AN ABSTRACT OF THE THESIS OF

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Title  A Study of the Photoconductivity of Color Centers in Alkali

_____Halides_____

Abstract approved

(Major Professor)

The original objectives in this investigation were to determine the nature of the photocurrent in crystals containing the colloidal absorption band and also in crystals containing the broad R'-band.

A special cell was constructed for holding the crystal during the photoconductivity measurements. Also a micromicroammeter was constructed which was capable of measuring photocurrents of the order of $10^{-11}$ amperes. A Beckman model DU spectrophotometer with an external optical system was used as the light source.

The initial primary photocurrent in additively colored KCl and KBr crystals containing various concentrations of F-centers was measured at room temperature. It was found that the spectral distribution of photocurrent in crystals containing low concentrations of F-centers was similar to the absorption curve. However, it was also observed that the amount of photocurrent produced by F-band illumination greatly decreased upon prolonged illumination with F-band light. In crystals containing relatively high concentrations of F-centers the photocurrent distribution exhibited a dip in the F-band region with photocurrent maxima only at the R- and N-bands. From these results it was concluded that the F-band must consist of two types of absorbing centers.

The spectral distribution of photocurrent in KCl crystals containing the colloidal band was found to agree in shape with the photocurrent curves for blue rocksalt containing metallic sodium. However in the case of KCl the photocurrent maximum was found to have been shifted to a higher wavelength, as would be predicted by theory.

After the formation of the R'-band in KCl crystals by means of arc illumination a large decrease of the photocurrent in the F-, R-, and N-band regions was observed. This decrease of the photocurrent indicates that these bands are destroyed during the formation of the R'-band.

A STUDY OF THE PHOTOCONDUCTIVITY OF
COLOR CENTERS IN ALKALI HALIDES

by

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A THESIS

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## ACKNOWLEDGMENT

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# A STUDY OF THE PHOTOCONDUCTIVITY OF
## COLOR CENTERS IN ALKALI HALIDES

## I.  INTRODUCTION

The term photoconductivity pertains to the change
in conductivity of a substance upon illumination and is
generally described as the volume photoelectric effect.
The effect can be interpreted in terms of the elevation
of electrons to a conduction level throughout the given
volume of substance which is illuminated.  In the case of
insulators the existence of these free electrons can be
detected by the application of an electric field across
the photoconducting material.  An electric current will
then flow through it during the period of illumination.

The magnitude of the observed photocurrent is
dependent upon the wavelength of the light as well as
upon its intensity.  Therefore the term "spectral distri-
bution of photocurrent" will refer to the photocurrent
observed per unit incident light energy striking the
sample, the values taken over a given range of the
spectrum.

The first measurements of the spectral distribution
of photocurrent in colored alkali halides appear to have
been carried out by Röntgen (15,pp.116-195).  His
experiments were made on rocksalt (sodium chloride)
crystals colored yellow by x-rays, and on naturally
occurring blue rocksalt crystals.

Later Pohl and his co-workers began an extensive investigation of the mechanism of photoconductivity in colored alkali halides and other materials. A complete bibliography of their publications in this field between 1925 and 1937 has been given by Pohl (13,pp.52-54). Reviews on the theory and mechanism of photoconductivity in colored alkali halides have been given by Hughes and DuBridge (4,pp.284-321), Pohl (12,pp.15-20), Seitz (18, pp.563-571; 19,pp.387-392), and Mott and Gurney (7, pp.117-137).

Pohl was able to demonstrate that the observed photocurrent is often composed of two distinct currents, which he called the primary and secondary currents. The primary current is due directly to the motion of electrons toward the anode as they are raised to the conduction level throughout the illuminated volume. This portion of the total current attains its maximum value instantly upon illumination and also dies down instantly when the light is cut off. During the primary current flow no electrons enter the crystal from the cathode and therefore a space-charge is set up within the crystal which changes the internal field. As a result of this polarization the photocurrent rapidly decreases upon prolonged illumination.

In some crystals, particularly at higher temperatures, the photocurrent does not reach its maximum value

instantly, but increases slowly with time. It also takes
a finite time to die down when the light is cut off. This
time dependent current, known as the secondary current,
may or may not die down upon prolonged illumination,
depending upon the experimental conditions (2,pp.654-657).
The secondary current is believed to be caused by at least
two factors: (1) the thermal migration of electrons after
their initial release which does not reach a saturation
value instantly, and (2) a resistance break-down of the
crystal which allows electrons to enter it from the
cathode. This flow of current from cathode to crystal
is probably caused by field emission from the cathode
after a high space charge has been induced in the crystal
from the flow of the primary current.

The primary photocurrent has been shown to be
proportional to the light intensity striking the crystal
and roughly proportional to the field strength at low
voltages. However, as the field increases, the photo-
current approaches a saturation value. The strength of
the electric field necessary to produce the saturation
current takes on widely different values for different
substances (7,p.121).

In view of the above considerations the following
mechanism has been postulated for the release of photo-
electrons. In the absence of an electric field the

absorption of light raises the trapped electrons to the
conduction level. The released electrons execute a
Brownian type motion and eventually again become trapped
after traveling a mean free distance, l. In the presence
of a weak field the released electrons travel a mean
range, w, in the direction of the anode before becoming
trapped although l remains the same. If a thin slice of
the crystal is illuminated at a distance, b, from the
anode, the total charge transfer recorded by the gal-
vanometer will be

$$Q = ne \frac{w}{d} \tag{1}$$

where n is the number of electrons released, d the
distance between the electrodes, and e the charge per
electron. If the field strength is now increased, w will
become larger. With a sufficiently high field, w
becomes comparable to b, and a saturation current is
observed. The maximum charge transfer which can be
obtained during a given amount of illumination should be
given by

$$Q_{max} = ne \frac{b}{d} . \tag{2}$$

It is therefore possible to calculate the number
of electrons released since $Q_{max}$, b, and d can be experi-
mentally measured. If the amount of absorbed light is
known, it is then also possible to calculate the quantum
yield, $\eta$ , defined by

$$\eta = \frac{\text{number of electrons released}}{\text{number of quanta absorbed}} \qquad (3)$$

Although this measurement has been made for silver bromide, experimental difficulties have made it impossible in the case of the alkali halides (1,p.790).

Equations 1 and 3 may be combined with a slight modification to yield

$$\eta \left(\frac{W}{E}\right) = \frac{i}{J} \frac{d}{E} \frac{h\nu}{e} \quad . \qquad (4)$$

In this equation i is the initial primary photocurrent, J the energy per second of the absorbed light, d the distance between electrodes, E the field strength, $\nu$ the frequency of the absorbed light, e the electronic charge, and h is Planck's constant. By means of equation 4 the product $\eta$ times w/E can hence be calculated from experimentally determined quantities.

Early experiments by Pohl on the absorption spectra of the colored alkali halides showed that the resulting curves contained bell-shaped absorption maxima at a characteristic wavelength for each salt. These bell-shaped bands became known as the F-bands.

Measurements of the spectral distribution of photocurrent have been carried out on several of the colored alkali halides containing F-centers. In each case it was found that the photocurrent curve had a shape similar to the absorption curve with a maximum value at the same wavelength as the peak of the F-band. These

results indicated that a loosely bound electron is present in an F-center and that it is liberated when the center absorbs a photon of suitable energy.

Pohl later discovered that when a crystal containing the F-band was irradiated with light of the wavelength absorbed by the band, the F-centers disappeared with the appearance of a new band which he called the F'-band. The F'-band appeared as a wide band on the long wavelength side of the F-band and was observed only at low temperatures. It was found that the F'-centers could also be converted back to F-centers by the absorption of light in the region of the F'-band.

This phenomenon gave a definite clue to the nature of F-centers when Pick (11, pp.371-374) determined the quantum yield $\phi$ for the transformation $F \rightarrow F'$ in KCl and KBr, with $\phi$ defined by

$$\phi = \frac{\text{number of destroyed F-centers}}{\text{number of absorbed light quanta}} \ .$$

Pick determined the concentration of F-centers optically, making use of the Smakula formula (20, p.607). It was found that the quantum yield attained a value of two in KCl at temperatures above $-130^\circ$ centigrade.

These results could be fully interpreted only by assuming that F-centers are electrons trapped in the crystal lattice, and that F'-centers are F-centers to which an electron has been added. Thus when a photon

strikes an F-center, the electron is released and wanders through the crystal until it is captured by another F-center.

By the use of equation 4 the product $\eta$ (w/E) has been calculated over a wide range of temperatures for many of the alkali halides containing F-centers (12,p.18). In the case of KCl this product remains constant between -130 and -80° centigrade.

It is significant that the value of $\phi$, determined by Pick, approaches two at this same temperature of -130° for KCl. In the above temperature range it is therefore probable that each absorbed photon liberates one electron, and $\eta$ in equation 4 can be set equal to one.

By using this procedure the value w/E has been determined for KCl at -100° centigrade with crystals containing various concentrations of F-centers (12,p.19). It was found that the mean range w was inversely proportional to the concentration of F-centers throughout a wide range of concentrations. These results further substantiate the belief that the F-centers themselves are the active trapping agents.

At present it is believed that an F-center is an electron which has become trapped in a negative ion vacancy (7,pp.111-113). Mott has postulated that the F- absorption band corresponds to a transition of the

electron from an s-like state to the lowest p-like state
which it can assume, by analogy with an alkali metal
atom (6,p.196). By this hypothesis there is more than
one discrete energy level below the ionization continuum,
and the activated electron must absorb a certain amount
of thermal energy to be raised to the conduction level.

The presence of other absorption bands, in addition
to the F- and F'- centers, have been noted in colored
alkali halides by several workers (19,pp.406-407).
Molnar observed the formation of a second band (the M-
band), in addition to the F-band, when KCl was colored by
means of x-rays. It was found that the F- and M-bands
could be interconverted when the crystal was irradiated
with light of the wavelength absorbed by the respective
band. However, during this conversion two new bands,
named the R-bands, appeared between the F- and M-bands.
Irradiation in the F-band region also often caused the
appearance of another band, named the N-band, on the long
wavelength side of the M-band.

The rate of conversion of F-centers to M-centers
in KCl has been measured by Petroff (10,pp.449-450). He
reported that the transformation apparently takes place
by means of an intermediate stage which has an absorption
peak corresponding to the F-band. These results suggest
that the F-absorption band may consist of two types of

centers.

Oberly and Burstein have recently made photo-current measurements on KCl and KBr crystals containing the F-, R-, M-, and N-bands in the absorption spectra (8,p.1257; 9,p.79). They found that crystals colored by means of x-rays gave photocurrent maxima at wavelengths corresponding to the F- and M-bands. They also made measurements on KCl crystals colored with an excess of alkali metal and found that in this case the photocurrent showed little response in the F- and M-band regions, however had definite peaks at wavelengths corresponding to the R- and N-bands. In KBr crystals colored by x-rays they noted that the photocurrent peak decreased to a much greater extent than the absorption peak upon bleaching with F-band light. Oberly suggested that two types of F-centers may exist: a soft center which is photo-conducting and also readily bleached by light, and a hard F-center which is not photoconducting and is relatively unaffected by light.

Markham (5,p.86) suggested that the decrease in the product $\eta w$ which Oberly observed during the bleaching of the F-band could be due to a decrease in the electron range $w$, instead of the decrease in the quantum yield $\eta$ which would occur if there are the two types of F-centers. He attributed the decrease in the electron range to an

increase in the concentration of negative ion vacancies
resulting from the F-band irradiation.

It was noted by Glaser that the irradiation of KCl
containing the F-, R-, and M-bands with intense white
light from a carbon arc caused by their coagulation into
one broad band. This broad band became known as the
R'-band, and its thermal and optical properties were
studied by Scott and Bupp (16,pp.341-346). One of the
original objectives in the present investigation was to
study the photoelectric properties of the R'-band.

In the preparation of KCl crystals containing high
concentrations of F-centers Scott and Smith noted the
development of a new distinct band on the high wavelength
side of the F-band (17,pp.982-986). Their experiments
indicated that these new centers were in heterogeneous
thermal equilibrium with the F-centers, and thus they
concluded that they were of a colloidal nature. Another
objective in this present investigation was to determine
the nature of the photocurrent spectral distribution in
crystals containing the colloidal band. Measurements of
the spectral distribution of photocurrent on blue NaCl
containing colloidal metal have been carried out by
Gyulai (3,p.413). He found that the photocurrent curve
in this case did not follow the absorption curve. The
photocurrent distribution, however, did coincide roughly

with the surface photoelectric current obtained with
metallic sodium, which implied that the colloidal
particles were large enough to emit electrons in a manner
similar to the bulk metal.

As has been stated, this investigation was under-
taken with the following objectives in mind:

1.  To determine the nature of the photocurrent
in KCl crystals containing the colloidal band.  The shape
of the photocurrent distribution curve in this case
should be similar to that obtained by Gyulai for blue
rocksalt, although shifted toward higher wavelengths
because of the lower work function of metallic potassium.

2.  To determine the nature of the photocurrent
in crystals containing the broad R'-band.  If this band
contains R- and M-centers as has been suggested, their
existence may be detected through photocurrent studies.

## II. EXPERIMENTAL

EXPERIMENTAL SYSTEM. The photocurrent obtained
with colored alkali halides crystals is on the order of
$10^{-11}$ to $10^{-12}$ amperes when the measurements are carried
out under the conditions which are described below. In
order to investigate these small photocurrents experi-
mentally the crystal must be mounted between two electrodes
which are in contact with opposite faces. A suitable
potential difference is then applied to the electrodes.
Also a sensitive galvanometer is connected in series with
the crystal and potential source.

Plate 1 shows the experimental arrangement which
was used throughout this investigation with the exception
of the light source for illuminating the crystal. In
general the apparatus consists of

1. A power supply which furnishes 150 volts for
the micromicroammeter and 450 volts for the potential
difference across the crystal.

2. The amplifying circuit of the micromicro-
ammeter.

3. The shield and the electrometer tube for the
micromicroammeter.

4. The photoconductivity cell.

5. A condenser which when charged to 450 volts
serves as the potential source for the crystal.

6. A switch which allows the condenser to be charged or discharged at will.

One shielded cable supplies +150 volts to the micromicroammeter and 6 volts A.C. to its tube filaments. Another shielded cable connects the components of the electrometer tube with the rest of the amplifying circuit. An insulated wire supplies +450 volts to the photoconductivity cell. The crystal to be investigated is placed in the photoconductivity cell between two carbon blocks which serve as electrodes.

MICROMICROAMMETER. The instrument was constructed from a circuit designed by Roberts (14, pp.181-183). A simplified schematic diagram of the circuit showing the essential components is given in plate 2 where

$T_1$ is a 6C6 sharp-cutoff pentode which is used as the electrometer tube in the instrument.

$T_2$ is a 6K5G high-mu triode used in the second stage of amplification.

$R_1$ is a high-megohm resistor having a value of $6 \times 10^9$ ohms.

$R_2$ is composed of a variable resistor of 3000 ohms ($R_{2B}$) in series with a fixed resistor of 3500 ohms ($R_{2A}$). A toggle switch allows $R_{2A}$ to be omitted from the circuit at will.

$R_4$ is a potentiometer of 1000 ohms resistance.

The power supply for the meter is similar to the one described by Roberts, employing an 80 dual-diode as the rectifier tube. The power supply was mounted on a separate chassis apart from the micromicroammeter.

With the exception of $T_1$ and $R_1$ the components of the meter were mounted in a 6 x 6 x 9 inch metal cabinet. However, the 60 microammeter shown in the circuit diagram is a separate unit with leads from the cabinet connected to it. Mounted on the front panel of the cabinet from left to right are S, $R_4$, $R_{2A}$, and $R_{2B}$.

S allows the instrument to be turned on and off. $R_4$ determines the zero point of the meter. Before each measurement it is adjusted until the bridge circuit is balanced. $R_{2A}$ and $R_{2B}$ together determine the sensitivity of the instrument. The amount of input current necessary to produce full scale deflection of the meter can be changed by a factor of thirty with their adjustment.

The 6C6 tube ($T_1$) and high-megohm resistor ($R_1$) were installed together in a light-proof shielded tube as shown in plate 3. It was necessary to make the shield light-proof to prevent a decrease in the sensitivity of the instrument.

As indicated in plate 3 sulfur serves as a support for the conductor rods and as an insulator in both the shield and photoconductivity cell. Trials with various

substances indicated that sulfur was the best insulator
for this purpose.

To prevent current leakage along the glass envelope
of the 6C6 tube, it was treated as follows before
installing in the shield. The glass surface was cleaned
by placing it in the vapor of boiling carbon tetrachloride.
The envelope was then washed with absolute ethanol and
allowed to dry. Finally a coating of Q-dope (a solution
of polystyrene) was applied to the glass surface and
allowed to dry.

The theory of the operation of this micromicro-
ammeter has been discussed by Roberts who shows that the
following formula is valid

$$I_1 R_1 = I_2 R_2 = E_1 \tag{5}$$

where $I_1$ is the input current with the input leads
connected to terminals HI and G (plate 2), $I_2$ is the
current flowing through the 60 microammeter, and $E_1$ is
the voltage drop across the terminals HI and LO. From
this formula it can be seen that the ratio $R_2/R_1$ determines
the sensitivity of the instrument.

Therefore the calibration of the meter consists
essentially of determining the value of the high-megohm
resistor $R_1$. This calibration was carried out by using
the micromicroammeter as an electrometer. A standard
condenser having a capacitance of $0.0500 \times 10^{-6}$ farads

was charged to about 0.2 volt with a potentiometer and
then allowed to discharge across the terminals HI and LO.
The time required for the condenser to drop down to a
given fraction of its original voltage was recorded with
a stopwatch, and the resistance $R_1$ was then calculated
from the formula

$$2.30 R_1 C \log (E_o/E_t) = t$$

using the slope method. In the above formula C is
capacitance and $E_t$ is the measured voltage at time t. In
this manner it was found that

$$R_1 = 6.08 \times 10^9 \text{ ohms} \pm 1\% .$$

The potentiometer voltage required to produce full
scale meter deflection when applied across the terminals
HI and LO was found to be

$$E_1 = 0.193 \text{ volts, when } R_2 = 3000 \text{ ohms} .$$

Therefore $I_1 = (0.193)/(6.08 \times 10^9)(60)$

$$= 5.29 \times 10^{-13} \text{ amps per scale division} .$$

PHOTOCONDUCTIVITY CELL. The design of the cell is
shown in plate 3. The copper shielding tubes (7) extend
through two holes in the cell base (12). The circular
groove (13) cut into the base is filled with Cenco
"softseal tackiwax" which allows an airtight seal to be
obtained when the brass cylinder (14) is forced on. This
brass cylinder can be readily removed to insert a crystal
into the holder. Not shown in the diagram is a glass vial

containing magnesium perchlorate which rests inside the cell on the base. The cylinder (14), base (12), and electrometer tube shield (7) are all grounded to a water pipe.

CONDENSER FOR POTENTIAL SOURCE. The potential source shown in plate 1 is a 4 microfarad, 600 volt, oil-filled condenser. Since the current drain on the condenser is very low, no noticeable voltage drop could be detected during the photocurrent measurements.

LIGHT SOURCE. Throughout this investigation a Beckman spectrophotometer, model DU, with a tungsten filament lamp served as the light source. An optical system of three mirrors and a condensing lens brought the light from the spectrophotometer and focused it on the surface of the crystal in the photoconductivity cell. The light was focused into a line about 1/2 mm wide and 2 mm long.

The spectral distribution of energy of the light after passing through the optical system was determined by means of a copper-copnic, seventeen junction thermopile. The thermopile potential was measured with a Leeds and Northrup type HS galvanometer. During these measurements it was assumed that the galvanometer deflection was proportional to the light intensity. It was found that the distribution of energies agreed fairly closely with

that calculated for a tungsten filament operating at a
block body temperature of 2100° Kelvin as indicated in the
following table.

| wavelength (m$\mu$) | E$_{exp}$ (cm deflection) | E$_{calc}$ (arbitrary) |
|---|---|---|
| 450 | 1.8 | 1.94 |
| 500 | 5.1 | 5.08 |
| 550 | 11.7 | 10.8 |
| 600 | 20.7 | 19.3 |
| 650 | 31.7 | 30.5 |
| 700 | 43.7 | 43.7 |

In this table E$_{exp}$ represents the galvanometer
deflection observed at the given wavelength. The values
of E$_{calc}$ are proportional to those calculated from the
formula

$$E_\lambda = e_\lambda J_\lambda$$

where e$_\lambda$ is the emissivity of tungsten and J$_\lambda$ is the
intensity of an ideal black body at 2100° K. In photo-
current measurements below 500 m$\mu$ the calculated energy
values are used in preference to the experimental values
when determining the spectral distribution of photocurrent.

An absolute determination of the light intensity
striking the crystals was made by comparing its intensity
with a calibrated, carbon filament light obtained from
the National Bureau of Standards. The comparison was
carried out by means of the thermopile previously mentioned.
It was found that at a wavelength of 700 m$\mu$ and with the
spectrophotometer slit width at 2.0 mm,

$$E = 3.82 \times 10^{-5} \text{ calories sec.}^{-1} .$$

CRYSTAL PREPARATION.  The dimensions of the crystals used for the photocurrent measurements never exceeded 2 x 3 x 4 mm and were oftentimes much smaller.  Usually the crystals were washed in absolute ethanol before inserting in the cell to remove any surface layer of water.  A dry atmosphere in the photoconductivity cell was maintained by means of magnesium perchlorate.  With these precautions it was found that no observable surface conductivity occurred, making it unnecessary to evacuate the cell.
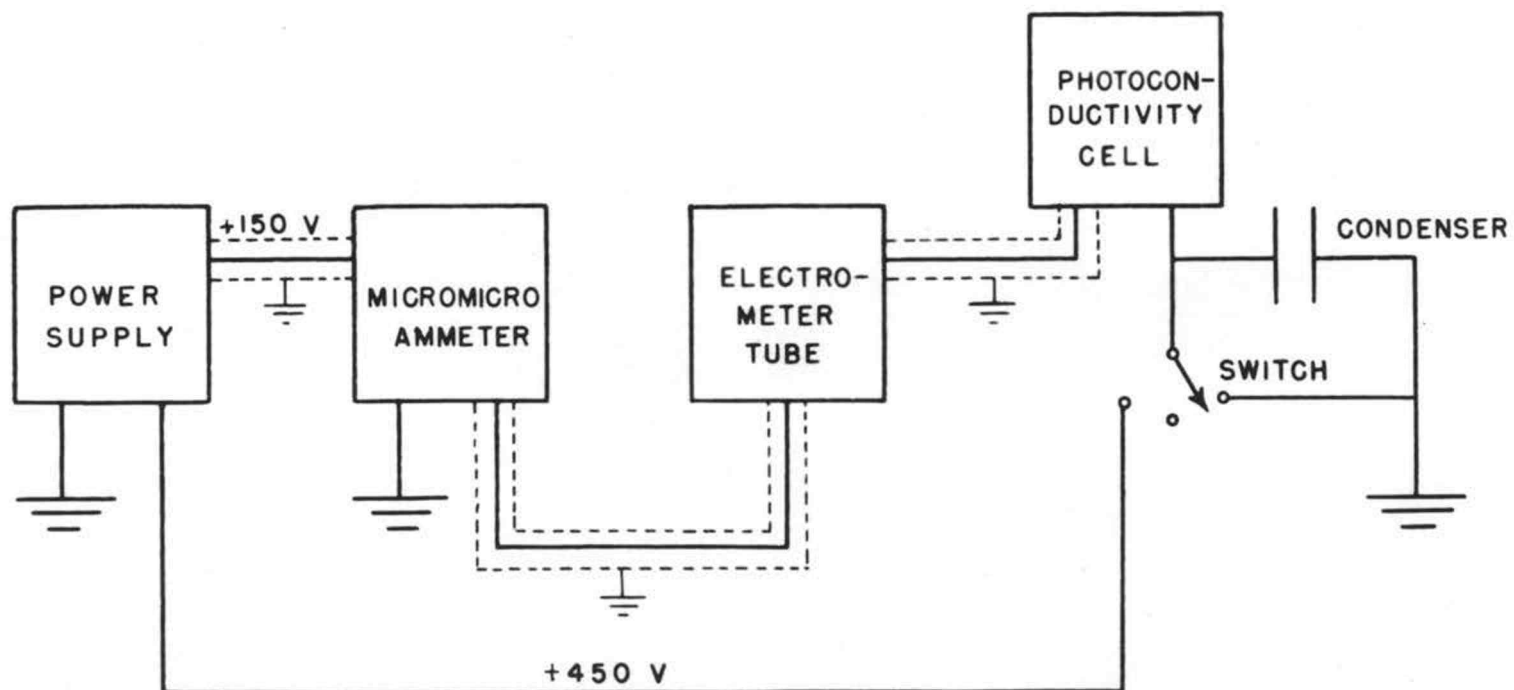
CURRENT MEASUREMENT.  Throughout this investigation all of the photocurrent measurements were made at room temperature.  At this temperature the dark current is generally too small to be detectable, and therefore the crystal may be illuminated at any time after the field is applied.  With currents of about $10^{-11}$ amperes or less, the photocurrent instantly attained a maximum value upon illumination and then slowly decreased as polarization occurred.  This initial current after illumination was always recorded as the primary photocurrent.  It was found necessary to use a low light intensity in order to prevent the initial rate of polarization from becoming too great. After each measurement at a given wavelength the condenser serving as the potential source was discharged and the crystal was illuminated for the same length of time as

with the field applied.  In most measurements this duration
of illumination was five seconds with and without the field
as determined with a stopwatch.  By this procedure the
effects of polarization could be kept to a minimum, and
reproducible results were obtained.

PLATE I
BLOCK DIAGRAM OF
EXPERIMENTAL SYSTEM

POWER SUPPLY · MICROMICRO AMMETER · ELECTRO-METER TUBE · PHOTOCON-DUCTIVITY CELL · CONDENSER · SWITCH

+150 V · +450 V

PLATE 2
SIMPLIFIED CIRCUIT OF
MICROMICROAMMETER

HI

$R_1$

$T_1$

$T_2$

22.5 V
− |||| +

LO

60
μA

$R_2$

$R_3$

G

S

$R_4$

− 150 V +
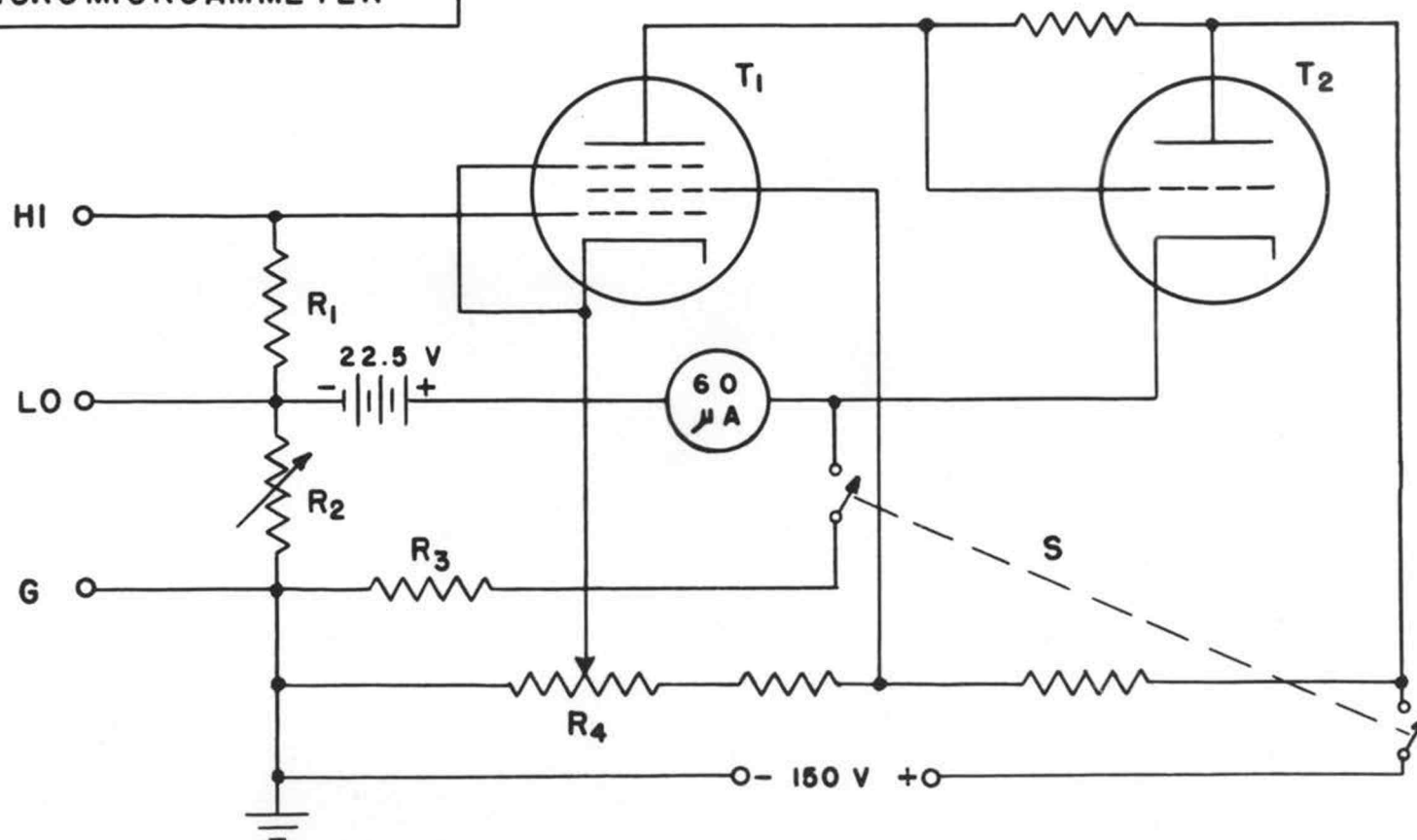
PLATE 3

PHOTOCONDUCTIVITY CELL AND
ELECTROMETER TUBE SHIELD
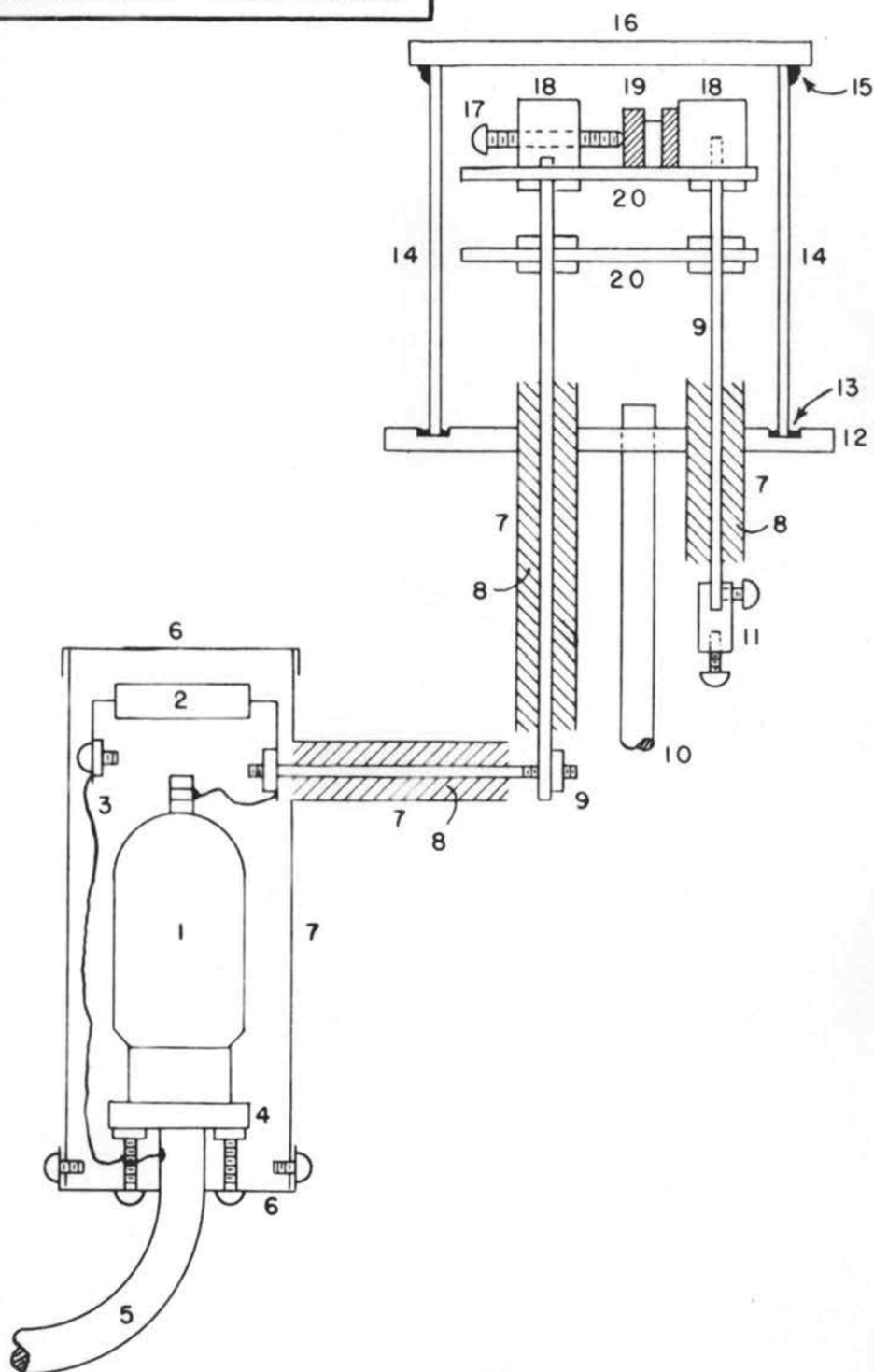
LEGEND  (Plate 3)

1.  6C6 electrometer tube

2.  Resistor of $6 \times 10^9$ ohms $(R_1)$

3.  Insulated wire to cable

4.  Tube socket

5.  Shielded cable to micromicroammeter cabinet

6.  Aluminum covers

7.  Copper tubes

8.  Sulfur

9.  Brass rods

10. Tube for cell evacuation

11. Connector for lead from positive potential source

12. Brass plate for cell base

13. Circular groove cut in base plate

14. Brass cylinder, 5 cm in diameter and 15 cm high

15. Apiezon-W wax which seals optical window to cylinder

16. Optical glass window

17. Brass screw for securing electrode

18. Brass blocks with cross section of 1 x 1 cm

19. Carbon blocks for electrodes

20 "Teflon" strips

# III.   DISCUSSION OF RESULTS

PHOTOCURRENT IN CRYSTALS CONTAINING F-CENTERS.
Graphs 1, 2A, and 3 show typical curves for the observed
spectral distribution of photocurrent in KCl crystals
containing various concentrations of F-centers.  In every
case the photocurrent values are given on the basis of a
field strength of 450 volts $mm^{-1}$.  The concentrations of
F-centers in the various samples were calculated by means
of the Smakula equation, setting the oscillator strength
equal to unity as was done by Scott and Smith (17, p.984).
All of the samples used in this investigation were pre-
pared by additive coloration.

On graph 1, curve A, is shown the distribution of
photocurrent obtained with a KCl sample containing approxi-
mately $3.7 \times 10^{15}$ F-centers $cm^{-3}$.  The measurement was
carried out in the direction of increasing wavelengths.  In
the region of higher absorption the photocurrent curve falls
off faster than would be expected, as is indicated by the
dashed curve.  At the completion of these measurements the
field was removed, and the crystal illuminated for three
minutes with light of 560 mµ.  The photocurrent measurements
were then repeated and the results are shown in curve B.

Graph 2A, curves A and B, show the photocurrent
distribution obtained with a freshly colored KCl crystal

before and after illumination with light of 560 m$\mu$.  The
same curves in graphs 2B show the corresponding change in
the absorption spectrum of the crystal before and after
illumination.  It can be seen from these curves that
illumination in the F-band region causes a much greater
decrease in the photocurrent than in the extinction
coefficient.  It should be noted that this decrease of
photocurrent occurs entirely in the F-band region, and the
photocurrent in the R-band region remains unchanged.
Although not shown in graph 2A because of its small magni-
tude, a photocurrent maximum in the N-band region (at
about 10000 m$\mu$) remains unaltered during the F-band
illumination.

Curve A of graph 3 shows the distribution of photo-
current in a KCl crystal containing a moderately high
concentration of F-centers.  It is to be observed that a
dip in the photocurrent curve occurs in the region of
greatest absorption.  The photocurrent in the R-band region
is relatively large, and there is a photocurrent maximum in
the N-band region at about 1000 m$\mu$.  Results similar to
these were always obtained with crystals containing high
concentrations of F-centers.

Measurements with KBr containing various concentra-
tions of color centers gave results which were in general
agreement with those given above for KCl.

PHOTOCURRENT IN CRYSTALS CONTAINING COLLOIDAL

CENTERS. Curve B of graph 3 gives the spectral distribu-
tion of photocurrent which was obtained from a KCl crystal
containing the colloidal absorption band at 760 m$\mu$. Curve
A shows the photocurrent distribution of an identical
crystal before treating to form the colloidal band. A
photocurrent maximum at 1075 m$\mu$ was also observed in addi-
tion to the peak at 470 m$\mu$ with KCl crystals containing
colloidal potassium. This is possibly a shift of the
N-band which was observed in KCl crystals containing
F-centers alone.

PHOTOCURRENT IN CRYSTALS CONTAINING R'-CENTERS.
Curve C of graph 2A indicates the type of photocurrent
distribution obtained after the development of the broad
R'-band in KCl. Curve C of graph 2B shows the corresponding
absorption spectrum. The R'-band was developed in the
crystals by exposing them to the white light of a carbon
arc for about 10 minutes. It should be observed that there
was a relatively large decrease of the photocurrent in the
R-band region upon the formation of the R'-band. Also it
is possibly significant that the photocurrent in the N-band
region was almost entirely destroyed by the development of
the R'-band.

This destruction of the photocurrent was noted in
all cases where the shape of the resulting R'-absorption

band was similar as that in graph 2B.  However during the
formation of the R'-band in crystals having an original
high concentration of F-centers, the peak of the R'-band
occasionally occurred near the peak of the original F-band.
In these cases the resulting photocurrent curves gave
evidence of the F- and R-bands and on one occasion gave
evidence of the colloidal band.

DARK CURRENT IN KBr.  While conducting photocurrent
measurements on colored KBr, it was noted that a dark
current of the order of $10^{-11}$ amperes was always present.
Also it was observed that this dark current sometimes did
and other times did not tend to polarize the crystal.  This
dark current was found to be dependent upon the time from
the previous illumination as is shown in graph 4.  In this
experiment light of 800 mμ was used to illuminate the
crystal since this wavelength was found to produce the
maximum photocurrent.  The crystal was illuminated for
exactly 30 seconds with no applied field.  After turning
off the light, the field was applied at the end of the time
interval indicated on the graph.  It was found that a ten
minute interval after illumination was sufficient to
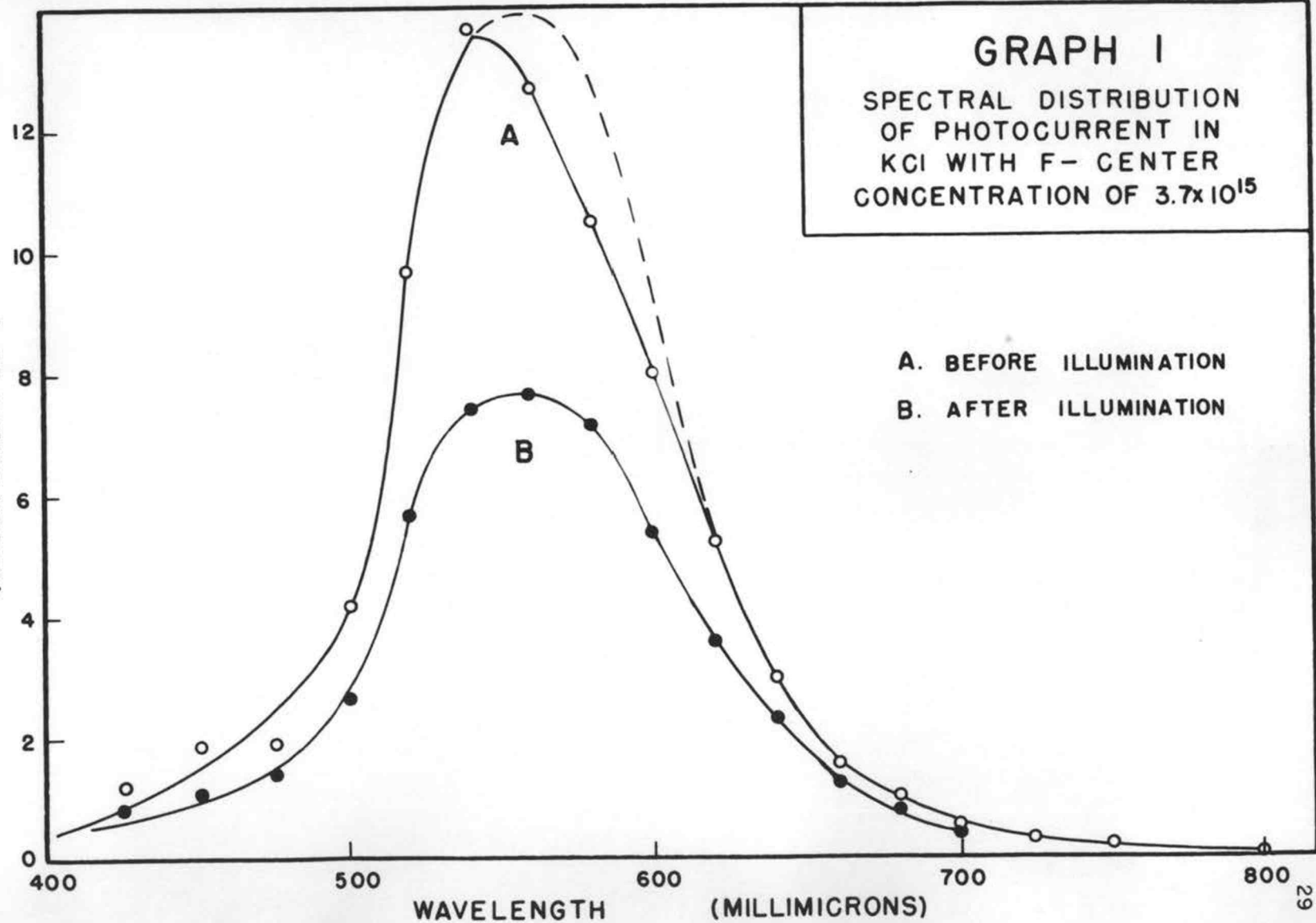destroy this enchanced activity.

GRAPH I

SPECTRAL DISTRIBUTION OF PHOTOCURRENT IN KCl WITH F- CENTER CONCENTRATION OF $3.7 \times 10^{15}$

A. BEFORE ILLUMINATION

B. AFTER ILLUMINATION

GRAPH 2A

SPECTRAL DISTRIBUTION
OF PHOTOCURRENT FOR
KCl WITH F – CENTER
CONCENTRATION OF $1.6 \times 10^{16}$

A. ORIGINAL SAMPLE OF KCl
B. AFTER ILLUMINATION WITH
   560 m$\mu$ LIGHT FOR 30 MINUTES
C. AFTER ILLUMINATION WITH
   ARC LIGHT FOR 10 MINUTES

PHOTOCURRENT PER INCIDENT ENERGY (COUL./CAL. $\times 10^5$ )

WAVELENGTH (MILLIMICRONS)

GRAPH 2B

ABSORPTION SPECTRA OF KCl WITH F—CENTER CONCENTRATION OF $1.6 \times 10^{16}$

A. ORIGINAL SAMPLE OF KCl
B. AFTER ILLUMINATION WITH 560 mμ LIGHT FOR 30 MINUTES
C. AFTER ILLUMINATION WITH ARC LIGHT FOR 10 MINUTES

EXTINCTION COEFFICIENT (CM⁻¹)

WAVELENGTH (MILLIMICRONS)

GRAPH 3

SPECTRAL DISTRIBUTION
OF PHOTOCURRENT FOR
KCl WITH F-CENTER
CONCENTRATION OF $3.9 \times 10^{17}$

A. ORIGINAL SAMPLE OF KCl

B. AFTER FORMATION OF COLLOIDAL BAND

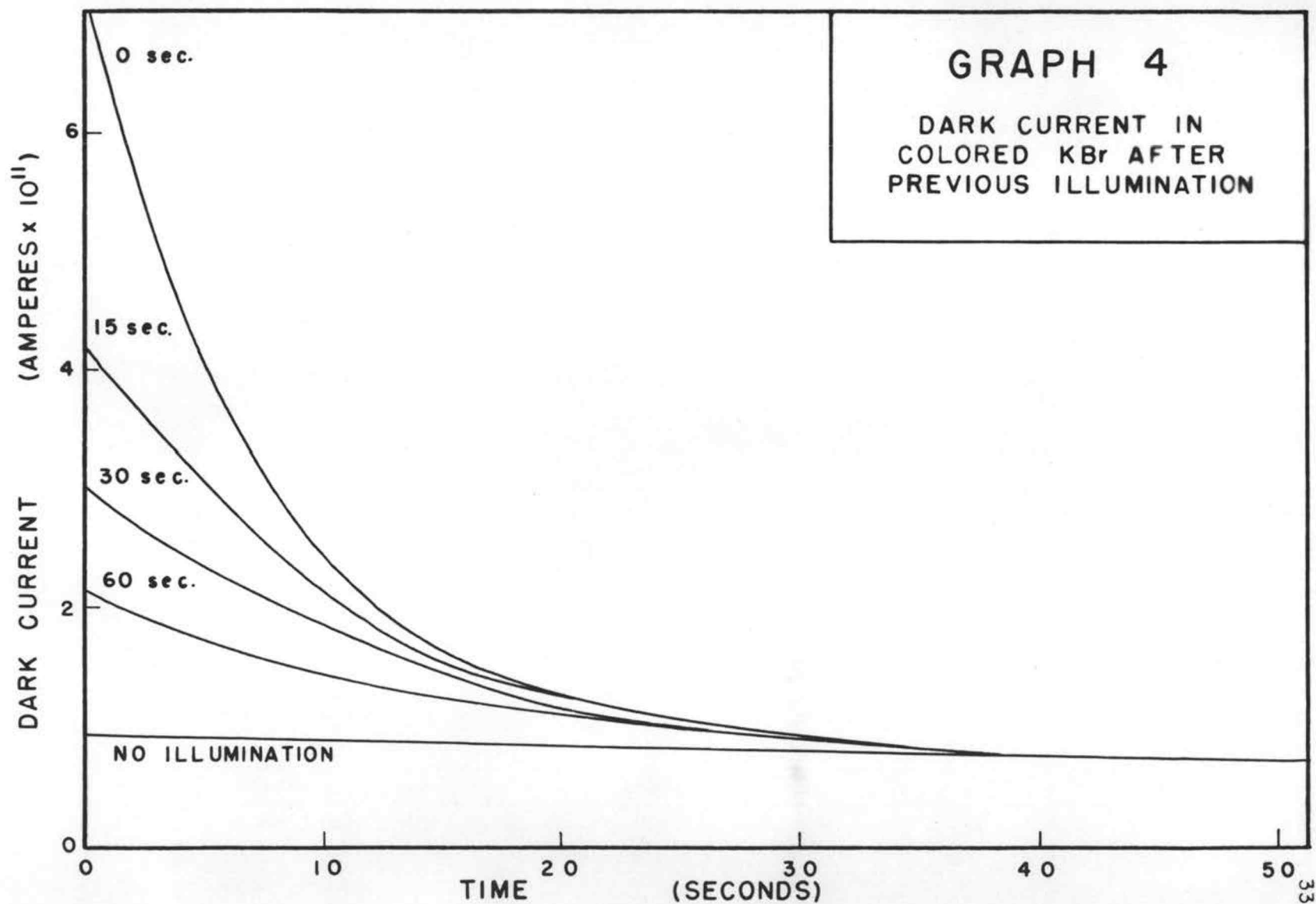PHOTOCURRENT PER INCIDENT ENERGY (COUL./CAL. x $10^6$)

WAVELENGTH (MILLIMICRONS)

GRAPH 4

DARK CURRENT IN COLORED KBr AFTER PREVIOUS ILLUMINATION

## IV.  CONCLUSIONS

METASTABLE CENTERS IN KBr.  From the results of the
dark current studies with KBr it is apparent that the
released photoelectrons become trapped in unstable centers
and then fall back to a lower energy level.  In the case
studied the conduction electrons are probably released
from R-centers.  Pick has found from optical studies that
the lifetime of the F'-band in KBr is several minutes at
room temperature.  Therefore it appears likely that the
above effect is caused by the formation of unstable
F'-centers.

NATURE OF F-CENTERS.  By comparing graphs 1 and 3
it can be seen that the product $\eta$w, in the region of the
F-band absorption, decreases as the F-center concentration
increases.  The experimental results can be best explained
by assuming that this decrease in $\eta$w is caused by a
decrease in the quantum yield $\eta$ .  This implies that the
F-band is composed of two types of centers, with only one
of the types being photoconducting, as was postulated by
Oberly.  This is apparently the only mechanism which can
satisfactorily explain the dip of the photocurrent curve
in the region of maximum absorption with crystals contain-
ing relatively large concentrations of F-centers.

NATURE OF THE COLLOIDAL BAND.  The spectral distri-
bution of photocurrent in KCl crystals containing the

colloidal band was found to agree in shape with the photo-
current curve obtained by Gyulai for blue rocksalt con-
taining colloidal sodium.  However, the position of the
photocurrent maximum was found to have been shifted to a
higher wavelength in the case of KCl, as would be predicted
by theory.

NATURE OF THE R'-BAND.  The decrease of the photo-
conductivity in the F-, R-, and N-bands after the formation
of the R'-band, indicates that these centers are destroyed
during the formation.  Also the failure to detect a colloid
photocurrent indicates that the size of the R'-centers is
below colloidal size.

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