

## Low-Temperature Optical Bleaching of $F$ Centers in KCl\*

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Optical bleaching of  $F$  centers in x-rayed and additively colored KCl has been studied at 77°K with pulse irradiation methods. Constant “ $F$  light” incident on the colored crystal establishes a photostationary equilibrium between  $F$  and  $F'$  centers. The application of a high-intensity light flash of appropriate spectrum displaces the system from equilibrium to either direction. The return to equilibrium is exponential in time, with a rate controlled by the intensity and spectrum of the constant light, but not depending on the  $F$ -center concentration or the method of coloration. The results are in agreement with a kinetic model involving only  $F$ -to- $F'$  center interconversions. Prior room-temperature optical bleaching inhibits the extent and rate of low-temperature bleaching, probably due to the growth of other bands under the  $F$  band. The saturation of the extent of bleaching at high pulse-light intensity and a lower bleaching efficiency for the additively colored crystal indicate that the distribution of  $F$  centers in the crystal is significant in low-temperature bleaching.

### INTRODUCTION

**$F$**  CENTERS in KCl can be bleached by irradiation with “ $F$  light” and the mechanism depends on the bleaching temperature. Near and above room temperature, optical bleaching causes several new bands to appear at longer wavelengths than the  $F$  band. The  $M$  band increases until a maximum height is reached, after which time it diminishes, while the  $R_1$  and  $R_2$  bands at shorter wavelength continue to increase.<sup>1</sup> Although the details of the process are not known, it is believed that the migration of vacancies is involved. Below about 190°K, the  $M$  and  $R$  bands do not appear on optical bleaching, but instead the very broad  $F'$  band grows. The  $F'$  center consists of two electrons trapped in a negative-ion vacancy and is produced by the photoionization of an  $F$  center and the subsequent capture of the electron at another  $F$  center. The efficiency with which  $F$  centers are converted to  $F'$  centers diminishes at low temperatures. In the region where  $F'$  centers are easily produced and are thermally stable, a two-step bleaching process occurs; optical excitation of the  $F$  center is followed by a thermally-activated release of the electron to the conduction band. At 170°K approximately 80% of the  $F$  band can be converted to the  $F'$  band.<sup>2,3</sup> Saturation occurs for two reasons: First, the  $F'$  band overlaps the  $F$  band so that continued irradiation also bleaches  $F'$  centers; and second, negative-ion vacancies compete with  $F$  centers for the electrons released from  $F$  centers. Photoconductivity measurements show that the bleaching quantum efficiency at 177°K is about 100 times larger than at 77°K.<sup>3</sup> Markham, Platt, and Mador<sup>4</sup> made a careful investigation of the optical

bleaching of KBr between 4° and 77°K and found that the rate depends on the temperature of x-ray irradiation and furthermore, did not detect optical bleaching in additively colored crystals. They suggested that tunneling accounts for the observed low-temperature bleaching, assuming that some  $F$  centers in x-rayed KBr are clustered, while  $F$  centers in additively colored KBr are uniformly distributed at distances too large for tunneling. It was shown in a previous publication<sup>5</sup> that substantial transient changes in transmission occur when x-rayed KCl is irradiated with a bright light flash at low temperature. Irradiation with a flash of green “ $F$  light” causes a fast decrease in the  $F$  band with a subsequent recovery after about 0.2 sec, and irradiation with a flash of red “ $F'$  light” causes a fast increase in the  $F$  band with a decay requiring approximately the same duration. This paper reports further investigation of these effects. In the experiments reported here, the x-raying was done at room temperature to minimize the effects of unstable  $V$  bands. Results for crystals x-rayed at low temperature will be reported at a later time. The earlier conclusion is substantiated that  $F$ -to- $F'$  center conversions are involved, new information is given on the influence of the constant monitoring lamp, and a simple kinetic model is proposed which explains many of the results.

### EXPERIMENTAL METHODS

The samples used were Harshaw KCl cleaved into 1×1 cm wafers, varying in thickness from 0.03–0.10 mm. They were irradiated in the dark at room temperature with 45-kv copper x rays, inside an evacuated metal sample holder with three 2-mm fused-silica optical windows and a 0.8-mm beryllium window for x-ray irradiation. In all experiments, except those requiring prior room-temperature bleaching, the irradiated crystals containing  $10^{16}$ – $10^{17}$   $F$  centers per cc were rapidly cooled to 77°K and optically bleached to saturation with “ $F$  light” in a Beckman DU spectrophotometer.

\* A. R. Reinberg and L. I. Grossweiner, *J. Chem. Phys.* **30**, 1616 (1959).

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<sup>1</sup> F. Seitz, *Revs. Modern Phys.* **18**, 384 (1946); **26**, 7 (1954).

<sup>2</sup> R. W. Pohl, *Proc. Phys. Soc. (London)* **49**, 13 (1937).

<sup>3</sup> H. Pick, *Ann. Physik* **31**, 373 (1938).

<sup>4</sup> J. J. Markham, R. T. Platt, and I. L. Mador, *Phys. Rev.* **92**, 597 (1953).

The flash-bleaching experiments were then performed in the apparatus shown in Fig. 1. The constant light source was a tungsten-filament lamp operated from a 6-v storage battery. The beam was focused on the front slit of a Bausch & Lomb "large wavelength" prism spectrometer. The light intensity at the rear slit was monitored with a 1P28 photomultiplier, whose signal was coupled to a Tektronix 545 oscilloscope. The flash light source was an Edgerton FX-1 flashtube with a 1-in. gap. It was energized from a 2- $\mu$ f capacitor at 8 kv and provided a 10- $\mu$ sec flash with a continuous spectrum from 220  $m\mu$  to the near infrared. The crystal was located between the constant lamp and spectrometer, and the crystal face made an angle of  $45^\circ$  to both the constant lamp and the flash lamp. The intensity of the constant and flash irradiation was varied with Bausch & Lomb neutral density filters. The flash-lamp spectrum was separated into two general regions with broad-band filters. The "green" light flash covered 450–610  $m\mu$ , peaking at 525  $m\mu$ , and the "red" light flash covered from 610  $m\mu$  to about 3  $\mu$ . Three spectral distributions were considered in each experiment: the constant lamp incident on the crystal, the flash lamp, and the monitoring wavelength of the spectrometer. Transient changes in optical transmission, as measured with the photomultiplier, can be converted into optical densities with the following equation:

$$- \Delta D = \log_{10}(V_s + V_{dc}) / V_{dc}, \quad (1)$$

where  $V_{dc}$  is the steady photoelectric signal at the monitoring wavelength and  $V_s$  is the instantaneous voltage change measured on the oscilloscope. Changes in transmission of one part in ten thousand were readily measured.

## RESULTS

For the purpose of this discussion, the return of optical density toward the original value after a mo-

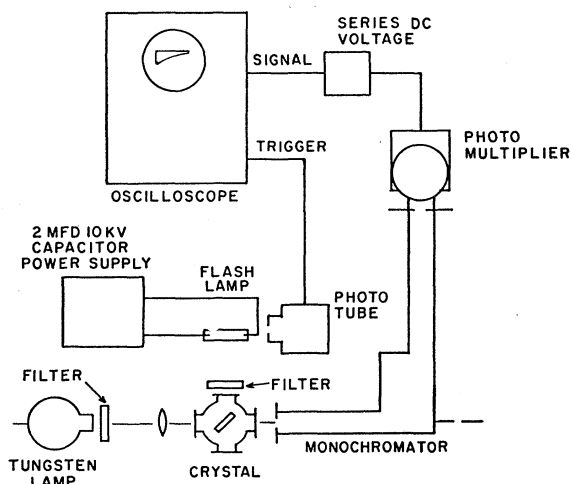


FIG. 1. Experimental arrangement for kinetic spectrophotometry.

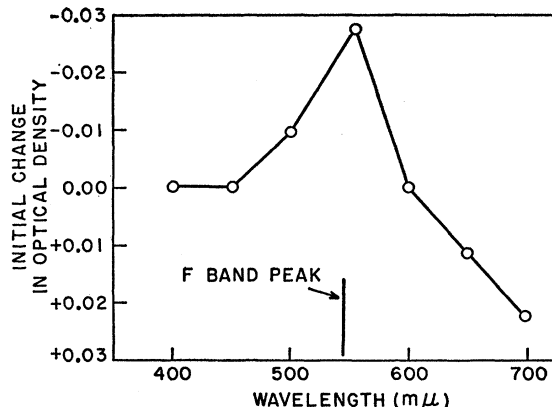


FIG. 2. Dependence of the initial extent of bleaching at 540  $m\mu$  on the wavelength of flash irradiation.

mentary increase is called a "decay" and the return after a momentary decrease is called a "recovery."

### 1. Identification of the Bands Bleached by Flash Irradiation

Although irradiation with a green light flash increases the transmission at 540  $m\mu$  and irradiation with a red light flash decreases the transmission at 540  $m\mu$ , this is not adequate proof that  $F$  and  $F'$  centers are bleached. For example, Compton and Klick<sup>6</sup> found that a complex series of bands appeared and disappeared while KCl containing  $R$  and  $M$  centers was exposed to "R" or "F light" at low temperature. Figure 2 shows how the initial change in optical density at 540  $m\mu$  varies with the wavelength of the flash irradiation. The latter was varied in 50- $m\mu$  steps with Farrand narrow-band interference filters from 400–700  $m\mu$ . The largest optical density decrease coincides with irradiation in the maximum of the  $F$  band, establishing that green flash irradiation bleaches  $F$  centers. The optical density increase at 540  $m\mu$  due to irradiation above the  $F$  band strongly suggests that  $F'$  centers are bleached. In other experiments the crystal was irradiated with red flash light and the monitoring wavelength was varied. Figure 3 shows the initial change in optical density at various monitoring wavelengths. For comparison, the absorption spectrum of a KCl crystal x-rayed at room temperature and measured in the Beckman DU spectrophotometer at 77°K is normalized to the same maximum height. The coincidence of the wavelength maxima is further evidence that the red flash light converts  $F'$  centers to  $F$  centers. The optical density decrease on either side of the  $F$  band is interpreted as the bleaching of  $F'$  centers. The narrower width of the flash-produced  $F$  band on the short-wavelength side can be explained by assuming that the "pure"  $F$  band is being measured, since the experimental method automatically subtracts absorptions that are not due to the  $F$  center. The observed half-

<sup>6</sup> W. D. Compton and C. C. Klick, Phys. Rev. **112**, 1620 (1958).

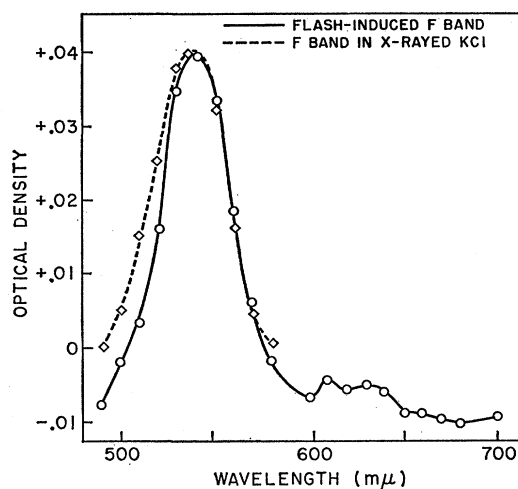


FIG. 3. Initial extent of bleaching at various wavelengths due to red-flash irradiation.

width is 0.16 ev, which is 0.03 ev smaller than the value reported for the "pure"  $F$  band by Konitzer and Markham.<sup>7</sup> It is interesting to compare the optical density decrease at 540  $m\mu$  to the optical density increase at 610  $m\mu$  after bleaching with a green light flash. Figure 4 shows the dependence of these quantities at various times after a flash irradiation. The linearity

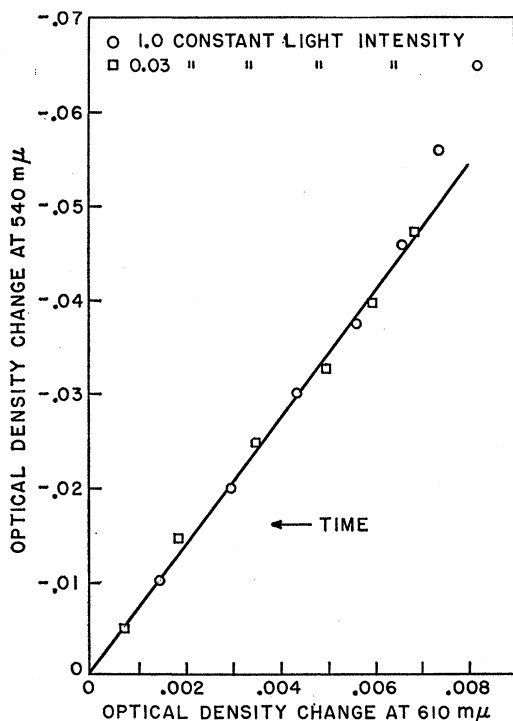


FIG. 4. Comparison of optical density change at 540  $m\mu$  to optical density change at 610  $m\mu$  for various times after green-flash bleaching.

<sup>7</sup> J. D. Konitzer and J. J. Markham, J. Chem. Phys. 32, 843 (1960).

shows that the number of  $F$  centers bleached is always proportional to the number of  $F'$  centers produced, and further substantiates the identification of these processes as  $F$ -to- $F'$  center interconversions.

## 2. Kinetics of the Bleaching Processes

### (a). Red-Flash Bleaching

When crystals containing  $F$  centers are bleached with red flash light, additional  $F$  centers are produced due to absorption in the  $F'$  band. The subsequent decay of  $F$  centers measured at 540  $m\mu$  is due to the bleaching of the "excess"  $F$  centers by the constant lamp. Figure 5 shows representative decay data plotted as exponential functions of time for various constant lamp intensities. There is good agreement with first-order decay. It is convenient to measure the bleaching rate as  $(1/\tau)$ , where  $\tau$  is the time required for the number of "excess"  $F$  centers to fall to  $e^{-1}$  of the value at any chosen time.

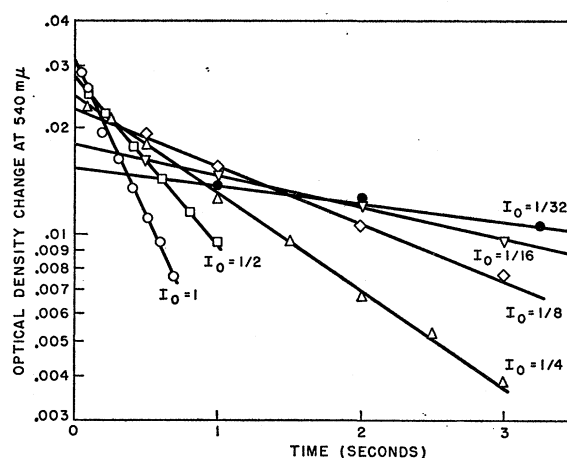


FIG. 5. Decay of "excess"  $F$  centers after red-flash bleaching, as a function of time and the constant lamp intensity.

Figure 6 shows the dependence of  $(1/\tau)$  on the constant lamp intensity for various total  $F$ -center concentrations. The constant lamp intensity was modified with neutral density filters so that the spectrum remained unchanged. The  $F$ -center concentrations were modified by varying the x-ray time from 5 to 600 min at 15-ma anode current. The straight line passing through the origin shows that the rate of bleaching of "excess"  $F$  centers is directly proportional to the intensity of the constant lamp and that the latter is entirely responsible for the return to the original  $F$ -center concentration, at the constant lamp intensities used. One set of points are for an additively colored crystal containing  $5.8 \times 10^{16}$   $F$  centers per cc.<sup>8</sup> Although the initial optical density change is about four times smaller than for a corre-

<sup>8</sup> The additively colored crystal was obtained from Zenith Radio Corporation, through the courtesy of J. J. Markham.

sponding x-rayed crystal, the decay time and its variation with constant lamp intensity coincide with the values for x-rayed crystals. The measured bleaching decay rates depend on the spectrum of the constant lamp. When the latter was restricted to 540 m $\mu$  with a narrow-band filter, the initial extent of optical bleaching was larger and the rate of decay was slower. The explanation for the former is that the constant lamp produces a higher concentration of *F'* centers when it is restricted to the *F*-band maximum. The slower decay rate is due to a combination of lower total intensity and spectral effects.

Red-flash bleaching makes it possible to measure the number of *F'* centers produced by the constant lamp, although their spectrum cannot be resolved in the spectrophotometer under usual conditions. Table I shows optical densities at the *F*-band maximum for crystals which had been x-rayed at room temperature for various times. Columns (2) and (3) show  $D_o$ , the optical density after x-raying and  $D_s$ , the optical density

TABLE I. Comparison of *F* centers bleached by constant "*F* light" to *F* centers recovered by red flash bleaching.  $D_o$  is the optical density at the *F*-band maximum after x-ray irradiation,  $D_s$  is the optical density after bleaching with constant "*F* light" to saturation, and  $\Delta D_i$  is the change due to red-flash irradiation.

(1) x-ray time (minutes)	(2) $D_o$	(3) $D_s$	(4) $\Delta D_i$	(5) $\frac{1}{2}\Delta D_i/D_s$	(6) $\Delta D_i/(D_o - D_s)$
5	0.161	0.126	0.0027	0.011	0.08
15	0.287	0.250	0.0070	0.014	0.19
35	0.342	0.296	0.0090	0.015	0.20
75	0.432	0.382	0.012	0.016	0.24
155	0.668	0.612	0.022	0.018	0.39
275	0.980	0.910	0.030	0.017	0.43
575	1.492	1.412	0.040	0.014	0.50

after bleaching to saturation at 77°K with "*F* light." The initial optical density change obtained by bleaching with a strong red light flash is shown in column (4). The ratio of  $\frac{1}{2}\Delta D_i$  to  $D_s$  in column (5) should be the actual *F'*-to-*F* center ratio, noting that each *F'* center bleached produces two *F* centers and that saturation data given below shows that most of the *F'* centers are bleached by the red light flash. The constancy of this quantity over the range of *F*-center concentrations indicates that the *F* and *F'* centers are in equilibrium with the constant lamp. It is interesting to note that the measured number of *F'* centers is smaller than the number of *F* centers bleached. Column (6) shows that their ratio increases with the *F*-center concentration. The apparent explanation is that other centers produced during the early stages of x-ray irradiation compete with *F* centers for the electrons released from bleached *F* centers. It is probable that these centers also are in equilibrium with *F* and *F'* centers during bleaching, to account for the constant ratio in column (5).

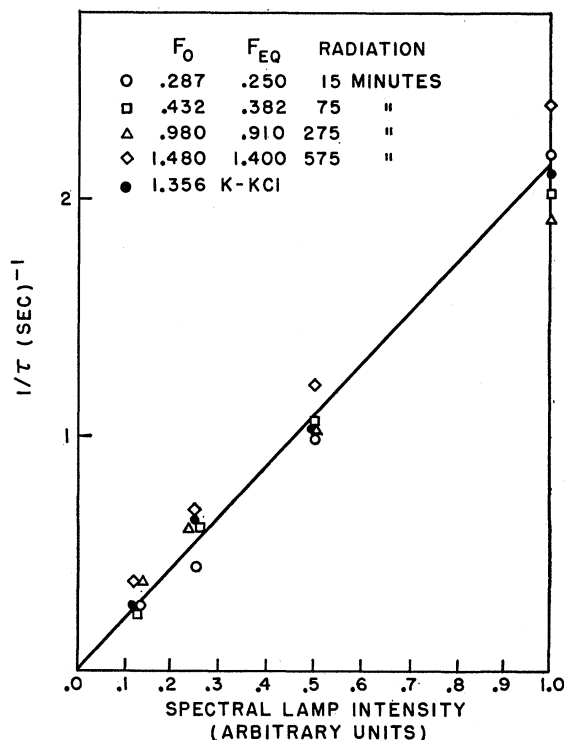


FIG. 6. Dependence of the red-flash bleaching decay rate on the constant lamp intensity.

### (b). Green-Flash Bleaching

When x-rayed crystals are bleached to saturation with the constant lamp at 77°K and are then irradiated with a green light flash, the *F* band is further bleached and subsequently recovers to the saturation optical density. Figure 7 shows representative recovery data for various constant lamp intensities. In contrast to the red-flash bleaching decay, the optical density change is exponential only at longer times. Figure 8 shows a

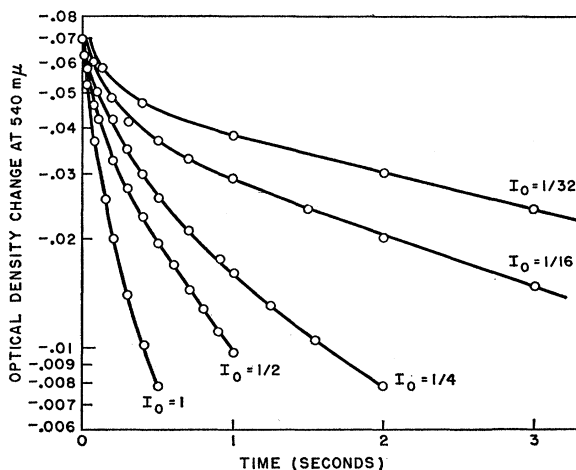


FIG. 7. Recovery of bleached *F* centers after green-flash bleaching, as a function of time and the constant lamp intensity.

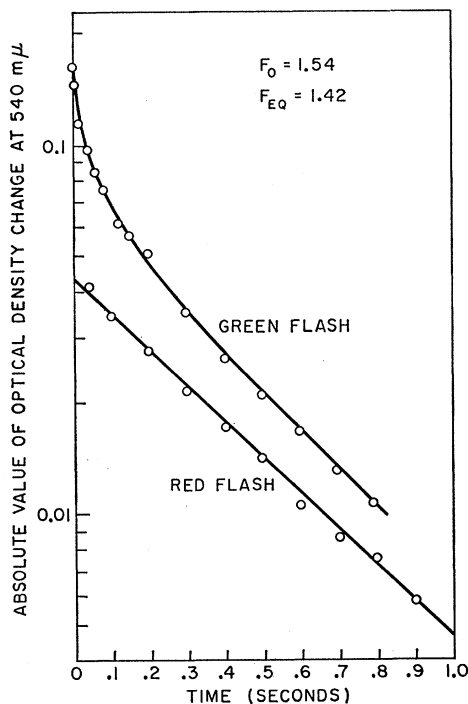
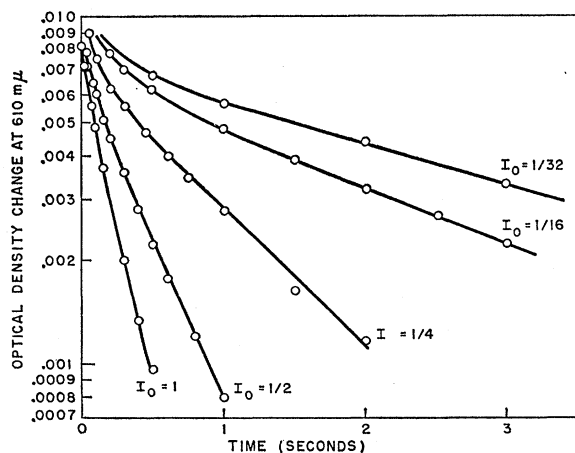
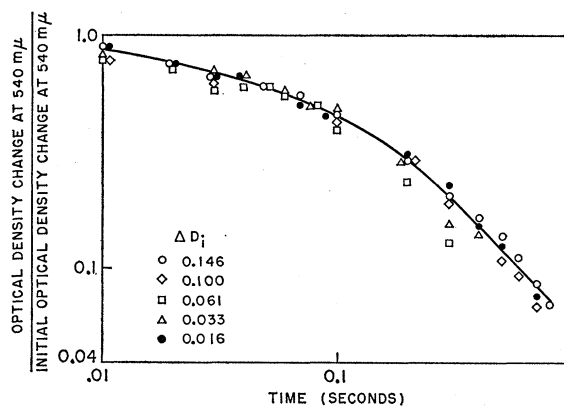


FIG. 8. Comparison of red- and green-flash bleaching.

comparison of a red-flash decay and a green-flash recovery under otherwise similar conditions. The exponential portions of both processes have the same rate. The recovery after green-flash bleaching is due to a bleaching of  $F'$  centers by the constant lamp, including wavelength regions where the  $F$  band and  $F'$  band overlap. This is an efficient process at low temperatures. The decay of  $F'$  centers can be followed directly by monitoring the transmission changes above the  $F$  band, Fig. 9. The dependence on time and the constant lamp intensity is consistent with the corresponding changes in the  $F$  band shown in Fig. 7.

FIG. 9. Decay of  $F'$  centers at 610  $m\mu$  after green-flash bleaching.FIG. 10. Dependence of the  $F$ -center recovery rate after green-flash bleaching on the initial extent of bleaching.

Although the green bleaching recovery deviates from exponential at short times, the process can be shown to be of first order in the number of bleached  $F$  centers by varying the intensity of the flash lamp under otherwise constant conditions. In a first-order process, the time required for completion of any chosen fraction of the process is independent of the starting point. In Fig. 10, green bleaching recovery curves are compared for runs where the initial extent of bleaching was varied from 0.016 to 0.146 optical density by changing the flash-lamp intensity. In each case, the instantaneous fraction of the unrecovered initial bleaching is plotted against time. (This only shifts the curves vertically on the figure, so that a visual comparison can be made.) The superposition of the data for various initial displacements shows that the process is of first order in the number of bleached  $F$  centers. The data points for the additively colored crystal fall on the same line.

### (c). Saturation of Flash Bleaching

Table II shows how the initial extent of red-flash bleaching and the corresponding decay time vary with the intensity of the flash lamp. The initial bleaching saturates at high flash-lamp intensities. The decay time is almost constant, with a possible slowly decreasing trend at low flash intensities. Figure 11 shows the variation of the initial extent of red-flash bleaching with the

TABLE II. Dependence of the initial extent of red flash bleaching and decay time on the intensity of the flash lamp.

Flash lamp intensity (relative)	$\Delta D_i$	Decay time (sec)
1.000	0.044	0.43
0.500	0.036	0.39
0.250	0.029	0.34
0.125	0.020	0.33
0.063	0.014	0.28
0.032	0.0070	0.31
0.016	0.0040	0.27
0.008	0.0025	0.36

constant lamp and flash-lamp intensities, where the former was monochromatic at  $540\text{ m}\mu$  to provide larger bleaching signals. There is a small variation of bleaching efficiency with constant lamp intensity, and saturation occurs at the highest constant lamp intensity used. The variation of the initial extent of green-flash bleaching with flash-lamp intensity is shown in Fig. 12 for two  $F$ -center concentrations. Saturation occurs in this case also, the implications of which are discussed below.

#### (d). Prior Room-Temperature Bleaching

The above results show that the rates of decay and recovery after flash bleaching are independent of the  $F$ -center concentration in the range studied. However, prior room-temperature bleaching markedly changes the flash-bleaching properties at  $77^\circ\text{K}$ . Table III shows how the initial extent of red-flash bleaching and the decay rate vary with the magnitude of the  $M$  band produced by room-temperature optical bleaching. The  $F$ -band optical density is always sufficient to absorb almost all

TABLE III. Effect of prior room-temperature bleaching on red-flash bleaching at  $77^\circ\text{K}$ .

Room temperature bleaching time (min)	$\Delta D_i$	$F$ -band <sup>a</sup> optical density	$M$ -band <sup>a</sup> optical density	Bleaching decay rate (arb.)
0	0.036	1.82	0.12	1.000
10	0.028	1.71	0.16	1.070
40	0.026	1.53	0.24	0.885
100	0.025	1.40	0.32	0.550
220	0.027	1.12	0.44	0.440
460	0.012	0.94	0.36	0.258

<sup>a</sup> As measured at band maximum in Beckman DU spectrophotometer.

incident light; nevertheless, the results indicate that only 25–30% of the original  $F$  band is effective in low-temperature bleaching processes after 460 min of room-temperature bleaching. The largest decrease in the extent of initial flash bleaching takes place after the  $M$  band has attained its maximum height and has started to diminish. Possible explanations are suggested below.

#### DISCUSSION

The characteristic features of the low-temperature bleaching of  $F$  centers are the low quantum efficiency and the small extent of ultimate yield. The low quantum efficiency has been explained by assuming that thermal activation is required to ionize the excited  $F$  center.<sup>9</sup> It does not explain the small extent of bleaching at and below  $77^\circ\text{K}$ , or why the bleaching efficiency depends on the method of coloration. Our results show that major factors limiting the extent of low-temperature bleaching

<sup>9</sup> N. F. Mott and R. W. Gurnery, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1948).

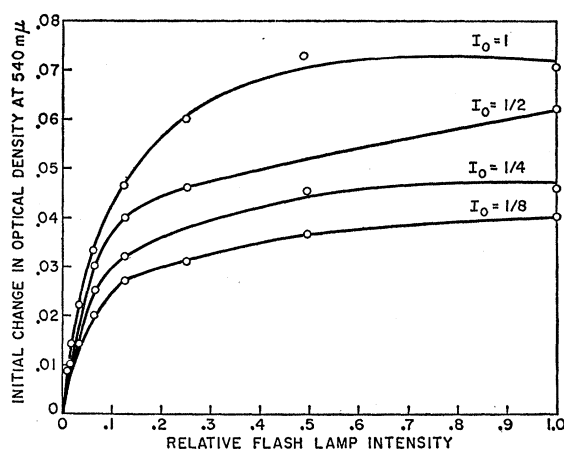


FIG. 11. Dependence of the initial extent of red-flash bleaching on the intensity of the flash lamp and the constant lamp.

of KCl are the overlap of the  $F'$  band and  $F$  band and the high bleaching efficiency of the former at low temperatures. The simplest kinetic model consistent with the results is one in which  $F$  and  $F'$  centers are the only imperfections involved in low-temperature bleaching and where the differential bleaching rates are proportional to the rate of light absorption in the respective bands; let

$$(dF/dt) = -AkI_F + Ak'I_{F'}, \quad (2)$$

where  $F$  is the number of  $F$  centers,  $A$  is the irradiated face area of the crystal,  $k$  and  $k'$  are rate-constants, and  $I_F$  and  $I_{F'}$  are the rates of light absorption in the  $F$  and  $F'$  bands. The latter quantities are related to the respective number of color centers by

$$I_F = \int I(\lambda) \{1 - \exp[-2.303F\sigma_F(\lambda)/A]\} d\lambda, \quad (3)$$

$$I_{F'} = \int I(\lambda) \{1 - \exp[-2.303F'\sigma_{F'}(\lambda)/A]\} d\lambda,$$

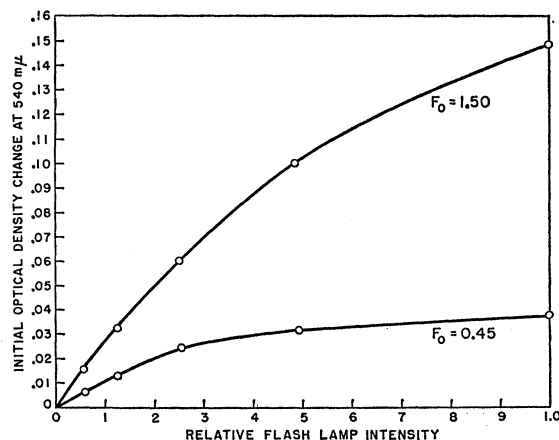


FIG. 12. Dependence of the initial extent of green-flash bleaching on the flash lamp intensity for two  $F$ -center concentrations.

where  $I(\lambda)$  is the incident light intensity per unit wavelength and  $\sigma$  is an absorption cross section related to the optical density by:  $D(\lambda) = N\sigma(\lambda)/A$ , where  $N$  is the number of absorbing centers. To obtain a solution in closed form we assume that  $D \ll 1$ . This is a very good approximation for integration over the  $F'$  band, but the neglect of the nonlinear terms introduces a possible error in the integral over the  $F$  band—this point is discussed below. With this approximation,

$$AI_F = 2.303F \int I(\lambda)\sigma_F(\lambda)d\lambda = cI_0F, \quad (4)$$

$$AI_{F'} = 2.303F' \int I(\lambda)\sigma_{F'}(\lambda)d\lambda = c'I_0F',$$

where  $c$  and  $c'$  are constants which depend only on the spectrum of the incident light and  $I_0$  is the total incident light intensity. Substitution of Eq. (4) into Eq. (2) gives

$$(dF/dt) = -kcI_0F + k'c'I_0F'. \quad (5)$$

Several solutions to Eq. (5) are pertinent. The equilibrium condition holds when  $(dF/dt)$  is equal to zero:

$$(F')_{eq}/F_{eq} = kc/k'c'. \quad (6)$$

Equation (6) shows that the equilibrium ratio of  $F'$ -to- $F$  centers is independent of the incident light intensity and the number of  $F$  centers, but does depend on the lamp spectrum. This is in good agreement with the data of Table I. To obtain the transient solutions, it is assumed that all optically bleached  $F$  centers produce  $F'$  centers.<sup>10</sup> The approach to equilibrium under the constant lamp is given by

$$F = F_{eq}\{1 + (2kc/k'c') \exp[-(kc + k'c'/2)I_0t]\}, \quad (7)$$

where

$$F_{eq} = [\frac{1}{2}k'c'/(kc + \frac{1}{2}k'c')]F_0 \quad (8)$$

and  $F_0$  is the number of  $F$  centers present immediately after x-ray irradiation. The transients after flash bleaching can be obtained by assuming that  $F = F_{eq} \pm \Delta F_i$  at  $t=0$ , where  $\Delta F_i$  is the initial displacement from equilibrium produced by the flash lamp; the solution is

$$F - F_{eq} = \pm \Delta F_i \exp[-(kc + \frac{1}{2}k'c')I_0t]. \quad (9)$$

The quantity  $(F - F_{eq})$  is directly proportional to  $\Delta D$  in Eq. (1). Equation (9) predicts an exponential return to equilibrium after displacement in either direction, with a rate-constant linear in the constant lamp intensity and varying with its spectrum. This is in agreement with the data of Figs. 5–10. The independence of the rate constants of the extent or method of coloration (for crystals which have not been exposed to “ $F$  light” at room tem-

perature) is taken as evidence that the mechanism for low-temperature bleaching is the same for all stages of x-ray coloration and is the same for the x-rayed and the additively colored crystal.

The saturation of flash bleaching shown in Figs. 11 and 12 indicates that an appreciable fraction of the available color centers are bleached. The instantaneous rate of  $F'$  center (red flash) bleaching is given by

$$(dF'/dt) = -A \int I(\lambda, t)\eta(\lambda) \times \{1 - \exp[-2.303F'\sigma_{F'}(\lambda)/A]\}d\lambda, \quad (10)$$

where  $I(\lambda, t)$  is the instantaneous incident light intensity per unit wavelength of the flash lamp and  $\eta(\lambda)$  is the quantum efficiency for photobleaching the  $F'$  band. As before, the exponential can be expanded, giving

$$(dF'/dt) = -GI_0(t)F', \quad (11)$$

where

$$GI_0(t) = 2.303 \int I(\lambda, t)\eta(\lambda)\sigma_{F'}(\lambda)d\lambda \quad (12)$$

and  $I_0(t)$  is the instantaneous total incident light intensity of the flash lamp. Integration of Eq. (11) gives

$$(F')_f = (F')_{eq}e^{-GE}, \quad (13)$$

where  $(F')_f$  and  $(F')_{eq}$  are the final and initial numbers of  $F'$  centers, and  $E$  is the total incident light in the flash. It is convenient to express Eq. (13) in terms of the initial change in the  $F$  band after red-flash bleaching:

$$\Delta F_i = 2(F')_{eq}(1 - e^{-GE}). \quad (14)$$

Equation (14) predicts that the extent of initial red-flash bleaching is linear in the flash-lamp intensity at low intensities (for a constant pulse shape), and saturates to twice the number of available  $F'$  centers at high intensities. This is in good agreement with the shape of the lines in Fig. 11. An analogous expression can be derived for green-flash bleaching, involving the equilibrium number of “bleachable”  $F$  centers and a  $G$  characteristic of the  $F$  band. A comparison of Figs. 11 and 12 shows that the initial slope of the lines is higher for red-flash bleaching. This must be due to a much larger quantum efficiency  $\eta$  for bleaching  $F'$  centers since all other quantities in Eq. (12) are smaller for the red-flash case. The observed saturation of green-flash bleaching indicates that only a small fraction of the  $F$  centers are “bleachable” at 77°K and justifies the expansion of the exponential in Eq. (4).

Experimental deviations from these equations should be noted. The departure of the green-flash bleaching recovery from exponential at short times cannot be explained at present. The results in Fig. 10 suggest that the exact dependence may be a superposition of exponential functions of different time constants, but there is no apparent reason for this to occur. Another

<sup>10</sup> The data in Table I show that some bleached  $F$  centers do not produce  $F'$  centers, but go to other centers instead. If the number of such centers is constant in time, then the rate equations are modified only to the extent that  $F_0$  is not the measured initial number of  $F$  centers, but some smaller constant value.

unexplained deviation is the small dependence of the initial extent of red bleaching in Fig. 11 on the intensity of the constant lamp. Finally, there may be a small systematic dependence of the rate for red flash-bleaching decay on flash-lamp intensity as shown in the data of Table II.

Despite the deviations, the proposed model predicts the experimental findings with reasonable success. The essential feature is that the constant lamp establishes an equilibrium between  $F$  and  $F'$  centers, which can be displaced to either direction by a light flash. These processes are shown schematically in Fig. 13, where time and optical density changes are drawn to scale. Since the rate-controlling steps are optically excited, the kinetics cannot give direct information on whether tunneling or electron transport is responsible for the conversion of  $F$  centers to  $F'$  centers. Evidence for tunneling or another distribution-controlled process is the lower bleaching efficiency for the additively colored crystal and the measurements showing that only part of the  $F$  band contains "bleachable"  $F$  centers.

The decrease in the low-temperature bleaching rate after room-temperature optical bleaching, Table III, suggests that a large fraction of the light incident on the  $F$  band is no longer effective in bleaching the "excess"  $F$  centers produced by red-flash bleaching. In fact, when the optical density at the  $F$  peak has been reduced to approximately one-half its original value, the bleaching decay rate-constant indicates that only 25% of the remaining absorption is actually due to  $F$  centers. A possible explanation is that the effective incident light is reduced by the inner-filtering action of other bands under the  $F$  band, which are due to room-temperature bleaching.<sup>11,12</sup> An alternative explanation is based on the proposal of Lambe and Compton<sup>13</sup> that excited  $F$  centers transfer energy to  $M$  and  $R$  centers by a resonance process. This could compete with bleaching and reduce the measured rate. If tunneling is important in low-temperature bleaching, then this mechanism is not consistent with the results in Table III. Continued room-temperature bleaching steadily diminishes the bleaching rate, but the extent of initial bleaching is almost constant during 10–220 min of room-temperature bleaching. Therefore, room-temperature bleaching has not appreciably reduced the number of "bleachable"  $F$  centers during this period. However, one would expect that the closely distributed "bleachable"  $F$  centers would be the first converted to  $M$  centers at room temperature. Our results show that the  $F$ -center distribution does influence the low-temperature bleaching of KCl, in agreement with the results for KBr,<sup>4</sup> and we favor the first explanation relating to inner-filtering by other bands under the  $F$  band.

In conclusion, it might be noted that no attempt has

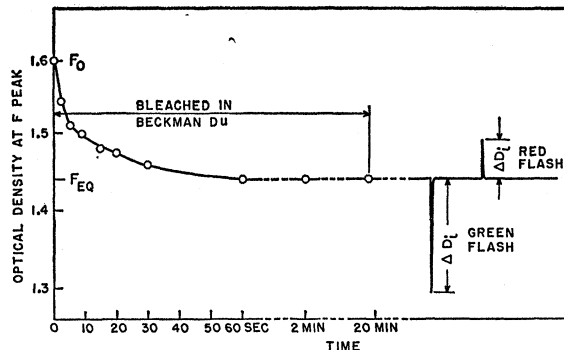


FIG. 13. Schematic representation of low-temperature bleaching processes.

been made to interpret the experimental results in terms of specific elementary processes involving the pertinent point-imperfections. The above measurements show that the rate-controlling steps are the rates of light absorption, and do not distinguish between alternative subsequent processes. This is particularly true for tunneling processes, where the initial and final states of the color centers are not known.

### CONCLUSIONS

1. Constant " $F$  light" incident on an x-rayed or additively colored KCl crystal at 77°K establishes a photostationary equilibrium between  $F$  and  $F'$  centers. The equilibrium concentration ratio for x-rayed crystals is independent of the light intensity and the total number of color centers.
2. The relative concentration of color centers can be temporarily displaced to either direction by a light pulse of appropriate wavelengths. The extent of this process saturates at high pulse-light intensities, indicating that only a fraction of the  $F$  centers are bleachable at low temperature. All  $F$  centers bleached do not produce  $F'$  centers, and the fraction which go to  $F'$  centers increases with the extent of x-ray coloration.
3. The return to the equilibrium condition after pulse irradiation takes place by a process which is exponential in time, with a rate which varies linearly with the constant light intensity and is independent of the direction of displacement. The bleaching rates are independent of the  $F$ -center concentration for x-rayed KCl and are the same for an additively colored crystal. However, the bleaching efficiency of the additively colored crystal is considerably smaller, indicating that the distribution of  $F$  centers is significant.
4. The results can be explained by a simple kinetic model which assumes that the bleaching rates of  $F$  and  $F'$  centers are proportional to the light absorption in the respective bands.
5. The presence of  $M$  centers, due to prior room-temperature bleaching, decreases the measured low-temperature bleaching rates. This is probably due to the production of new bands under the  $F$  band which absorb " $F$  light."

<sup>11</sup> C. Z. van Doorn and Y. Haven, Philips Research Rept. 11, 479 (1956).

<sup>12</sup> S. Petroff, Z. Physik 127, 443 (1950).

<sup>13</sup> J. Lambe and W. D. Compton, Phys. Rev. 106, 684 (1957).