing. If, as suggested by the work of Waldner and Wood, the rise is due to the necessity of filling trapping states, then the different dependence of these rise characteristics on annealing for the luminescence and photocurrent suggests that different traps are involved in the two processes.

IV. MODELS FOR TEMPERATURE-DEPENDENT DECAY CURVES

The temperature dependence of the decay curves can be explained by the simple model represented in Fig. 7(A), which is treated in detail in the Appendix. In this model the density of recombination centers, c , is assumed to be much greater than the density of free

carriers, n , and is considered constant during the decay. All quantities are assumed independent of position. While the capture probabilities at the recombination and trapping centers are taken as independent of temperature, the escape probability from the trap has the usual exponential temperature dependence. If retrapping during the decay is neglected, a solution to the differential equations which describe the decay is

$$n = n_0[(1-S) \exp(-t/\tau_1) + S \exp(-t/\tau_2)], \quad (2)$$

where n_0 is the density of electrons at the start of the decay process, and τ_1 , τ_2 , and S are given by the relations

$$\tau_1 = 1/\text{probability per second for capture at a recombination center}, \quad (3a)$$

$$\begin{aligned} \tau_2 &= 1/\text{probability of thermal ionization of a trap per second} \\ &= 1/b_2 = (1/b_0) \exp(E/kT), \end{aligned} \quad (3b)$$

$$S = \frac{b_2 k_2 N_T}{(k_1 c - b_2)(k_2 n_0 + b_2)}. \quad (3c)$$

N_T is the total density of trapping centers, k_1 is the probability of capture at a recombination center per second per unit center density, and k_2 is the corresponding probability for a trapping center. Therefore the decay is composed of two exponential terms and the time constant of one, and the magnitude of both are temperature dependent. Decay curves calculated from Eq. (2) as a function of temperature are given in Fig. 8.

Two points are of interest in Fig. 8: (1) The time required to decay to some value n_1 increases and then decreases with increasing temperature. (2) The decay curves cross each other. The observed dependence of the time constant τ_0 on temperature may then be a direct consequence of trapping effects. As shown in Fig. 6, both the luminescence and the photocurrent time constants have maxima as a function of temperature, and the decay curves are made up of exponential sections for some conditions. In addition, the luminescence decay curves cross in the same manner (see Fig. 4). The fact that the luminescence decay

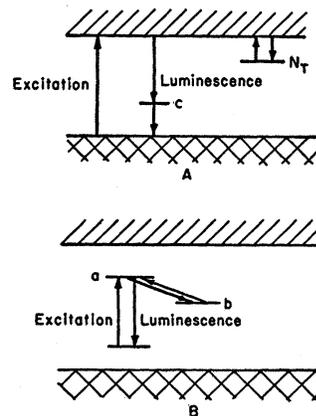


FIG. 7. Possible models for luminescence and photoconductivity.

¹⁹ J. Colwell and H. S. Sack (private communication).

curves are not composed of exponential sections suggests that the model in the form considered is too simple, and that the capture processes are not strictly monomolecular. However, it should also be noted that the curves of Fig. 8, which are the sum of two exponential sections, are not clearly broken up into these sections for the time range given.

Qualitatively the behavior of the decay curves may then be understood by the following considerations. At a low temperature, such that the lifetime of electrons in the conduction band is much shorter than that of electrons in traps, and at a high temperature, such that the inverse holds, the initial parts of the decay curves which are of interest here are determined by the lifetime of free electrons. However, at some intermediate temperature, where the lifetime of trapped electrons is of the same order of magnitude as that of the free electrons, the decrease of the density of free electrons during the decay is slowed because of replenishment from the trapping states. Thus an increase and decrease of the decay time with increasing temperature is observed. This mechanism is treated in a qualitative fashion by Garlick and Wilkins.²⁰

As pointed out by Garlick and Wilkins, there should be a thermoluminescent glow peak associated with each of the maxima in the curve of luminescence decay time ν s temperature. While Moore² did not make measurements below liquid nitrogen temperature, he did observe glow peaks at 80°K and 240°K. The glow peak at 80°K

may therefore be associated with the maximum at about 80°K in Fig. 6.

If the simple considerations of the model of Fig. 7(A) apply, the luminescence magnitude should be directly proportional to the density of electrons in the conduction band so that the luminescence decay should be the same as the photocurrent decay. As indicated in Figs. 4, 5, and 6 and in the above discussion, the decay times, the forms of the decay curves, and the annealing dependence of the decay times for luminescence and photocurrent differ. However, it must also be pointed out that the differential equations of Model A also apply to another model, that of Fig. 7(B). In this model, which only concerns luminescence, the temperature-independent lifetime of state a and the temperature-independent transition probability from a to b replace the probabilities for capture at the luminescence center and the trap, respectively, while the temperature-dependent transition probability from b to a replaces the escape probability from the trap. The number of centers in the excited state, a , of Fig. 7(B), and thus the luminescence, which is proportional to this number, is then given by a relationship of the same form as (2). Therefore, while the temperature dependence of the photocurrent decay time can be explained by the mechanism of Model A, the temperature dependence of the luminescence decay time can be attributed to the mechanisms of either Model A or Model B.

V. DISCUSSION

The experimental results indicate that the complete luminescence process most probably does not take place in an isolated center such as that of Model B, Fig. 7. No excitation band characteristic of a luminescent center was found; the luminescence is excited by the same wavelengths which produce photocurrent in the region of fundamental absorption. This alone is a rather strong argument against isolated centers. However, there are also other facts which support this point of view. In the first place, annealing changes the luminescence decay and rise characteristics without seriously altering the luminescent emission band. In addition, the parameters associated with the nonradiative competing recombination process are the same for different materials and independent of the decay time. It seems rather doubtful that it could be possible to alter the metastable states associated with the luminescent center without altering the whole electronic configuration of the center, and thereby producing a change in the emission band and the energy and jump frequency associated with the nonradiative transition. It should also be noted that this luminescent center would have to be rather complex since it must account not only for the nonradiative transition, but also for the two metastable states associated with the two maxima in the curve of decay time ν s temperature (Fig. 6). Quantum efficiency measurements at low tem-

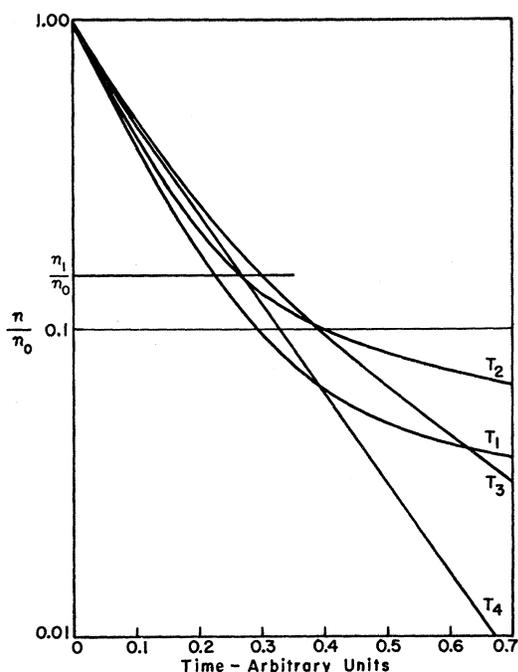


FIG. 8. Decay curves from Eq. (2). Increasing subscripts of T_1 , etc. indicate increasing temperature.

²⁰ G. Garlick and M. Wilkins, Proc. Roy. Soc. (London) A184, 408 (1945).

peratures can be taken as further evidence that isolated luminescence centers are not acceptable. Meidinger²¹ found the luminescence quantum yield to be close to unity for silver halide emulsion, while Lehfeldt¹⁵ found the quantum yield for photoelectrons in crystalline AgCl to be 0.5. In addition, Moore² found the ratio of luminescence quanta to number of photoelectrons to be approximately 10^{-4} at 198°K. However, as shown in Fig. 1, the luminescence efficiency increases by a factor of 2.5×10^5 with decreasing temperatures between 198° and 40°K, indicating a ratio of luminescence quanta to photoelectrons of about 0.25 at the low temperature. These measurements suggest that many of the exciting quanta producing mobile electrons must also be effective in producing luminescence, and that luminescence is a major form of energy dissipation. It therefore appears that the luminescence transition must take place when either a mobile electron or hole is captured.

Before discussing the possible relationship between the luminescence and the photoconductivity if luminescence does occur when mobile charges are captured, a remark is necessary concerning the photocurrent. The frequency dependence of the photocurrent can be interpreted in terms of a polarization at the electrodes which influences the internal electric field.¹⁶ Therefore, the photocurrent decay is a measure not only of the decrease of the density of mobile carriers, but also of changes in the polarization and internal field. While direct measurements of the internal field were not made, several observations indicate that polarization does not influence appreciably the initial part of the decay which is of interest here. In fact, the decay time is practically independent of frequency between 2.0×10^2 cps and 2.0×10^5 cps at 77°K while the conductivity changes by a factor of about 20, presumably due to a variation in polarization. This seems to indicate that the photocurrent decay is not influenced by changes in polarization during the decay but is a measure of the decay of the density of mobile charges. In addition, the conductivity increases approximately linearly with intensity and as the square route of the applied voltage while the initial decay is fairly insensitive to these quantities.

If luminescence occurs when mobile electrons are captured at a center such as *c* of Fig. 7(A), then for a simple monomolecular recombination process the luminescence and photocurrent decay should be the same. Yet, as already noted, the time constants and the forms of the decay curves are different, thus indicating that the model, at least in this simple form, is not correct. In addition the time constants changed by different amounts with vacuum annealing, and under most conditions the luminescence decays faster than the photocurrent. However, if the recombination process is more complex, e.g., if it is bimolecular, then differences in the decay curves can be expected. For other than mono-

molecular recombination the time constants should be intensity dependent and the magnitudes of the luminescence and photocurrent should not depend on intensity in the same functional way. In the present work the time constants were found to be relatively insensitive to the exciting intensity and both the luminescence and photocurrent increased in the same functional way with intensity, thus suggesting that the recombination processes are essentially monomolecular and that luminescence does not occur as a result of electron capture.

It is also possible that there are several types of centers, such as *c* in Fig. 7(A), at which electrons may be captured, but that visible luminescence occurs only at one of these. However, the quantum efficiency measurements cited above suggest that at low temperatures there may be only one important recombination center, the one at which the luminescence occurs. More accurate quantum efficiency measurements are needed. Finally, the rise characteristics of the luminescence were altered appreciably by annealing, whereas the rise characteristics of the photocurrent were altered little, if any, by the same treatment. If this rise time is interpreted as the time required to fill traps, then the traps associated with the luminescence rise cannot be the same as the electron traps associated with the photocurrent rise.

While it cannot be conclusively argued that the luminescence does not occur when mobile electrons are captured, all of the above considerations seem to indicate that it does not. It is therefore suggested that luminescence occurs when a hole is captured at a recombination center as illustrated in Fig. 9. Recombination may then take place by the capture of a hole at the center with the emission of a luminescent quantum, followed by the capture of an electron to complete the recombination process. It is possible to obtain a self-consistent interpretation of the observations by such a model. The temperature dependence of the luminescence and photocurrent decays are then determined by the hole and electron lifetimes and trapping times, respectively, with the possibility of coupling via the recombination center.²² The temperature dependence of the decay times may then be explained by the trapping mechanism considered in connection with Model A, Fig. 7. For instance, PT_1 and PT_2 in Fig. 9 indicate two hole-trapping levels to

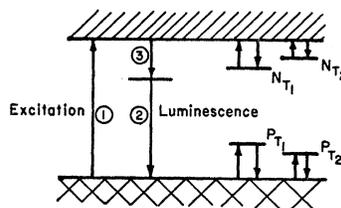


FIG. 9. Combined model for luminescence and photoconductivity.

²² A discussion of the model and a summary of the data has been previously presented [D. A. Wiegand, Bull. Am. Phys. Soc. Ser. II, 1, 205 (1956)].

²¹ W. Meidinger, Physik Z. 40, 517 (1939).

be associated with the two maxima in the curve of luminescence decay time vs temperature of Fig. 6.

The magnitudes of the luminescence and photocurrent decay times of Kodak, Harshaw, and annealed Cornell AgCl indicate on the basis of the model of Fig. 9 that the hole lifetime may be considerably shorter than that of the electron. This is in agreement with the observations of Lehfeldt,¹⁵ Waldner,³ Brown,²³ Werman,²⁴ and others whose measurements indicate that electrons give a much larger contribution to the photocurrent than holes. However, there is still an unresolved question concerning the mobility of holes in AgCl. While Brown has been unable to observe mobile holes and has placed an upper limit on the hole range of 1/10 that of the electron range for equal mobility of holes and electrons between 86° and 150°K, Moore² and Werman have found evidence of mobile holes at 198° and 77°K, respectively. Werman, however, observed a hole schubweg of less than 1/10 that of the electron.

The increase of both the luminescence and photocurrent decay times with annealing indicates a decrease in the density of the recombination centers and/or a change in the density of traps. The fact that the photocurrent decay changed by a larger amount could be due to the different effects of annealing on electron and hole traps. The dependence of the rise-time measurements on annealing seem to support this hypothesis. The recombination centers and trap densities may be decreased because of an annealing out of imperfections or increased because of a diffusion in of impurities from the surface. The similarity of the annealed Cornell material and the as received Kodak AgCl suggest the former explanation.

If luminescence does occur when a mobile charge is captures, the increase of the photocurrent with temperature between 14° and 50°K cannot be ascribed to a temperature-dependent generation efficiency of mobile charges since the luminescence does not increase in the same temperature range. This increase must then be ascribed to effects such as polarization, mobility, or lifetime. The temperature dependence of the dielectric properties indicates that it is not due to polarization.¹⁶ The data of Allemand and Rossel,²⁵ and Brown and Dart²⁶ indicate an increase in the drift mobility with temperature between 40° and 80°K, so that the observed increase in photocurrent may be due to mobility considerations. The increase of drift mobility can be associated with either impurity scattering or trapping. The decrease of the photocurrent decay time, τ_0 , in the temperature range from 28° to 40°K could indicate a decrease in the electron lifetime. However, this decay time is also influenced by trapping and if the

density of traps is sufficiently large the complete observable decay will be determined by the rate of escape from traps. The large decrease of τ_0 between 28° and 40°K suggests a trapping mechanism. Therefore independent measurements of electron lifetime and microscopic mobility as a function of temperature are necessary before a conclusion can be reached.†

The author would like to advance tentatively the idea that the recombination centers are silver ion vacancies, which are known to exist in the silver halides. If this is the case, the hole lifetime might be expected to be shorter than the electron lifetime, since holes will be attracted by a Coulomb-like force while after hole capture there will be no long-range forces of attraction for electrons. Annealing might be expected to decrease the density of colloidal silver. The observed increase in the decay times after vacuum annealing can then be accounted for by this mechanism. The work of Luckey²⁷ indicates that chlorine can be taken up and evolved from AgCl. Chlorine may be absorbed by an increase in the density of holes and silver ion vacancies in the lattice. When the external chlorine atmosphere is removed after annealing, the chlorine will tend to escape, thus decreasing the density of silver ion vacancies. The effect of annealing in a chlorine atmosphere on the decay times and the change in the decay times with time after the annealing can then be explained at least in a qualitative fashion by these considerations.

VI. ACKNOWLEDGMENTS

The author is deeply indebted to Professor Henri S. Sack, who suggested the problem, for his guidance and direction throughout the course of this study. He also wishes to thank Dr. Michael Waldner and Dr. Irving Ames for many fruitful discussions and suggestions, and Howard Maine and John Gelvey for technical assistance.

APPENDIX

In considering the model of Fig. 7(A) the following assumptions have been made:

- (1) The excitation and the charge distribution are independent of position in the crystals.
- (2) The density of recombination centers is much larger than n and so can be considered constant, independent of the state of excitation.

The differential equations of balance are then

$$dn/dt = R - k_1cn - k_2n(N_T - n_i) + b_2n_i, \quad (4a)$$

$$dn_i/dt = k_2n(N_T - n_i) - b_2n_i, \quad (4b)$$

²³ F. C. Brown, *Phys. Rev.* **97**, 355 (1955).

²⁴ M. Werman, thesis, Cornell University, Ithaca, New York, 1956 (unpublished); M. Werman, Office of Naval Research Technical Report No. 1, Contract No. Nonr-401(16) NR 017-402, September 15, 1956 (unpublished).

²⁵ C. Allemand and J. Rossel, *Helv. Phys. Acta* **27**, 212 (1954).

²⁶ F. C. Brown and F. Dart, *Phys. Rev.* **108**, 281 (1957).

† *Note added in proof.*—Recent measurements by K. Kobayashi and F. Brown (private communication) show that the Hall mobility decreases continuously with increasing temperature above 20°K, thereby indicating that the increase in photocurrent between 20° and 50°K is due to trapping rather than microscopic mobility considerations.

²⁷ G. Luckey (private communication).

where R is the excitation rate of free charge, n_t is the density of trapped electrons, and the other terms have been defined earlier. Equations (4) are nonlinear simultaneous differential equations. As a first approximation let us assume that the retrapping term $k_2n(N_T - n_t)$ is small during the decay. Then with $R=0$ at $t=0$, Eqs. (4) may be rewritten as

$$dn/dt = -k_1cn + b_2n_t, \quad (5a)$$

$$dn_t/dt = -b_2n_t. \quad (5b)$$

A solution of these equations is

$$n_t = n_{t_0}e^{-b_2t}, \quad (6a)$$

$$n = n_0 \left[\left(1 - \frac{b_2k_2N_T}{(k_1c - b_2)(k_2n_0 + b_2)} \right) e^{-k_1ct} + \frac{b_2k_2N_T}{(k_1c - b_2)(k_2n_0 + b_2)} e^{-b_2t} \right], \quad (6b)$$

where n_0 and n_{t_0} are the values at $t=0$ and the relationship between them is obtained from setting (4b) equal to zero for the steady-state condition (8).

The assumption that the retrapping term can be neglected is valid if

$$k_1cn \gg k_2n(N_T - n_t), \quad (7a)$$

$$b_2n_t \gg k_2n(N_T - n_t). \quad (7b)$$

Equation (7a) may be readily satisfied at low temperatures since then $n_{t_0} \approx N_T$ and n_t changes slowly with time during the decay. Equation (7b) is certainly not valid at the start of the decay because at equilibrium

$$b_2n_{t_0} = k_2n_0(N_T - n_t). \quad (8)$$

However, at low temperatures n decreases much faster than n_t during the decay, so that (7b) will be satisfied for times shortly after the start of the decay.

By considering the temperature dependence of the time, t_1 , for n to decay to some constant value n_1 , it can be shown that t_1 has a maximum as a function of temperature at temperatures such that

$$k_1c > b_2. \quad (9)$$

Equation (9) is satisfied at low temperatures.

Length and Resistivity Changes in Germanium upon Low-Temperature Deuteron Irradiation and Annealing*†

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Simultaneous measurements of the length change and resistivity of high-purity germanium single crystals were made upon irradiation and annealing. The specimens were initially irradiated at 25°K with deuterons of average energy 10.2 Mev to an integrated flux of 6.2×10^{16} deuterons/cm² and annealed to room temperature. The specimens were then irradiated at 85°K to an additional flux of 9.2×10^{16} deuterons/cm² and annealed to 364°K. The specific length expansion for both bombardments was $\Delta L/L = (1.5 \pm 0.3) \times 10^{-21}/(\text{deuteron/cm}^2)$. The annealing after both irradiations showed a gradual recovery of the expansion which was observable only after warming to above 200°K. The precise determination of the onset of annealing was limited by the accuracy of the expansion measurements ($\sim 20\%$). Recovery was $\sim 50\%$ complete by 300°K and $\sim 85\%$ complete by 360°K.

I. INTRODUCTION

RADIATION damage produced in semiconductors by high-energy particle irradiation has been the subject of considerable interest in recent years.¹⁻⁶

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‡ Now at Sandia Corporation, Albuquerque, New Mexico.

¹ F. Seitz and J. S. Koehler, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 305.

The resistivity measurements agreed generally with previous results. A large increase in resistivity occurred during the low-temperature bombardments. The specimens became p -type after bombardment and annealing. On the first warmup after the bombardment at 25°K the resistivity decreased irreversibly by a factor of 10^8 between 65°K and 300°K with a large part of the decrease coming apparently between 150°K and 225°K. On the warmup from the second bombardment at 85°K an irreversible resistivity increase occurred on warming to 140°K. The resistivity then decreased irreversibly by a factor of 10^3 between 150°K and 200°K. Extensive resistivity annealing, therefore, occurred in an earlier stage of the recovery process than did the experimentally observable length change annealing.

Electrical measurements have been the prime tool in the great majority of investigations because of their sensitivity to lattice defects. Unfortunately, electrical

² J. W. Glen, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1955), Vol. 4, p. 381.

³ H. Brooks, in *Annual Review of Nuclear Sciences* (Annual Reviews, Inc., Stanford, 1956), Vol. 6, p. 215.

⁴ H. Y. Fan, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 283.

⁵ H. Y. Fan and K. Lark-Horovitz, in *Report of the Bristol Conference on Defects in Crystalline Solids, July, 1954* (The Physical Society, London, 1955), p. 232.

⁶ G. J. Dienes and G. H. Vineyard, *Radiation Effects in Solids* (Interscience Publishers, Inc., New York, 1957).