When color centers are introduced into a crystal of potassium chloride, an absorption band called the F band appears in the visible region of the spectrum and imparts a violet color to the crystal. When exposed to light lying in this absorption band, the crystal becomes photoconductive. With continued F light illumination, the F band decreases in intensity and secondary absorption bands appear in the spectrum on the long wavelength side of the F band. Concurrently, the photosensitivity, which is given by the quotient of the photoconductivity, $\sigma$, and the rate at which photons are absorbed by unit volume of the crystal in unit time, $I$, decreases rapidly. The basic relation for the sensitivity,

$$\frac{\sigma}{I} = e \mu \eta T$$

where $e$ = electronic charge

$\mu$ = electron mobility
$\eta =$ photoionization quantum efficiency

and $\tau =$ mean photoelectron lifetime,

shows that any change in sensitivity upon F light illumination must reflect changes in either $\eta$, $\tau$, or both quantities.

Recognizing that the decrease in sensitivity probably stems from changes in both $\eta$ and $\tau$, an explanation is advanced on the premise that only $\eta$ is involved. The decrease in $\eta$ is experimentally related to the process of optical bleaching with the attendant appearance of the secondary absorption bands.

The results of the investigation demonstrate that neither $\eta$ nor $\tau$ can be neglected in accounting for changes in the photosensitivity. A decrease in the effective quantum efficiency for photoionization of the F center occurs with the formation of the secondary centers for two reasons. First, excited states of the secondary centers absorb light in the F band region. This F light is reemitted as luminescence and therefore does not yield conduction electrons. Although the M center is primarily responsible because of its low photoionization quantum efficiency, the presence of N centers may also contribute to the decrease in $\eta$. In crystals containing alkaline earth ions, the formation of $Z_1$ centers also causes a decrease in $\eta$ because the $Z_1$ band greatly overlaps the F band and the $Z_1$ center has a low quantum efficiency for photoionization. The second reason for the decrease
in a process of energy transfer which occurs readily at low temperature and is assumed to occur at room temperature. In this process, light absorbed directly by the F center is transferred to M centers which, in turn, luminesce rather than yield photoelectrons.

Changes in the mean lifetime of the conduction electrons and hence in the sensitivity are brought about by the trap-replacement process, in which electrons ionized from F centers are trapped at impurity centers, thereby increasing the concentration of isolated anion vacancies. If the trapping cross section of the impurity center is less than that of the isolated anion vacancy, then the photoelectron lifetime and the sensitivity will decrease. An example of an impurity center of this nature is an anion vacancy adjacent to a sodium ion, which upon trapping an electron becomes the A center. If, on the other hand, the trapping cross section is greater than that of the isolated anion vacancy, then the photoelectron lifetime and the sensitivity will increase. This behavior was noted in the case of the calcium-doped crystals. It is believed that the initial rapid changes in the sensitivity are the result of this trap-replacement process, which yields isolated anion vacancies and consequently results in the initiation of the process by which F-aggregate centers such as the M center are formed.
INTERACTIONS OF ELECTRONS AND TRAPS
IN POTASSIUM CHLORIDE CONTAINING COLOR CENTERS

by

ROBERT EARL WOODLEY

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INTERACTIONS OF ELECTRONS AND TRAPS IN POTASSIUM CHLORIDE CONTAINING COLOR CENTERS

INTRODUCTION

Pure potassium chloride is neither photoconductive nor exhibits any absorption bands in the wavelength region between its first fundamental absorption band with maximum at 162 mµ and its infrared absorption band with maximum at 70.7 µ. Upon the introduction of color centers into the crystal however, its optical and electrical properties are profoundly altered. An absorption band, which imparts a violet color to the crystal, appears in the visible region of the spectrum at a wavelength of 560 mµ. When exposed to light lying in this absorption band, the crystal becomes photoconductive, that is its conductivity increases during illumination.

The F Center

According to the model proposed by deBoer (7, p. 308), color centers, more commonly called F centers from the German word for color, Farbe, are electrons bound electrostatically to anion vacancies, an anion vacancy having a net positive charge as a result of its six nearest neighbor cations.

F centers may be introduced into a crystal in a number of ways but those most frequently employed are the addition of a stoichiometric excess of an alkali metal or exposure of the crystal to ionizing
radiation such as x-rays. Only the former method was employed in the present investigation, because the coloration exhibits a greater relative stability in that processes involving the recombination of electrons and holes are precluded.

The mechanism by which F centers enter the crystal during additive coloration is believed to be as follows (7, p. 307). Atoms of the vaporized metal are adsorbed on the crystal surface where they undergo ionization. The free electrons wander into the crystal ultimately to be trapped at negative ion vacancies. Halide ions diffuse from the interior to the surface where they form new layers of the crystal with the adsorbed metal ions. As a result of the addition of one anion vacancy for each F center formed, the density of the crystal decreases. Witt (60, p. 19) has observed a decrease in density which, within experimental error, is consistent with the one-to-one correspondence between F centers and anion vacancies. Seitz (52, p. 34), on the other hand, has pointed out that the observed density decrease in itself does not constitute proof of deBoer's model, because the decrease could be associated with an increase in the average lattice spacing.

**Optical Bleaching**

When a crystal containing F centers is exposed to light lying in the F absorption band, bleaching of the crystal occurs. The
absorption of light of wavelength 560 mµ, hereafter termed \( F \) light, results in the promotion of the \( F \) center electron to an excited state 2.2 ev above the ground state. Because this excited state lies only about 0.1 ev below the conduction band, thermal activation at room temperature is sufficient to yield a conduction electron. The conduction electron wanders randomly through the crystal until it is trapped either by an anion vacancy to reform an \( F \) center or by some other trapping center. The continued exposure of the crystal to \( F \) light leads to a reduction of the \( F \) band and results in the formation of new centers which exhibit absorption bands on the long wavelength side of the \( F \) band.

Unfortunately, the bleaching process cannot be fully explained by the simple capture of photoelectrons by trapping centers already present in the crystal. Several mechanisms have been proposed to account for the bleaching of \( F \) centers at room temperature by light lying in the \( F \) band. Possible processes include (1.) a purely electronic, temperature independent process, (2.) a temperature dependent process involving the migration of vacancies, or (3.) a combination of these two extremes, the latter being the most likely. Examples of (1.) are annihilation of photoelectrons by holes associated with \( V \) centers, capture of photoelectrons by \( F \) centers to form \( F' \) centers, and trapping of photoelectrons by divalent cations incorporated substitutionally into the alkali halide lattice. An example of
is the migration of vacancies to form a vacancy cluster which in turn traps a photoelectron to form a secondary center.

In additively colored crystals, the absence of V centers precludes the possibility of electron-hold annihilation. In KCl, the F' center is at best only momentarily stable at room temperature which obviates the possibility of capture by F centers. The trapping of photoelectrons by impurity ions, on the other hand, is very important at room temperature, irrespective of the mode of coloration. Kawamura and Okura (17, p. 161) have shown that when a crystal is purified by recrystallization from the melt, it cannot be bleached unless it is deformed and even then the extent of bleaching is barely evident. Deformation of a crystal results in the formation of vacancies and clusters of vacancies which serve as trapping centers for electrons ionized from F centers. In their experiments, however, the vacancy clusters were presumably removed by pulse annealing at 400°C for one minute.

As a possible vacancy migration bleaching mechanism, Ueta and Känzig (55, p. 1592), employing suggestions originally put forth by Seitz (51, p. 406-407), have postulated that the relatively fast, initial bleaching corresponds to direct trapping of photoelectrons by vacancy clusters already present in the crystal as a consequence of rapidly quenching the crystal to room temperature following additive coloration. The vacancy clusters consist of two positive and two
negative ion vacancies on neighboring lattice sites, i.e. a quartet of vacancies, which upon the capture of a photoelectron ejects a cation vacancy in order to maintain electrical neutrality. The slow bleaching, which subsequently occurs, would then correspond to the pairing of the ejected cation vacancy with an ionized F center, the migration of the pair of vacancies to another pair forming a quartet, and the eventual capture of a photoelectron by the newly-formed quartet. In this mechanism, the cation vacancy serves, in a sense, as a catalyst.

Bron and Nowick (2, p. 114-121) have pointed out that a means of distinguishing between various bleaching mechanisms is in terms of their temperature dependence. From Petroff's data (43, p. 449) on the temperature dependence of M center formation and from their own results, they conclude that the activation energy for the bleaching process is on the order of 0.35 ev. Delbecq (8, p. 565) found a value of 0.46 ev for the activation energy of M center formation, in reasonable agreement with this value. These results tend to preclude the Seitz-Ueta-Känzig mechanism because there the activation energy should approach 0.8 ev, the activation energy for cation vacancy migration.

Bron and Nowick further indicate that the rate controlling step in the bleaching process may be the migration of vacancy pairs present in the crystal. They point out that according to Dienes (9, p. 631)
the activation energy for vacancy pair migration is about 0.4 ev which agrees well with their value. Tharmalingam and Lidiard (53, p. 1159) have since shown, however, that the activation energy for pair migration is at least as great if not greater than that for the migration of a single vacancy. Their calculations are substantiated by the experimental results of Laurance (27, p. 60). In addition, the equilibrium concentration of vacancy pairs at room temperature is too small to account for the observed rate of bleaching, thereby requiring the postulation of additional processes for their rapid formation, processes which may or may not prove to be feasible.

More recently it has been suggested that electrostatic forces play an important role in the bleaching process. For example, Delbecq (8, p. 578-581) has proposed a mechanism for M center formation which involves the attractive forces between anion vacancies and F' centers. Whereas electrostatic forces most likely do play an important role, it may be generally stated that any proposals concerning the mechanism of the bleaching process can be considered at best only conjectural in that present knowledge is insufficient to allow a precise definition of the mechanism. In any event, bleaching of the F absorption band results in the formation of secondary centers which will be considered in the following section.
The Secondary Centers

According to Petroff (43, p. 448), the first products of F center bleaching are A and B centers. The A absorption band, which lies on the long wavelength side of the F band, appears as a broadening of the latter and may be obtained to a satisfactory approximation by subtraction. Its development proceeds through a maximum and ultimately attains a constant value somewhat less than the maximum value. The B band extensively overlaps the F band where its presence is implied by a broadening of the F band toward shorter wavelengths (22, p. 685). van Doorn and Haven (57, p. 488) explain the B band as an excited state of the M band underlying the F band, whereas Ohkura and Awane (38, p. 1349) apparently neglecting the presence of the B band contend that early in the bleaching process A centers are formed exclusively. In a later paper however, Ohkura and Uchida (40, p. 2114-2115) demonstrate the reversible optical conversion between A and B centers in additively colored KCl at -180° C. The foregoing observations on A and B centers have been recently explained quite satisfactorily in an important series of papers by Kojima, et al. (20, p. 121-122; 32, p. 576-577; 21, p. 2033-2044). They have shown that the A center in KCl is an F center adjacent to a substitutional sodium ion. Perturbation resulting from the presence of the sodium ion causes a splitting of the triply-degenerate excited state of the F
center into two levels, one at the longer wavelength side of the F band and the other at a slightly shorter wavelength than the F band. These two levels thus correspond to Petroff's A and B bands, respectively, and the optical conversion between A and B centers is nothing more than an optically-induced reorientation of the same center. It is also interesting to note that A centers can be thermally converted to F centers by heating to 50°C in the dark. The activation energy for the process is 0.43 ev, which apparently represents the energy required to dissociate the A center into an F center plus an isolated sodium ion.

With continued F light illumination, the M band is the next in a succession of new absorption bands to appear. It was first studied extensively by Molnar (30, p. 944), after whom it is designated, and independently by Petroff (43, p. 449-454), who believed the B center to be the M center precursor. Ohkura and Awane (38, p. 1350) observed a linear dependence between the decreasing A center concentration and the increasing concentration of M centers before the appearance of the R bands. Their observation thus agrees with that of Petroff, because as is now known A and B centers are identical. In a manner similar to that of the A center, the M center concentration eventually attains a maximum value after which it decreases to a more-or-less constant value. As pointed out above, the maximum value and its rate of attainment are strongly temperature dependent,
activation energies of 0.35 and 0.46 ev having been obtained for the process of M center formation.

Because of its early formation, Seitz (51, p. 404-405) proposed a model for the M center consisting of an F center plus an adjacent vacancy pair, the presumably highly-mobile vacancy pair attaching itself to an F center during the initial stages of bleaching. It was later shown, however, that the M center must possess inversion symmetry (42, p. 722). To bring the Seitz model into accord with this finding, Knox (19, p. 88) suggested that the cation adjacent to the M center spends most of its time between the two anion vacancies. This model is also known to be incorrect because the M center was found to be diamagnetic (37, p. 2076). Following the proposal of van Doorn and Haven (57, p. 487), it is now recognized that the M center consists of two adjacent F centers with its axis directed along one of the six [110] directions.

Other studies of the M center have yielded results of interest to the present investigation. In particular, studies of M center luminescence have yielded valuable results. van Doorn and Haven (57, p. 487) found that the development of the M band in a crystal led to a new emission band which arose not only when the crystal was irradiated in the M band but also in the F band. This new M emission band occurs at room temperature in contrast to the F emission band which only occurs at temperatures below about 170° K. van Doorn
(59, p. 299-300) later demonstrated that the quantum efficiency for F center fluorescence decreases rapidly as the M center concentration increases. For example, when the ratio of the absorption constants of the M and F bands increased from about 0.01 to 0.09, the quantum efficiency dropped from 0.91 to 0.34. van Doorn and also Lambe and Compton (26, p. 692-693) suggested that energy was transferred from F to M centers when M center fluorescence occurred as a result of F light exposure.

Following the demonstration of the anisotropic nature of the M center by Ueta (56, p. 107-109), a number of investigations of M center dichroism have been undertaken. Particularly noteworthy is the study by Okamoto (41, p. 1090-1097) which led to the establishment of a number of excited states of the M center, two of which coincide fairly closely with the maximum of the F center absorption peak. These M center absorptions under the F band thus readily explain the observance of M center luminescence upon F light excitation.

Before leaving the subject of the M center, it is of interest to note an experimental result obtained by Kanzaki (16, p. 1064). He found that during the development of the M band, its maximum shifts to lower energies and a relative increase in absorbance on the low energy side of the band occurs. While it can only be postulated, this may imply that the M band as well as the F band is a composite structure.
Shortly following the appearance of the M band, the $R_1$ and $R_2$ bands arise. Petroff (43, p. 451) demonstrated that the growth rate of the $R_2$ band is proportional to the M center concentration, thereby identifying the M center as the precursor of the $R_2$ center. This relationship is also supported by the fact that the sum of the M and $R_2$ center concentrations approaches a fixed maximum during the bleaching process (5, p. 1465).

Although Seitz (51, p. 407) has proposed different models for the centers leading to the two R bands, sufficient evidence has been obtained to indicate that the two bands in reality probably originate from different transitions of the same center. It has been shown that over a wide range of R center concentrations, the ratio of the two peak heights is essentially constant (14, p. 90). Also, at the temperature of liquid nitrogen, excitation in either of the R bands results in the same emission band (57, p. 488; 26, p. 687; 6, p. 1622), whereas bleaching in the $R_1$ band bleaches the $R_2$ band also (6, p. 1622).

The models proposed by Seitz for the R centers consist of a pair of neighboring anion vacancies containing either one electron (the $R_1$ center) or two electrons (the $R_2$ center). Experimental investigations, particularly those of van Doorn and Haven (57, p. 488) and Okamoto (41, p. 1094), have since shown that the dipoles associated with the R bands are oriented along the $[111]$ directions of the crystal. This fact led van Doorn (58, p. 322) and later Pick (44, p. 72)
to propose a model consisting of three adjacent F centers at the corners of an equilateral triangle lying in a [111] plane. This model has recently received support from electron spin resonance experiments (23, p. 193) and x-ray coloration equilibrium studies (49, p. A228).

As was pointed out above, excitation in either R band leads to the same emission peak. This peak also results upon exposure to F light, thereby indicating the presence of an excited state of the R center under the F band. As was the case for the M center, the R emission occurs at room temperature, although the efficiency is much lower (26, p. 686-687).

The excited states of the R center have been investigated by Okamoto (41, p. 1094), who found that at least one of them, his so-called R\textsubscript{3} band, has its maximum absorption at a wavelength which results in the broadening of the high energy side of the F band as R centers are formed. This phenomenon had been noticed by several investigators.

The N absorption band was discovered on the long wavelength side of the M band by Petroff (43, p. 447) and independently by Burstein and Oberly (3, p. 1254). More recent measurements demonstrate that the N band actually consists of two bands (14, p. 89; 6, p. 1621), now termed the N\textsubscript{1} and N\textsubscript{2} bands. Petroff believed that the N band arose after the appearance of the R bands; however, from the data of Herman, Wallis, and Wallis (14, p. 89) it appears more
likely that the N and R bands arise more or less simultaneously. Results obtained in the present investigation are in agreement with the latter observation.

The N bands have not been studied as thoroughly as the other defect bands because ordinarily they are not obtained in high concentrations and moreover they overlap extensively in KCl. Nevertheless a number of observations on the N bands have been published. It is generally agreed that the two N bands arise from different defect centers. The $N_2$ band resembles the R bands (41, p. 1094; 13, p. 1456) both with respect to its rate of growth and its [111] orientation. However, Schnatterly and Compton have presented evidence that indicates the $N_2$ and R bands actually result from different defect centers. Their results imply that the $N_2$ center consists of four associated F centers as was proposed by Pick (44, p. 72). They also suggest that the $N_1$ center is closely related to the M center, because both show a [110] orientation and a linear relationship was found to exist between their absorption coefficients.

On the other hand, Hattori (13, p. 1462) states that no relationship exists between the M and N bands, although he does imply that Pick's model of the $N_1$ center may be correct. This model consists of four adjacent F centers lying in the [111] plane at the four corners of a parallelogram. It is readily apparent from the above considerations that additional research effort must be expended before the N centers
can be rigorously characterized.

In crystals containing divalent cations of the alkaline earth metals, another absorption band arises. It is termed the $Z_1$ band and it generally appears early in the bleaching process as a shoulder on the long wavelength side of the F band. In crystals which contain a moderate concentration of the divalent cation, the $Z_1$ band tends to predominate over the other secondary absorption bands. It is not altered by exposure to light lying in the band, but it is transformed upon heating into the $Z_2$ band. Because $Z_2$ centers were not encountered in this work, further mention of them will not be made.

Seitz (50, p. 137) has proposed a model for the $Z_1$ center consisting of an isolated divalent cation which has captured an electron. Pick (45, p. 130), on the other hand, has suggested that the $Z_1$ center consists of a combined divalent cation and cation vacancy plus an electron. Although experimental evidence has been offered in support of both models, Lidiard (28, p. 419) has pointed out that it is likely that neither of them is correct. He argues that under conditions where mobile electrons are formed but vacancies are immobile no $Z_1$ centers are formed. Hence, it appears that the production of $Z_1$ centers may involve the anion vacancies of the transformed F centers as well as their electrons.
Photoconductivity

The phenomenon wherein the electrical conductivity of a material increases upon illumination is termed photoconductivity and the material itself is called a photoconductor. The increased conductivity is, in general, a consequence of the excitation of electrons into the conduction band by the absorption of photons of the proper wavelength or energy. The positive holes that remain behind also contribute to the increase in conductivity if they are mobile. In the alkali halides however, the "holes" are immobile and hence the photoconductivity is purely electronic. The conduction electron, even in the absence of an applied field, executes a Brownian motion in the conduction band until it is trapped either by a hole, in the present case an anion vacancy, or by some other imperfection in the crystal. If the trapping center plus electron is thermally stable at the temperature of the experiment, the electron remains trapped until released by the absorption of light of the proper wavelength. If, on the other hand, the trapping center is thermally unstable, the electron may be thermally released to perform its random motion until captured by a thermally stable trap. Under the influence of an applied field, a net preferential drift in the field direction occurs, and the presence of a current measuring device in the circuit demonstrates the existence of a photocurrent. The mean distance over which the electrons drift in the
field direction, the Schubweg, is given by

\[ d = v_d T = \mu F T \]  \hspace{1cm} (1)

where \( v_d \) = drift velocity,

\( T \) = mean lifetime of conduction electrons,

\( \mu \) = electron mobility or drift velocity per unit field strength,

and \( F \) = electric field strength.

The actual distance traveled by the electron is given by the product \( v T \), where \( v \) is the thermal velocity of the electron, and is of the order of a centimeter. In contrast, the Schubweg in KCl, under the conditions of the present study, is less than this by a factor of about \( 10^3 \).

For an electronic conductor, the conductivity may be represented by the relation

\[ \sigma = n e \mu \] \hspace{1cm} (2)

where

\( n \) = concentration of conduction electrons

and

\( e \) = electronic charge.

In the special case of a photoconductor, the concentration of conduction electrons is given by

\[ n = f T \] \hspace{1cm} (3)
where

\[ f = \text{rate of excitation of electrons into the conduction band/unit volume of crystal}, \]
\[ \eta = \text{quantum efficiency for generation of photoelectrons}, \]
and

\[ I = \text{rate of absorption of photons/per unit volume of crystal}. \]

Combining Equations (2) and (4) and rearranging, the relation

\[ \sigma / I = e \mu \eta \tau \] (5)

is obtained. The quantity \( \sigma / I \) is termed the sensitivity of the photoconductor. Because the electronic charge is universally constant and the mobility is constant at a given temperature for a given material, the sensitivity is completely characterized by the product \( \eta \tau \) and any change in the sensitivity with exposure to light must either result from a change in \( \eta \), in \( \tau \), or in both quantities.

The quantum efficiency for the generation of photoelectrons for a composite absorption band, that is an absorption band resulting from the presence of more than one species absorbing light at the band wavelength, can be written

\[ \eta = \sum_i f_i \eta_i \] (6)

where

\[ f_i = \text{fraction of light absorbed by } i^{th} \text{ species} \]
and \[ \eta_i = \text{quantum efficiency of } i^{\text{th}} \text{ species.} \]

If changes in the concentrations of the absorbing species occur with exposure of the photoconductor to light, it is obvious that \( \eta \) and hence the sensitivity will also be affected, particularly in instances where the \( \eta_i \) are quite different from one another.

Similarly, the mean lifetime is related to the concentration of traps in the photoconductor by

\[
\tau = \left[ v \sum \frac{n_j S_j}{S_j} \right]^{-1} \tag{7}
\]

where

\[
v = \text{thermal velocity of electron,}
\]

\[
n_j = \text{concentration of traps of } j^{\text{th}} \text{ kind,}
\]

and

\[
S_j = \text{trapping cross section of traps of } j^{\text{th}} \text{ kind.}
\]

Thus, it is readily apparent that any changes in the concentrations of traps upon illumination of the photoconductor will affect the electron lifetime and, in turn, the sensitivity.

Coloration of potassium chloride yields a material which meets the specifications of a photoconductor, in that exposure of the crystal to F light yields photoelectrons. Those aspects of the photoconductivity exhibited by colored KCl pertinent to the present study will now be considered.

When the sensitivity, \( \sigma / I \), of the F band is examined as a function
of temperature in the range $-180^\circ C$ to room temperature without allowing bleaching to occur, it is found upon increasing the temperature from $-180^\circ C$ to $-130^\circ C$ that the sensitivity increases about one hundred-fold (46, p. 18-19). This increase is attributed to an increase in the quantum efficiency, $\eta_F$, for ionizing F centers. At $-130^\circ C$ it is believed that $\eta_F = 1$, that is for every photon of F light absorbed one F center is ionized. Because the F center contains only one electron, this is the maximum value that $\eta_F$ can attain and hence the room temperature value of $\eta_F$ will also be unity.

In the temperature range from $-130^\circ C$ to about $-80^\circ C$, the sensitivity remains essentially constant. Over this region, every electron which is released by an F center is trapped by another F center to yield an F' center. Thus two F centers are destroyed for each photon absorbed, the one from which the electron was ejected and the one which captured the electron.

As the temperature is increased above $-80^\circ C$, the sensitivity again increases and when room temperature is reached the sensitivity has essentially attained its maximum value. This second increase in sensitivity with temperature is attributed to the decreasing stability of the F' center. In other words, the electron trapping ability of the F center decreases so that the mean range of the electrons and hence the sensitivity increase.

It is of interest to mention with regard to the $F \rightarrow F'$ conversion
that the presence of secondary centers causes a considerable reduction in the ability to convert F to F' centers (39, p. 934; 47, p. 1734-1741). Two explanations have been advanced to explain this effect. Ohkura et al. (39, p. 934) suggest that the electron range is decreased by the presence of the secondary centers and newly formed anion vacancies both of which act as traps. On the other hand, Reinberg and Grossweiner (47, p. 1741) believe that the effective incident light intensity is reduced by the inner-filtering action resulting from the presence of other bands under the F band.

When the photoconductive sensitivity is examined as a function of the wavelength of the exciting light, the sensitivity spectrum obtained depends to a great extent on prior exposure of the crystal to F light. In the case of a freshly-quenched crystal which has received no prior illumination, the sensitivity spectrum in the F band region is much like the absorption spectrum (31, p. 298-299; 1, p. 373-374). A prominent peak occurs at the normal F band location. If, however, the crystal has undergone appreciable bleaching, the sensitivity spectrum no longer resembles the absorption spectrum but should be proportional to the quantum efficiency of the particular defect being excited. During an investigation of the photoconductivity of the Z bands, Cole and Friauf (4, p. 389) made use of this fact to obtain relative quantum efficiencies for ionization of the various secondary centers. Barth (1, p. 375), in a somewhat similar study, measured
the relative quantum efficiencies of the F and M bands and obtained for their ratio, $\eta_F/\eta_M = 10.5$, a value which readily indicates the low sensitivity to be expected from the M band as compared to the F band. A similar value for this ratio was obtained in a very interesting study by Kuwabara et al. (24, p. 1623). Some care must be employed in the use of these values because of the overlap of the absorption bands.

During bleaching of a colored KCl crystal and particularly during the early stages of bleaching, the photoconductive sensitivity in the F band decreases rapidly, much more rapidly than the optical absorbance in the band. This phenomenon has been studied by several investigators and is the primary subject of the present thesis. As was shown in Equation (5), the sensitivity is characterized by the product $\eta \tau$, so that any change in the sensitivity with exposure must reflect changes in either $\eta$, $\tau$, or both quantities.

In a series of papers, Oberly and Burstein (34, p. 217; 35, p. 228; 36, p. 1257-1258) proposed that the F band is in reality a superposition of absorption bands composed of what Oberly later called "hard" and "soft" F centers. The "hard" F centers are essentially nonphotoconducting and hence their quantum efficiency for ionization must approach zero. In contrast, the "soft" F centers are photoconducting, have a quantum efficiency near unity, and hence can be readily bleached. Upon bleaching, the ratio of "hard" to "soft" centers increases with a consequent decrease in the effective quantum
efficiency of the absorption band. The decrease in the photosensitivity is thus attributed solely to the decrease in the quantum efficiency. In addition, Oberly (35, p. 228) mentioned that the wavelength of the peak absorption for "hard" F centers corresponds to the wavelength of Petroff's B band.

It was later suggested by Markham (29, p. 433) that an alternative explanation for the decrease in sensitivity is a decrease in the electron range, and hence $\tau$, resulting from the increasing concentration of anion vacancies as F centers are destroyed, the anion vacancies being effective electron traps. This mechanism obviates the necessity for two kinds of F centers.

Neilson and Scott (31, p. 300) further pointed out that, if both "hard" and "soft" F centers exist, the quantum efficiency for the liberation of a photoelectron could never be greater than the ratio of "soft" F centers to the total number of F centers. Because it is highly probable that the quantum efficiency for F center ionization at room temperature is unity, the lower quantum efficiency implied by Oberly's theory appeared to be irreconcilable with $\eta_F = 1$. They therefore supported Markham's contention that the electron range rather than the quantum efficiency decreases upon bleaching.

Hardtke (11, p. 1-117) continued this program of investigation and developed the trap-replacement theory to the point where it would account reasonably well for the observed decrease in sensitivity with
exposure (12, p. 545-548). The theory envisages traps $T$ of trapping cross section approximately two orders of magnitude less than the trapping cross section for the anion vacancy. The rapid capture of photoelectrons by the traps $T$ during the initial stages of bleaching results in a rapid increase in the anion vacancy concentration and hence a rapid drop in the conduction-electron lifetime, $T$. The photosensitivity and the optical absorbance approach a limiting value, because in the presence of a high concentration of anion vacancies the majority of the photoelectrons are trapped to reform F centers. No attempt was made, however, to determine the nature of the traps $T$, and it was assumed that only one type of trap was involved in order to keep the mathematics from becoming too cumbersome. Considering the changes which occur in the absorption spectrum with bleaching, this is quite obviously an oversimplification.

The relationship between the decrease in sensitivity and F center bleaching was further examined by Hirai and Scott (15, p. 2864-2867), who studied the phenomenon as a function of temperature in the range from $-30^\circ$ C to room temperature. Except at the lower temperatures where a new trap which is not stable above $0^\circ$ C had a pronounced effect on the results, their findings were similar to those of Hardtke et al. (12, p. 544-549) and they concluded that the trap-replacement mechanism accounted for the major features of their observations.

Kuwabara et al. (24, p. 1621-1624) in their study of F and M
center photoconductivity attributed part of the decrease in sensitivity with bleaching to a decrease in the ionization probability of the F center as the M band increased. In other words, an appreciable proportion of the energy absorbed by the F center is reemitted as M center luminescence. Thus, in essence, they ascribed the decreasing sensitivity to a decreasing quantum efficiency for photoionization of the F center. However, because the luminescence increased linearly with M center concentration whereas the photoconductivity fell off more rapidly, it was felt that at least part of the decrease in sensitivity might result from a decreasing electron range.

Kuwabara (25, p. 345) later suggested that the photoionization efficiency of the center responsible for dichroic absorption in the F band region is far less than that of the F center. This again implies that the growth of the M band is responsible for the decrease in sensitivity as a consequence of a decrease in the effective quantum efficiency of the F band.

Finally, Noble and Markham (33, p. 1351-1352) believe that upon bleaching the F band is replaced by a band which they refer to as the B band. After prolonged bleaching, the F band is completely destroyed and the absorption band in the F band region is due solely to their B center. Furthermore, they state that the decrease in photoconductivity may result from a change in the process of thermal ionization whereby electrons are released from the first excited state
into the conduction band. This interpretation thus joins the ranks of those suggesting a change in the quantum efficiency rather than the photoelectron lifetime.

**Objective**

The interpretations advanced for the decrease in sensitivity with F light bleaching are almost as many in number as the number of investigators studying the phenomenon. It is hoped that, by comparing the changes produced in the absorption spectrum of colored potassium chloride, both pure and containing added impurities, with the change in sensitivity simultaneously produced by F light bleaching, some additional understanding of photoconductive fatigue can be gained.
EXPERIMENTAL PROCEDURE

Sample Preparation

Only single crystals of potassium chloride were employed in this investigation. The crystals of "ordinary" purity were cleaved from a large single crystal obtained from the Harshaw Chemical Company and are designated by the prefix, H. The remaining crystals were grown by the Kyropoulis technique in this laboratory. The "pure" crystals were supplied by P. Gruzensky, who grew the crystal designated by the prefix P-1 from doubly-recrystallized KCl using a reactor-grade graphite crucible in order to avoid the incorporation of metallic impurities into the crystal. During its growth, an atmosphere of argon was maintained around the crystal. The pure crystal designated by the prefix P-2 was grown in the same manner from KCl purified by the Hay process. The crystals doped with SO$_4^{2-}$ ion and with Ca$^{++}$ ion were grown by H. Coker and C. Gorham respectively. In both cases, the crystals were grown in air from a platinum crucible. The sulfate ion and calcium ion concentrations presented in this thesis are the concentrations of these ions added to the melt. In the case of the calcium ion, Kelting and Witt (18, p. 700) estimate that only about one-tenth of the divalent salt in the melt eventually appears in the single crystal. The sulfate-doped crystals are designated by the prefix S, while the crystals containing calcium ions are designated
by the prefix C.

The additive coloration of the above crystals was accomplished as follows. Coloring bombs were constructed of 17 mm o. d. pyrex tubing with a constriction about six inches above the lower sealed end. A more-than-adequate supply of potassium metal was placed in the chamber below the constriction while the single crystal was positioned in the upper chamber and was supported by the constriction. The crystal was wrapped in copper foil to preclude the possibility of exposure to stray illumination during the coloration period. After evacuation, the bomb was sealed at a point about 2.5 inches above the constriction yielding an overall length of about 8.5 inches. The completed bomb was then inserted into a pair of vertical furnaces whose temperatures were independently controlled by means of two Powerstats. The lower furnace, whose temperature controlled the potassium metal temperature and hence the extent of coloration, was generally maintained at about $340^\circ$ C. The upper furnace, whose temperature controlled the crystal temperature, was maintained at about $540^\circ$ C. To achieve homogeneity, coloration periods of from 50 to 90 hours were employed. Following the coloring period, the entire assembly was removed to a dark room where the bomb was removed from the furnaces, placed in a metal trough, and smashed with a hammer. The foil-wrapped crystal was quickly removed from the debris and cooled in a stream of compressed air. The entire
removal operation was conducted under the dim light from a red safety lamp positioned about ten feet away. The copper foil was not removed from the crystal until the crystal was to be cleaved for optical or photoconductivity measurements.

Except during actual measurements, the colored crystals were only handled under a lamp from which light in the wavelength range corresponding to the F band in KCl had been removed. This lamp consisted of a six watt tungsten light bulb installed behind two superimposed liquid filters one of which contained an approximately 0.1 N solution of Cu(NH$_3$)$_4$SO$_4$ while the other contained an approximately 0.007 M solution of KMnO$_4$. According to Hardtke, better than 99 percent of the illumination from this lamp is confined to wavelengths shorter than 490 mµ and longer than 620 mµ (11, p. 31). Although the liquid filters were unstable over extended periods of operation, it was quite simple to replace the solutions each time the lamp was to be used. The use of this lamp thus eliminated any possibility of premature exposure of the crystal to light lying within the F band.

To prepare a crystal for optical or photoconductivity measurements, the following procedure was employed. The crystal was first removed from its covering of copper foil and then slices approximately one mm thick were cleaved from all outer surfaces. The outer surfaces thereby eliminated were usually clouded, and for both optical and photoconductivity measurements a freshly cleaved
surface was desirable from the standpoint of light transmission.

Cleavage of the crystal to specific dimensions was accomplished by means of a device in which the crystal could be clamped into a position in which a razor blade, guided by two vertical posts and given a sharp tap, would sever a slice of the desired thickness. The crystal's position and hence its size was preset by means of a small metric scale incorporated into the design of the cleaving device. Whereas in the case of photoconductivity measurements, the crystal dimensions were not critical, for optical measurements the length of the crystal had to be maintained within certain tolerances, so that the crystal would be held properly in the crystal holder. To obtain this length with reasonable accuracy, an aluminum blank of the proper dimension was employed to preset the crystal position in the cleaving device. In order to obtain comparable results during optical and photoconductivity measurements, the small crystals used were cleaved from adjacent positions in a slice of the larger crystal.

Optical Measurements

All bleaching and spectral measurements were accomplished in a Beckman Model DK-1 recording spectrophotometer. The design of the crystal holder employed for these measurements is shown in Plate 1. Its essential components consisted of a slit, S, a viselike device for positioning the crystal, C, over the slit, and a small
aluminized mirror, M, to reflect the bleaching light back through the crystal thereby enhancing the uniformity of bleaching. The holder and attached "vise" were milled from aluminum. All of the metallic parts were painted with a flat black paint except where they came into contact with the crystal.

The slit was one mm wide and usually very nearly six mm in length depending upon the length of the crystal. Because of spatial restrictions, the travel of the movable arm of the "vise" was limited, and it was for this reason that the length of the crystal had to be maintained within certain tolerances as previously mentioned.

The small mirror was made from a piece of microscope slide cover glass which was aluminized by the vacuum evaporation of aluminum foil entwined in a tungsten filament. Because of a slight oxidation of its outer surface during preparation, it was used as a second surface rather than first surface mirror. A thin layer of Apiezon T stopcock grease was employed to hold the mirror to the crystal holder.

In order to calculate the integrated exposure of a crystal to the bleaching light, it was necessary to know the reflectivity of the mirror. The reflectivity of a surface is a function of the material, the wavelength of the incident light, and the angle of incidence. Because bleaching was accomplished with F light normally incident on the crystal, the reflectivity of the mirror was measured with F light at
an angle of incidence as close as possible to 90°. The value obtained was 0.545.

As shown in Plate 2, the crystal holder was attached to a Dewar cell. Spectral measurements could thus be performed at the temperature of liquid nitrogen to improve the resolution of the various absorption bands. To provide adequate thermal contact and thereby ensure proper cooling of the crystal, the void volume remaining between the crystal holder and the copper cold finger was filled with a mixture of powdered graphite and Lubrisal stopcock grease. Once the crystal holder was properly positioned on the cold finger, it was never removed. However, two fine lines were etched on these respective components in the event that removal necessitated repositioning of the crystal holder. Reference lines were also etched on both halves of the standard taper joint which connected the inner and outer components of the cell, one line on the outer component and two on the inner component. Rotation of the two halves of the joint with respect to one another allowed the alignment of either of the two lines on the inner component with the line on the outer component. In one position, the bleaching position, F light passed through the thinnest dimension of the crystal, impinged on the small mirror, and was reflected back through the crystal. In the other position, the position for spectral measurements, the light passed through the slit, through a somewhat thicker dimension of the crystal, and then
to the detector.

To initiate a series of optical measurements, the empty cell was evacuated to a pressure of about 0.5 micron Hg and placed in a cell holder which also served as a lid for the spectrophotometer sample compartment. In addition, the cell holder supported the reference aperture which was a small circular hole of about the same area as the sample aperture. After cooling the cell to liquid nitrogen temperature, the contribution to the absorbance resulting from the differences in the sample and reference apertures was determined over the pertinent wavelength range. The cell was then warmed to room temperature and removed to the dark room where a crystal, cleaved to the proper dimensions, was carefully positioned over the slit of the crystal holder and the "vise" closed. To avoid compression of the crystal in the "vise", a small drop of Duco cement was placed on one end of the crystal and the "vise" closed to the point where it just touched the crystal. It was thus actually the cement which held the crystal in place. To ensure that no absorption bands appeared in the wavelength region of interest as a result of the cement, the spectrum of an uncolored crystal was measured both before and after being smeared with the cement. Aside from a general increase in the baseline, the region from 400 to 1400 m\(\mu\) was entirely free from spurious absorption bands.

The loaded cell was again placed in the cell holder and covered
with a cylindrical cardboard tube lined with black paper. This tube covered the upper portion of the cell but allowed access to the stopcock and line used for its evacuation. During removal from the dark room and evacuation, two blackened corks filled the holes in the cell holder which during measurements normally allowed passage of the monochromatic light through the cell. Following evacuation, the cell and holder were transferred to the vicinity of the spectrophotometer, covered with a double thickness of black cloth, and the two blackened corks removed. The cell holder was then carefully seated in the spectrophotometer sample compartment and the black cloth removed. During this entire operation, the colored crystal was exposed only to light from which the F band was filtered.

Following the addition of liquid nitrogen to the Dewar cell, the initial spectrum of the crystal was measured in the wavelength range 1400 m\(\mu\) to 350 m\(\mu\). Compressed air dried with anhydrous CaSO\(_4\) was blown across both windows of the cell during the spectral measurements to prevent condensation of moisture on the windows. A shutter, which was in reality the filter holder on the spectrophotometer, was then closed and the liquid N\(_2\) siphoned from the cell. Warming of the cell to room temperature was accomplished by blowing compressed air into the well, which had contained the liquid N\(_2\), for a period of about twenty minutes. The cell was then rotated to the bleaching position, the shutter opened to allow exposure of the
crystal to F light, and a timer simultaneously started to record the duration of exposure. The timer employed was a Precision Time-It Timer made by the Precision Scientific Company. Following a suitable period of bleaching, the shutter was closed and the timer stopped. The cell was then rotated to the measuring position, liquid N₂ added, and the resulting spectrum measured. Further measurements involved repetitions of the above cycle and were continued until spectral measurements indicated that bleaching had proceeded to the desired extent.

In order to compute the rate at which photons were absorbed per unit volume of the crystal during bleaching, it was necessary to know the absorbance, the dimensions of the crystal, and the incident light intensity. The absorbance as a function of exposure was determined from the spectral measurements described above. The dimensions of the crystal were measured with a micrometer following the optical measurements. The incident light intensity was determined by placing a thermopile in the position which had been occupied by the crystal. The thermopile was constructed and calibrated by Hardtke, who has described these operations in detail (11, p. 40-42). Measuring the thermopile output by means of a Leeds and Northrup Type HS galvanometer with a scale about two meters distant and employing a calibrated carbon filament lamp obtained from the National Bureau of Standards, he obtained a sensitivity of 5.06 x 10⁻⁷ watt/mm² per
centimeter of deflection. This value has been used throughout the present investigation. Thus by determining the galvanometer deflection, the rate at which photons of a given wavelength were impinging on the crystal was readily calculated.

**Photoconductivity Measurements**

The photoconductivity apparatus is shown diagramatically in Plate 3. The amplifier and power supply were constructed by G. Neilsen following a design published by Roberts (48, p. 181-183). Both units were modified by F. Hardtke to increase their usefulness for the purpose at hand.

The power supply, whose input was stabilized by a Sola constant voltage transformer, furnished the filament and plate voltages to the amplifier and also provided a selection of seven different voltages with which the eight µf oil-filled capacitor could be charged. The voltages ranged from 50 to 300 volts in 50 volt increments plus an additional voltage of 450 volts. The capacitor, in turn, supplied the field across the electrodes between which the crystal was held.

The gain of the amplifier could be conveniently varied from $10^6$ to $10^7$ by means of a variable resistance. The amplifier was also provided with the output circuitry necessary to supply a recorder and to bring the recorder's readings into alignment with a microammeter incorporated into the amplifier circuit. The amplified
photocurrent could then either be read on the microammeter or recorded.

The recorder employed was a Brown recording potentiometer, Model 153X12V-X-9. By replacing the standard drive motor with a high speed synchronous motor, the chart speed of the recorder was increased by a factor of about 36 to the value, 1.16 inches/second, as determined by measurement. As will be more fully explained later, the increased chart speed allowed a more precise measurement of photocurrents which rapidly decayed as a result of polarization of the crystal.

The colored crystal was held securely between spring-loaded graphite electrodes which were insulated from each other and from the cell in which they were housed by teflon insulation. The F light entered the cell through a glass window and impinged on the crystal in a direction perpendicular to the direction of the applied electric field. To prevent scattering of the light beam, small metallic mirrors were mounted between the electrodes and the crystal. The mirrors were held to the electrodes by Cenco Softseal Takiwax, which had been rendered conducting by admixture with powdered graphite. The electrode spacing was thus determined solely by the thickness of the crystal. A small strip of dull black paper was mounted behind the crystal to give a surface whose reflectivity was near zero.

A shallow dish of magnesium perchlorate was also enclosed
within the cell to maintain a dry atmosphere and thereby eliminate surface conductivity due to moisture. The desiccant was replaced each time a new crystal was installed between the electrodes.

The cell, in turn, was mounted in a light-proof housing. The thermopile, mentioned previously on page 34, was mounted in the same housing. Either the cell or thermopile could be conveniently and reproducibly positioned in the light beam simply by sliding the housing back and forth in a cradle.

A double prism monochromator constructed by Hardtke from the remnants of a demonstration model was employed as the source of F light for the photoconductivity measurements. The monochromator light source consisted of a 300 watt tungsten lamp in conjunction with the optical system from a 35 mm slide projector. Adequate cooling of the 300 watt lamp was provided by a small blower. Because of its limited range, the monochromator was used only as an F light source, and hence the positions of the prisms and exit slit remained fixed. In addition, the exit slit width was fixed at a value of 1.5 mm. Variation of the light intensity was accomplished by varying the voltage supplied to the 300 watt lamp and/or adjusting the width of the entrance slit by means of a thumb screw having 60 scale divisions around its circumference. The slit width was calibrated with a thickness gauge at various thumb screw settings. In this manner it was found that the change in slit width per revolution (60 divisions) of
the thumb screw amounted to 0.426 mm. A shutter synchronized with SPDT switch S-3 covered the entrance slit except during photocurrent measurements and depolarization periods. With the shutter closed, switch S-3 allowed the input of a constant but preselected voltage to the recorder, thereby considerably reducing the pen lag when relatively large photocurrents were to be measured. With the shutter open, switch S-3 passed the output of the amplifier to the recorder.

When the dependence of the photoconductivity upon wavelength was determined, a Beckman Model DU spectrophotometer was employed as a light source, everything else remaining the same. Here the light intensity could be conveniently varied by changing the exit slit width. The filter holder served as a shutter.

Hardtke's motor-driven switch was replaced by switch S-2. It was constructed from the metallic parts of a commercial DPDT switch whose ceramic base was replaced with a base of teflon. Copper extensions on the metal contacts reduced the time of switching between the two closed positions. The two halves of the switch were shielded from one another by a double thickness of sheet metal, and the entire switch was shielded from its surroundings by means of a grounded, sheet metal cover. Thereby, operation of the switch did not induce undesirable currents in the amplifier. Measurements were made with the switch closed in the upper position (refer to Plate 3); whereas when it was closed in the lower position, the crystal
was grounded for depolarization.

Switch S-4 was another new addition to the apparatus. It allowed the measurement of currents without the necessity of opening the shutter switch, S-3. Thus when the contribution of dark currents or currents resulting from surface moisture were to be determined, switch S-4 was closed in the upper position rather than opening the shutter switch with the attendant possibility of stray illumination striking the crystal.

To commence a series of photoconductivity measurements, the cell was removed to the dark room where a small crystal, previously cleaved to the proper dimensions, was washed in absolute ethyl alcohol to remove surface moisture and then positioned between the spring-loaded electrodes of the photoconductivity cell. The crystal dimensions commonly employed for these measurements were approximately $4 \times 4 \times 1 \text{ mm}^3$, with the electric field acting across the smallest dimension. After replenishing the anhydrous Mg(ClO$_4$)$_2$, the cell was closed and its window covered with aluminum foil. It was then returned to its housing in the photoconductivity apparatus, the electrical connections made, and the foil removed from the cell window. During the cell loading operation, the crystal was only exposed to the lamp from which light lying in the F band had been removed by filtering.

After the power supply was turned on and the voltage to be
applied to the crystal was selected, a few minutes were allowed for the amplifier to warm up before supplying the amplifier plate voltages. The oil-filled capacitor was then charged to the selected operational voltage, usually about 300 volts, by closing switch S-1 to the right (refer to Plate 3), again allowing a few minutes for the amplifier to recover. Each time the capacitor was charged its voltage was measured during charging with a Triplett voltmeter, Model 630, because some periodic variation resulted from the varying extent of power consumption in the building. After charging, the capacitor was isolated from the power supply and thus from minor line voltage fluctuations which otherwise had a pronounced effect on the stability of the amplifier output.

With switch S-2 closed in the upper position but with the crystal remaining in the dark, the microammeter was zeroed. Thus, any contribution to the amplifier output resulting from dark currents was automatically excluded from measurement. If it was impossible at this time to zero the microammeter, it was obvious that excessive moisture was present on the crystal surface thereby necessitating further rinsing in absolute alcohol. After the microammeter was zeroed, the amplifier output was switched to the recorder whose reading was also adjusted to zero if necessary. This process was then repeated at some upper scale reading, usually 150 µa, on the microammeter and the recorder reading again brought into alignment.
The standardization of the recorder in this manner was performed before every series of photocurrent measurements. The apparatus was now ready for use.

With the shutter still closed, some intermediate recorder reading was obtained by adjusting the variable resistor, $R_1$. As previously mentioned, the input of this constant voltage to the recorder reduced the pen lag when measuring relatively large photocurrents. If the adjustment was properly made, the recorder reading was of the same magnitude as the initial photocurrent. If not, the reading was easily adjusted after the first photocurrent measurement to the proper position for subsequent measurements.

To perform the first measurement, it was now only necessary to start the chart drive and then immediately open the shutter allowing F light to illuminate the crystal. Because blocking electrodes were employed, electrons could neither enter nor leave the crystal, and hence space charge polarization rapidly resulted. Consequently the photocurrent decayed exponentially with time thereby limiting the duration of individual measurements to about five or ten seconds, after which the shutter was closed and the chart drive stopped. At this time, if necessary, the capacitor was recharged, although the usual practice was to charge the capacitor only after every second or third measurement.

To depolarize the crystal, it was grounded by switching $S-2$ to
the lower position and then exposed to F light for a period of exactly one minute. While the duration of this interval of illumination was somewhat arbitrary, it was found that longer periods were unnecessary unless additional bleaching of the crystal was desired, whereas appreciably shorter periods were not completely effective in removing the polarization field. Ten seconds after closing the shutter at the end of the depolarization interval, switch S-2 was moved to the upper position. After an additional ten seconds, the chart drive was started and the shutter opened to initiate another photocurrent measurement. This cyclic procedure was continued usually until from thirty to fifty individual photocurrent measurements were completed.

With the exception of the periods of actual measurement, all intervals were carefully timed. The duration of the individual measurements was obtained by measurement of the length of the recorded current trace, the chart drive speed being accurately known. A knowledge of the duration of illumination was necessary in order to compute the integrated exposure of the crystal to F light. Also required was the absorbance of the crystal as a function of exposure. This, however, was determined independently on a separate slice of crystal as previously described. Careful timing of the dark period, the interval of 20 seconds between the end of the depolarization period and the start of the current measurement, was necessitated by the existence of a photocurrent lag time, that is the time required to
achieve an equilibrium concentration of conduction electrons. This phenomenon, which was discussed by Hardtke (11, p. 6-8), will not be dwelt upon at length here but presumably arises as a consequence of the presence of thermally unstable trapping centers in the crystal. Only by standardizing the dark interval could reproducible results be readily obtained.

To illustrate the method employed to ascertain the value of the photocurrent which would have obtained in the absence of space charge polarization, the reader is referred to Graph 1, which is a facsimile of a typical recorder tracing as obtained by measurement. In region 1, the constant current trace, line AB, results from the input of the preselected constant voltage to the recorder. During this period the crystal remained in the dark. The abrupt break in the curve at \( t = 0 \) is due to opening shutter switch S-3. In region 2, the crystal was exposed to F light and the constant voltage replaced by the actual amplifier output. After a momentary instrumental lag resulting in the small dip in the curve, point C, the recorded photocurrent increased slightly and then rapidly decayed with polarization of the crystal.

At \( t = 6 \) seconds, another sharp break in the curve occurs upon closing the shutter switch. In region 3, the crystal was no longer illuminated and the constant voltage, line FG, was again recorded. As previously explained, the duration of exposure was accurately defined by the distance between the two sharp discontinuities in the current.
trace. Also illustrated in Graph 1, is the photocurrent trace in the absence of space charge polarization. Here the photocurrent eventually attains a saturation value, line HJ, resulting from the equilibrium of photoelectrons with thermally unstable traps. Because a current trace of this nature could not be obtained experimentally, it was assumed that the short linear extrapolation, line DE, of the exponential portion of the current trace to \( t = 0 \) yielded the desired equilibrium photocurrent. While justification for this method is somewhat uncertain, it was the method employed throughout the investigation. In certain instances however, the exponential current decay was so rapid that a linear extrapolation was not felt to be justified. Here it was assumed that, at least during the exponential portion of the curve, the current could be represented by \( I = I_0 e^{-kt} \), thereby allowing the calculation of \( I_0 \) by means of the relation

\[
\log I_0 = \frac{t_2 \log I_1 - t_1 \log I_2}{t_2 - t_1},
\]

where \( I_1 = \) photocurrent at \( t_1 \)

and \( I_2 = \) photocurrent at \( t_2 \).
EXPERIMENTAL RESULTS

Optical Bleaching

Measurements of the absorbance changes which occurred upon illumination with F light of the colored crystals employed in this study are illustrated in Graphs 2 through 8. In general, the absorbance index, that is the absorbance per unit thickness of crystal, is plotted against the integrated exposure for those absorption bands whose height could be measured with some degree of precision. Ideally, the integrated exposure is given by

\[ It = I_o \int_0^t \left[ 1 - e^{-2 \cdot 303 A(t)} \right] dt \]  

(9)

where \( I = \) number of photons absorbed per unit volume in unit time,
\( I_o = \) number of incident photons per unit volume per unit time,
\( t = \) time,
and \( A(t) = \) absorbance.

Because an analytic function for \( A(t) \) as a function of time was not known for each crystal, it was necessary to sum the exposure intervals

\[ I_o \left( 1 - e^{-2 \cdot 303 A_i} \right) \Delta t_i \]  

(10)

over periods, \( \Delta t_i \), during which either the absorbance, \( A_i \), could be
considered reasonably constant or an average value of the absorbance could be assumed. As mentioned in the preceding section, ordinarily the absorbance measurements were performed at 77° K on a relatively thick dimension of the crystal whereas bleaching was carried out at room temperature through a thin dimension of the crystal perpendicular to the measurement direction. In this way, concentration gradients along the path of measurement could be avoided. Only the periods of room temperature bleaching are included in the integrated exposure because the extent of bleaching at 77° K is insignificant.

Referring now to Graph 2, the absorbance measurements on Harshaw KCl, it should be pointed out that this was the only case where two separate slices of a given crystal were used for the measurements. This was done so that a thicker slice of the crystal could be used to measure the secondary absorption bands, thereby improving the accuracy of measurement. It should also be mentioned that in this particular case the F band absorbance was measured at room temperature, whereas the absorbances of the secondary bands were measured at liquid nitrogen temperature. In all other instances, i.e. Graphs 3 through 8, the measurements were performed at 77° K. The wavelengths at which the various absorption bands were measured are tabulated in Table I.

Although the absorbance measurements on the secondary centers were performed at 77° K, considerable overlap of the N bands still
TABLE I. WAVELENGTHS OF THE ABSORPTION BANDS WHICH OCCUR IN COLORED POTASSIUM CHLORIDE.

<table>
<thead>
<tr>
<th>Absorption Band</th>
<th>Wavelength (mµ)</th>
<th>At 77° K</th>
<th>At room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>540</td>
<td>560</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>593</td>
<td>617</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>801</td>
<td>820</td>
<td></td>
</tr>
<tr>
<td>R₁</td>
<td>655</td>
<td>670</td>
<td></td>
</tr>
<tr>
<td>R₂</td>
<td>724</td>
<td>730</td>
<td></td>
</tr>
<tr>
<td>N₁</td>
<td>~1000</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>~1055</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Z₁</td>
<td>602</td>
<td>620</td>
<td></td>
</tr>
</tbody>
</table>

occurred. In order to obtain the individual absorbances, it was necessary to assume a symmetrical shape for the N₁ band and subtract its absorbance from the total to obtain that for the N₂ band. The long-wavelength side of the N₁ band was therefore assumed to be a mirror image of the short-wavelength side, which was free from overlapping absorption bands. This method is believed to be justified, because at low exposures where only the N₁ band appeared, it did exhibit a reasonably symmetrical shape.

While it is not shown on Graph 2, at exposures in excess of about 1 x 10^{17} photons/cm^3 a new absorption band appeared. It is a broad band centered at a wavelength of approximately 1250 mµ. Unfortunately, its development did not proceed to the point where accurate measurements could be performed.

In Graph 3, which illustrates the results on the "pure" KCl
purified by the Hay process, it is seen that a prominent A band grew rapidly and suppressed the initial development of the M and R bands as compared to the Harshaw crystal for which no A band was found. Although the detailed procedure followed during the purification of this KCl is not known, it appears that the presence of Na\(^+\) may have resulted from the use of pyrex vessels with an alkaline solution employed in the Hay process. During the entire series of measurements on this crystal, no indication of an N band, either N\(_1\) or N\(_2\), was ever apparent.

In the case of KCl purified by recrystallization, Graph 4, the F band did not bleach appreciably, even after considerable exposure to F light. Consequently, the growth of the M and R bands was restricted. Only a very small N band appeared and then only at the longest exposure. No A band appeared. Both "pure" crystals were colored in the same coloring bomb.

Graph 5 illustrates the results for a crystal which was grown from a melt containing 0.001 mole percent CaCl\(_2\). This low concentration of impurity did not have any pronounced effect on the growth of the secondary centers. The impurity band was small and it is not known with certainty whether it actually stems from the presence of the Ca\(^{++}\) ion or is due to the presence of a small concentration of Na\(^+\) ion.

In contrast, the crystal which was grown from a melt containing
0.01 mole percent CaCl$_2$ exhibited a very pronounced $Z_1$ band upon bleaching. This is illustrated in Graph 6. Once again, the appearance of a large impurity band suppressed the formation of the secondary centers, although the M band finally showed appreciable growth in the later stages of the exposure. This crystal was colored in the same bomb with the other calcium-doped crystal.

In Graphs 7 and 8 are shown the results obtained on crystals doped with K$_2$SO$_4$ and colored together. The crystal grown from a melt containing 0.03 mole percent K$_2$SO$_4$, Graph 7, behaved essentially normally with the secondary absorption bands appearing as expected during illumination. Not indicated on the graph is the presence of the $N_2$ band which appeared at exposures in excess of about $2 \times 10^{17}$ photons/cm$^3$, but not to the extent at which it could be accurately measured.

In the case of the crystal grown from a melt containing 0.1 mole percent K$_2$SO$_4$, Graph 8, the initial F center concentration was only half that produced in the other sulfate-doped crystal with which it was colored. No explanation for this result can be given. The secondary absorption bands could not be measured accurately, because even at 77$^\circ$K their resolution was very poor. Only the M band absorbance could be measured successfully. The R and N bands did arise during bleaching but only projected slightly above the background presumably resulting from the presence of the sulfate ion.
Photoconduction Fatigue

Graph 9 and Graphs 11 through 16 illustrate the decrease in the photosensitivity with exposure to light lying in the $F$ band exhibited by the various crystal employed in this investigation. It should be recalled that the crystals employed for photoconductivity measurements and those used for absorbance measurements were cleaved from adjacent positions in the larger crystal employed in the coloration process. In each case, the sensitivity as given by the quotient of the conductivity, $\sigma$, in units of reciprocal time and the rate of photon absorption, $I$, in units of photons absorbed in unit volume per unit time is plotted against the integrated exposure. This latter quantity was obtained in a manner identical to that used in the optical bleaching measurements. Here, however, both the exposure during the actual measurements and that during the depolarization periods had to be summed. Generally, the measurements were carried beyond the maximum exposures indicated on the graphs, but the decrease in sensitivity at the higher exposures was very limited compared to the large initial drop and ordinarily approached some limiting value.

For the most part, the results agree with those of other investigators, showing a general decrease in sensitivity with $F$ light exposure. At least one difference should be noted however. It is the
increase in sensitivity observed during the initial periods of exposure of the two calcium-doped crystals, Graphs 13 and 14. Although Hirai and Scott (15, p. 2865) observed similar increases in ordinary KCl, the increases occurred only at a temperature of $-15^\circ C$ or below. In the present study, all of the photoconductivity measurements were performed at room temperature.

The dashed lines present on some of the curves mark intervals during which the light intensity was increased to increase the exposure rate. Because this was ordinarily done by increasing the entrance slit width, the increased band pass probably resulted in less light actually being absorbed than was calculated on the basis of all of the light being absorbed at the peak wavelength. As a consequence, an apparent decrease in the sensitivity occurred. The one exception appears in Graph 16. In this one instance, the exposure rate was increased by increasing the lamp voltage but at the same time decreasing the slit width. The effect is therefore just the opposite of that discussed above.

Graph 10, while not illustrating results on photoconduction fatigue, will nevertheless be mentioned in this section with the other photoconductivity measurements. It pictures the absorption spectrum and also the photosensitivity spectrum for a well-bleached crystal of Harshaw KCl, that is a crystal in which the secondary absorption bands are well developed. Both sets of measurements were made at
room temperature, and it is for this reason that the various absorption bands are not well resolved, although all are definitely present. It is readily apparent that the maxima and minima of the two spectra do not coincide.

**Thermal Annealing of Photoconduction Fatigue**

A limited number of measurements were performed on the thermal annealing of photoconduction fatigue. In these measurements, a well-bleached crystal, whose residual conductivity was known, was heated for a given period of time at a given temperature. Its conductivity was then remeasured. After again bleaching the crystal until approximately the same low residual conductivity resulted, it was reannealed for the same period of time but at a different temperature. In this manner, several measurements were made over the temperature range from room temperature to 265°C. They are presented in Graph 17. By plotting the logarithm of the fractional increase in conductivity versus the reciprocal of the absolute temperature, it was found that an activation energy in the range of 0.30 to 0.35 ev obtained for the annealing process.

The absorption spectrum of another slice of this crystal was measured both before and after annealing. Before annealing, a reduced F band and the usual secondary absorption bands were displayed. Following a 12 minute anneal at about 200°C however,
spectral measurements indicated that all of the secondary centers had been destroyed and the F band considerably enhanced. The absorbance of the F band did not attain its pre-bleaching value, however.
DISCUSSION AND CONCLUSIONS

The process of optical bleaching and the consequent appearance of the secondary absorption bands are believed to be intimately related to the decrease in sensitivity. The basic relation for the sensitivity,

\[ \frac{\sigma}{I} = e \mu \eta \tau, \quad (11) \]

shows that any change in sensitivity with illumination must reflect changes in either \( \eta \), \( \tau \), or both of these quantities. Although it is realized that the decrease in sensitivity probably results from changes in both \( \eta \) and \( \tau \), an explanation will be advanced on the premise that only \( \eta \) is involved. Maximum use will be made of the bleaching results obtained in the present investigation and by other investigators.

Effect of Bleaching on the Photoelectron Lifetime

In examining the mean photoelectron lifetime, \( \tau \), we are led to a reconsideration of the trap-replacement mechanism. According to this mechanism traps pre-existing in the crystal capture photoelectrons ejected from F centers, thereby forming isolated anion vacancies. The increase in the anion vacancy concentration results in a corresponding decrease in the electron lifetime, \( \tau \). The capture of photoelectrons by pre-existing traps also yields the secondary
absorption bands. In other words, we are considering a purely electronic, temperature-independent process. If all of the observable changes took place by this mechanism, then the same decrease in sensitivity, the same optical bleaching, and the same secondary absorption bands should occur irrespective of the temperature as long as photoelectrons can be created by the absorption of F light.

At -100°C, the quantum efficiency for the photoionization of the F center electron is unity. While no measurements of photoconduction fatigue at this temperature are known, absorbance changes have been measured. The only change in the absorption spectrum with one known exception results from the formation of F' centers by the capture of photoelectrons by the F centers themselves. The one known exception is the formation of the A' center, a center resulting from the capture of a second electron by the A center (21, p. 2036). This interesting result indicates that A centers must also be formed at this low temperature and therefore that their formation at all temperatures must result from a purely electronic process and not one involving vacancy migration. The only other possibility for the formation of a defect center at -100°C by purely electronic means might be one in which the absorption band of the center formed is hidden by either the F or F' bands. This does not seem likely, however, because the major portion of the F band is replaced by the broad, low F' band. If another absorption band of any consequence developed,
it would surely be noticeable in the spectrum, if not as a peak, at least as a shoulder on one of the existing bands. Moreover, unless it displayed the same thermal instability as the F' center, thermal destruction of the F' band should reveal any underlying band. Because none of the other secondary centers are formed at -100° C, it is likely that their formation takes place by the migration of vacancies, a process which requires a somewhat higher temperature in order to proceed at a measurable rate. From the above considerations, it is concluded that at least part of the reduction in sensitivity with exposure, which occurs at room temperature, may result by a trap-replacement mechanism, that is by the formation of A centers. This conclusion will, however, depend on the ultimate fate of the anion vacancies produced.

**Effect of Bleaching on the Quantum Efficiency for Photoionization**

In examining the effect of the quantum efficiency, \( \eta \), it is necessary to consider how this quantity must vary with exposure in order to account for the accompanying decrease in sensitivity. The variation of the quantum efficiency will depend on the nature of the centers which absorb light in the F band region and on their individual quantum efficiencies as was shown in Equation (6).
The A Center

The A center, whose absorption bands, the A and B bands, greatly overlap the F band at room temperature, will be considered first. It can immediately be decided that the presence of this center cannot have any pronounced effect on the effective quantum efficiency in the F band region. Kojima et al. (21, p. 2036) have shown that when a crystal containing A centers is illuminated with light lying in the A band at any temperature between -50 to -130°C, the A' band grows rapidly. This fact readily indicates that the quantum efficiency for the photoionization of the A center is probably close to unity even at these low temperatures and most assuredly is unity at room temperature. Therefore, the replacement of F centers by A centers should have no net effect on the quantum efficiency of the composite absorption band.

The Z1 Center

The Z1 center also arises early in the irradiation when divalent cations are present in the crystal. In this case, however, an entirely different result obtains. The Z1 band extensively overlaps the long-wavelength side of the F band. By employing the room temperature position and half-width of the Z1 peak and assuming a Gaussian line shape, one can calculate that the absorbance of the Z1 band at 560 mµ,
the wavelength of the F band maximum, is approximately 56% of the maximum Z₁ band absorbance. Furthermore, according to Seitz (50, p. 134) the Z₁ band cannot be bleached at room temperature with light lying in the band. Cole and Friauf (4, p. 389), on the other hand, found a quantum efficiency of 0.30 ± 0.03 for the photoionization of the Z₁ center electron. Their value is probably too high, because they assumed a unit quantum efficiency for the F band after considerable bleaching had occurred. We may conclude that the Z₁ center electron is not readily promoted into the conduction band. Hence, as the Z₁ band grows, its presence will have an increasing influence on the effective quantum efficiency of the composite "F" band. Of course, the presence of divalent cations is a necessary prerequisite for the presence of a Z₁ band. While CaCl₂ was actually only added to two of the crystals of the present study, alkaline earth cations are a likely impurity in all of the other crystals also. Duerig and Markham (10, p. 1044) have published analyses of Harshaw KCl which indicate the presence of up to about 0.01% calcium, which is more than was present in either of the crystals doped with calcium in the present study. Thus, it seems probable that a small concentration of divalent cations may be present in all of the crystals employed with the possible exception of the specially purified crystals.
The M Center

Probably the most important of the F-aggregate centers with respect to its effect on the quantum efficiency is the M center. Okamoto (41, p. 1095) has demonstrated the existence of two excited states of the M center which are essentially completely hidden by the F band. At 77°K where the maximum absorption of the F band lies at a wavelength of 540 mµ, the maximum absorptions of the M₂ and M'₂ bands lie at 546 mµ and 538 mµ respectively. The wavelengths of their maximum absorptions at room temperature, where that of the F band is 560 mµ, are estimated to be 564 mµ and 560 mµ respectively. Thus, for all practical purposes they overlap completely with the F band. Assuming that the increase in their half-widths upon increasing the temperature from 77°K to room temperature is in direct ratio to the increase in the half-width of the M band, the ratio of their respective peak heights to that of the M band is unaffected by the temperature increase and the values given by Okamoto can be employed directly. This leads to the following correction to the F band absorbance at room temperature:

\[
A_F^{(corrected)} = A_F - 0.78A_M \quad (12)
\]

where \(A_F\) and \(A_M\) are the measured absorbances in the F and M bands respectively.
Looking now at the quantum efficiency to be expected for the photoionization of the M center in these two excited states, it is recalled that several investigators found a ratio for the quantum efficiency for the ionization of the M center to that of the F center of about 0.1, as was pointed out on page 21. Because of the composite nature of the "F" band after other centers are formed, \( \eta < 1 \). Therefore, the quantum efficiency for M center ionization must be somewhat less than 0.1, and it seems likely that the quantum efficiency for photoionization of electrons from either of the two excited states is also on the order of 0.1.

The R Center

Although Okamoto (41, p. 1094) has found an excited state of the R center whose absorption band is hidden by the F band, it is doubtful that it exerts much if any influence on the composite "F" band. As Oberly and Burstein (34, p. 217) pointed out, the R bands exhibit considerable photoresponse indicating a relatively high quantum efficiency. The measurements of Cole and Friauf (4, p. 389), while lacking precision, yielded values of 0.9 and 0.5 for the quantum efficiencies of the \( R_1 \) and \( R_2 \) centers respectively. As pointed out previously, these values are based on a unit quantum efficiency for the F band in a crystal which has undergone considerable bleaching. They are therefore somewhat high but nevertheless indicate that the
quantum efficiency for ionization of the $R_3$ center must be nearly unity. Thus, like the $A$ center, the presence of $R$ centers in the crystal will not have any pronounced net effect on the quantum efficiency of the composite absorption band.

The $N$ Centers

Pick (44, p. 73-74) has proposed $N$ center models which include excited states having absorption bands in the $F$ band region. While some experimental evidence for these absorption bands exists (41, p. 1094), any evidence relating to their magnitude and position is lacking. As in the case of the $R$ center, Oberly and Burstein (34, p. 217) have indicated that the $N$ band exhibits considerable photoresponse. This result is in contrast to the findings of the present investigation which will be discussed shortly. Unfortunately, little can be said regarding the possible effects of the $N$ bands on the effective quantum efficiency of the composite "$F$" band. If their individual quantum efficiencies approach unity, then their effect will be small; but if these quantum efficiencies are small, as is indicated by the present study, then the presence of $N$ centers in the crystal could have a pronounced effect on the sensitivity. Fortunately, it is often found experimentally that the growth of the $N$ bands is not excessive. In any case, their effect on photoconductance fatigue will necessarily be neglected.
The F Center

Finally, it appears necessary to examine the quantum efficiency of the F center itself. As was pointed out previously, in the absence of other centers and at temperatures above \(-130^\circ C\), the quantum efficiency for photoionization of the F center is unity. However, Kuwabara et al. (24, p. 1623) have found that the efficiency of F center emission at \(-170^\circ C\) decreases linearly with the increasing M center concentration even though the amount of F light absorbed by the excited states of the M center hidden under the F band is taken into account. This fact supports the proposal that energy absorbed by the F center itself is transferred to the M center. van Doorn (59, p. 300) has presented similar evidence in support of an energy transfer process. The extent to which energy transfer affects the F center quantum efficiency at room temperature is not known, however it appears likely that the effective quantum efficiency for photoionization of the F center decreases with exposure as a consequence of an energy transfer process rather than remaining constant at a value of unity. The linear decrease in F center emission found by Kuwabara suggests that the F center quantum efficiency can be represented by an equation of the form

\[
\eta_F = 1 - k A_M \tag{13}
\]

where \(k = \text{constant}\). At \(I_t = 0\), when only F centers are present in
the crystal and $A_M = 0$, $\eta_F = 1$, but with the initiation of bleaching with the attendant formation of $M$ centers, $\eta_F$ decreases. In view of the fact that $\eta_F$ can be considerably less than unity in a well-bleached crystal, it is again emphasized that the quantum efficiencies of the other defect centers are appreciably less than the literature values which are based on a unit quantum efficiency for the $F$ center.

**Effect of the Quantum Efficiency on the Sensitivity**

Graph 10 illustrates the wavelength dependence of the sensitivity. Because in a given crystal the photoelectron lifetime should be independent of the source of electrons, a plot of the sensitivity as a function of the wavelength of the absorbed light depends only on the quantum efficiency of the absorption band illuminated. In the wavelength region between 950 $\mu m$ to 1100 $\mu m$ where the N bands occur, it is seen that the sensitivity is relatively low implying a low quantum efficiency for the N bands. At the M band maximum at 820 $\mu m$, the sensitivity is still low but is somewhat higher than that in the N band region, probably as a result of overlap with the $R_2$ band. In the region of the R bands, the sensitivity is high, particularly for the $R_1$ band, and indicates that the R centers are readily ionized. Upon approaching the F band maximum, the sensitivity falls off rapidly, reaching a minimum at about 570 $\mu m$, the region of the $M_2$ band. It then increases rapidly in the region of the $R_3$ band as one would
expect for a higher excited state of the R center. Unfortunately, measurements could not be performed at lower wavelengths because the low light intensity of the spectrophotometer could not be accurately measured there. While these results are for the most part qualitatively similar to those of other investigators, as was mentioned above, the relative quantum efficiency in the N band region is small in contrast to the findings of Oberly and Burstein. This implies that absorption bands of the N centers lying under the F band could contribute to the decrease in sensitivity during the bleaching process.

All of the above considerations can be summarized by the following equation which relates changes in the sensitivity to the absorbance changes which occur when the colored crystals are bleached. It is obtained by combining Equations (5), (6), and (7).

\[
\frac{\sigma}{I} = \frac{e\mu}{v} \sum \frac{f_i \eta_i}{n_j S_j} \quad (14)
\]

where \( \sigma /I \), the \( f_i \), the \( n_j \), and \( \eta_F \) are all functions of the integrated exposure. At \( I = 0 \) when only F centers are present in the crystal, \( f_i = f_F = 1 \) and \( \eta_i = \eta_F = 1 \) so that

\[
(\sigma /I)_o = \frac{e\mu}{v} \sum \frac{n_j^o}{n_j S_j} \quad (15)
\]

The \( n_j \) include the concentrations of the anion vacancies, both isolated and adjacent to sodium ions. The initial trap concentrations, \( n_j^o \), and
their electron capture cross sections, $S_j$, essentially define the initial sensitivity, $(\sigma / I)_o$, and are, in turn, related to the purity of the crystal. For example, upon comparing the initial sensitivities of the specially purified KCl, Graph 11, and the sulfate-doped KCl, Graph 16, it is seen that they differ by a factor of about 30. The low sensitivity of the sulfate-doped crystal may result from the additional anion vacancies introduced into the crystal with the sulfate ion.

In order to test Equation (14) or its equivalent, two approximations are necessary. First, it is assumed that the electron trapping cross section of an anion vacancy adjacent to a potassium ion is identical to that of an anion vacancy adjacent to a sodium ion. Because the formation of A centers has no effect on the quantum efficiency of the composite "F" band, this assumption allows us to neglect the A center completely. In other words, it is assumed that the electron lifetime, $\tau$, is constant. Its value is obtained from Equations (7) and (15), viz.

$$\tau = \tau_o = \frac{(\sigma / I)_o}{e^\mu} \quad (16)$$

Equation (16) may, in turn, be substituted into Equation (14) to yield

$$\sigma / I = (\sigma / I)_o \sum_i f_i \eta_i \quad (17)$$
Equation (17) can also be written

\[ \frac{\sigma / I}{(\sigma / I)_0} = \eta = \sum_i f_i \eta_i \]  

(18)

The second approximation is necessary because the absorbances and quantum efficiencies of the excited states of the N centers are unknown. Thus, we must neglect the presence of N centers in the crystals and hence any influence they might have on the quantum efficiency of the composite absorption band. As a result of this approximation, Equation (18) may be written as follows:

\[ \frac{\sigma / I}{(\sigma / I)_0} = \eta_f f_F + \eta_M f_M + \eta_{Z_1} f_{Z_1} \]

\[ = (1 - kA_M) f_F + \eta_M f_M + \eta_{Z_1} f_{Z_1} \]

\[ \text{(19)} \]

where

\[ f_F = \frac{1 - e^{-2.303(A_F - 0.78A_M - 0.56A_{Z_1})}}{1 - e^{-2.303A_F}} \]

(20)

\[ f_M = \frac{1 - e^{-2.303 \times 0.78A_M}}{1 - e^{-2.303A_F}} \]

(21)

and

\[ f_{Z_1} = \frac{1 - e^{-2.303 \times 0.56A_{Z_1}}}{1 - e^{-2.303A_F}} \]

(22)

Ordinarily, both products \( \eta_M f_M \) and \( \eta_{Z_1} f_{Z_1} \) are small, so that

\[ \frac{\sigma / I}{(\sigma / I)_0} \sim (1 - kA_M)f_F \]

(23)
or \[
\frac{1}{I_F} \left[ \frac{\sigma/I}{(\sigma/I)_0} \right] \approx 1 - kA_M
\] (24)

Therefore, a plot of the left-hand side of Equation (24) versus \(A_M\) should yield a straight line of slope \(k\) if the decrease in sensitivity is primarily a consequence of a decrease in the effective quantum efficiency of the composite "F" absorption band. Plots of this function for four of the crystals are shown in Graph 18. Some curvature is exhibited in each case, thereby indicating that changes in the photoelectron lifetime must also contribute to the decrease in sensitivity with illumination.

Values of \(k\) calculated from the results on the Harshaw crystal are presented below to indicate the magnitude of the change in slope as a function of exposure. The Harshaw results were selected because of the greater accuracy with which the secondary absorption bands were measured and because the sensitivity fatigue curve, Graph 9, exhibited normal behavior.

TABLE II. VARIATION IN \(k\) WITH EXPOSURE FOR HARSHAW KCL.

<table>
<thead>
<tr>
<th>(10^{-15} (\text{photons absorbed/cm}^3))</th>
<th>(k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>20.7</td>
</tr>
<tr>
<td>50</td>
<td>21.4</td>
</tr>
<tr>
<td>100</td>
<td>18.5</td>
</tr>
<tr>
<td>300</td>
<td>16.0</td>
</tr>
</tbody>
</table>
It is seen that $k$ is reasonably constant considering the approximations employed and realizing that over this same exposure interval the sensitivity varies by a factor of six. The variation in $k$ can probably be attributed to a decrease in the photoelectron lifetime, although secondary effects may also result from the neglect of the N bands which had developed to an appreciable extent in this crystal.

In the case of the calcium-doped crystals, the mechanism proposed in this thesis cannot be used to account for the sensitivity increase observed during the early periods of illumination. Because the F band has a unit quantum efficiency at $I_t = 0$, it cannot increase and the sensitivity increase must therefore be attributed solely to an increasing photoelectron lifetime. Absorbance measurements did not indicate the abrupt formation of any secondary center during the sensitivity increase, and therefore it is not possible to identify the trapping center responsible with certainty. It is, of course, highly probable that this center is associated with the presence of calcium, even though abnormal growth in the $Z_1$ band during this period of illumination was not observed. The sensitivity increase also indicates that these trapping centers must have an electron capture cross section appreciably greater than that of the anion vacancy.

The "Hay process" KCl crystal, Graph 11, although showing the high initial sensitivity typical of specially-purified material, exhibits a remarkable decrease in sensitivity which can only be accounted for
by the similarly remarkable growth in the A band during the same period of exposure. This result indicates that the electron trapping cross section of an anion vacancy adjacent to a sodium ion must be considerably less than that of an anion vacancy adjacent to a potassium ion. Therefore, the use of the approximation, whereby the photo-electron lifetime was assumed to remain constant during bleaching, is to be avoided when a prominent A band is present.

The other specially-purified KCl crystal, Graph 12, not only shows a high initial sensitivity but also exhibits only a relatively minor decrease in sensitivity during its illumination. This is the result anticipated for a crystal from which potential electron traps have been removed by purification. Similarly, the extent of F band bleaching with the attendant formation of secondary centers is greatly reduced indicating that impurities by acting as electron traps essentially initiate the bleaching process. This may be seen from the following scheme, in which $\alpha$ represents an isolated negative-ion vacancy.

$$\begin{align*}
F & \xrightarrow{hv} e^- + \alpha & (a) \\
A^+ + e^- & \rightarrow A & (b) \\
F + e^- & \rightarrow F' & (c) \\
F' + \alpha & \rightarrow M & (d)
\end{align*}$$

In this example, ionized A centers, $A^+$, serve as the impurity electron trap. Equations (c) and (d) indicate a possible means by
which $F$-aggregate centers are formed. It is seen that for each electron trapped to form an $A$ center, an anion vacancy remains behind irrespective of the fact that vacancies are incorporated into the secondary centers. When no impurities are present to remove the electrons, they can only recombine with anion vacancies to reform $F$ centers and no bleaching or sensitivity loss occurs.

The behavior exhibited by the sulfate-doped crystals was similar to that shown by the Harshaw crystal. The presence of $SO_4^-$ ion, while diminishing the magnitude of the initial sensitivity, apparently has no pronounced effect on the bleaching rate or on the rate at which the sensitivity decreases with exposure. It thus appears that the anion vacancies introduced with the $SO_4^-$ ion may remain associated with the impurity and may not exert any appreciable influence on the changes induced by illumination.

**Thermal Annealing of Photoconduction Fatigue**

The influence of the secondary centers on the sensitivity is also indicated by the limited number of thermal annealing measurements performed during the present study and shown in Graph 17. Only one crystal was used for these measurements and it was bleached to the point where its residual photoconductivity was approximately the same low value before each annealing run. It is therefore believed that the initial state of the crystal was always essentially the same with
respect to the concentrations of the various secondary centers.

At a temperature near $80^\circ$ C, no recovery of the photoconductivity occurred. Only R centers are readily destroyed at this temperature (54, p. 493). Because R centers have no appreciable effect on the quantum efficiency of the composite absorption band, it is reasonable that their loss should not effect a conductivity increase. Between 100 and $130^\circ$ C where N centers are thermally unstable, a small increase in the conductivity occurred over the time interval employed. Above $130^\circ$ C, M centers decompose thermally and recovery from photoconduction fatigue proceeded rapidly. Unfortunately, no information was obtained on the possible occurrence of A centers in the crystal used for the annealing measurements. Because A centers are also readily decomposed at the temperatures employed for these measurements (21, p. 2035-2036), their contribution to the observed photoconductivity increase is unknown but could be appreciable. For this reason, the extent of the contribution to the photoconductivity increase resulting from the destruction of M centers cannot be ascertained quantitatively.

Because the initial state of the crystal was approximately the same before each thermal treatment, the measured rate was assumed proportional to the specific rate constant and an activation energy calculated for the recovery process. The apparent activation energy obtained in this manner was about 0.30 to 0.35 ev and is of about
the magnitude of the activation energy (0.43 ev) for the thermal destruction of the A center (21, p. 2036). It is also of about the magnitude of the activation energy (0.3 ev) found by Bron and Nowick (2, p. 121) for the bleaching process, and of the activation energy found for M center formation. It appears possible that the rate-determining process in each case may be the diffusion of one of the components of the secondary centers, perhaps the F center itself.

Conclusions and Recommendations

The results of this investigation demonstrate that neither the quantum efficiency for photoionization of the F center nor the photoelectron lifetime can be neglected in accounting for changes in the photosensitivity of colored potassium chloride upon exposure to F light. A decrease in the effective quantum efficiency for photoionization of the F center occurs with the formation of the secondary centers for two reasons. First, as a consequence of excited states of the secondary centers which absorb light in the F band region, F light absorbed by the crystal is reemitted, primarily as M center luminescence, and does not yield conduction electrons. Although the M center is primarily responsible because of its low photoionization quantum efficiency, the presence of N centers in the crystal may contribute to the quantum efficiency decrease. In crystals containing alkaline earth ions, the formation of Z\textsubscript{1} centers also causes a
quantum efficiency decrease because the $Z_1$ band greatly overlaps the F band and the $Z_1$ center has a low quantum efficiency for photoionization. The second reason for the decrease in the effective quantum efficiency for photoionization of the F center is a process of energy transfer which occurs readily at low temperature and is assumed to occur at room temperature. In this process, light absorbed directly by the F center is transferred to M centers which, in turn, luminesce rather than yield photoelectrons.

Changes in the mean lifetime of the conduction electrons and hence in the sensitivity are brought about by a trap-replacement process, in which electrons ionized from F centers are trapped at impurity centers, thereby increasing the concentration of isolated anion vacancies. If the trapping cross section of the impurity center is less than that of the isolated anion vacancy, then the photoelectron lifetime and the sensitivity will decrease. An example of an impurity center of this nature is an anion vacancy adjacent to a sodium ion. Upon trapping an electron, this center becomes the A center. If, on the other hand, the trapping cross section is greater than that of the isolated anion vacancy, then the photoelectron lifetime and the sensitivity will increase. This behavior was noted in the case of the calcium-doped crystals. It is believed that the initial rapid changes in the sensitivity are the result of this trap-replacement process, which yields isolated anion vacancies and consequently results in the
initiation of the process by which F-aggregate centers such as the M center are formed.

In future investigations of photoconduction fatigue, it is recommended that the absorbance and photoconductivity measurements be made in situ. The use of a single piece of crystal will preclude the possibility of differences between adjacent slices of a larger crystal. These differences could include concentration or impurity gradients occurring during crystal growth and coloration.

The use of a series of sodium-doped crystals with varying concentrations of the impurity will allow the determination of the relative contributions of the quantum efficiency and the mean photoelectron lifetime to the decrease in sensitivity with exposure. For example, it would be of interest to compare the sensitivities of crystals having the same M-center concentration but different A-center concentrations. A series of crystals of this nature would also indicate the importance of trap replacement on the rate of formation of the F-aggregate centers.

Interesting experiments can also be based on the process of thermal annealing. The different thermal stabilities of the secondary centers would allow the estimation of the extent by which the different centers influence the effective quantum efficiency of the F center.

Probably the most important problem for future investigators is to unravel the complex nature of the absorption band which replaces
the pure $F$ band. Irrespective of the theory proposed for the decrease in sensitivity with $F$ light exposure, one cannot rely on the absorbance at the $F$ band location to give a true indication of the number of $F$ centers present in the crystal after illumination has been initiated.
PLATE I
CRYSTAL HOLDER FOR SPECTRAL MEASUREMENTS
PLATE 2
DEWAR CELL FOR SPECTRAL MEASUREMENTS
GRAPH 1
A TYPICAL PHOTOCURRENT MEASUREMENT
SPECTRAL MEASUREMENTS ON HARSHAW KCl

CRYSTAL H-1
$N_e^0 = 3.3 \times 10^{16}$

CRYSTAL H-2
$N_e^0 = 3.3 \times 10^{16}$

$\alpha \times 10^6$ (MM$^2$)

$I_t \times 10^{17}$ (PHOTONS / CM$^3$)
GRAPH 3
SPECTRAL MEASUREMENTS ON "PURE" KCl

CRYSTAL P-2-1
N⁺ = 3.7 x 10⁶

α (mm⁻¹)

α x 10² (mm⁻¹)

I t = 10⁻⁷ (photons/cm³)

I t = 10⁻⁴ (photons/cm³)
GRAPH 4
SPECTRAL MEASUREMENTS
ON "PURE" KCl

CRYSTAL P-I-1

\[ N_e = 3.7 \times 10^{16} \]

\[ \alpha \times 10^3 \text{(MM}^2\text{)} \]

\[ \alpha \times 10^6 \text{(MM}^2\text{)} \]

\[ I^* \times 10^{-7} \text{(PHOTONS/CM}^3\text{)} \]
GRAPH 5
SPECTRAL MEASUREMENTS
ON Ca$^{++}$ DOPED KCl
CRYSTAL C-1-1 (0.001 M% Ca$^{++}$)
$N_F^* = 4.4 \times 10^{16}$

\[ \alpha = \frac{x}{\lambda} (\text{Mm}^{-1}) \]

\[ \alpha = 10^2 (\text{Mm}^{-1}) \]

\[ I = 10^6 (\text{Photons / cm}^3) \]

83
GRAPH 6
SPECTRAL MEASUREMENTS
ON Ca⁺⁺ DOPED KCl
CRYSTAL C-2-I (0.01M % Ca⁺⁺)
N_f⁰ = 4.1 x 10¹⁷

α_f (MM⁻¹)

α = 10^² (MM⁻¹)

It x 10⁻⁶ (PHOTONS/CM³)

Z₁

OM

R₂

ON₁

0.6
0.5
0.4
0.3
0.2
0.1
0

10
5
2
1
0

2
4
8
10
GRAPH 7
SPECTRAL MEASUREMENTS ON $SO_4^-$-DOPED KCl CRYSTAL S-1-1 (0.03M% $SO_4^-$)
$N_F^0 = 2.3 \times 10^{16}$

$\alpha_{x} (\text{M.M.}^{-1})$

$I x 10^7 (\text{PHOTONS/CM}^3)$

$\alpha x 10^2 (\text{M.M.}^{-1})$
GRAPH 8
SPECTRAL MEASUREMENTS
ON $\text{SO}_4^{2-}$-DOPED KCl
CRYSTAL S-2-1(0.10M% $\text{SO}_4^{2-}$)
$N_e = 1.15 \times 10^{16}$
GRAPH 9
PHOTOCONDUCTION FATIGUE
IN HARSHAW KCl
CRYSTAL H-3
N° = 3.3 \times 10^6
GRAPH 10
PHOTOSENSITIVITY AND
ABSORPTION SPECTRA
FOR HARSHAW KCl
CRYSTAL H-4
○ PHOTOSensitivity
□ ABSORBANCE INDEX

α \times 10^3 \text{ (MM}^2\text{)} OR \sigma \times 10^7 \text{ (CM}^3\text{)}

WAVELENGTH (M\mu)

500 600 700 800 900 1000 1100 1200
GRAPH II
PHOTOCONDUCTION FATIGUE
IN "PURE" KCl
CRYSTAL P-2-2
$N_F = 3.7 \times 10^{16}$
GRAPH 12
PHOTOCONDUCTION FATIGUE IN "PURE" KCl
UPPER CURVE: CRYSTAL P-I-2
LOWER CURVE: CRYSTAL P-I-3
$N_0^R = 3.7 \times 10^{16}$
GRAPH 13
PHOTOCONDUCTION FATIGUE
IN Ca⁺⁺-DOPED KCl
CRYSTAL C-1-2
Nₓ = 4.4 × 10¹⁶
0.001 MOLE % Ca⁺⁺
GRAPH 14
PHOTOCONDUCTION FATIGUE
IN Ca\textsuperscript{2+} DOPED KCl
CRYSTAL C-2-2
\(N_v = 4.1 \times 10^{16}\)
0.01 MOLE \% Ca\textsuperscript{2+}
GRAPH 15

PHOTOCONDUCTION FATIGUE
IN SO_4^2- DOPED KCl
CRYSTAL S-1-2
N_p^0 = 2.3 \times 10^{16}
0.03 MOLE % SO_4^2-
PHOTOCONDUCTION FATIGUE
IN SO\(_2^-\)-DOPED KCl
CRYSTAL S-2-2
N\(_f^0\) = 1.15 \times 10^{16}
0.10 MOLE % SO\(_2^-\)

GRAPH 16

\(\sigma/IT \times 10^{16} \text{ (cm}^2\text{)}\)

I \(T \times 10^{-17} \text{ (photons/cm}^3\)
GRAPH 17
RECOVERY OF PHOTOCONDUCTIVITY UPON THERMAL ANNEALING

\[ \Delta \sigma \times 10^2 \text{ (sec}^{-1}) \]

\[ T (\text{°C}) \]

Points at:
- 100°C: \[ \Delta \sigma \] is approximately 0.
- 200°C: \[ \Delta \sigma \] shows a moderate increase.
- 300°C: \[ \Delta \sigma \] shows a significant increase.

The graph illustrates the recovery of photoconductivity as a function of temperature upon thermal annealing.
GRAPH 18
TEST OF EQUATION (24)

CRYSTALS       LINE
H-1,2,3        
P-2-1,2        
C-2-1,2        
S-1-1,2        

\[ 10 \left[ \frac{\sigma}{\sigma_0} \right] \] vs. \( A_M \times 10^2 \)


