

## **Thallous Sulfide PhotoConductive Cells II. Theoretical Discussion**

A. von Hippel and E. S. Rittner

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## Thallous Sulfide Photo-Conductive Cells

### II. Theoretical Discussion\*

A. VON HIPPEL AND E. S. RITTNER

*Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge, Massachusetts*

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A theory is formulated which is in substantial agreement with all facts reported in a previous paper on thallous sulfide photo-conductive cells. The underlying physical picture is that light is absorbed in the  $Tl_2S$  proper and in the presence of oxygen, positive "holes" and negative oxygen ions are formed. The "holes" and ions recombine at a rate proportional to the product of their concentrations. During their lifetime, the negative ions act as space charge compensators for the defect conduction and allow correspondingly higher currents to flow. This space charge compensating action, which is similar to the role played by positive ions in gas discharges, seems to be one essential mechanism of producing secondary photo-effects.

### INTRODUCTION

**I**N a previous paper<sup>1</sup> an account was given of an experimental study of thallous sulfide photo-conductive cells. A satisfactory theory should account for the following facts established by this study:

- (1) the dark current and photo-current are proportional to the applied voltage;
- (2) the dark conductance decreases exponentially with the reciprocal of the absolute temperature;
- (3) the photo-current, which represents a secondary photo-effect, is a non-linear function of the illumination and decreases rapidly with increasing temperature;
- (4) the introduction of solute oxygen atoms into the  $Tl_2S$  phase reduces the conductivity greatly, changes the material from an excess to a defect conductor, increases the photo-sensitivity many fold, but does not alter materially the transmission of the layer; and
- (5) the photo-current produced by a light flash of very short duration builds up to a maximum in about  $5 \times 10^{-5}$  second and decays exponentially with time except initially when the rate of decay is highest and increases with light intensity; the time constant of the exponential portion of the decay characteristic increases exponentially with the reciprocal of the absolute temperature.

### I. THE CONDUCTION MECHANISM IN THALLOUS SULFIDE

Crystalline thallous sulfide, according to Ketelaar and Gorter,<sup>2</sup> consists of  $Tl-S-Tl$  layers

\* This research was carried out under contract OEMsr-1036 with Division 16, Section 16.4 of the National Defense Research Committee and completed in June, 1945. Publication has been delayed because of the war.

<sup>1</sup> A. von Hippel, F. G. Chesley, H. S. Denmark, P. B. Ulin, and E. S. Rittner, *J. Chem. Phys.* **14**, 355 (1946).

<sup>2</sup> J. A. A. Ketelaar and E. W. Gorter, *Zeits. f. Krist.* **101**, 367 (1939).

arranged similarly to those in the cadmium iodide (C6) type of structure. The binding between thallium and sulfur atoms cannot be purely ionic as this would require the close juxtaposition of layers of positively charged thallium ions. Moreover, the thallium and sulfur atoms can best be accommodated in the structure by using atomic radii.<sup>2</sup> Similarly, the binding cannot be predominantly metallic because the electronic conductivity of thallous sulfide is too small ( $10^{-2}$ – $10^{-5}$  ohm<sup>-1</sup> cm<sup>-1</sup> at 25°C) for the metallic bond to contribute appreciably to the cohesion of the crystal. It appears likely, therefore, that the bonding between the sulfur and thallium atoms is covalent (possibly with partial ionic character) and that the attraction between adjacent thallium layers is the result of van der Waals forces similar to the cadmium iodide case. The electrical conductivity is probably restricted to the  $Tl-Tl$  planes, in which some of the thallium atoms lie nearly as close together as in thallium metal.

If the electrons or holes needed in the conduction process were not originally present in the compound but were to migrate in from the electrodes, space charge formation would restrict the current density to very small values. This follows from Poisson's equation:

$$\frac{dE}{dx} = \frac{4\pi\rho e}{\epsilon_{\infty}}, \quad (1)$$

where  $e$ =electron charge,  $E$ =field strength,  $\rho$ =density of charge carriers (is a function only

of  $x$ ), and  $\epsilon_\infty$ =optical dielectric constant. By replacing  $\rho$  by the current density,  $j$ ,

$$j = \rho ebE = \sigma E, \quad (2)$$

where  $\sigma$ =conductivity and  $b$ =mobility; and integrating, the following expression results:

$$E = \left( \frac{8\pi jx}{\epsilon_\infty b} + E_0^2 \right)^{1/2}. \quad (3)$$

Maximum space charge and current density will be attained when the field gradient,  $E_0$ , at the electrode from which the charge carriers emigrate ( $x=0$ ) is reduced to zero. By introducing the voltage,  $V$ , applied across the sample of length,  $d$ ,

$$V = \int_0^d E dx; \quad (4)$$

and integrating, the maximum current density possible under space charge conditions is found:

$$j_{\max} = \frac{V^2 b \epsilon_\infty}{d^3} (10^{-15}) \text{ amp./cm}^2. \quad (5)$$

Equation (5) predicts that for a sample of unit length ( $d=1$  cm) with 100 volts applied, a mobility of the charge carriers,  $b=100$  cm/sec. per volt/cm,<sup>3</sup> and an optical dielectric constant of the order of 10, a current density  $j_{\max} \sim 10^{-8}$  amp./cm<sup>2</sup> would be obtained. However, the relation between current density and voltage for  $\text{Ti}_2\text{S}$  is given by Ohm's law (Part I,<sup>1</sup> Section IB, Eq. (1)) rather than by Eq. (5), and a current density of about 1 amp./cm<sup>2</sup> would be observed under the conditions stated.

A more likely assumption is that thermal ionization creates an equilibrium density of electrons and holes in the material:

$$\rho_d = \rho_0 e^{-Q/kT}, \quad (6)$$

where  $Q$ =ionization energy and  $\rho_d$ =equilibrium density of electrons=equilibrium density of holes. If these charge carriers can traverse the compound with mobilities  $b_e$  and  $b_h$  without

space charge formation, a dark current density,  $j_d$ , would result:

$$j_d = \rho_d e E (b_e + b_h). \quad (7)$$

The motion of charge carriers in semiconductors is normally an intermittent process.<sup>4</sup> The electron or hole travels a mean distance  $\bar{w}$  in the field direction for an average time,  $t_f$ , and is then trapped for a time,  $t_t$ . The mobility of the carrier is thus given by

$$b = \bar{w}_0 / (t_f + t_t), \quad (8)$$

where  $\bar{w}_0 = \bar{w}/E$ . The activation energy,  $u$ , required to release the trapped carrier is supplied by thermal vibration; hence,  $t_t$  will depend on temperature in accordance with Eq. (9):

$$t_t = t_0 e^{u/kT}. \quad (9)$$

For  $t_t \gg t_f$ , which is usually the case, the mobility may be written

$$b = b_0 e^{-u/kT}. \quad (10)$$

It follows from (6), (7), and (10) that the current density can be expressed as

$$j_d = \rho_0 e E \cdot e^{-Q/kT} (b_{e0} \exp[-u_e/kT] + b_{h0} \exp[-u_h/kT]). \quad (11)$$

(Subscripts  $e$  and  $h$  refer to electrons and holes, respectively.)

It will be recalled that unoxidized  $\text{Ti}_2\text{S}$  (sample No. 2) proved to be an excess conductor and that on oxidation the resistance of the material increased rapidly, while the thermo-voltage changed its sign to indicate defect conductivity (Part I,<sup>1</sup> Section VI, Fig. 17). Consequently, pure thallosulfide appears to be an "intrinsic" semiconductor in which electrons and holes are mobile, the mobility of the former dominating ( $b_e \gg b_h$ ).

In Part I,<sup>1</sup> Section V, Eq. (4), an empirical relation between conductance,  $G_0$ , and temperature had been found:

$$G_0 = a e^{-U/kT}.$$

Also, Table II had indicated that the activation

<sup>3</sup> This value corresponds to the maximum excess electron mobility in the alkali halides (A. Smakula, Goettinger Nachrichten Math. Phys. Kl. 1, 62 (1934)), to the hole mobility in  $\text{Cu}_2\text{O}$  (E. Engelhard, Ann. d. Physik 17, 501 (1933)), and to the order of magnitude of the electron mobility in metals.

<sup>4</sup> A. von Hippel, J. App. Phys. 8, 815 (1937); Phys. Rev. 8, 605 (1940).

energy,  $U$ , varied appreciably from cell to cell and that no simple relation existed between  $U$  and the state of oxidation. Equation (11) clarifies this situation somewhat. One of the exponential terms involving the mobility normally dominates. In the single exponential function remaining,  $U$  is not a simple activation energy but the sum of an ionization energy  $Q$  and an activation energy  $u$ . It is likely that  $Q$  and  $u$  will be affected by oxidation. In addition, there is some evidence that in the very thin photo-cell layers  $a$  and  $U$  are functions of the layer thickness. Moreover, the insulating compound,  $\text{Ti}_2\text{SO}_2$ , formed in the oxidation, will influence  $U$  and  $a$  in accordance with the amount formed and its location. Therefore, the random variation in  $U$  from cell to cell is not surprising.

For the unoxidized material according to (11) the conductivity can be written:

$$\sigma = \rho_0 e b_{e0} \exp [(Q + u_e)/kT]. \quad (12)$$

On a thin layer of pure  $\text{Ti}_2\text{S}$  ( $\sim 500\text{\AA}$ ) values of  $\sigma = 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$  and of  $U = Q + u_e = 0.54$  electron volt were obtained. The magnitude of  $\rho_0$ , which corresponds to the number of Ti atoms per  $\text{cm}^3$  of thallous sulfide, is  $1.1 \times 10^{22}$ . Hence the maximum mobility of the electrons at room temperature is  $b_{e0} = 57 \text{ cm/sec. per volt/cm}$ , in good agreement with values obtained from other systems.<sup>3</sup>

From a consideration of the available space in the  $\text{Ti}_2\text{S}$  structure,\* it would appear that the most likely sites for the solute oxygen atoms are in spaces interleaving the Ti-Ti layers. This disposition provides twenty-seven possible locations in the unit cell for accommodating oxygen atoms—the same as the number of sulfur atoms already present. Such strategic location of the oxygens permits them to exert a profound influence on the conductivity. Owing to their large electron affinity, the oxygen atoms serve as electron traps, but the electrons apparently can be released again by thermal agitation. With increasing oxygen content the mobility of the excess electrons must rapidly decrease and the mobility of the holes, while somewhat impaired by lattice distortion, begins to dominate (Part I,<sup>1</sup> Section VI, Fig. 17).

\* The advice of F. G. Chesley has been most helpful in these structural considerations.

## II. QUALITATIVE DISCUSSION OF THE PHOTO-EFFECT

Two alternative explanations might be offered for the fact that oxygen photo-sensitizes thallous sulfide. A new, photoelectrically active, absorption band may result from the oxidation, or the absorption of the  $\text{Ti}_2\text{S}$  proper may lead to a photoelectric effect when oxygen is present. The transmission measurements (Part I,<sup>1</sup> Section VII) suggest the latter to be the case.

Since the flash response characteristics show that a time of  $5 \times 10^{-5} \text{ sec.}$  is required for the build-up of the photo-current (Part I,<sup>1</sup> Section VIIIB), it appears that initially an excited state is formed which persists for a short time before giving rise to longer-lived disturbance centers responsible for the secondary photo-effect. The details of this process are probably the following. By the absorption of a light quantum an electron is transferred instantaneously into an excited state. The creation of this state alters the potential field of the neighboring atoms; the nuclei swing into new equilibrium positions, and the lifetime of the excited state is lengthened to about  $10^{-5} \text{ sec.}$  The electron can then either return to its original state accompanied by realignment of the lattice, or it can be ejected leaving behind a positive hole.

In insulators the latter process would initiate only a primary photo-effect: that is, if electron and hole were to migrate through the material to the electrodes, a maximum photoelectric yield of one electron per ionizing light quantum would be recorded. In semiconductors an additional secondary photo-current should be observed, if the electron and hole do not leave the substance at the same rates.

As is known from gas discharges, one positive ion moving slowly from anode to cathode can allow many fast electrons to pass in the opposite direction because it compensates at any moment the space charge density of the electron current. In the same way a slow hole moving from anode to cathode in pure  $\text{Ti}_2\text{S}$  ( $b_e \gg b_h$ ) would allow  $b_e/b_h$  "extra" electrons to flow through the material. Unoxidized thallous sulfide has been found (Part I,<sup>1</sup> Section VIIIB) to exhibit such a photo-response, although the yield obtained is lower than that of the oxidized material by a factor of  $10^4$  to  $10^5$ .

The presence of an oxygen atom, with its large electron affinity, enormously increases the probability that a photoelectrically excited electron will escape from its parent atom leaving behind a positive hole\*\* and forming a relatively immobile  $O^-$  ion. This ion represents the disturbance center producing the secondary photo-effect, and until it recombines with a positive hole, a number of mobile holes can traverse the material. The rate of disappearance of centers is proportional to the total number of  $O^-$  ions and also to the total number of positive holes present at any time.

The possibility of effecting conversions from one wave-length to another by means of the  $a$  factors in the plots of  $\Delta I$  vs. light intensity (Part I,<sup>1</sup> Section VD) and the lack of dependence of the shape of the decay characteristic on the wave-length of the monochromatic light flash (Part I,<sup>1</sup> Section VIIIB) indicate that the same kind of disturbance center is produced at different wave-lengths.

### III. QUANTITATIVE DISCUSSION OF THE PHOTO-EFFECT

#### A. Response to Steady Illumination

A calculation of the photo-response according to the picture just presented consists of an evaluation of the charge density of electrons and holes prevailing in the material and its change as a function of intensity of illumination.

When thermal equilibrium is established in the dark, the rates of formation,  $d\rho_f/dt$ , and of recombination,  $d\rho_r/dt$ , of the charge carriers are equal. Since the recombination rate is proportional to the number of electrons and to the number of holes present at any time, at equilibrium these rates will be proportional to the square of the charge density,  $\rho_d$ .

$$\frac{d\rho_f}{dt} = \frac{d\rho_r}{dt} = B\rho_d^2. \quad (13)$$

( $B$  = probability of recombination.)

Under constant illumination a new balance between the rates of recombination and formation is established and the charge density in-

creases from  $\rho_d$  to  $\rho$ . Hence,

$$B\rho^2 = B\rho_d^2 + cJ, \quad (14)$$

where  $c$  represents the number of charge carrier pairs created per second per unit of volume under an illumination,  $J$ , of  $1 \mu\text{watt}/\text{cm}^2$ . The increase in charge carrier density is therefore

$$\Delta\rho = \rho - \rho_d = -\rho_d + \left(\rho_d^2 + \frac{cJ}{B}\right)^{\frac{1}{2}} \quad (15)$$

and

$$\frac{\Delta\rho}{\rho_d} = -1 + \left(1 + \frac{cJ}{B\rho_d^2}\right)^{\frac{1}{2}}. \quad (16)$$

Since the photo-current density is given by

$$\Delta j = \Delta\rho eEb_h, \quad (17)$$

while the dark current density is given by

$$j_d = \rho_d eE(b_e + b_h), \quad (18)$$

the ratio of light current to dark current density follows from (16)–(18):

$$\frac{\Delta j}{j_d} = \frac{b_h}{b_e + b_h} \left[ -1 + \left(1 + \frac{cJ}{B\rho_d^2}\right)^{\frac{1}{2}} \right]. \quad (19)$$

In the sensitive, oxidized cell where  $b_e \ll b_h$ , (19) reduces to

$$\frac{\Delta j}{j_d} = -1 + \left(1 + \frac{cJ}{B\rho_d^2}\right)^{\frac{1}{2}}. \quad (20)$$

Values of  $\Delta j/j_d$  calculated from (20) for a sensitive cell agree within experimental error with measured values of  $\Delta I/I_0$ , as can be seen in Table I.

TABLE I. Agreement between measured and calculated response to continuous illumination.

Source	Illumination $\mu \text{ watts}/\text{cm}^2$	$\Delta I/I_0$ observed	$\Delta j/j_d$ calculated	
White light	9.35	2.33	2.30	$\frac{c}{B\rho_d^2} = 1.05$
	23.0	3.94	4.02	
	42.1	5.85	5.72	
	84.5	9.0	8.46	
	214	14.3	14.1	
	758	24.6	27.2	
$\lambda = 0.9\mu$	0.0877	0.176	.165	$\frac{c}{B\rho_d^2} = 4.07^*$
	0.175	0.33	.315	
	0.263	0.45	.440	
	0.351	0.55	.560	
	0.438	0.64	.670	
	0.527	0.71	.778	

\*\* The positive holes can probably be identified with  $Tl^+$  ions located at lattice points.

\* The value of  $c/B\rho_d^2$  at any other wave-length for this cell is given by  $(4.07) \times (a \text{ factor})$ . (Part I (reference 1), Section VD.)

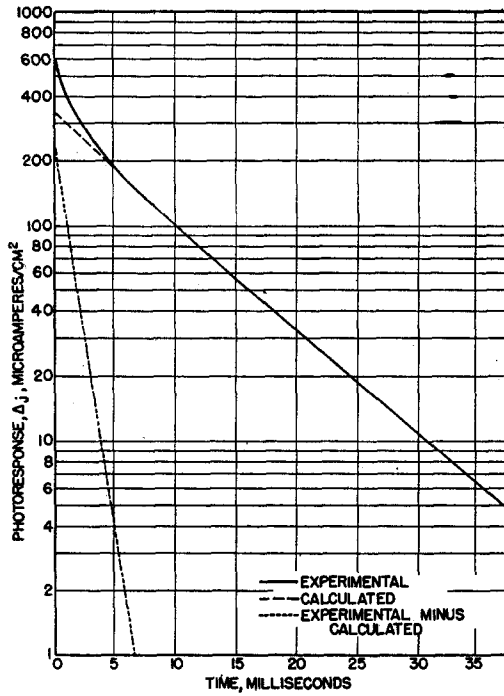


FIG. 1. Experimental and calculated decay characteristics ( $j_d$  = microamperes/cm<sup>2</sup>).

For incompletely oxidized cells (19) fits the data better than (20) because the excess conductivity is still appreciable.

### B. Response to Flash Illumination

Under flash illumination the rise of the current occurs as soon as the charge carrier pairs are created. The number of these charge carriers should be proportional to the number of quanta absorbed. If the rate of formation of the pairs is much faster than the rate of their recombination, the peak of the current transient should be proportional to the light intensity.

The decay characteristic can be calculated from the differential equation expressing the rate of disappearance of charge

$$d\rho/dt = B(\rho_d^2 - \rho^2). \quad (21)$$

Introducing  $\Delta\rho$ , the increase in charge carrier density above  $\rho_d$ ,

$$d\Delta\rho/dt = -B\Delta\rho(\Delta\rho + 2\rho_d), \quad (22)$$

rewriting (22)

$$d\Delta\rho \left( \frac{1}{\Delta\rho} - \frac{1}{\Delta\rho + 2\rho_d} \right) = -2\rho_d B dt, \quad (23)$$

and integrating (23)

$$\frac{\Delta\rho}{2\rho_d + \Delta\rho} = \frac{\Delta\rho_p}{2\rho_d + \Delta\rho_p} \exp(-2\rho_d B t) \quad (24)$$

( $\Delta\rho_p$  = maximum charge carrier pair density produced by the light flash at  $t=0$  which corresponds to about  $5 \times 10^{-5}$  sec. after occurrence of the flash), the equation for  $\Delta\rho$  is obtained:

$$\begin{aligned} \Delta\rho &= \frac{\Delta\rho_p^2 \rho_d \exp(-2\rho_d B t)}{2\rho_d + \Delta\rho_p(1 - \exp(-2\rho_d B t))} \\ &= \frac{\Delta\rho_p \exp(-2\rho_d B t)}{1 + \frac{\Delta\rho_p}{2\rho_d}(1 - \exp(-2\rho_d B t))}. \end{aligned} \quad (25)$$

The photo-current density,  $\Delta j$ , plotted logarithmically as function of time, should therefore follow the law

$$\ln \Delta j = \ln \Delta j_p - 2\rho_d B t$$

$$-\ln \left[ 1 + \frac{\Delta\rho_p}{2\rho_d}(1 - \exp(-2\rho_d B t)) \right], \quad (26)$$

where  $\Delta j_p = \Delta\rho_p e E b_h$ .

Differentiating (26), the slope is found to be  $-(2\rho_d + \Delta\rho_p)B$  at  $t=0$  and  $-2\rho_d B$  at  $t=\infty$ . Hence, the final slope of the decay curve is independent of light intensity while the magnitude of the initial slope increases with the illumination level, in qualitative agreement with the experimental data (Part I,<sup>1</sup> Section VIII B, Fig. 20).

The constants needed to calculate the decay characteristic from (26) can be obtained in the following way. The quantity  $2\rho_d B$  is equal to the final slope of the curve, and the extrapolation of this straight line to  $t=0$  gives an intercept

$$\alpha = \frac{\Delta\rho_p}{2\rho_d} 2j_d / \left( 1 + \frac{\Delta\rho_p}{2\rho_d} \right), \quad (27)$$

from which  $\Delta\rho_p/2\rho_d$  can be computed. Substituting the known value,  $\Delta j_1$ , at  $t_1$  ( $t_1 \gg 1/2\rho_d B$ ) in (26), the initial intercept,  $\Delta j_p$ , is obtained.

Agreement between experimental decay characteristics and those calculated from (26) is not very good at the initial portion of the curves (Fig. 1). The difference between experimental

and theoretical characteristics is shown by the dotted curve in the figure, the height and shape of which suggest that an appreciable fraction,  $[\Delta\rho_p' / (\Delta\rho_p + \Delta\rho_p')]$ , of the total number of disturbance centers decay at a faster rate than that predicted by (26).

This situation may be accounted for by the following hypothesis. When the oxygen content of the solid solution is high, the electron affinity of an oxygen atom will be lowered by the presence of a close oxygen neighbor and the probability of recombination of the corresponding  $O^-$  ion with a  $Tl^+$  hole will be increased to  $B'$ . In general, the number of oxygen close neighbors surrounding an oxygen atom will vary statistically from zero to six and a similar statistical distribution of time constants is to be expected. It is the longest of these time constants, however, that exerts by far the profoundest effect on the response to steady illumination.

### C. Lifetime of the Photoelectric Centers

On the basis of the preceding discussion, the average lifetime,  $\tau$ , of the disturbance centers can now be calculated.

If an initial charge density,  $\Delta\rho_p$ , is created by a light flash,  $\tau$  is defined by the equation

$$\tau = \int_0^\infty \frac{\Delta\rho_p dt}{\Delta\rho_p}, \quad (28)$$

or according to (25)

$$\tau = \int_0^\infty \frac{2\rho_d \exp(-2\rho_d B t) dt}{2\rho_d + \Delta\rho_p(1 - \exp(-2\rho_d B t))}. \quad (29)$$

By introducing  $x = \exp(-2\rho_d B t)$  and

$$dx = -2\rho_d B \exp(-2\rho_d B t) dt,$$

Eq. (29) can be rewritten

$$\begin{aligned} \tau &= \frac{1}{B} \int_0^1 \frac{dx}{2\rho_d + \Delta\rho_p(1-x)} \\ &= -\frac{1}{B\Delta\rho_p} [\ln \{2\rho_d + \Delta\rho_p(1-x)\}]_0^1 \\ &= \frac{1}{B\Delta\rho_p} \ln \left( 1 + \frac{\Delta\rho_p}{2\rho_d} \right). \end{aligned} \quad (30)$$

The average lifetime, therefore, decreases with

increasing light intensity. For very small light intensities ( $\Delta\rho_p \ll 2\rho_d$ )  $\tau$  becomes

$$\tau = \frac{1}{2\rho_d B} = \frac{1}{\kappa} \quad (31)$$

(for definition of  $\kappa$  see Part I,<sup>1</sup> Section VIIIB).

### D. Frequency Response

Runge and Sewig<sup>5</sup> have proposed a theory to account for the photo-effect in thallosulfide photo-conductive cells based on the assumption that light creates disturbance centers which decay exponentially with time. This theory is inadequate to explain most of the data obtained in our work.<sup>1</sup> However, their assumption is valid at very low intensity levels, as is shown by flash response results (Part I,<sup>1</sup> Section VIIIB, Fig. 20). Hence, the equation derived by these authors for the photo-current produced by a square-wave modulated light signal can be employed to calculate the frequency response of the cell at the low intensity levels employed in the standard test set.<sup>6,7</sup> In this equipment the d.c. component and all harmonics of the photo-current above the fundamental frequency are eliminated by the amplifier system. Therefore, the relationship between the instantaneous photo-current,  $\Delta i$ , and the time,  $t$ ; the frequency,  $\omega/2\pi$ ; the d.c. current,  $\Delta i_p$ , produced by steady illumination of the peak value; and the time constant,  $1/\kappa$ , is given by

$$\Delta i = \frac{2\kappa\Delta i_p}{\pi} \left( \frac{\omega}{\omega^2 + \kappa^2} \sin \omega t + \frac{\kappa}{\omega^2 + \kappa^2} \cos \omega t \right) \quad (32)$$

or

$$\Delta i = \frac{2\kappa\Delta i_p}{\pi(\omega^2 + \kappa^2)^{\frac{1}{2}}} \sin(\omega t + \theta), \quad (33)$$

where  $\tan \theta = \kappa/\omega$ . The peak amplitude,  $A$ , of the current is thus given by

$$A = 2\kappa\Delta i_p / \pi(\omega^2 + \kappa^2)^{\frac{1}{2}}, \quad (34)$$

or the r.m.s. voltage,  $S$ , developed across the

<sup>5</sup> I. Runge and R. Sewig, *Zeits. f. Physik* **62**, 726 (1930).

<sup>6</sup> W. L. Hole, N.D.R.C. Report No. 16.4—Special No. 9 (1944).

<sup>7</sup> L. N. Holland, N.D.R.C. Report No. 16.4—Special No. 6 (1944).

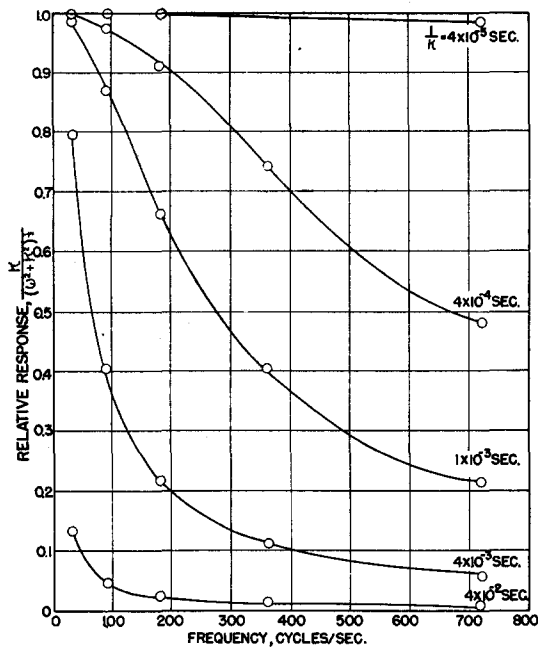


FIG. 2. Relative response vs. frequency for different values of the time constant.

load resistor,  $R_L$ , of the input circuit amounts to

$$S = \frac{2\kappa\Delta i_p R_L}{\pi(\omega^2 + \kappa^2)^{1/2}(2)^{1/2}}. \quad (35)$$

The quantity  $\kappa/(\omega^2 + \kappa^2)^{1/2}$ , representing the relative response with frequency, has been plotted in Fig. 2 as function of the modulating frequency for different values of the time constant,  $1/\kappa$ . For cells which decay quite slowly ( $\kappa^2 \ll \omega^2$ ) the relative response is inversely proportional to the frequency and independent of  $\kappa$ ; while when  $\kappa$  becomes of the same order as  $\omega$ , the shape of the response characteristic is highly dependent upon the magnitude of the time constant.

It follows from (35) that the frequency response of a cell can be calculated if  $\kappa$  is determined from flash response data and if the photocurrent,  $\Delta i_p$ , resulting from the exposure to an unmodulated signal flux of one microhololumen is measured.\* Tables II and III show that satisfactory agreement between calculated and measured values of  $S$  is obtained.

\*  $\Delta i_p$  can also be calculated from Eq. (27) of Part I (reference 1) using the value of  $c/B\rho_d^2$  obtained from measurements at higher levels of illumination and correcting for the fact that only a fraction of the cell surface is illuminated in the test set.

It is of interest to consider the change in cell response resulting from a change in the time constant,  $1/\kappa$ , keeping all other factors constant. Since  $\Delta i_p$  is proportional to the average lifetime of the disturbance centers and hence proportional to  $1/\kappa$  at low levels of illumination,  $(\omega^2 + \kappa^2)^{-1/2}$  should be representative of the peak amplitude,  $A$ . Values of  $(\omega^2 + \kappa^2)^{-1/2}$  for various values of  $1/\kappa$  and for  $\omega/2\pi = 90$  cycles are shown in Table IV. The output at 90 cycles increases with time constant; however, there is little to be gained in increasing  $1/\kappa$  beyond the values of the time constants of the majority of cells made by present methods. Improvement of the frequency response, which requires a reduction in the time constant, can be obtained only at the expense of the absolute signal level.

Since  $\kappa = 2\rho_d B$ , any means which can be utilized to increase  $\rho_d$  (or the apparent  $\rho_d$ ) can be employed in reducing the time constant. Such means include exposure of the cell to high temperatures or to background unmodulated illumination.

### E. Photoelectric Yield

The space charge compensating action of the disturbance centers during their average life-

TABLE II. Comparison of calculated and measured signal voltages at 90 cycles.

Cell No.	$1/\kappa$ , sec.	$\Delta i_p$ , $\mu$ amp.	$R_L$ , megohms	Signal, db (reference level 0.1 $\mu$ volt = 0 db)	
				Calculated	Measured
50B	$3.6 \times 10^{-2}$	0.20	2.5	101	98
54B	$2.1 \times 10^{-2}$	0.07	10	108	108
84B	$8.7 \times 10^{-3}$	0.02	40	117	115
40B	$5.2 \times 10^{-3}$	0.025	20	117	114
66B	$4.2 \times 10^{-3}$	0.015	40	111	110
18A	$3.3 \times 10^{-4}$	**	0.5	—	58

\*\*  $\Delta i_p$  too small to measure; calculated value from measured signal =  $3.6 \times 10^{-4}$   $\mu$  amp.

TABLE III. Comparison of calculated and measured frequency response.

Cell No.	Frequency, cycles/sec.	30	90	180	360	720
		S, db calculated	S, db calculated	S, db calculated	S, db calculated	S, db calculated
50B	S, db calculated	107	101	95	89	83
	measured	104	98	93	86	81
54B	S, db calculated	114	108	102	96	90
	measured	112	108	103	94	88
18A	S, db calculated*	58	58	57.5	56	53
	measured	58	58	58	56	53

\* Calculations made relative to measured response at 90 cycles.



time,  $\tau$ , allows  $z$  holes to traverse the length,  $d$ , of the semiconductor where

$$z = \tau b_h E / d. \quad (36)$$

If the fraction of the incident radiation absorbed by the layer is  $f$ , and if the photoelectrically excited electrons escape from their parent atoms with a probability,  $P$ , the quantum yield is given by

$$\eta = f P \tau b_h E / d. \quad (37)$$

The photoelectric yield is a function of temperature for several reasons. As is shown by the data of Table IV, Part I,<sup>1</sup> the variation of the peak of the flash response curve with temperature can be expressed by an equation of the form

$$\Delta G_p / G_0 = p - qT, \quad (38)$$

where  $p = 2.0$  and  $q = .0222$  for  $T$  in  $^{\circ}\text{C}$  and for the particular cell measured; or

$$\begin{aligned} \Delta G_p &= pG_0 - qG_0T \\ &= pa e^{-U/kT} - qT a e^{-U/kT}. \end{aligned} \quad (39)$$

(See (4), Part I.<sup>1</sup>) Hence,  $\Delta G_p$  increases at first and later decreases with temperature, becoming zero at  $90^{\circ}\text{C}$ . Since  $\Delta G_p$  is proportional to  $fP$ , this product also varies with temperature in accordance with (39).

The density of charge carriers,  $\rho_d$ , increases rapidly with temperature according to (6); therefore, if  $B$  is constant, the time constant for low light intensities should increase exponentially with the reciprocal of the absolute temperature. This has been experimentally verified (Part I,<sup>1</sup> Fig. 22); however, the slope of the plot of  $\log 1/\kappa$  vs.  $1/T$  was steeper than the corresponding plot of  $\log G_0$  vs.  $1/T$ . This suggests that  $B$  is not a constant but varies with temperature in the following way:

$$B = B_0 e^{-s/kT}. \quad (40)$$

Finally,  $b_h$  should increase somewhat with temperature (10), but the activation energy,  $u_h$ , is so small (see IIIF) that this effect is of minor importance.

The  $b$  factors (Part I,<sup>1</sup> Fig. 15) representing the over-all yield as a function of temperature are defined by the relation

$$\begin{aligned} b &= \eta T^{\circ}\text{K} / \eta_{300^{\circ}\text{K}} \quad (\text{for } \lambda = \text{constant}) \\ &= f T^{\circ}\text{K} P T^{\circ}\text{K} \tau T^{\circ}\text{K} / f_{300^{\circ}\text{K}} P_{300^{\circ}\text{K}} \tau_{300^{\circ}\text{K}}. \end{aligned} \quad (41)$$

TABLE IV. Dependence of  $(\omega^2 + \kappa^2)^{-1/2}$  on  $1/\kappa$  at 90 cycles.

$(\omega^2 + \kappa^2)^{-1/2}$	$1/\kappa$ , sec.
$4 \times 10^{-5}$	$4 \times 10^{-5}$
$3.9 \times 10^{-4}$	$4 \times 10^{-4}$
$8.7 \times 10^{-3}$	$1 \times 10^{-3}$
$1.6 \times 10^{-3}$	$4 \times 10^{-3}$
$1.76 \times 10^{-3}$	$4 \times 10^{-2}$
$1.767 \times 10^{-3}$	$\infty$

## F. Calculation of Fundamental Constants

If the value of one constant is assumed, it is possible to calculate the values of the other fundamental constants from experimental measurements. This has been done for the sensitive cell No. 84B.

The hole mobility,  $b_h$ , can be obtained from (37) using measured values of quantum yield ( $\eta = 1.8$  electrons/quantum at  $\lambda = 0.6\mu$  and  $E = 124$  volts/cm), time constant at low levels of illumination ( $\tau = 9.13 \times 10^{-3}$  second, from final slope of Fig. 1), distance between alternate grids ( $d = 0.19$  cm), fraction of the incident radiation absorbed by the layer ( $f = 0.75$  at  $0.6\mu$  from absorption measurements), and assuming the probability that a photoelectrically excited electron will escape from its parent atom,  $P$ , to be about 0.4:

$$b_h = 0.96 \frac{\text{cm}}{\text{sec.}} \bigg/ \frac{\text{volt}}{\text{cm}}.$$

The maximum charge carrier pair density,  $\Delta\rho_p$ , produced by a single light flash (of unknown absolute intensity) can be computed from the calculated initial intercept of the flash response curve ( $\Delta j_p = 347 \times 10^{-6}$  amp./cm<sup>2</sup> at  $\lambda = 0.9\mu$  and  $E = 215$  volts/cm), the calculated value of  $b_h$ , and (26).

$$\Delta\rho_p = 1.0 \times 10^{13} \text{ cm}^{-3}.$$

The extrapolation of the straight line portion of the flash curve yields a value of  $\Delta\rho_p / 2\rho_d = 0.22$ . Hence,

$$\rho_d = 2.4 \times 10^{13} \text{ cm}^{-3}.$$

Since the final slope,  $2\rho_d B$ , is  $109.5 \text{ sec.}^{-1}$ , the recombination probability,  $B$ , is

$$B = 2.3 \times 10^{-12} \text{ cm}^3 \text{ sec.}^{-1}.$$

Similarly, the average probability of recombination,  $B'$ , of the faster decaying centers is about

$$B' \sim 1.6 \times 10^{-11} \text{ cm}^3 \text{ sec.}^{-1},$$

and these centers comprise about 43 percent of the total number. (See initial intercepts of Fig. 1.)

From the calculated value of  $\rho_d$ , the known values of  $\rho_0$  ( $1.1 \times 10^{22}$ ) and  $T$  (300°K), and (6), the thermal ionization energy can be calculated.

$$Q = 0.51 \text{ electron volt.}$$

This value agrees with the measured thermal activation energy,  $U$ , within experimental error. Hence,

$$u_h = U - Q = 0.$$

The quantum yield measured under steady illumination yields a value of  $c/B\rho_d^2 = 11.0$ , which together with the values of  $B$  and  $\rho_d$  gives the number of charge carrier pairs created per second per unit of volume under an illumination of  $1 \mu\text{watt}/\text{cm}^2$  ( $\lambda = 0.6\mu$ ).

$$c = 1.4 \times 10^{16} \text{ cm}^{-3} \text{ sec.}^{-1} \mu\text{watt}^{-1} \text{ cm}^2.$$

This corresponds to an equilibrium charge density created by this illumination of  $\Delta\rho = 5.9 \times 10^{13} \text{ cm}^{-3}$ .

The constant,  $c$ , can also be calculated directly from the number of effective quanta absorbed in the photo-sensitive layer of thickness  $\delta$  ( $\delta = 5 \times 10^{-5} \text{ cm}$ ).

$$c = \frac{5.03 \times 10^{12} \lambda_\mu f P}{\delta}$$

$$= 1.8 \times 10^{16} \text{ cm}^{-3} \text{ sec.}^{-1} \mu\text{watt}^{-1} \text{ cm}^2. \quad (42)$$

In view of the uncertainty in the magnitude of  $P$ , this result is in good agreement with the previous calculation.

Finally, the capture cross section,  $A$ , of an oxygen ion defined by

$$A = B/v \quad (43)$$

can be obtained if an estimate is made of the "instantaneous" velocity,  $v$ , of a thallium hole. The maximum frequency with which a  $\text{Tl}^+$  hole can be exchanged from thallium to thallium neighbor by thermal vibration can be calculated to a first approximation from the Debye temperature of thallium metal:

$$\nu_{\max} = k\theta/h$$

$$= 2.1 \times 10^{12} \text{ sec.}^{-1}. \quad (44)$$

where  $k$  = Boltzmann constant,  $h$  = Planck constant, and  $\theta$  = Debye temperature = 100°K. Multiplying  $\nu_{\max}$  by the average thallium-thallium distance in  $\text{Tl}_2\text{S}$  ( $4 \times 10^{-8} \text{ cm}$ ), the maximum velocity,  $v_{\max}$ , of a thallium hole is found to be

$$v_{\max} = 8.4 \times 10^4 \text{ cm sec.}^{-1}$$

$$= v \text{ for } u_h = 0$$

yielding a capture cross section of

$$A = 2.74 \times 10^{-17} \text{ cm}^2,$$

an area which is unreasonably small. This indicates that many thallium holes collide with oxygen ions without recombining. Evidence has already been cited to support this supposition (see (40)), an activation energy,  $s = 0.11$  electron volt, having been measured on a different cell (Part I,<sup>1</sup> Section VIIIB). If this value of  $s$  also applies to cell No. 84B, the maximum probability of recombination is

$$B_0 = 1.61 \times 10^{-10} \text{ cm}^3 \text{ sec.}^{-1},$$

leading to a value of

$$A = 19.1 \times 10^{-16} \text{ cm}^2,$$

which corresponds to a circular cross section of radius 2.46Å. This is a reasonable order of magnitude as the distance from center to center of a  $\text{Tl}^+$  ion and  $\text{O}^-$  ion in contact is about 2.5Å.

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Shortly before this work was completed, Dr. Uhlenbeck informed us about the theoretical treatment of the thallous sulfide cell and the measurements carried out at the University of Michigan, which were submitted to Division 16.4 of N.D.R.C. as "Special Report 26" by A. W. Ewald, W. L. Hole, and G. E. Uhlenbeck. The calculations of these authors have been based on the model of an excess semiconductor with impurity centers, as used by Mott and Gurney.<sup>8</sup> This mathematical treatment can be adapted with slight modification to the discussion of thallous sulfide as an "intrinsic" semiconductor, and we have profited from it for our discussion of response to continuous and to flash illumination.

<sup>8</sup> N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), p. 191.