

## Low-Temperature Photoconductivity of Additively Colored KCl\*

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 (Received October 17, 1960)

The transient photoconductivity of additively colored crystals of KCl has been investigated at temperatures down to 10°K. The spectral response reflects the structure in optical absorption in the ultraviolet reported by Lüty. Quantum yields are found to be less than 1.0 at 10°K but are much higher in the region of the  $L_1$  (3.6 eV) and  $L_2$  (4.2 eV) bands than in the  $K$  band on the high-energy side of the  $F$  band. The beginning of electron collection or saturation effects was found in the case of thin, lightly colored crystals which indicates that electron ranges were in the vicinity of  $10^{-6}$  cm<sup>2</sup>/volt at 10°K. Shallow traps effective below 26°K were found in the crystals studied so far. These traps have a large product of concentration times cross section and compete favorably with the  $F$  center at 10°K. They can be partly filled following illumination at low temperature with the result that enhanced photoresponse is produced in the red and near infrared.

### I. INTRODUCTION

TRANSIENT photoconductivity in additively colored alkali halide crystals has provided a sensitive method for studying the electronic structure of these crystals. Recently Lüty<sup>1</sup> has reported three new absorption bands on the high-energy side of the  $F$  band whose optical absorption is proportional to the  $F$ -center concentration in heavily colored alkali halides. The photoelectric response of KBr and KI at 80°K has been found to show some of this same structure<sup>2</sup> and similar results were recently obtained by Robe<sup>3</sup> in an investigation of the photoresponse in KBr at liquid helium temperatures. The main emphasis in the present work is on the low-temperature yield and transport properties of carriers released by light absorbed in the  $F$ ,  $K$ , and so-called Lüty bands at higher energy. The early experiments of Pohl and coworkers<sup>4-7</sup> show that primary photocurrents may be interpreted in a simple way in terms of a mean electron range (Schubweg) governed by a uniform volume distribution of traps. It was shown in KCl at -100°C that the  $F$  center itself is the main trap for concentrations of  $F$  centers between about  $2 \times 10^{15}$  and  $10^{17}$  per cubic centimeter. Inchauspé<sup>2</sup> found that traps other than the  $F$  center may be important in lightly colored crystals of KBr at 80°K. It will be shown in this paper that traps other than the  $F$  center become dominant at very low temperatures in lightly colored KCl.

Primary photocurrents are characterized by a saturation behavior with increasing collection field. If the range can be determined from saturation data, and if the optical absorption is known, it is possible to compute the quantum efficiency defined as the number of conduction electrons released per absorbed quanta. In the early work on alkali halides the saturation field was found to be so high that only extremely thin crystals could be used in which case the optical absorption could not be measured. In the present experiments it was found that partial saturation could be obtained in lightly colored crystals of KCl in which the  $F$ -band absorption could be measured. It is thus possible to obtain the quantum efficiency if we assume that the absorption of these high-energy bands is proportional to the  $F$ -center concentration.

In order to explain the temperature dependence of the observed photoconductivity it is necessary to know the way in which carrier mobility varies with temperature. Results are presented in the following article<sup>8</sup> on the Hall mobility of photoelectrons in KCl as a function of  $F$ -center concentration and temperature in the range 6° to 100°K. It was found that the Hall mobility rises steeply as the temperature is lowered but that the photoconductivity does not reflect the rise in mobility apparently because of shallow traps. The existence of these traps can be demonstrated by enhanced long-wavelength sensitivity following illumination at low temperature as well as by electrical glow phenomena during warming.

### II. EXPERIMENTAL METHODS

#### A. Sample Preparation

Samples for the photoconductivity measurements were all prepared from the same shipment of Harshaw KCl. In order to avoid passing the impurities over the KCl stock during processing, potassium was vacuum distilled three times with the final distillation entering

\* Supported in part by the U. S. Air Force Office of Scientific Research and the National Science Foundation.

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<sup>1</sup> F. Lüty, presented at The International Symposium of Color Centers in Alkali Halides, Corvallis, Oregon, September, 1959 (unpublished).

<sup>2</sup> N. Inchauspé, *Phys. Rev.* **106**, 898 (1957).

<sup>3</sup> J. Robe, Ph.D. thesis, University of Illinois, June, 1960 (unpublished).

<sup>4</sup> W. Flechsig, *Z. Physik* **46**, 788 (1928).

<sup>5</sup> G. Glaser and W. Lehfeldt, *Nachr. Akad. Wiss. Göttingen, Math.-physik Kl. 2*, 109 (1936).

<sup>6</sup> N. Mott and R. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), Chap. 4.

<sup>7</sup> R. W. Pohl, *Proc. Phys. Soc. (London)* **49**, 16 (1937).

<sup>8</sup> F. C. Brown and N. Inchauspé, following paper [*Phys. Rev.* **121**, 1303 (1961)]. Preliminary results were reported at the International Symposium of Color Centers in Alkali Halides, Corvallis, Oregon, September, 1959 (unpublished).

TABLE I. *F*-center concentration, thickness, and the low temperature at which photoresponse was investigated for the different samples.

| KCl crystal | $C_F(\text{cm}^{-3})$ | $l(\text{cm})$ | $T_{PC}(\text{°K})$ |
|-------------|-----------------------|----------------|---------------------|
| 1           | $4.87 \times 10^{17}$ | 0.122          | 9.5                 |
| 2           | $3.38 \times 10^{17}$ | 0.0915         | 9.5                 |
| 3           | $2.78 \times 10^{17}$ | 0.0915         | 12.                 |
| 4           | $1.6 \times 10^{16}$  | 0.094          | 9.5                 |
| 5           | $5.1 \times 10^{15}$  | 0.0635         | 15.                 |
| 6           | $5.3 \times 10^{15}$  | 0.0635         | 8.5                 |

a sidearm containing the uncolored crystal. The Pyrex tube containing the crystal and potassium was placed within a double inclined oven with the lower oven controlling the vapor pressure of potassium and the upper oven, containing the crystal, held at 600°C. After 12 hours, the samples were rapidly quenched in liquid paraffin. The crystals were kept in the dark and only briefly exposed to red-light during cleaving and mounting in the cryostat. Information on the samples is listed in Table I. The optical absorption of all crystals was measured at room temperature as well as several samples at liquid helium temperatures in a Cary recording ultraviolet spectrophotometer, Model 14R. The *F*-center concentration was determined from the optical density using Smakula's equation<sup>9</sup> with an oscillator strength of 0.81. Both the optical absorption and photoconductivity were found to change with aging at room temperature. Thus, freshly colored crystals were prepared for all sets of measurements. The absorption data on freshly prepared crystals at liquid helium temperatures was found to agree quite well with those measured by Lüty.<sup>1</sup> The dotted curve in Fig. 1 shows the optical density for a crystal ( $C_F = 3.4 \times 10^{17} \text{ cm}^{-3}$ ) from which the reflection and absorption losses in an uncolored blank at liquid helium temperature has been subtracted. The importance of making these measurements on freshly colored crystals should be emphasized.

### B. Transient Photoconductivity

In order to measure primary as distinguished from secondary photoconductivity, it is necessary to observe several precautions. Charge entering the crystal from the electrodes, space charge, and charge multiplication must not be allowed. The first of these was eliminated by blocking layers between the crystal and electrodes. Space charge was not a problem in the present experiments because of low light intensities and a very small amount of released charge. KCl with its high dielectric constant and band gap would not be expected to show charge multiplication effects at the fields employed, and a nearly linear photoresponse with collecting field proved that it did not.

For our experimental case, consider a single crystal of thickness  $l$ , placed between plane parallel electrodes,

<sup>9</sup> A. Smakula, Z. Physik **63**, 763 (1930).

and illuminated through the cathode. Electrons released by absorbed light will be swept into the crystal by the electric field until they become trapped. If  $n_0$  electrons are released at  $t=0$ , the number remaining at time  $t$  is given by  $n = n_0 e^{-t/\tau}$ , where the mean time for trapping  $\tau = 1/C_t \sigma u$ .  $C_t$  is the trap density,  $\sigma$  the cross section for trapping, and  $u$  is the thermal velocity. The average range or Schubweg,  $w = \mu E \tau$ , where  $\mu$  is the electron drift mobility and  $E = V/l$  is the electric field. The range per unit field,  $w_0 = \mu \tau$ , is a useful property of the crystal. Using  $t = x/\mu E$  and the definition of range, the number of electrons left after traveling a distance  $x$  is given by  $n = n_0 e^{-x/w}$ . The electrometer will register a charge  $q = ex/l$  for every electron of charge  $e$  that drifts a distance  $x$  in the crystal.

Using these concepts and considering the absorption, penetration, and reflection of the light, Van Heyningen and Brown<sup>10</sup> used the following formula for the charge measured by the electrometer,

$$Q = e \eta_a N_0 (1 - R) (1 - e^{-kl}) \psi, \quad (1)$$

where  $\eta_a$ , the quantum efficiency, is the number of conduction electrons released per absorbed quanta;  $N_0$  is the number of incident quanta,  $R$  is the reflection coefficient,  $k$  is the absorption constant, and  $\psi$  is a saturation factor which takes into account the mean range of electrons and the depth of optical absorption.  $\psi = \bar{x}/l$ , where  $\bar{x}$  is the total displacement of all the electrons divided by their number. For our case of small optical absorption, the whole crystal is uniformly illuminated, i.e.,  $k \approx 0$ , and the formula for  $\psi = \psi_{i_0}$  has been given by Hecht.<sup>11</sup>

$$\psi_{i_0} = \frac{w}{l} \left[ 1 - \frac{w}{l} (1 - e^{-l/w}) \right]. \quad (2)$$

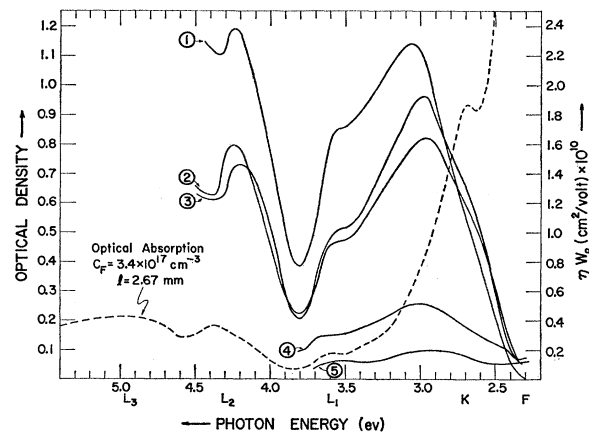


FIG. 1. Transient photoresponse  $\eta w_0$  versus photon energy for the KCl crystals and temperatures listed in Table I. The optical density of heavily colored crystals is shown by a dotted line.

<sup>10</sup> R. S. Van Heyningen and F. C. Brown, Phys. Rev. **111**, 462 (1958).

<sup>11</sup> K. Hecht, Z. Physik **77**, 235 (1932).

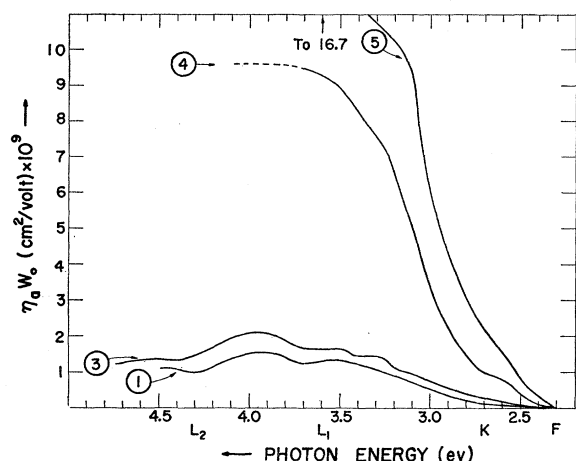


FIG. 2. Photoresponse in the vicinity of  $10^\circ\text{K}$  corrected for optical absorption. Notice that  $\eta_a w_0$  is very low in the  $K$  and  $F$  region but rises steeply at shorter wavelengths.

Equation (2) approaches 0.5 for complete saturation of the photocurrent, i.e.,  $w = \infty$ . Note that Eq. (1) requires a linear dependence of  $Q$  on incident light intensity. This point was tested using neutral density filters, and the response of the crystal was found to be linear over at least three orders of magnitude. For the case where saturation and collection effects can be ignored, i.e.,  $w \ll l$ , Eq. (1) can be rewritten as follows, remembering that  $w = \mu E \tau$  and  $\psi_{t0} \approx w/l$ :

$$Q = \frac{e \eta_a N_0 (1-R) (1 - e^{-kl})}{l} \mu E \tau. \quad (3)$$

The product  $\eta_a \mu \tau = \eta_a w_0$  can be determined from this equation, a knowledge of the optical absorption, and the observation of  $Q$ .

If two traps are effective instead of just one, for example, the  $F$  center (or closely associated trap) and a second shallow trap, then the trapping probability

$$\frac{1}{\tau} = \frac{1}{\tau_F} + \frac{1}{\tau_t} = (C_F \sigma_F + C_t \sigma_t) u. \quad (4)$$

The observed charge per absorbed photon may be computed using  $w_0 = \mu \tau$ , Eq. (3) and Eq. (4). The result is

$$Q / [N_0 (1-R) (1 - e^{-kl})] = (eE/l) (\eta_a w_0), \quad (5)$$

where

$$\eta_a w_0 = \eta_a \mu / [u (C_F \sigma_F + C_t \sigma_t)]. \quad (6)$$

From Eq. (6) it is seen that if the  $F$  center is the dominant trap, as it is at  $-100^\circ\text{C}$ , then  $\eta_a w_0$  is inversely proportional to the concentration of  $F$  centers. If the shallow traps become dominant ( $C_t \sigma_t \gg C_F \sigma_F$ ), which is the case for low temperatures and small  $F$ -center concentration, then the observed  $\eta_a w_0$  tends toward a constant value as a function of  $1/C_F$ . These are quali-

tative considerations only as it may be necessary to take more than two traps into account.

The low temperatures for the photoconductivity measurements were maintained in a helium cryostat similar to that described by Mapother and Witt.<sup>12,10</sup> The crystals were gently held between plane parallel electrodes located in a copper chamber clamped to the bottom of the helium reservoir. Helium exchange gas could be admitted to the copper chamber to maintain thermal contact. Temperatures were measured with a copper constantan thermocouple and a carbon resistance thermometer each calibrated against a standard platinum resistance thermometer. The lower transparent electrode was a 1-mm thick NESA-coated quartz slide<sup>13</sup> connected to a highly insulated battery voltage supply. A shielded lead from the upper spring-loaded metallic electrode was connected to the input of an Applied Physics Corporation vibrating reed electrometer used in the "open" position to measure charge. The electrodes were blocked with insulating layers to prevent charge from entering or leaving the crystal. The upper metallic electrode was blocked with 0.5-mil Mylar plastic, and the lower transparent electrode with a 5.5 mil optical quality quartz plate. The amplified output of the electrometer was fed into a recording potentiometer. The background noise level was well below  $10^{-16}$  amp and the charge released by a 7.5-sec light pulse was in the vicinity of  $10^{-12}$  Coulomb. The electrometer and recording potentiometer were calibrated directly from standard charge pulses.

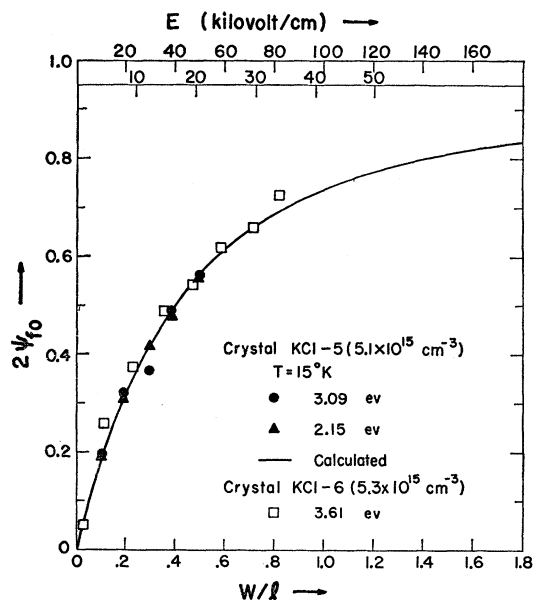


FIG. 3. Saturation curves for crystals 5 and 6 at low temperature. Two scales for electric field are given—the upper one applies to crystal 5, the lower to crystal 6. Crystal 6 had the longer range as given in Table III.

<sup>12</sup> D. E. Mapother and F. E. L. Witt, Rev. Sci. Instr. **26**, 843 (1955).

<sup>13</sup> D. N. Lyon and T. H. Geballe, Rev. Sci. Instr. **21**, 769 (1950).

TABLE II. Ratio of the photoresponse at 10°K and 78°K for various crystals at a photon energy of 3.6 ev.

| KCl crystal | $C_F$ (cm <sup>-3</sup> ) | $\eta_a w_0$ (10°K) / $\eta_a w_0$ (78°K) |
|-------------|---------------------------|---|
| 1           | $4.87 \times 10^{17}$     | 2.0                                       |
| 2           | $3.38 \times 10^{17}$     | 1.4                                       |
| 3           | $2.78 \times 10^{17}$     | 1.3                                       |
| 4           | $1.6 \times 10^{16}$      | 1.1                                       |
| 5           | $5.1 \times 10^{15}$      | 1.1                                       |

The light source for the ultraviolet photoconductivity measurements was a Hanovia quartz hydrogen lamp dispersed with high spectral purity by a Leiss double monochromator using quartz prisms. A front silvered mirror reflected the uniform image of the second prism face on the crystal surface. The mirror could be rotated 90° to reflect the same image on a calibrated cesium antimony photocell.<sup>14</sup> A contact switch on the input of the electrometer enabled it to be used to measure the photocell current and the crystal pulse in turn. It was thus possible to monitor the light intensity point by point if desired, or to check the light intensity at any time. The photoconductivity measurements in the near infrared were taken with a regulated tungsten lamp as a source and its output was measured with a Perkin-Elmer radiation thermocouple calibrated against the cesium antimony photocell.

III. RESULTS

A. Photoconductivity Response

In order to plot the photoresponse as a function of wavelength for the case when saturation or collection effects are absent, ( $\psi = w_0 E / l$ ), it is convenient to rewrite Eq. (1) as follows:

$$\eta w_0 = Ql / N_0 e E, \tag{7}$$

where  $\eta = \eta_a (1 - R) (1 - e^{-kl})$  is now the quantum efficiency per incident photon,  $w_0$  is the range per unit field, and the experimentally determined quantities are

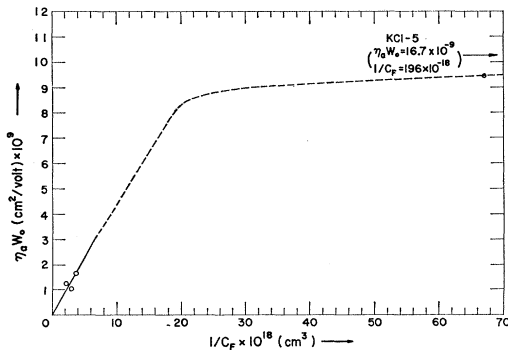


FIG. 4. Showing the position of the points for  $\eta_a w_0$  as a function of  $1/C_F$ . Data for the heavily colored crystals is at least consistent with a line drawn through the origin, whereas the lightly colored crystals lie far from this line. The dotted line is a plot of Eq. (6).

<sup>14</sup> Kindly furnished by Dr. L. Apker, General Electric Research Laboratory, Schenectady, New York.

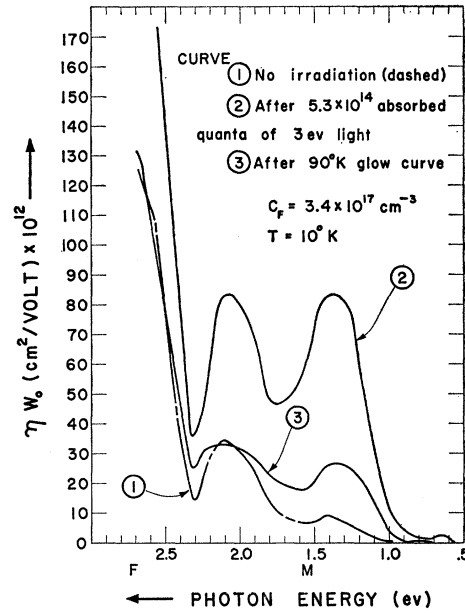


FIG. 5. Long wavelength photoresponse in a heavily colored crystal before and after irradiation at 10°K.

on the right. The low-temperature behavior of  $\eta w_0$  vs photon energy for 5 specimens of KCl containing  $F$  centers in a range of concentration from  $5.1 \times 10^{15}$  to  $4.87 \times 10^{17}$  per  $\text{cm}^3$  is plotted in Fig. 1. The optical absorption at 20°K as a function of photon energy for a 2.67-mm thick crystal of KCl with  $3.4 \times 10^{17}$   $F$  centers per  $\text{cm}^3$  is also included. This latter curve has been corrected for reflection losses and background absorption but not for absorption associated with the coloration. The structure of the photoconductivity curves for the more heavily colored samples clearly delineates the first two so-called Lüty bands with the third lying outside the reach of the apparatus. The peak photoresponse of the  $K$  band lies on the high-energy side of the  $K$  absorption peak. Since the range per unit field,  $w_0$ , should be constant with wavelength, this represents a sharp rise in the quantum efficiency in the vicinity of 2.9 ev. No significance is attached to the crossover of curves 2 and 3 in the  $L_2$  region since low incident light intensity in this case caused a fairly large scatter in the data.

Values of  $\eta_a w_0$  vs photon energy for these same curves, as plotted in Fig. 2, are obtained by correcting for absorption under the assumption that the absorption in the Lüty bands as well as in the  $K$  band, is proportional to the  $F$ -center concentration over the entire range and may be obtained from the measured optical density. The values for KCl-2 were not plotted since they fall between curves 1 and 3 and confuse the detail. The quantum efficiency rises from a minimum in the region of the  $F$  band to a fairly constant value in the region of the  $L_1$  and  $L_2$  wavelengths. The structure in this region is probably a reflection of the difficulty of

correcting for absorption rather than a variation in the quantum efficiency for absorbed light.

The photoresponse  $Q$  of the various crystals was observed point by point as the temperature was lowered in order to see if  $\eta_a w_0$  would reflect the increase in Hall mobility observed at low temperatures.<sup>8</sup> Little change with temperature was found for lightly colored crystals; however, the more heavily colored samples invariably showed a gradual increase below 80°K and a leveling off below about 50°K. A gradual increase below liquid nitrogen temperature was also reported in the early work of reference 7. For the present case the ratio of  $\eta_a w_0$  at 10°K to  $\eta_a w_0$  at 78°K is given in Table II for light absorbed in the  $L_1$  band. The observed increase only partly reflects the increasing Hall mobility because of the effects of shallow traps.

### B. Saturation Effects and Quantum Efficiency

The thickness of the thin cleaved samples of KCl was in most cases less than one millimeter as shown in Table I. Well over 1000 volts could be applied to the crystals without leakage largely due to the use of blocking layers, careful shielding, and placement of leads. Therefore, it was expected that saturation effects due to the collection of electrons according to Eq. (2) could be observed.<sup>15</sup> In addition, field ionization might also be possible at high electric fields for wavelengths which excite into states below the bottom of the conduction band.

Effects which appear to be due to field ionization were observable for light absorbed in the  $F$  and the  $K$  bands at 78°K. A plot of  $Q/N_0 e$  vs  $E$  at these wavelengths was concave upwards at high fields except in the case of very lightly colored crystals. These results at 78°K represent the combined effects of thermal and field ionization as shown by the work of Lüty.<sup>16</sup> At low temperature, 10°K, the superlinear effects in electric field were barely observable (moderate or heavily colored crystals) and only for light absorbed in the region of the  $K$  band. For the higher energy photons of the  $L_1$  band, the photoresponse was linear with electric field in heavily colored crystals. This result as well as the general behavior of the  $\eta_a w_0$  curves of Fig. 2 strongly indicates that light absorbed in the  $F$  and  $K$  bands excite electrons into discrete states below the bottom of the conduction band, whereas the higher energy  $L_1$  light excites into final states which overlie the bottom of the conduction band.

The situation was somewhat different in the case of lightly colored crystals. At 78°K collection effects appear to straighten out the upward bending of the  $Q/N_0 e$  versus  $E$  curves for the  $F$  and  $K$  region. Clear evidence for the beginning of saturation was obtained particularly at low temperature for light in the  $L_1$

TABLE III. Electron range  $w_0$  determined from saturation curves. The quantity  $(\eta_a w_0)'$  is the charge collected/absorbed photon,  $Ql/[N_0 e(1-R)(1-e^{-kl})E]$ . The extrapolated  $\eta_a w_0$  is the product of efficiency and unit range which would apply in the absence of collection effects [Eq. (3)]. The last column shows the quantum efficiency obtained in two ways as explained in the text.

| Crystal | $w_0$<br>(cm <sup>2</sup> /volt) | $(\eta_a w_0)'$<br>(cm <sup>2</sup> /volt) | Extrapolated<br>$\eta_a W_0$<br>(cm <sup>2</sup> /volt) | $\eta_a$             |
|---------|----------------------------------|--|---|----------------------|
| KCl-5   | $6.3 \times 10^{-7}$             | $16.7 \times 10^{-9}$                      | $22.8 \times 10^{-9}$                                   | $3.6 \times 10^{-2}$ |
| KCl-5   | $6.3 \times 10^{-7}$             | Calculated                                 |   | $2.4 \times 10^{-2}$ |
| KCl-6   | $1.5 \times 10^{-6}$             | $27.6 \times 10^{-9}$                      | $58.2 \times 10^{-9}$                                   | $3.9 \times 10^{-2}$ |
| KCl-6   | $1.5 \times 10^{-6}$             | Calculated                                 |   | $3.9 \times 10^{-2}$ |

band (3.61 eV).<sup>17</sup> Figure 3 presents the low-temperature saturation data for two lightly colored crystals, KCl-5 and KCl-6, which are almost identical physically except for their initial unknown impurity content. KCl-5 was colored from Harshaw stock and KCl-6 has been zone refined.<sup>18</sup> Saturation data for KCl-5 was obtained at two wavelengths lying on opposite sides of the  $F$  band, and that for KCl-6 was obtained at 3.61 eV. The intensity of the incident light for this run on KCl-6 was made as great as possible by using wide slits and running the hydrogen lamp at maximum power in order to decrease the scatter in the data at this wavelength.

Table III lists values of  $w_0$ ,  $\eta_a w_0$ , and the resulting values of  $\eta_a$ . Two different determinations of  $\eta_a$  are given for each crystal. The first are found by observing  $Q$  as a function of  $E$  and extrapolating the low-field points as straight lines as if there were no collection effects. This results in the extrapolated values of  $\eta_a w_0$  as shown in Table III. The efficiency  $\eta_a$  is then determined by dividing the extrapolated  $\eta_a w_0$  by  $w_0$ . This is the more reliable of the two methods since a graphical average over several points is involved. The second method of finding  $\eta_a$  is by determining  $Q$  at one high-field point, and then calculating the result using Eqs. (1) and (2). Of the four values of  $\eta_a$  listed, the one calculated by the second method for KCl-5 is the most uncertain. The low incident light intensity and the necessity of choosing a single datum point for the calculation shows up in its deviation from the other three. A value of  $\eta_a = 0.04 \pm 0.01$  appears to be the best weighted average-taking into account the uncertainties in the measurements. This estimate does not consider any errors made in assuming that the optical absorption in this region is proportional to the  $F$ -center concentration as shown by Lüty. The corresponding quantum efficiencies for the  $F$ - and  $K$ -band regions are  $\eta_a(F)$

<sup>17</sup> High-field or hot-electron effects are apparently not as important as might be suspected, as evidenced by the fact that the downward bending of the  $Q$  versus  $E$  curves appeared at moderate as well as very low temperature. The general trend with  $F$ -center concentration and crystal thickness also makes it reasonable to ascribe the observations mainly to collection effects.

<sup>18</sup> Zone-refined by the Anderson Physical Laboratory, Urbana, Illinois.

<sup>15</sup> H. Witt, Z. Physik 128, 442 (1950).

<sup>16</sup> F. Lüty, Z. Physik 153, 247 (1958).

$= (2.7 \pm 0.5) \times 10^{-4}$  and  $\eta_a(K) = (4.6 \pm 0.5) \times 10^{-3}$  both at  $10^\circ\text{K}$ .<sup>17</sup>

With the above measurements of  $\eta_a w_0$ ,  $\eta_a$ , and  $\mu$ , we can now check the dependence of  $\eta_a w_0$  on the trapping by  $F$  centers and other traps as expressed by Eq. (6). Figure 4 shows a few points for the photoresponse,  $\eta_a w_0$  (at 3.6 eV), located according to the reciprocal of the  $F$ -center concentration. For very high coloration a nearly linear relationship is expected with the curve passing through the origin. The data at least lends itself to a linear plot for the heavily colored crystals but approaches saturation for intermediate and lightly colored crystals. The dotted curve of Fig. 4 is a plot of the way  $\eta_a w_0$  varies with  $1/C_F$  as predicted by Eq. (6) using values of mobility estimated from the data of reference 8 and a thermal velocity corresponding to  $10^\circ\text{K}$ . Equation (6) has been adjusted to the data for samples KCl-3 and KCl-4 by choosing appropriate values of  $\sigma_F$  and  $C_t \sigma_t$  and using the measured values of  $\mu$  and  $\eta_a w_0$ . The result is

$$\eta_a w_0 = \frac{3.7 \times 10^{-2} \mu}{u(1.7 \times 10^{-14} C_F + 6400)} \quad (8)$$

The cross section for trapping at an  $F$  center (or closely associated traps) is seen to have a value of  $1.7 \times 10^{-14} \text{ cm}^2$ . This value obviously depends somewhat on the concentration and trapping cross section of shallow traps which are probably due to impurities. For example, if the corrected value of  $\eta_a w_0$  for KCl-5 which would be expected in the absence of saturation and collection effects were used in the curve fitting, a value of  $C_t \sigma_t = 2800 \text{ cm}^{-1}$  would be required. This value would yield  $\sigma_F = 3 \times 10^{-14} \text{ cm}^2$ . Thus, the effective value of  $\sigma_F$  would lie somewhere in the vicinity of  $(1 \text{ to } 3) \times 10^{-14} \text{ cm}^2$ . If the shallow traps are due to impurities present in concentrations from 1 to 10 parts per million, they would have to have trapping cross sections in the region of  $10^{-12}$  to  $10^{-13} \text{ cm}^2$ . Activation analysis of Harshaw KCl indicates the above concentration of sulfur and nickel—but more like 70 ppm of Br.<sup>19</sup>

### C. Enhanced Photoresponse and Trap Filling

Efforts were made to fill traps at  $10^\circ\text{K}$  and thus increase the Schubweg. This was not found possible apparently because of the high density of traps and low efficiency for yield of electrons. Figure 5 shows the photoresponse in the near infrared before and after the absorption of  $5.3 \times 10^{14}$  quanta of 3-eV light in KCl-2, a heavily colored crystal ( $C_F = 3.38 \times 10^{17} \text{ cm}^{-3}$ ). Although the photoresponse at 3 eV<sup>20</sup> was enhanced by a factor of about 2, the field dependence of the response

<sup>19</sup> S. Anderson, J. S. Wiley, and L. S. Hendrichs, J. Chem. Phys. **32**, 949 (1960).

<sup>20</sup> It is quite likely that the sensitivity at 3 eV and  $10^\circ\text{K}$  is not due to transitions commonly associated with the  $F$  center at all, but rather there is weak underlying absorption. The quantum yield at this wavelength is of the order of  $10^{-4}$  to  $10^{-3}$ .

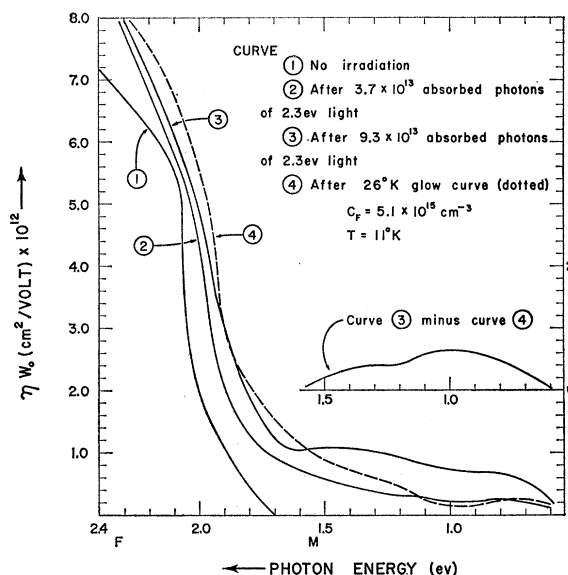


Fig. 6. Long wavelength photoresponse in a lightly colored crystal before and after irradiation at  $11^\circ\text{K}$ . Note that the situation is different than in a heavily colored crystal.

was linear before and after the irradiation. Notice, however, that there is an enhanced photosensitivity on the long wavelength side of the  $F$  band. Also, upon warming, there was an electrical glow peak with a maximum at  $90^\circ\text{K}$  after which the photoresponse dropped, but did not return to the original curve. (See curve 3, Fig. 5.) Although some  $F$  centers may be formed, the glow peak at  $90^\circ\text{K}$  is not the thermal emptying of the  $F'$  center which has been observed to take place at about  $205^\circ\text{K}$ .<sup>21</sup> The enhanced sensitivity would appear to be closely associated with the  $F$ -center concentration, since it augments structure present in the unirradiated crystal and underlies the  $F$  and  $K$  bands.

It was thought that the  $M$  center might trap an extra electron at low temperature to form what might be called an  $M'$  center in analogy with the similar situation in the  $F \rightarrow F'$  center. Experiments to tie in these low-temperature bands with the dichroism of the  $M$  center were negative. Heavily colored and lightly colored KCl crystals were bleached at room temperature with light in the  $M$  band polarized in a  $[110]$  direction, and then cooled as rapidly as possible to  $10^\circ\text{K}$ . Since the  $M$  center has been shown to be dichroic and to have predominantly  $[110]$  symmetry by formation and optical bleaching experiments,<sup>22</sup> it was expected that the photoresponse at low temperature would reflect the results of this bleaching. No such dichroic behavior of the photoresponse in the two directions of polarization  $[110]$  and  $[\bar{1}\bar{1}0]$ , was found. It may be that the  $M$  center was not an important trap at low temperature, or that the bleaching at room temperature with  $M$

<sup>21</sup> D. Dutton and R. Maurer, Phys. Rev. **90**, 126 (1953).

<sup>22</sup> F. Seitz, Revs. Modern Phys. **26**, 7 (1954).

light polarized in the  $[110]$  direction destroyed a majority of  $M$  centers of both orientations. The optical density of the  $M$  center was not measurable in light or moderately colored crystals, but in the above heavily colored crystal, it was of the order of 0.2 times the optical density in the  $F$  band.

Contrasting behavior upon illumination at low temperature was observed for the case of lightly colored crystals. Figure 6 shows the results obtained with KCl-5 ( $C_F = 5.1 \times 10^{15} \text{ cm}^{-3}$ ) before and after absorption of about  $10^{14}$  photons of  $F$  light at  $11^\circ\text{K}$ . The pronounced structure of the heavily colored crystal is missing, and a sizable amount of the enhanced response disappears after a thermal glow curve peaked at  $26^\circ\text{K}$ . An analysis of the glow curve in a manner discussed by Dutton and Maurer<sup>21</sup> yields a thermal depth for this trap of about 0.05 eV. When the response after the thermal emptying of the trap is subtracted from the enhanced response before warming, it is seen that the maximum of this enhancement occurs at a photon energy of about 1 eV (see Fig. 6). The quantum efficiency for emptying these traps is quite high and with a tungsten lamp as a source, the charge released in the crystal is of comparable magnitude for these infrared wavelengths as it is in the  $K$  and  $F$  bands. This fact can lead to erroneously high readings for photoconductivity when low-temperature photoconductivity is measured using white light or light passing through an optical filter having significant transmission in the near infrared. The measurement itself can significantly charge these traps and alter the apparent photoconductivity.

#### IV. CONCLUSIONS

Additively colored crystals of KCl are found to be photoconducting at  $10^\circ\text{K}$ , as well as at  $78^\circ\text{K}$ , on the high-energy side of the  $F$  band. The spectral response reflects the absorption structure found by Lüty.<sup>1</sup> After correction for absorption, the product of quantum yield and carrier range  $\eta_a w_0$  at  $10^\circ\text{K}$  is nearly constant with wavelength in the  $L_1$  and  $L_2$  band (3.6 and 4.2 eV, respectively) but drops sharply in the region of the  $K$  and  $F$  band. This would agree with the suggestion that

the  $K$  band (as well as  $F$  band) results from excitations to states below the bottom of the conduction band. The importance of a configuration coordinate diagram and also of nonvertical transitions is not yet clear.

The range of carriers can be estimated from curves which begin to show saturation or collection effects in lightly colored crystals. Unit ranges in the vicinity of  $10^{-6} \text{ cm}^2/\text{volt}$  were found at  $10^\circ\text{K}$ . An estimate of the quantum yield in the  $L_1$  band can be made assuming that optical absorption relates to absorption in the  $F$  band as found by Lüty.<sup>1</sup> The result,  $\eta_a = 0.04 \pm 0.01$ , indicates the existence of a competing process but is tentative pending a measure of the absorption in the ultraviolet region and also the preparation of crystals having longer electron ranges.

As the temperature is lowered below  $78^\circ\text{K}$ , the transient photoconductivity does not closely follow the increasing Hall mobility observed in separate experiments.<sup>8</sup> This is because of the existence of shallow traps which decrease the drift mobility and, at very low temperatures, effectively compete with the  $F$  center as a trap. Two cases have to be considered, that of lightly colored crystals and that of heavily colored crystals. When  $C_F < 2 \times 10^{17} \text{ cm}^{-3}$ ,  $w_0$  is nearly independent of  $C_F$  at  $10^\circ\text{K}$ . Moreover, illumination fills shallow traps and produces enhanced photosensitivity in the infrared. The traps release electrons upon warming in the vicinity of  $26^\circ\text{K}$ . For these traps the product of concentration and cross section,  $C_t \sigma_t$ , is from 1000 to  $4000 \text{ cm}^{-1}$ , which suggests a large cross section or a very high concentration. On the other hand, for crystals with  $C_F > 2 \times 10^{17} \text{ cm}^{-3}$ , electrons may be trapped at  $F$  centers or at closely related centers. If one assumes that  $F$  centers are the main trap, the trapping cross section at  $10^\circ\text{K}$  is  $\sigma_F \simeq 10^{-14} \text{ cm}^2$ .

#### ACKNOWLEDGMENTS

The authors would like to express their appreciation for the interest and help of Professor R. J. Maurer. The assistance and suggestions of Dr. J. A. Cape, Mr. R. Swank, and Professor J. W. Mitchell are much appreciated.