## On the Conductivity Produced in CdS Crystals by Irradiation with Gamma-Rays\*

RUDOLF FRERICHS

Department of Physics, Northwestern University, Evanston, Illinois

(Received August 1, 1949)

By combining the theory of secondary photo-currents developed by Hilsch, Pohl, Schottky, and others, with the model of a crystal phosphor by Johnson and Seitz and by Riehl and Schoen a theory of the photoconductivity in CdS crystals is given. The theory agrees qualitatively with the results of previous and present experiments. A quantitative energy scheme, which is the basis for this theory, has been determined from measurements of the emission and absorption spectra of these crystals. According to the new determined sign of the thermal e.m.f.: CdS against Cu, the photo-current in CdS is predominantly carried by electrons. The dark current follows the usual law:  $\log \sigma \sim 1/T$  with the constants  $\epsilon = 0.67$  ev and  $\sigma_0 = 1.7 \cdot 10^{-3}$  mho cm<sup>-1</sup>. In accordance with the theory the final current reached after prolonged irradiation is proportional to the square root of the intensity of irradiation. The final current follows Ohms law. The initial slope of the decay curve is proportional to the intensity of irradiation. Under periodical irradiation with gamma-rays the amplitude of the resulting alternating current slowly increases to a final value. If the electric field is temporarily removed the original conductivity is slowly restored. When a CdS crystal is heated and then cooled to liquid air temperature irradiation produces a small primary current of less than  $10^{-13}$  amp. at first. With continuous irradiation and after a slight delay this current suddenly increases until it reaches a constant value of 10<sup>-8</sup> amp.

## INTRODUCTION

SINCE the appearance of the first papers on the use of crystals for detecting nuclear rediction (1) of crystals for detecting nuclear radiation (diamond,<sup>1</sup> silver chloride<sup>2</sup> and cadmium sulfide<sup>3</sup>) there has been a growing interest in these so-called "counting crystals." <sup>4</sup> Further, a volume of literature on the photoelectric properties of CdS crystals has now accumulated.<sup>3, 4a, 5-21</sup> Inasmuch as CdS and the other counting crystals are phosphors, without exception,<sup>22</sup> and inasmuch as the mechanism of the photo-conductivity of a crystal phosphor was not yet explained, the author felt a detailed investigation of the relation

- <sup>10</sup> K. Weiss, Zeits. f. Naturfwiss 34, 212 (1947).
   <sup>10</sup> K. Weiss, Zeits. f. Naturforsch. 2a, 650 (1947).
   <sup>11</sup> H. Kallmann and R. Warminsky, Ann. d. Physik 4, 69 (1948).
   <sup>12</sup> H. Kallmann, Research 2, 62 (1949).
   <sup>13</sup> H. Kallmann and R. Warminsky, Research 2, 87 (1949).
   <sup>14</sup> L. Rozerr and H. Kallmann, Ang. d. Bhysik (6) 3, 217 (1048).
- <sup>14</sup> I. Broser and H. Kallmann, Ann. d. Physik (6) 3, 317 (1948).

<sup>15</sup> H. Kallmann and R. Warminsky, Research 2, 389 (1949).
<sup>16</sup> H. Kallmann, Ann. d. Physik 4, 61 (1948).
<sup>17</sup> G. C. Goldsmith and K. Lark Horowitz, Phys. Rev. 75, 526 (1949)

<sup>14</sup> R. Frerichs and A. F. J. Siegert, Phys. Rev. 74, 1875 (1948).
 <sup>19</sup> Rose, Weimer, and Forgue, Phys. Rev. 76, 179 (1949).
 <sup>20</sup> Fassbender, Moglich, Rompe, Ann. d. Physik (6) 3, 327

(1948)

between photo-conductivity and phosphorescence was warranted.

This paper attempts to give a model for this mechanism in CdS and describes several experiments which are the basis for the model.

#### A. The Mechanism of the Photo-Conductivity in CdS Crystals

Kallmann and Warminsky<sup>11</sup> were the first to point out that those CdS crystals which show large secondary currents are strongly phosphorescent. Thus the secondary currents in CdS as well as other crystal phosphors must be explained on the basis of the collective electron model for crystal phosphors. It will be shown, by combining the theory of secondary currents in photo-conductors, first proposed by Hilsch, Pohl, and Schottky,23 with the generally accepted model for a crystal phosphor of Seitz, Johnson, Riehl, and Schoen, that the effects observed in CdS crystals can be explained.

Irradiation of a crystal phosphor by light or by fast particles produces a positive hole at an activating impurity.<sup>24</sup> The hole is produced either by a direct lifting up of the electron from the impurity state into the conduction band or it may first be produced in the filled valence band and then shift to an activating impurity by transfer of an electron. In each case the net result is a positive hole localized in the lattice at the position of the activating impurity. It is fundamental to the mechanism described in this paper that the positive charges remain stationary. This type of photo-

<sup>\*</sup> This work was sponsored by the U. S. Navy, Bureau of Ships. <sup>1</sup>G. Stetter, Berh. d. D. Phys. Ges. 22, 13 (1941); see W. Jentschke, Phys. Rev. 73, 77 (1948). <sup>2</sup>P. J. Van Heerden, "The crystal counter," dissertation, Utrecht, 1945.

<sup>&</sup>lt;sup>3</sup> R. Frerichs and R. Warminsky, Naturwiss 33, 251 (1946).

<sup>&</sup>lt;sup>6</sup> R. Frerichs and K. Warminsky, Naturwiss 33, 251 (1940).
<sup>4</sup> A review of this development is given by: R. Hofstadter, Nucleonics 4, No. 4, 1; No. 5, 29 (1949).
<sup>4a</sup> S. G. Sizzo and J. B. Platt, Phys. Rev. 76, 704 (1949).
<sup>6</sup> R. Frerichs, Naturwiss 33, 281 (1946).
<sup>6</sup> R. Frerichs, Phys. Rev. 72, 594 (1947).
<sup>7</sup> R. Frerichs, Research 1, 208 (1948).
<sup>8</sup> C. J. Humphreys, J. Opt. Soc. Am. 39, 664A (1948).
<sup>9</sup> J. Fassbender, Naturwiss 34, 212 (1947).
<sup>10</sup> K. Weiss Zeits f. Naturforsch. 2a, 650 (1947).

 <sup>&</sup>lt;sup>21</sup> G. Hohler, Ann. d. Physik (6) 4, 371 (1948).
 <sup>22</sup> ZnS and diamond have been used in the early investigations on subjective counting of scintillations. Type II diamonds, which are best suited as crystal counters are according to Pohl and to Robertson, photo-conductors as well as phosphors. AgCl is a phosphor at low temperatures.

<sup>23</sup> R. Hilsch and R. W. Pohl, Zeits. f. Physik 108, 55 (1937); 112, 252 (1939); R. Schottky, Das freie Electron in Physik and Technik (Verlag, Julius Springer, Berlin, 1940), p. 57; R. Pohl and F. Stockmann, Ann. d. Physik (6) 1, 275 (1947).

<sup>&</sup>lt;sup>24</sup> The nature of the impurity states has been discussed by N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1948), second edition, Chapter VI.

conductivity therefore has to be distinguished from other types<sup>25</sup> in which holes and electrons both move.

How does the excitation behave when a strong electric field is applied to the crystal? We first assume a good insulating crystal, as for instance CdS at low temperatures. In this case the electron lifted up into the conduction band follows the field without delay. If the field is high enough the electron will eventually reach the anode. When the liberation of the electron takes place near the cathode the maximum current is attained. One electron is moved across the crystal per one quan-



FIG. 1. Band scheme of CdS.

tum of energy effective. Since no electrons can enter the crystal at the cathode, this process is complete as soon as the electron reaches the anode. At low fields the electron will be captured in trapping states or will recombine with the positive hole. But above a certain field, determined by the lifetime of the free electron, it reaches the anode before this trapping or recombination occurs. Further increase of the field strength does not increase the current; the current is saturated.

If we assume instead a crystal with a small electron conductivity, as for instance CdS crystals at room temperature, the process will be different. A small number of electrons will be continually lifted up by thermal impact into the conduction band from the highest intermediate filled states between the valence and the conduction band. These states may be due either to filled electron traps or to activating impurities which can give up electrons to the conduction band. There are many more of the latter, hence the transition from the activating impurities represents a more probable process. If one electron is lifted up by irradiation the positive charge of the hole as well as the negative charge of the electron become neutralized by a redistribution of the density of the conduction electrons within the crystal. The hole attracts electrons and the electron produced repels other electrons. The net effect is that an extra electron is now available in the conduction band. When the electron leaves the crystal at the anode another electron enters at the cathode. The current due to these electrons is given by

$$i = e \cdot v \cdot (P/l) \cdot \tau, \tag{1}$$

where v = mobility of the electron, P = potential applied, l = distance between the electrodes,  $\tau =$  lifetime of the hole. If a large number of primary electrons is lifted up into the conduction band and if the lifetime of the holes is long then an electron chain results, giving a large secondary current.

We consider the processes which interrupt the chain and thus restore the crystal to its original state. Electrons can be prevented from reaching the anode in three ways. They can recombine with a positive hole at the activating impurity, emitting light in this process. They can return to the activating impurity with a simultaneous loss of their energy to the lattice as "phonons." Finally they can be captured by an electron trap. The electron traps may be cracks, interfaces between crystals or dislocations of the lattice.<sup>26</sup> Storage of electrons in traps and their subsequent release accounts for the phosphorescence. The return of the electrons, which transfer some of their energy as heat, causes energy losses observed in phosphorescence.

The recombination with the activating impurities follows the usual quadratic law:  $dn/dt = -bn^2$ (b = coefficient of recombination), provided the number of holes is equal to the number of electrons *n* in the conduction band. The dark currents are of the order of  $10^{-11}$  to  $10^{-14}$  amp. but the photo-currents reach  $10^{-8}$ amp. and more. Thus the number of the electrons in the conduction band is given approximately by the number of electrons lifted up from the activating impurities and it is proportional to the absorbed energy of irradiation, *J*. The equation for the lifting up and recombining the electrons is represented by:

$$dn/dt = aJ - bn^2. \tag{2}$$

This equation neglects the capturing of electrons in traps. The trapping of a single electron affects the current in two ways. Its removal from the conduction band reduces the number of electrons available by one and at the same time the corresponding electron chain is broken. Releasing of the electron from the traps affects the current also in two ways. First it may be released into the conduction band and initiate an electron chain. This corresponds to "stimulation" in the terminology of phosphorescence. When the electron returns from the conduction band to the activating

<sup>&</sup>lt;sup>25</sup> The latter type has been thoroughly investigated by K. G. McKay, Phys. Rev. 74, 1606 (1948).

<sup>&</sup>lt;sup>26</sup> In phosphors of the ZnS type, the traps are generally assumed to be separate from the luminescent centers.

impurity, the crystal looses the trapping energy by emission of light. Second, in the alternative process, the electron may be released from the trap and lose its energy stepwise to the lattice in "phonons." It does not reach the conduction band and therefore does not take part in electron chain building. It returns to the activating impurities without emission of light. This process is the "quenching" in the terminology of phosphorescence. While stimulation temporarily increases the secondary current, quenching reduces it.

#### **B.** Experimental Results

#### a. The Band Scheme of CdS

Since the proposed theory is derived from the optical data it must agree with the band scheme of the electrons. The energies of the valence band, the conduction band, the activating impurities and the traps are given in Fig. 1. The ev values are plotted downward from the lower edge of the conduction band. For a crystal at room temperature the upper edge of the valence or highest filled band is situated at 2.41 ev below the lower edge of the conduction band. This energy difference varies inversely with the temperature,<sup>27</sup> and the levels shift correspondingly, as represented in Fig. 1.

The activating impurities, i.e., the luminescent centers, extended from 1.42 to 1.85 ev in the crystals investigated.28 These values were determined by mea-



FIG. 2. Temperature dependence of the conductivity of CdS.

<sup>27</sup> F. A. Kroger, Physica 7, 1 (1940); F. Moglich and R. Rompe, Zeits. f. Physik 119, 473 (1942); A. Radkovsky, Phys. Rev. 73, 749 (1948); G. Hohler, reference 21.

410-10 4/10-1 13/ Xamp ละเกิ 410 154 136 108 90 72 54 36 18 O sec

FIG. 3. Rise of the photo-current in CdS at liquid air temperature (curves taken with stepwise decrease of input resistances).

surements on the red and infra-red emission spectrum of the crystal under irradiation with ultraviolet light.<sup>29</sup> The luminescence corresponds to a transition from the lower edge of the conduction band into levels of the activating impurities and defines their position. At low temperatures a second set of equi-distant levels situated closely above the valence gives rise to a second system of emission bands in the green.<sup>30</sup> The energy of the traps is given by the range of the extinguishing infra-red radiation. This corresponds to a transition from these traps into the lower edge of the conduction band. The traps extend over a region with two maxima at about 0.9 and 1.5 ev.<sup>6,31</sup>

### b. The Nature of the Current Carriers

In this model we assume that the current is carried solely by electrons and that the positive holes are immobile. The sign of the current carriers was determined by the sign of the thermal e.m.f. between CdS and Cu in the temperature range 23°C and 70°C. The average thermal e.m.f. of nine crystals investigated amounted to  $7 \times 10^{-4}$  volt per degree centigrade when the crystals were in the dark. At strong irradiation with light or with gamma-rays it was about  $1.6 \times 10^{-4}$  volts/°C. Measurement of the thermal e.m.f. determines only the predominance of the one or the other sign of conductivity. Each of the nine crystals investigated showed predominantly electron conductivity under irradiation. Eight showed predominantly electron conductivity in the dark. The conductivity of one crystal in the dark was predominantly due to holes. But under irradiation the crystal showed predominantly electron conductivity. This behavior is not yet explained. The measurements were made with an electron tube voltmeter of high

<sup>&</sup>lt;sup>28</sup> The nature of the activating impurities in the crystal used is not known. By suitable activation for instance with silver, this

emission can be shifted. The resultant shift of the activator levels will change the activation energy of the dark current accordingly.

<sup>&</sup>lt;sup>29</sup> Photographs were taken with a Hilger wave-length spectrometer. The spectrum of the crystal investigated did not extend beyond 8700A.

<sup>&</sup>lt;sup>30</sup> F. A. Kroger, Physica 7, 1 (1940). <sup>31</sup> It is however possible that additional traps are situated between 0 ev and 0.7 ev. These traps would be empty at room temperature and are only effective in capturing at low temperatures.



input resistance (up to  $5 \times 10^{11}$  ohms). Dember effects were balanced out by reversing the terminals of the crystals.

## c. Low Temperature, No Irradiation

In a crystal which has been kept in the dark the highest occupied levels are at the activating impurities. Since the energy difference between the conduction band and the activating impurities is large, small conductivity is to be expected at low temperature. The dark current of some crystals investigated at liquid air temperature were less than  $1 \times 10^{-14}$  amp. This is the lower limit of the electronic voltmeter.

### d. Higher Temperatures, No Irradiation

According to the energy scheme a few electrons should be lefted up from the activating impurities into the conduction band by thermal impact. The conductivity was observed to follow the usual law:

$$\sigma = \sigma_0 e^{-(\epsilon/kT)}.$$
 (3)

Measurements in the range 25°C to 100°C gave  $\epsilon = 0.67$ and  $\sigma_0 = 1.7 \times 10^{-3}$  mho cm<sup>-1</sup>. Figure 2 shows the logarithm of the current plotted against 1/T. The crystal was not heated above 100°C to prevent deterioration.

The optical value of the activating energy usually is about twice the electrical value.<sup>32</sup> This was confirmed by these measurements. The electron donators fall well into the region of the activating impurities, which contain loosely bound electrons. They can be lifted up into the conduction band and thus account for the dark current. In a crystal which is irradiated and then placed in the dark some electrons remain trapped. They may be released by thermal impact and thus temporarily augment the dark current. The measurements of the dark current are thus found to be in agreement with the optically derived energy scheme.

#### e. Low Temperatures, Irradiation, Initial Stage

According to the crystal phosphor model, electrons lifted up from the activating impurities into the con-

duction band are captured by the traps and remain there at low temperatures. The photo-conductivity connected with this process should be small since the trapping probability is high.

The experiments to check this process were performed with gamma-rays. The crystal was in a brass tube which could be lowered into baths of various temperatures. The tube was airtight and kept dry by "drierite." It was possible to insert a radium needle (platinum 0.5-mm walls, 5-mg radium equivalent) through a tube to within 4 mm of the crystal. The irradiation was about 70 mr/sec. The curves were drawn by a paper tape recorder fed by a sensitive d.c. amplifier. The crystal in the tube was heated to 100°C before each measurement to empty the electrons from the traps. Ionization in the air surrounding the crystal was avoided by applying a low potential of 2.9 volts at the crystal. At liquid air temperature the dark current ( $\ll 10^{-13}$  amp.) reached  $8 \times 10^{-13}$  amp. in about three seconds after the radium was brought close to the crystal (Fig. 3).

## f. Low Temperature, Irradiation, Advanced Stage

In this part of the experiment the traps are filled slowly. The capture of electrons is reduced and they stay in the conduction band longer. It was found that the current was constant for 18 sec., then started to rise.<sup>32a</sup> After three hours the current reached  $1.5 \times 10^{-8}$  amp. but the final value had not yet been reached.

## g. Low Temperature, Irradiation, Interruption of Irradiation

The lifetime of electrons in traps is very long at low temperatures. According to our model, electrons are lifted up from the activating impurities into the traps and a metastable state of the crystal results. If under these conditions the irradiation is interrupted the photo-current immediately drops to values  $<10^{-13}$  amp., because the electrons in the conduction band recombine with the activating impurities. If the crystal is irradiated for a second time, a new delay does not occur. The current rises immediately and comes to the same value of  $1.5 \times 10^{-9}$  amp. as before.

## h. Low Temperature, Irradiation, Interruption of Irradiation, Warming up of the Crystal

The energy stored in a crystal phosphor at low temperatures can be released by warming it. If a crystal previously irradiated at liquid air temperature is heated to 70°C, there is a sudden surge of current. This current is several orders of magnitude larger than the dark current at this temperature. This agrees with the band scheme. Some filled traps are situated higher than the

<sup>&</sup>lt;sup>32</sup> T. H. de Boer and Ch. van Geel, Physica 2, 286 (1935); Mott and Gurney, reference 24, p. 160.

<sup>&</sup>lt;sup>32a</sup> Analogous observations were made by W. Lehfeldt, Göttinger Nachrichten II, 1, 171 (1935) with AgCl at low temperatures. AgCl is used as a crystal counter. This confirms our assumption (reference 22) that counting crystals are phosphors.

activating impurities (Fig. 1). In these experiments the additional charge carried across the crystal amounted to about  $1.7 \times 10^{-7}$  coulomb. Since this represents secondary currents no immediate conclusions concerning the number of traps and trapped electrons can be drawn.

If the experiment is repeated at 100°C there is a second and smaller surge of current of electrons coming from the deeper traps.

### i. Room Temperature, Irradiation

At room temperature the traps continually discharge electrons and the metastable state cannot be sustained (Fig. 4). The dark current,  $1.3 \times 10^{-12}$  amp. starts to rise immediately upon irradiation, and reaches  $1.8 \times 10^{-8}$ amp. after 72 seconds. If the traps are empty at the beginning of the irradiation the current at first rises slowly. As the traps are filled the current increases at a faster rate. Finally the rate of increase tapers off and the current reaches a constant value. Then the rate of raising the electrons into the conduction band equals the rate of recombination with the activating impurities. At high intensities the number of electrons in the conduction band equals the rate of recombination with the activating impurities. At high intensities the number of electrons in the conduction band exceeds the number of trapped electrons.<sup>33</sup> The number of electrons in the conduction band at equilibrium is given by

$$dn/dt = aJ - bn^2 = 0, \quad aJ = bn^2.$$
 (4)

To test this relation equilibrium currents under different irradiation intensities were measured. Measurements with four crystals gave averaged ratios of the photocurrents of 2.06:1 when the distance between radium needle and crystal was increased from 28 to 56 mm.

## j. Room Temperature, Intermittent Irradiation

If the irradiation is interrupted, Eq. (4) changes to

# $dn/dt = -bn^2$ .

The crystal was irradiated for a period of hours until the current at the recorder became constant. Then the radium was withdrawn for two seconds and immediately replaced. At a chart speed of 19 mm=4.1 sec. a small dip in the curve was observed. The current returned to its former value within a few seconds after the radium was replaced. This indicates that during the interruption the occupancy of the traps is not seriously affected. Measurements were made at relative intensities of irradiation of 4 and 1. The corresponding ratio of the downward slope of the short decay curves was 4.3:1.

When the irradiation was kept constant and the potential applied at the crystal increased in steps from 1:2:3 the initial downward slope of the decay curve

increased from 1 to 2.1 to 2.9. When the distance between radium and crystal was varied so that the current remained constant at different potentials V the initial downward slope of the decay curves was proportional to 1/V. Both of the results agree with the theory. Equation (2) giving the initial slope of the decay curve cannot be expected to hold for the rise curve. This is because the initial state of the crystal depends strongly on the occupancy of the traps. If some electrons remain in the traps at the beginning of the experiment the current rises faster than in a crystal with empty traps.

# k. Room Temperature, Non-Equilibrium Conditions

At equilibrium the photo-current is proportional to the square root of the intensity of irradiation. Also the number of electrons captured per second by the traps is equal to the number of electrons thermally released per second into the conduction band. From the proportionality of n with J it follows that the number of electrons captured per second is a constant fraction of the number in the conduction band. This relation can only hold if enough empty traps are available. The capturing is determined then by the number of electrons available and not by the number of empty traps. At room temperature the traps discharge rapidly and a large number of empty traps is always available.

Non-equilibrium conditions were observed as follows: The photo-current was kept at a chosen constant value by the rate at which the radium needle was withdrawn. When the photo-current was kept at a constant value and the exposure time varied, it was found that the initial slope of the decay curve decreased markedly with increasing exposure time. This experiment indicates traps extending over a wide region in the energy diagram in accordance with the optical observations of the



FIG. 5. Current produced in CdS by periodical irradiation with  $\gamma$ -rays.

<sup>&</sup>lt;sup>33</sup> Preparation and characteristics of solid luminescent materials Cornell Symposium of the American Physical Society, p. 115, ff.



FIG. 6. Curves showing that the building up of stationary positive space charges is independent of the electric field to the first approximation. Continuous curve: Field applied at the CdS crystal during irradiation. Interrupted curve: Field periodically removed during irradiation.

extinguishing absorption. The electrons captured in the traps of different depths rearrange themselves with time until finally predominantly deeper traps are filled. This experiment further shows that the interpretation of these curves offers the same difficulties as the interpretation of the optical decay curves of phosphors with more than one trap level.

### l. Room Temperature, Periodical Irradiation

To produce periodic gamma-ray pulses, the needle was attached to the end of a long lever and moved by a cam. A five seconds irradiation period at 1.0 cm was followed by a five second period at 35 cm. Travel time per cycle was less than a second. When the crystal is irradiated periodically the current builds up according to Fig. 5. This curve is explained qualitatively as follows. At each period of irradiation equal numbers of electrons are lifted up from the activating impurities into the conduction band. This number decreases by recombination during the period of irradiation as well as during the intermission and this decrease is proportional to the square of n. If the quadratic dependence of the rate of recombination holds for this curve we would expect that the amplitudes of the increasing steps and the decreasing steps would become equal and equilibrium would be reached. However the amplitude of the increasing steps is small in the beginning and grows with time. This can be explained by the capture of electrons in traps. At first the number of empty traps is large, many electrons are trapped and are lost to the process of conductivity. In time the traps fill up, fewer electrons are captured and the rate of increase of the conducting electrons becomes greater.

## m. Effect of Combined Irradiation with Visible Light and Particles

Kallmann and Warminsky<sup>11, 33a</sup> found that pulses due to nuclear particles in CdS crystals are large when the crystal is also irradiated with white light or with electrons. This irradiation fills the traps with

<sup>33a</sup> See also A. G. Chynoweth, Phys. Rev. 76, 310 (1949).

electrons in agreement with our model. The capturing probability is smaller and the electrons remain in the conduction band for a longer time.

## n. Unipolar Conductivity in CdS Crystals

CdS crystals show unipolar conductivity when one end of the crystal is irradiated. The current is stronger when the cathode is irradiated.

These unipolar effects, first observed by Gudden and Pohl in ZnS, have been emphasized by Kallmann and Warminsky<sup>11</sup> as well as by Rose, Weimer, and Forgue.<sup>19</sup> According to the model assumed, positive stationary holes are formed close to the origin of the liberated electron. If a positive stationary space charge occurs close to the cathode the entrance of the electrons is made easier and longer electron chains will result.

## o. Irradiation, Raising and Lowering the Temperature

The final current in a crystal irradiated with constant intensity depends upon the temperature of the crystal. At low temperatures the photo-current is large, at high temperatures it is small. According to measurements of Brentano and Davis<sup>34</sup> the photo-conductivity reaches a maximum at about  $-120^{\circ}$ C and decreases again at lower temperature. The decrease of photo-conductivity at high temperatures parallels the quenching of phosphorescence. At high temperature an increased number of direct recombinations between the electron and the activating impurities can take place. The energy difference is transformed in "phonons." This increased probability of recombination reduces the maximum current and decreases the inertia in accordance with the observations. The processes involved at very low temperatures, where the current again decreases, cannot be explained. It might be possible that the appearance of the green system of phosphorescence bands offers an additional way for the return of the electron to low states. Thus it would diminish the number of electrons in the conduction band.

## p. Crystal Irradiated at Room Temperature, Electrical Fields Periodically Interrupted

The building up of stationary positive space charges in the body of the crystal is independent of the electric field to the first approximation. Figure 6 shows two curves which were taken, one on top of the other, with the same irradiation and field. In the continuous curve the irradiation on the crystal was interrupted after 27 seconds. In the discontinuous curve the conditions were unchanged but the field was interrupted periodically. If the initial deviations due to the capacitance of the crystal have disappeared this procedure gives the same results on both the rise curve and the decay curve. These experiments have to be performed with strong irradiation and weak fields. Then the formation and the

<sup>34</sup> J. M. C. Brentano and D. H. Davis, Phys. Rev. 74, 711 (1948).

lifetime of the positive space charges is determined by the individual absorption processes of incident gammaradiation and by the recombination rate of the electrons lifted up into the conduction band.

At strong fields and weak irradiation the shift of the electrons simultaneously shifts the location of the recombination processes towards the anode. Finally a uniform distribution of positive space charges in the crystal is achieved. The slow restoration of the conductivity can be accelerated by application of alternating fields. If the potential at the electrodes is reversed every 10 seconds the final current for each phase is reached immediately. This experiment is related to the important observations of McKay on diamonds irradiated with slow electrons.

### C. Other Theories of Photo-Conductivity in CdS

Kallman and Warminsky<sup>11</sup> first clarified the amplification process when they pointed out that photoconductivity and phosphorescence are closely related. They showed that strongly phosphorescent crystals yield the largest secondary current. They did not, however, take recombination into account and deduced an exponential dependence of the decreasing current on the number of electrons in the conduction bands. This dependence does not agree with the measurements given here.

Rose, Weimer, and Forgue<sup>19</sup> assumed that the large secondary currents are due to "opening up" of multiple thin barriers between conducting sections of the crystal. They pointed out that irradiation with narrow pencils of light in CdS produces currents the intensity of which depends on the irradiated spot.

CdS crystals produced by the usual method consist often of many small crystals grown together in the form of ribbed strips. The short crystal needles are lined up side by side to form a ribbed polycrystal. Inspection of the ribbed areas under polarized light reveals crystal boundaries coinciding with the edges of the ribs. The photoelectric properties are identical whether the current flows parallel to the long axis, or crosswise. This proves that barriers between individual crystals do not affect the photo-currents. According to earlier measurements of the author, photo-currents can be observed in CdS at field strengths of less than 0.1 volt/cm. This is hard to explain by the barrier layer model.

Fassbender, Moglich, and Rompe<sup>20</sup> give an interpretation of the ideas of Hilsch, Pohl, Stockmann, and others on secondary currents by means of the collective electron model of solids. The differences between their theory and the one presented here should be pointed out. These authors considered a photo-conductor containing a set of discrete energy levels between valence and conduction band. Electrons are brought up into the conduction band thermally as well as by irradiation. They return to the discrete levels by recombination only. Thus if the dark current resulting from the thermal activation is small, the photo-current  $i_{final}$  is proportional to the square root of irradiation. The theory in this form however does not explain the present observations on CdS. The presence of traps, capturing and releasing of electrons, stimulating and quenching are not considered. In CdS the dark currents are so small that in the tail of the decay curve the trapped electrons determine exclusively the dependence of the current on time.

#### CONCLUSION

The collective electron model of the crystal phosphor is adequate to give a qualitative picture of the secondary photo-currents induced by irradiation in CdS crystals. The quantitative relations between current and irradiation and initial declining slope, after the irradiation has been interrupted, can be explained by simple assumptions. None of the properties observed up to now are in contradiction with this theory.

To summarize the observations:

a. The photo-current in a crystal phosphor is directly proportional to n, the number of electrons in the conduction band.

b. The luminescence intensity is proportional to the recombination rate  $bn^2$ .

#### ACKNOWLEDGMENT

The author acknowledges the valuable discussions and the kind help of Dr. R. J. Cashman, Dr. A. W. Ewald, Mr. L. W. Gildart, Dr. E. W. Lothrop Jr., and Dr. A. J. F. Siegert.



FIG. 5. Current produced in CdS by periodical irradiation with  $\gamma$ -rays.