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PHOTOELECTRIC CONDUCTIVITY IN SEMI-CONDUCTORS

26 July 1951



U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

NAVORD Report 2149

PHOTCELECTRIC CONDUCTIVITY IN SEMI-CONDUCTORS

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ABSTRACT: The equations relating the photocurrent to field strength, intensity of illumination, quantum efficiency, and electron and hole mobilities and concentrations in semiconductor crystals, are derived for the case when both holes and electrons are present. It is shown that in contrast to the case of induced conductivity in insulators, the measurement of time constant and of deviation from Ohm's Law does not yield sufficient information to determine either hole or electron mobility.

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The equations governing photoelectric conductivity in semi-conductors are presented. The work is a part of Task Number NOL-Re4e-126-1-52, a project to investigate the photoconductive process. The report is for information only, and does not request further action.

The author gratefully acknowledges the guidance of Dr. R. J. Maurer, who suggested the investigation and helped to clarify many basic points by discussion and interpretation.

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By direction

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REFERENCES

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- (2) T. S. Moss, T.R.E. Reprt T 2100 (Telecommunications Research Establishment) Nov. 1947
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Table of Symbols

Symbols to be used in the following paper are defined as follows:

Subscripts

e -- electrons
h -- holes
d -- dark
k -- cathode

Symbols

i -- current density (amps/cm²)
n -- concentration (of electrons or holes) (cm⁻³)
v -- mobility -- (cm/sec)/(volt/cm)
E -- field strength -- (volts/cm)
x, a -- position coordinates
l -- crystal length
 $\frac{dn}{dt}$ -- rate of elevation of electrons from full to conduction band (cm⁻³sec⁻¹)
 $-\frac{dn}{dt}$ -- rate of recombination of holes and electrons (cm⁻³sec⁻¹)
 $\mathcal{K}_e = n_e e v_e$ -- electronic conductivity (ohm⁻¹cm⁻¹)
 $\mathcal{K} = \mathcal{K}_e + \mathcal{K}_h$ -- total conductivity (ohm⁻¹cm⁻¹)
 $\mathcal{K}_e = \mathcal{K} / (\mathcal{K}_e + \mathcal{K}_h)$
 $\mathcal{K}_h = \mathcal{K} / (\mathcal{K}_e + \mathcal{K}_h)$
 τ -- time constant of recombination (sec)
w = schubweg = $\tau E v_e$ (cm) -- mean distance of travel of free electron
 μ -- quantum efficiency -- number of electrons elevated per incident quantum of light
Q -- number of quanta incident on the crystal per second per cm²

Conditions of Applicability

Assumptions made in the theory are:

1. Uniform, weak illumination
2. Steady state conditions
3. Single crystals
4. Monomolecular recombination

PHOTOELECTRIC CONDUCTIVITY IN SEMI-CONDUCTORS

Introduction

Theories of photoconductivity with which determinations of electron and hole mobilities may be made have been developed for materials of two principal types. A theory due to Hecht (reference (1)) treats the case of an insulator in which conductivity is induced, as by irradiation or by electron bombardment. This theory has been applied by Moss (reference (2)) to a determination of electron mobilities in PbS, by measurements of the photoconductive time constant and the deviation from Ohm's Law.

The case of photoconductivity in mixed conductors (materials displaying ionic plus electronic conductivity) was presented by Stöckmann (reference (3)). He showed that an application of the equations of Hecht to non-insulators does not lead to the correct value of mobility unless the conductivity is purely ionic. This results from the fact that the amount of deviation from Ohm's Law depends on the relative amounts of electronic and ionic conductivity: for a pure ionic conductor the equations of Hecht apply, while for a pure electronic conductor no deviation is to be expected. Thus a determination of mobility requires a knowledge of the relative electronic and ionic conductivity. No method of determining this ratio is presented in the theory.

A further disadvantage of the Stöckmann theory is that it does not handle the case where both electrons and holes are simultaneously present. Ionic conductivity is assumed to be independent of illumination and coordinates, so the equations cannot be applied to this case merely by considering the ionic conductivity as being due to the holes. He suggests an extension of the fundamental equations to cover this case, but does not develop the subject.

It is the purpose of the present paper to develop the equations applicable to the case of semi-conductors in which holes and electrons may be present simultaneously. As in Stöckmann's discussion a monomolecular recombination law will be assumed, so that the limitation of weak illumination must be imposed. The present theory will present equations which yield a lower bound for the mobility, just as in the case of Stockmann's calculations.

DERIVATION OF THE PHOTOCURRENT EQUATION

Ohm's Law in the differential form

$$(1) \quad i = (n_e e v_e + n_h e v_h) E$$

is believed to hold even in those cases where the integral form does not hold. If we consider only absolute values of mobilities, we must take $e_e = e_h = e$ as positive. Then we have without error

$$i = (n_e e v_e + n_h e v_h) E.$$

Since the time constant τ represents the mean time an electron is in the excited state, we may express the "schubweg" or mean drift distance traversed by an electron, as

$$w = \tau E v_e.$$

The equation of continuity of the total current in the sample under steady state conditions, $\text{div } i = 0$, becomes for the case of a linear conductor:

$$(2) \quad \frac{d i}{d x} = (n_e e v_e + n_h e v_h) \frac{\partial E}{\partial x} + e E \left(v_e \frac{\partial n_e}{\partial x} + v_h \frac{\partial n_h}{\partial x} \right) = 0$$

under the assumption that v_e and v_h are independent of illumination and position.

The continuity equation for electrons given in terms of the net source strength (difference between the rates of elevation $\delta n / \delta t$ and recombination $-\partial n / \partial t$) in the steady state is

$$\text{div } i_e = \frac{\partial p_e}{\partial t}$$

or

$$(3) \quad \frac{\partial n_e}{\partial x} e v_e E + n_e e v_e \frac{\partial E}{\partial x} = e \left(\frac{\partial n_e}{\partial t} + \frac{\delta n_e}{\delta t} \right)$$

To eliminate $\frac{\partial E}{\partial x}$ from (2) and (3) rewrite (2) as

$$\frac{\partial E}{\partial x} = -e E \left(v_e \frac{\partial n_e}{\partial x} + v_h \frac{\partial n_h}{\partial x} \right) / (n_e e v_e + n_h e v_h).$$

Then (3) becomes

$$(4) \quad \frac{\partial n_e}{\partial x} e v_e E + n_e e v_e \left[\frac{-e E \left(v_e \frac{\partial n_e}{\partial x} + v_h \frac{\partial n_h}{\partial x} \right)}{n_e e v_e + n_h e v_h} \right] = e \left(\frac{\partial n_e}{\partial t} + \frac{\delta n_e}{\delta t} \right).$$

Setting

$$\frac{n_e e v_e}{n_e e v_e + n_R e v_R} = \alpha_e$$

gives

$$\frac{\partial n_e}{\partial x} e E \left[v_e - \alpha_e \left(v_e + v_R \frac{\partial n_R / \partial x}{\partial n_e / \partial x} \right) \right] = e \left(\frac{\partial n_e}{\partial t} + \frac{\delta n_e}{\delta t} \right)$$

or

$$(5) \quad e v_e E \frac{\partial n_e}{\partial x} \left[1 - \alpha_e \left(1 + \frac{v_R}{v_e} \frac{\partial n_R / \partial x}{\partial n_e / \partial x} \right) \right] = e \left(\frac{\partial n_e}{\partial t} + \frac{\delta n_e}{\delta t} \right).$$

Eliminating $\partial n_e / \partial x$ from (2) and (3) yields

$$e v_e E \frac{\partial n_e}{\partial x} \left[1 + \frac{v_R}{v_e} \left(\frac{\partial n_R / \partial x}{\partial n_e / \partial x} \right) \right] = - \frac{\partial E}{\partial x} (n_e e v_e + n_R e v_R)$$

$$(6) \quad \frac{\partial E}{\partial x} \left[n_e e v_e - \frac{n_e e v_e + n_R e v_R}{1 + \frac{v_R}{v_e} \left(\frac{\partial n_R / \partial x}{\partial n_e / \partial x} \right)} \right] = e \left(\frac{\partial n_e}{\partial t} + \frac{\delta n_e}{\delta t} \right)$$

$$(7) \quad e \left(\frac{\delta n_e(x)}{\delta t} + \frac{\partial n_e(x)}{\partial t} \right) = \frac{\partial E}{\partial x} \left[\frac{n_e e v_R \left(\frac{\partial n_R / \partial x}{\partial n_e / \partial x} \right) - n_R e v_R}{1 + \frac{v_R}{v_e} \left(\frac{\partial n_R / \partial x}{\partial n_e / \partial x} \right)} \right]$$

$$= -\alpha_e \frac{\partial E}{\partial x} \left[\frac{\frac{\alpha_R}{\alpha_e} - \frac{v_R}{v_e} \left(\frac{\partial n_R / \partial x}{\partial n_e / \partial x} \right)}{1 + \frac{v_R}{v_e} \left(\frac{\partial n_R / \partial x}{\partial n_e / \partial x} \right)} \right].$$

Define

$$A \equiv \left[\frac{\frac{\alpha_R}{\alpha_e} - \frac{v_R}{v_e} \left(\frac{\partial n_R / \partial x}{\partial n_e / \partial x} \right)}{1 + \frac{v_R}{v_e} \left(\frac{\partial n_R / \partial x}{\partial n_e / \partial x} \right)} \right]$$

$$(8) \quad e \left(\frac{\delta n_e(x)}{\delta t} + \frac{\partial n_e(x)}{\partial t} \right) = -A \kappa_e \frac{\partial E}{\partial x}.$$

Under uniform illumination it is reasonable to assume that A is independent of coordinates. Integrating (8) under this assumption yields

$$\begin{aligned} (9) \quad e \int_0^x \left(\frac{\delta n_e(a)}{\delta t} + \frac{\partial n_e(a)}{\partial t} \right) da &= -A \int_0^x \kappa_e(a) \frac{\partial E(a)}{\partial a} da \\ &= -A \left[(\kappa_e E) \Big|_0^x - e v_e \int_0^x E \frac{\partial n_e}{\partial a} da \right] \\ &= -A \left[\kappa_e E(x) - \kappa_{ek} E_k - e v_e \int_0^x E \frac{\partial n_e}{\partial a} da \right] \end{aligned}$$

where $a=0$ represents the cathode and

$$E_k = i / (\kappa_{ek} + \kappa_{rk}).$$

Integrating (9) over the full length of the sample,

$$\begin{aligned} (10) \quad -\frac{1}{A} \int_0^l e dx \int_0^x \left(\frac{\delta n_e(a)}{\delta t} + \frac{\partial n_e(a)}{\partial t} \right) da \\ = \int_0^l \kappa_e E(x) dx - \int_0^l \kappa_{ek} i dx - \int_0^l e v_e dx \int_0^x E \frac{\partial n_e}{\partial a} da. \end{aligned}$$

In a single crystal, uniformly illuminated, $E(x)$ should not vary seriously with coordinates; it can thus be replaced by its average value and taken out of the integral. Then

$$\int_0^l \kappa_e E(x) dx = E e v_e \int_0^l n_e(x) dx$$

Eq. (10) then becomes

$$\begin{aligned}
 (11) \quad & -\frac{1}{A} \int_0^l e \, dx \int_0^x \left(\frac{\delta n_e(a)}{\delta t} + \frac{\partial n_e(a)}{\partial t} \right) da + \int_0^l e v_e \, dx \int_0^x E \frac{\partial n_e}{\partial a} da \\
 & = E e v_e \int_0^l n_e(x) \, dx - \alpha_{ek} i l.
 \end{aligned}$$

To determine $n_e(x)$ for these integrals we must consider the recombination rate, as well as (5) which relates $\partial n_e / \partial x$ and $\partial n_e / \partial t$. For weak illumination the number of available holes will be much greater than the number of optically excited electrons, and we may assume a monomolecular recombination law:

$$(12) \quad \frac{\partial n_e}{\partial t} = -\frac{n_e - n_{ed}}{\tau}$$

while (5) can be written

$$(13) \quad \frac{\delta n_e}{\delta t} + \frac{\partial n_e}{\partial t} = v_e E \frac{\partial n_e}{\partial x} (1 - \alpha'_e)$$

if we use the notation

$$\alpha'_e = \alpha_e \left[1 + \frac{v_h}{v_e} \left(\frac{\partial n_h}{\partial x} / \frac{\partial n_e}{\partial x} \right) \right].$$

Thus

$$(14) \quad \frac{\delta n_e}{\delta t} - \left(\frac{n_e - n_{ed}}{\tau} \right) = v_e E \frac{\partial n_e}{\partial x} (1 - \alpha'_e)$$

and we have

$$(14') \quad \frac{\frac{\partial n_e}{\delta t} - \frac{n_e - n_{ed}}{\tau}}{\frac{\partial n_e}{\delta t} - \frac{n_e - n_{ed}}{\tau}} = \frac{\partial x}{v_e E (1 - \alpha'_e)}$$

For uniform illumination $\delta n_e / \delta t$ is constant, and α'_e may be assumed to be independent of coordinates. (14') is then satisfied by

$$(15) \quad \frac{\delta n_e}{\delta t} - \frac{n_e - n_{ed}}{\tau} = C(t) e^{-\frac{x}{\tau E v_e (1 - \alpha_e')}}$$

or

$$n_e = n_{ed} + \tau \frac{\delta n_e}{\delta t} - \tau C(t) e^{-\frac{x}{\tau E v_e (1 - \alpha_e')}}$$

where $C(t)$ must satisfy (12).

$$(16) \quad \frac{\partial n_e}{\partial t} = C(t) e^{-\frac{x}{\tau E v_e (1 - \alpha_e')}} - \frac{\delta n_e}{\delta t} = \tau \frac{\partial C(t)}{\partial t} e^{-\frac{x}{\tau E v_e (1 - \alpha_e')}}$$

$$(17) \quad C(t) = C_1 e^{-\frac{t}{\tau}} + \frac{\delta n_e}{\delta t}$$

$$(18) \quad n_e = n_{ed} + \tau \frac{\delta n_e}{\delta t} - \tau \left[\frac{\delta n_e}{\delta t} + C_1 e^{-\frac{t}{\tau}} \right] e^{-\frac{x}{\tau E v_e (1 - \alpha_e')}}$$

It is apparent that

$$C_1 = \frac{n_e - n_{ed}}{\tau} \Big|_{x=0, t=0}$$

However, since we are considering the steady state case, we consider only time intervals for which $t \gg \tau$. Then we may write

$$(19) \quad n_e(x) = n_{ed} + \tau \frac{\delta n_e}{\delta t} \left[1 - e^{-\frac{x}{\tau E v_e (1 - \alpha_e')}} \right].$$

Integrating this over the length of the sample and inserting the notation $w_e = \tau E v_e$ gives

$$(20) \quad eE v_e \int_0^l n_e(x) dx = eE v_e \left[\int_0^l (n_{ed} + \tau \frac{\delta n_e}{\delta t}) dx - \int_0^l \tau \frac{\delta n_e}{\delta t} e^{-\frac{x}{w_e(1-\alpha_e')}} dx \right]$$

$$= eE v_e \left[n_{ed} l + \tau l \frac{\delta n_e}{\delta t} + \tau \frac{\delta n_e}{\delta t} w_e (1-\alpha_e') \left(e^{-\frac{l}{w_e(1-\alpha_e')}} - 1 \right) \right]$$

where

$$(21) \quad n_{ed} eE v_e = \alpha_{ed} (\alpha_{ed} + \alpha_{kd}) E = \alpha_{ed} i_d.$$

We may now insert (15) and (17) into (14) obtaining

$$(22) \quad \frac{\delta n_e}{\delta a} = \left[\frac{\delta n_e}{\delta t} e^{-\frac{a}{w_e(1-\alpha_e')}} \right] / v_e E (1-\alpha_e').$$

Inserting (13), (20), (21) and (22) into (11) yields

$$(23) \quad -\frac{\delta n_e}{\delta t} \int_0^l e dx \int_0^x \left(\frac{1}{A} - \frac{1}{1-\alpha_e'} \right) e^{-\frac{a}{w_e(1-\alpha_e')}} da$$

$$= \alpha_{ed} i_d l - \alpha_{ek} i_l + e \tau E v_e \frac{\delta n_e}{\delta t} \left[l - w_e (1-\alpha_e') \left(1 - e^{-\frac{l}{w_e(1-\alpha_e')}} \right) \right].$$

On dividing through by $\alpha_{ed} l$ and making the approximation $\alpha_{ek} \approx \alpha_{ed}$ (valid for weak illumination) we find

$$(24) \quad i - i_d = \frac{\tau E v_e e}{\alpha_{ed}} \frac{\delta n_e}{\delta t} \left[1 - \frac{w_e}{l} (1-\alpha_e') \left(1 - e^{-\frac{l}{w_e(1-\alpha_e')}} \right) \right]$$

$$+ \frac{\delta n_e}{\delta t} \int_0^l e dx \int_0^x \frac{1}{\alpha_{ed} l} \left[\left(\frac{1}{A} - \frac{1}{1-\alpha_e'} \right) e^{-\frac{a}{w_e(1-\alpha_e')}} da \right].$$

Expansion of the integral gives

$$(25) \int_0^1 dx \int_0^x e^{-\frac{a}{w_e(1-x_e')}} dx = l^2 \frac{w_e(1-x_e')}{l} \left[1 - \frac{w_e(1-x_e')}{l} \left(1 - e^{-\frac{l}{w_e(1-x_e')}} \right) \right]$$

Thus (24) becomes

$$(26) i - i_d = e \frac{\delta n_e}{\delta t} \frac{l}{A x_e} \frac{w_e}{l} (1 - x_e') \left[1 - \frac{w_e(1-x_e')}{l} \left(1 - e^{-\frac{l}{w_e(1-x_e')}} \right) \right]$$

Corresponding expressions from preceding theories are:

- (a) Hecht's theory for insulators containing free electrons:

$$(27) i - i_d = enl \frac{w}{l} \left[1 - \frac{w}{l} \left(1 - e^{-\frac{l}{w}} \right) \right]$$

- (b) Stöckman's theory for mixed conductors containing free electrons:

$$(28) i - i_d = enl \frac{w}{l} \left[1 - \frac{w}{l} (1 - x_e) \left(1 - e^{-\frac{l}{w_e(1-x_e)}} \right) \right]$$

In these two expressions n is identical with the present quantity $\delta n_e / \delta t$.

Since we have restricted ourselves to the case of weak illumination, we can express the rate of elevation of electrons in terms of the quantum efficiency μ , and Q , the number of light quanta falling on the crystal per second per cm^2 :

$$(29) \frac{\delta n_e}{\delta t} = Q \mu$$

Hence (26) can be written

$$(30) \quad i - i_d = Q \mu \frac{e l}{x_d A} \frac{w_e (1 - x_e')}{l} \left[1 - \frac{w_e (1 - x_e')}{l} \left(1 - e^{-\frac{l}{w_e (1 - x_e')}} \right) \right].$$

This equation gives us the photocurrent in terms of illumination and field strength, with quantum efficiency, electron and hole mobilities and concentrations, crystal size, and time constant as parameters. The photocurrent is plotted as Curve 1 in Figure 1, against the factor $w_e (1 - x_e')/l$ which is proportional to field strength.

It can be seen from the equation that the photocurrent does not obey Ohm's Law in the integral form, so long as x_e' is different from unity. It is this deviation which has been utilized to determine electron mobility in insulators.

MOBILITY

The method of measuring mobility from these equations may most easily be described by referring to (27). The extension to (26) and (28) will then follow directly.

Since $w = \tau E v$, (27) can be rewritten as

$$(31) \quad \frac{i - i_d}{E} = e n l \frac{\tau v}{l} \left[1 - \frac{\tau E v}{l} \left(1 - e^{-\frac{l}{\tau E v}} \right) \right].$$

This equation is plotted as Curve 2 in Figure 1. The initial tangent to this curve is the straight line

$$(32) \quad \frac{i - i_d}{E} = e n \tau v \left(1 - \frac{\tau E v}{l} \right)$$

shown as Curve 3. Since τ , E , and l are all independently measurable, v can be calculated directly from the slope of this line.

The difference between (30) and (29) is

$$(33) \quad f_1(E) = e n l \left(\frac{\tau v}{l} \right)^2 E e^{-\frac{l}{\tau E v}}.$$

Hence if this difference is divided by E and plotted on semi-log paper against $1/E$, a straight line of slope $-l/\tau v$

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will be obtained. This may also be used to calculate ν .

Now subject (26) or (28) to this same series of operations obtaining (31') through (33'). The analog of (32) contains too many undetermined coefficients to be of any use to us, but that corresponding to (33) is

$$(33') \quad f_2(E) = \frac{(1-\alpha_e')}{A} = \frac{\delta n_e}{\delta t} \frac{l}{\alpha_{ex}} \left(\frac{\nu_e \tau}{l} \right)^2 (1-\alpha_e') E e^{-\frac{l}{\tau \nu_e (1-\alpha_e')}}.$$

Thus the slope of $\log(f_2/E)$ vs. $1/E$ is $-\frac{l}{\tau \nu_e (1-\alpha_e')}$, of which l and τ may be independently determined. Unfortunately the value of

$$\alpha_e' = \alpha_e \left[1 + \frac{\nu_e}{\nu_e'} \left(\frac{\partial n_A}{\partial x} / \frac{\partial n_e}{\partial x} \right) \right]$$

is not known. Hence ν_e cannot be calculated in this manner.

Photocurrent in a thin film of PbS at room temperature was measured as a function of field strength, to check the form of (30) and (31'), although the condition that the sample be a single crystal is not satisfied for such a film.

The film was irradiated with monochromatic radiation of 2.4 microns wavelength at an intensity of 1 microwatt per square centimeter. The radiation was chopped at 90 cps to permit a-c amplification. A film having a time constant of 24 microseconds and an electrode spacing of 0.04 cm was used. The data are presented in Figure 2, along with data for PbS at -185°C reported by Moss (reference (2)). Rather good agreement with theory is seen in both sets of data.

A value of $.94 \text{ cm sec}^{-1}/\text{volt cm}^{-1}$ is found for $(1-\alpha_e')\nu_e$ at 20°C , while Moss reports a value of $.05 \text{ cm sec}^{-1}/\text{volt cm}^{-1}$ at -185°C , increasing with temperature. He terms this an "effective mobility" of the layer.

CONCLUSIONS

The equation relating photocurrent in a semi-conductor to illumination, field strength, and crystal parameters such as mobility, time constant, and quantum efficiency has been derived for single crystals of semi-conductors containing both free holes and free electrons, for the case of weak illumination. It is shown that the photocurrent may not obey Ohm's Law in the integral form. This is in contrast to the case for semi-conductors containing either but not both free electrons and free holes which should obey this law (reference (3)). The behavior of such a semi-conductor also differs from that of an insulator or a pure ionic conductor in that this deviation from Ohm's Law cannot be combined with a time constant measurement to determine the electronic mobility in the present case.

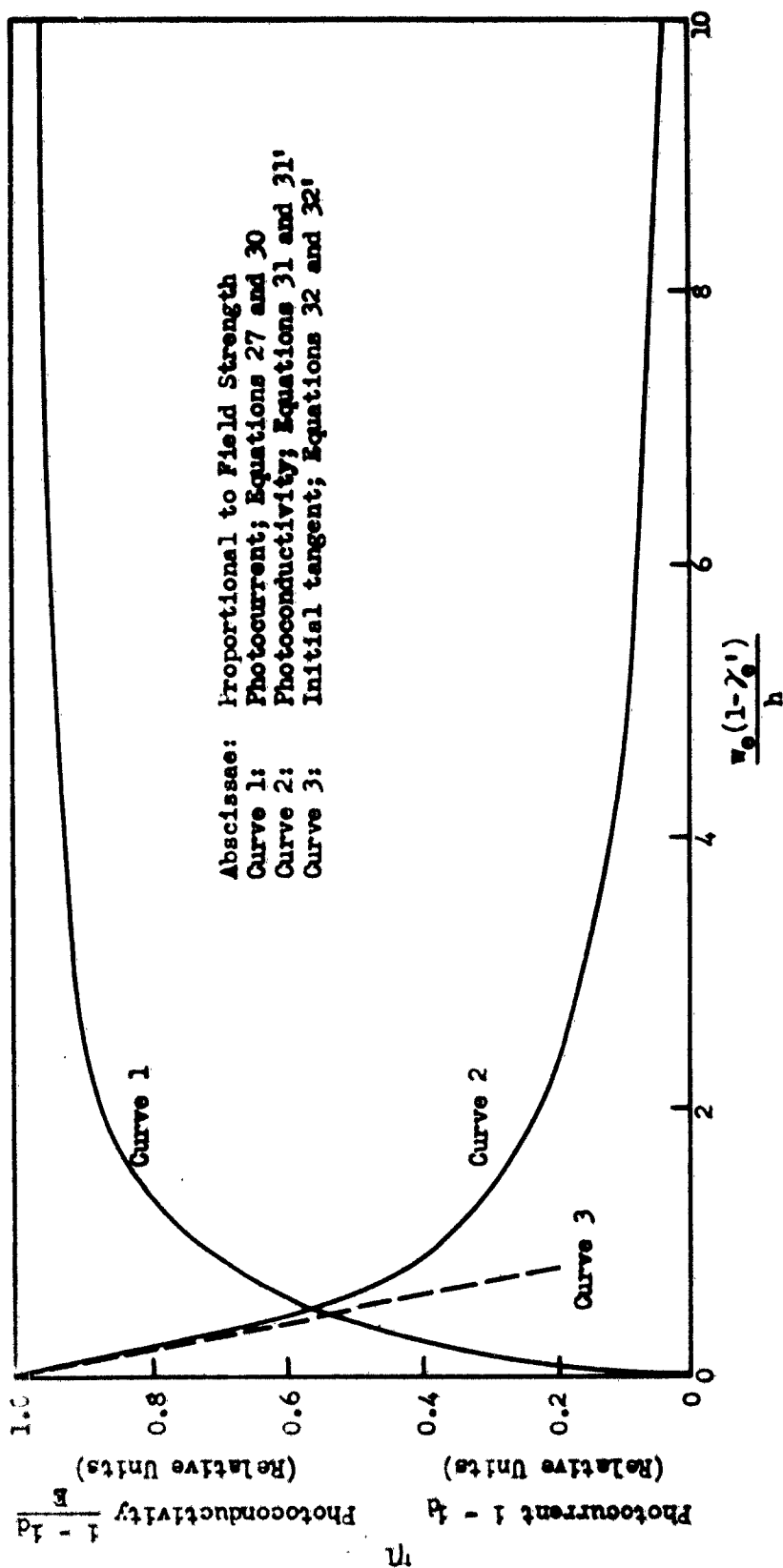


Fig 1 PHOTOCURRENT AND PHOTOCONDUCTIVITY, THEORETICAL

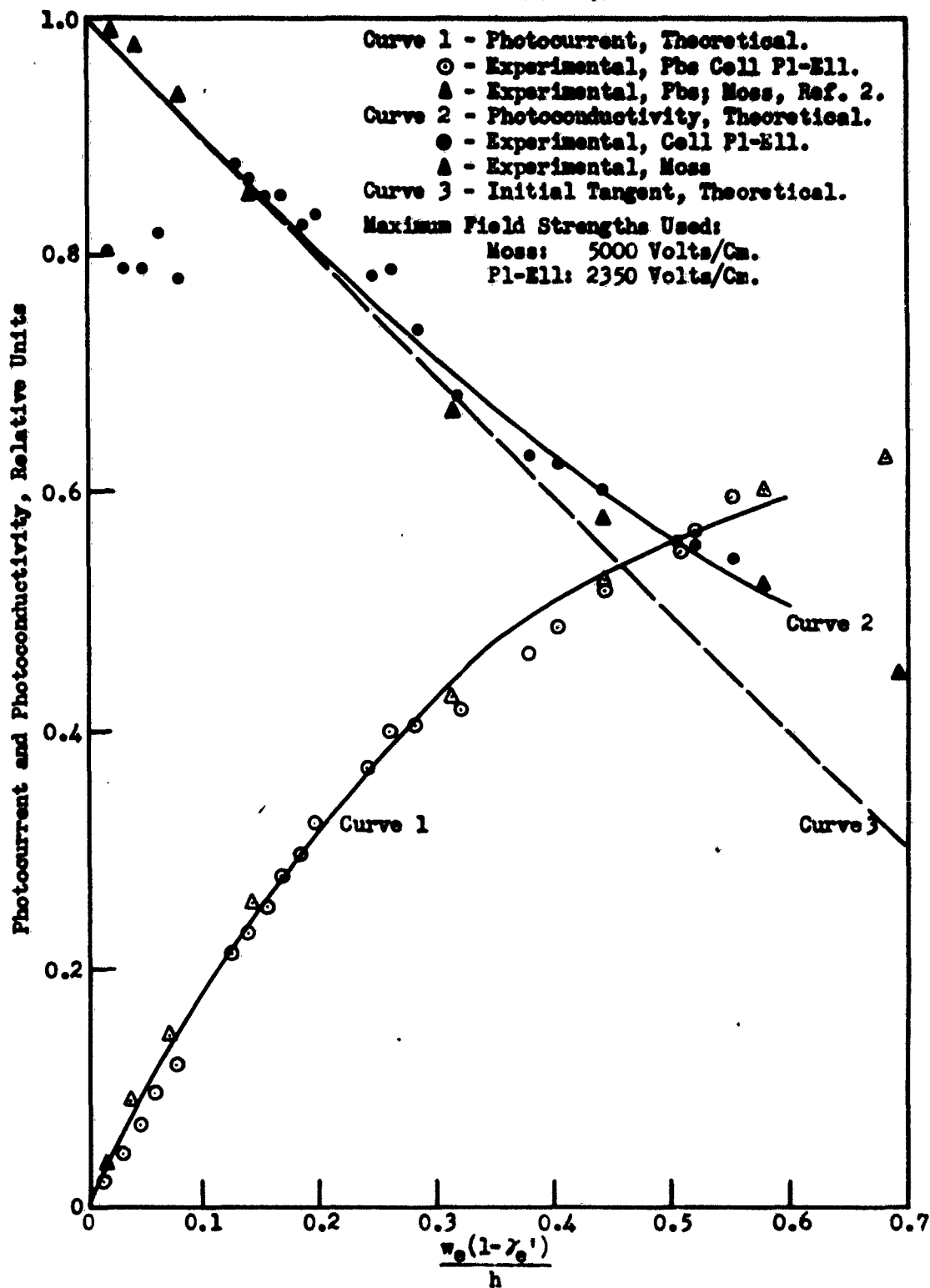


Fig 2 PHOTOCURRENT AND PHOTOCONDUCTIVITY, EXPERIMENTAL

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