

Photoequilibrium between KCl F and F' Centers at 80°K†

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The illumination of F centers in KCl at 80°K establishes a photoequilibrium between F' and F centers. The equilibrium transformations are reversible and are of the same magnitude for additively colored crystals and crystals x-rayed at 80°K and 300°K. The photostationary ratio of F' to F centers varies with the logarithm of the incident light intensity. Transitions between equilibrium levels approximate first-order processes, controlled by the rate of light absorption in the F and F' bands. A kinetic model is proposed in which the elementary steps are the photoionization of F and F' centers, and electron capture at F centers and negative-ion vacancies. The variation of light intensity and spectrum through the crystal is accounted for by assuming that temporal equilibrium is maintained in local regions and integrating the results over the crystal volume. The photoionization quantum efficiency of the F center at 80°K is calculated to be 0.020 ± 0.003 ; this quantity is one-half of the photobleaching quantum efficiency. A value of 0.016 ± 0.005 is obtained for the ratio of the electron-capture cross section of the F center to the chloride-ion vacancy.

INTRODUCTION

LIGHT absorption in the F band of alkali halide crystals at an appropriate temperature range (below 170°K in KCl) induces a bleaching of F centers and the growth of the F' band. The quantum efficiency for this process, and the reverse process of recovering the F band by irradiation with light in the F' band, was studied by Pick¹ for additively colored KCl. His investigation shows that the initial quantum efficiency is equal to two at the temperature at which maximum conversion of F into F' centers occurs; i.e., two F centers are destroyed for each photon absorbed in the F band. Photoconductivity experiments show that light absorbed in the F band produces conduction electrons and that the F center is the predominant electron trap above 70°K.^{2,3} These results establish that the F' center consists of two electrons trapped in a negative-ion vacancy and can be produced by photoionization of an F center and subsequent capture of the electron at another F center. The extent to which the F band can be bleached at a given temperature is limited by the overlap of the F and F' bands and the competition between negative-ion vacancies and F centers for the capture of photoelectrons; it decreases rapidly with decreasing temperature, reflecting the drop in the efficiency for photoionization of the F center.

The bleaching process is more complicated in crystals colored by ionizing irradiation presumably because of the presence of hole centers which are efficient traps for electrons. A characteristic difference between the capture of an electron by a hole center and by an F center is the reversibility of the latter process. Optical bleaching experiments^{4,5} at 78°K show that the extent

of bleaching depends on the temperature of x-ray irradiation. Only a part of the initial bleaching can be recovered by irradiation with " F' light," but after several cycles of bleaching and recovery the subsequent changes are completely reversible indicating that the F - to F' -center conversions remain. It should be noted that Markham *et al.*⁴ did not observe optical bleaching in additively colored KBr at 78°K in disagreement with our findings in KCl. They attributed the bleaching in x-rayed crystals to tunneling of electrons between clustered F centers.

The F - to F' -center conversion in KCl was studied recently at 80°K by pulse irradiation methods.⁶ Crystals colored by x rays at room temperature were bleached with steady " F light" until an equilibrium transmission at the peak of the F band was reached. A subsequent bright flash of light of the appropriate spectrum induced a fast displacement away from equilibrium, (a decrease in transmission with " F' light," an increase in transmission with " F light") followed by a return to the equilibrium value. It was shown that only F to F' center transformations are involved and that the rate of return to equilibrium is independent of the F -center concentration and varies linearly with the intensity of the steady light.

This paper reports the results of a more detailed investigation of the equilibrium between F and F' centers in KCl at 80°K under conditions of steady illumination and for crystals colored in various ways. The transformations are described by a set of kinetic equations involving F centers, F' centers, negative-ion vacancies and photoelectrons. Numerical solutions to the rate equations lead to values for the relative electron-capture cross sections of the F center and a chloride-ion vacancy and the photoionization efficiency of the F center.

EXPERIMENTAL METHODS

The crystals used were Harshaw optical grade KCl, additively colored and colored by irradiation with x

⁶ A. R. Reinberg and L. I. Grossweiner, *Phys. Rev.* **122**, 1734 (1961).

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¹ H. Pick, *Ann. Physik* **31**, 365 (1938); **37**, 421 (1940).

² G. Glaser and W. Lehfeldt, *Nachr. Akad. Wiss. Göttingen, Math-physik. Kl.* **2**, 91 (1936).

³ R. W. Pohl, *Proc. Phys. Soc. (London)* **49**, 13 (1937).

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

⁵ A. Smakula, *Z. Physik* **59**, 603 (1930).

TABLE I. Incident light intensity as measured with thermopile.

Lamp	Filter	Light intensity (photons/cm ² -sec)	Wavelength range (m μ)
Monitoring (tungsten)	CS 4-64	1.2×10^{15}	500-560
Monitoring (tungsten)	Interf. 540 m μ + CS 3-71	1.9×10^{15}	530-555
Saturation (mercury)	Interf. 540 m μ + CS 3-71	5.0×10^{16}	546
Saturation (tungsten)	CS 2-62	4.0×10^{18}	600-3000

rays at 80°K and 300°K. The samples were cleaved into 1×1 cm platelets of thickness from 0.05 to 0.07 cm. Coloration with 45 kvp silver target x rays was carried out in the dark inside an evacuated metal sample holder, provided with three optical windows of 2-mm fused silica and a 0.8-mm beryllium window for x rays. For most of the runs, the x rays were filtered by 0.56-mm aluminum to eliminate the soft component and obtain a more uniform coloration. The uniformity was estimated by cleaving a 0.1-cm thick crystal into 4 equal parts and measuring the optical density of the sections. It was found that the average F center concentration varied by about a factor of 2 between the front and back sections. Some experiments were performed with samples irradiated with unfiltered x rays where the F center concentration varied by a factor of 10. Unless otherwise noted, the data presented for x-rayed crystals pertain to filtered x rays. The additively colored crystals as received⁷ contained aggregate centers. They were pulse-annealed at 550°C for one to two minutes, quenched on a copper plate, and transferred to the sample holder under a red safelight.

All optical absorption measurements were made at 80°K. Optical density was measured with a Beckman DU spectrophotometer and transmission changes induced by light of various spectral distributions and intensity was measured in the apparatus shown schematically in Fig. 1. The instantaneous transmission at the peak of the F band was monitored with a de-operated tungsten filament lamp (monitoring light), an F -band filter, and a Bausch and Lomb constant-deviation monochromator coupled to a 1P28 photomultiplier tube. The photoelectric signal was measured on a Tektronix type 545 oscilloscope. The F -band filter consisted of either a Corning CS 4-64 band-pass filter peaking at 525 m μ , or a combination of a Bausch and Lomb narrow-band interference filter peaking at 540 m μ with a Corning CS 3-71 sharp-cut yellow filter cutting off below 470 m μ . The transformations were induced by high intensity light (saturation light) provided by an Osram HBO 109 mercury arc lamp for irradiation in the F band and a 30-watt tungsten filament lamp for irradiation in the F' band. The satura-

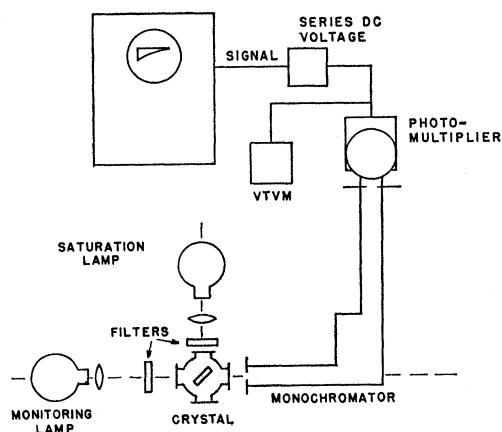


FIG. 1. Experimental arrangement.

tion filters used for the F band were a Bausch and Lomb 540-m μ narrow-band interference filter with a Corning CS 3-71, and for the F' band a Corning CS 2-62 transmitting from 600 m μ to 3000 m μ . The intensity of the monitoring and the saturation light was varied with calibrated Bausch and Lomb neutral density filters. Changes in optical density were calculated from changes in the photoelectric signal by the relation, $\Delta D = \log_{10}[V/(V + \Delta V)]$, where V is the steady photoelectric signal and ΔV is the change corresponding to the transmission change of the crystal. In correlating the transient measurements with data obtained from the Beckman DU spectrophotometer, it was necessary to correct the former for the 45° angle of incidence on the optical bench. A simple calculation including refraction through the crystal shows that the optical density measured at 45° incidence is 1.14 times larger than the optical density measured at 0° incidence.

Light intensity calibrations were made with an Eppley bismuth-silver junction thermopile. The intensity of the saturation light was reduced in each case by a known factor in order to bring the reading of the thermopile in the range for which the calibration constant was given. For the tungsten lamp, the spectral distribution was calculated from Planck's radiation law at the measured filament temperature. The geometrical factor was obtained by matching the numerically integrated light intensity to the total intensity as measured with the thermopile. For the case of the mercury arc lamp in combination with the 540-m μ interference filter and the Corning CS 3-71 filter, it was assumed that the incident light was due to the 546.1-m μ spectral line of mercury. Values of the various light intensities incident on the crystal are given in Table I.

A typical experiment proceeded as follows; after x-ray coloration or annealing of the additively colored samples the crystal was cooled rapidly to 80°K and was bleached to saturation with 540-m μ light in the Beckman DU spectrophotometer. The sample holder was transferred to the apparatus of Fig. 1 and the trans-

⁷ The additively colored crystals were obtained from Armour Research Foundation through the courtesy of G. Noble and D. Mergerian.

mission changes under various conditions of illumination on the crystal were measured.

RESULTS

The basis of these experiments is a determination of the transmission changes in a colored crystal induced by illumination with "F" or "F'" light." In drawing conclusions from such measurements about the physical properties of the F- to F'-center transformation, it is necessary to interpret the observed transmission changes as the combined effects of the monitoring and the saturation light, since the monitoring light establishes the initial condition of the crystal from which the changes induced by the saturation light are measured. The reversibility of the transformation was established first. The transmission of the crystal rapidly reached a constant value under the monitoring light for additively colored crystals, while for samples colored by x rays a slow bleaching was observed, which was more prominent for crystals x rayed at 80°K. Cross-illumination with strong "F light" from the saturation lamp induced an increase in transmission and when the "F light" was removed, the transmission for x-rayed crystals recovered to a value higher than the initial. After this cycle was repeated three or four times, the transmission changes became completely reversible for all crystals and no further changes were observed in the photoelectric signal under the monitoring light, while the crystal was kept at constant low temperature.

Representative data is shown in Fig. 2. The zero line corresponds to the equilibrium optical density at the peak of the F band under the monitoring light. In Fig. 2(a), "F' (red) saturation light" induces an increase in the optical density ΔD_r (corresponding to an increase

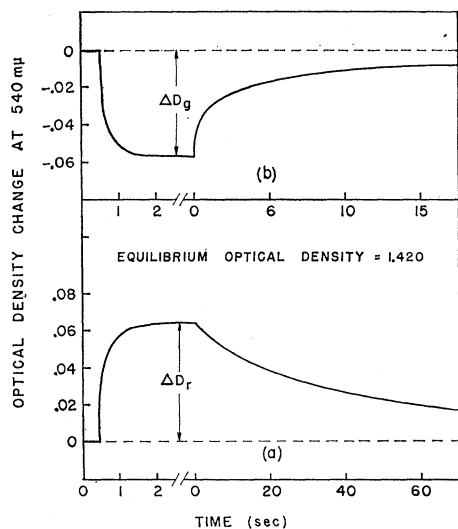


FIG. 2. Representative data showing transitions between equilibrium levels. Trace (a) shows transitions from weak "F light" to strong "F' light" and vice versa; trace (b) shows transitions from weak "F light" to strong "F light" and vice versa.

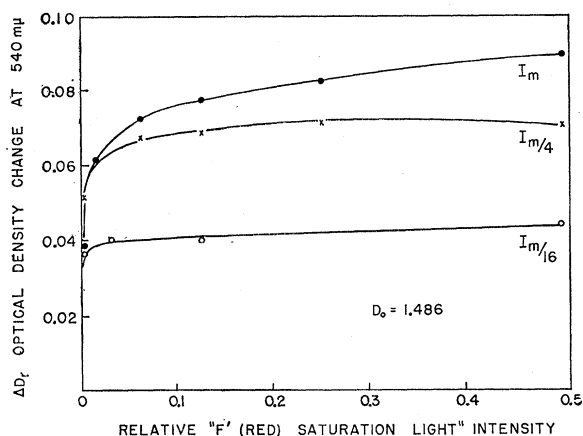


FIG. 3. Extent of F-band optical density change due to "F" saturation light" at various monitoring light intensities; for additively colored KCl.

in the number of F centers) and a new value of the equilibrium optical density is established. Upon removing the saturation light the optical density returns to the original equilibrium value under the monitoring light. Figure 2(b) shows the change ΔD_g induced by "F (green) saturation light." The F band optical density bleaches to a lower equilibrium value and then recovers under the influence of the monitoring light when the saturation light is removed. It is clear from these results that the relative concentrations of F and F' centers are determined by the total light incident on the crystal and that the observed transmission changes correspond to transitions between equilibrium concentrations of F and F' centers. The dependence of ΔD_g and ΔD_r on the monitoring and saturation light intensity, the F-center concentration, and the method of coloration were investigated, and the results applied to a description of the F to F' center conversion.

Equilibrium Under "F' Saturation Light"

An F' to F-center equilibrium was first established in the crystal by the monitoring light. Subsequent illumination with "F' saturation light" converted a fraction of the F' centers to F centers, depending on the intensity. The changes in the F-band optical density following illumination with "F' saturation light" are shown in Fig. 3 as a function of the saturation light intensity for three different intensities of the monitoring light. The extent of optical density change reaches a constant value at very low saturation light intensities, especially for the lower monitoring light intensities. This indicates that the F' centers are almost completely bleached and that the optical density change ΔD_r is a measure of the number of F' centers at equilibrium under the monitoring light. This transformation was also observed by bleaching additively colored crystals in the Beckman DU spectrophotometer with 540-mμ light. Subsequent illumination with 750-mμ

light restored the F band to the initial value. Figure 3 also shows that the apparent number of equilibrium F' centers depends on the intensity of the monitoring light, a point that is discussed in further detail below.

The dependence of the optical density change produced by " F' saturation light" on the equilibrium number of F centers is shown in Figs. 4 and 5. The data in Fig. 4 were obtained from two crystals colored at 300°K with filtered and unfiltered x rays, as indicated. Successively higher F center concentrations were obtained by continued x raying, since previous work^{8,9} on the recovery of the F band shows that the final state of the crystal is not affected by intermediate optical bleaching. The small difference in the extent of transformation for crystals of the same total optical density colored by filtered and unfiltered x rays indicates that the distribution of F centers does not appreciably influence the mechanism. Comparable data are shown in Fig. 5 for crystals colored in several ways. Again, the method of coloration is only a small factor in the equilibrium bleaching. The shape of the lines in Figs. 4 and 5 is of considerable interest. Based on comparable experiments with red flash irradiation, Reinberg and Grossweiner⁶ noted that the number of F' and F centers under continuous " F light" are in a constant ratio and concluded that a photoequilibrium occurs. It is surprising that a constant factor is observed at high F -band optical densities, where the light absorption is exponential in the F -center concentration. However, it is shown below that the equilibrium ratio of F' to F centers is not sensitive to small changes in light intensity. Thus, if it is assumed that equilibrium is established in local regions of the crystal, then the light

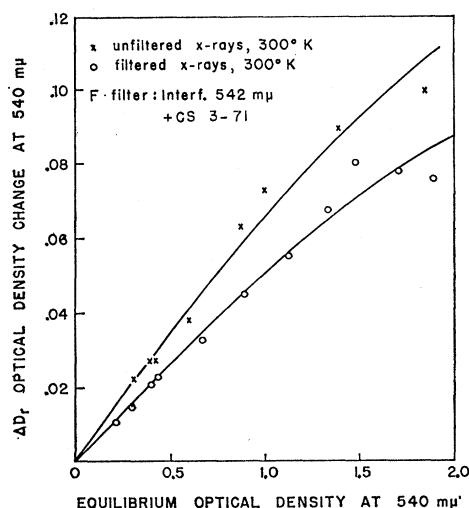


FIG. 4. Extent of F -band optical density change due to " F' saturation light" as a function of the equilibrium F -band optical density, for KCl x rayed at 300°K. The solid lines are a "least squares" fit to the data based on Eq. (23).

⁸ L. E. Silverman and L. I. Grossweiner, Phys. Rev. **121**, 1072 (1961).

⁹ W. Duerig, Phys. Rev. **94**, 65 (1954).

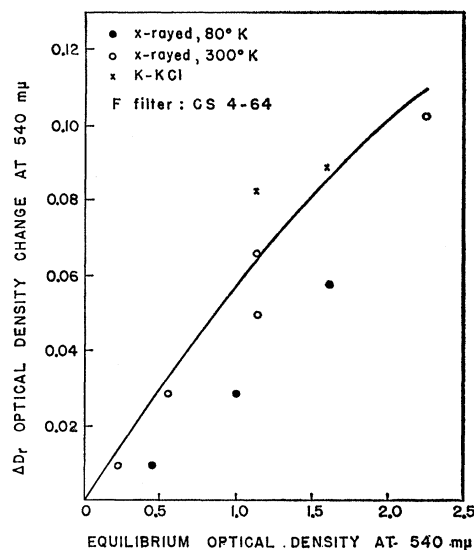


FIG. 5. Extent of F -band optical density change due to " F' saturation light" as a function of the equilibrium F -band optical density, for KCl colored in different ways. The solid line is a "least squares" fit to the data based on Eq. (23).

intensity gradient will not be significant. The small departure from linearity shown in Figs. 4 and 5 is due to the change in the spectral distribution of the light passing through the crystal. The specific functional dependence in the range of optical densities considered and for our light source is given in Eq. (23).

It should be emphasized that the results pertain only to the reversible part of the F -band bleaching. The total bleaching, i.e. the difference between the initial F -band optical density D_0 and the equilibrium F -band optical density D_q under steady " F light" varies with the method and extent of coloration. A summary of the available data is given in Table II. It is seen that the ratio of ΔD_r , the maximum reversible optical density change due to " F' light", to the total bleaching ($D_0 - D_q$) is unity for additively colored crystals, but is considerably smaller for x rayed crystals. Noting that the prior growth of aggregate centers at 25°C markedly reduces the extent of low-temperature bleaching for crystals x rayed at 300°K,⁶ the ratio of the M -band to the F -band maxima for the new data is shown in Table II. There does not appear to be any direct relationship between the presence of the M band and the extent of F - and F' -center equilibrium, and presumably the previous results are due to more complicated processes occurring during the prior room-temperature bleaching.

Equilibrium Under " F Saturation Light"

Illumination of the crystal with strong " F saturation light" induces a shift in the equilibrium number of F centers to a value below that established under the monitoring light. The decrease in optical density ΔD_0 due to the " F saturation light" is shown in Fig. 6 for

TABLE II. Comparison of reversible and irreversible F -band optical bleaching for different methods of coloration. D_0 is the initial F -band optical density, D_q is the F -band optical density after bleaching, and ΔD_r is the change in the F -band optical density corresponding to F centers converted into F' centers.

Method of coloration	D_0	D_q	ΔD_r	ΔD_r	
				$D_0 - D_q$	M/F
K-KCl (this work)	0.935	0.910	0.025	1.00	0.002
K-KCl (this work)	1.690	1.600	0.089	0.99	0.02
Hard x rays, 300°K (this work)	0.610	0.555	0.029	0.53	0.04
Hard x rays, 300°K (this work)	1.220	1.140	0.048	0.60	0.05
Hard x rays, 80°K (this work)	1.100	1.000	0.029	0.29	0.000
Hard x rays, 80°K (this work)	1.740	1.600	0.058	0.41	0.000
Soft x rays, 300°K (reference 6)	0.160	0.126	0.0027	0.08	
Soft x rays, 300°K (reference 6)	0.287	0.250	0.0070	0.19	
Soft x rays, 300°K (reference 6)	0.342	0.296	0.0090	0.20	
Soft x rays, 300°K (reference 6)	0.432	0.382	0.012	0.24	
Soft x rays, 300°K (reference 6)	0.668	0.612	0.022	0.39	
Soft x rays, 300°K (reference 6)	0.980	0.910	0.030	0.43	
Soft x rays, 300°K (reference 6)	1.492	1.412	0.040	0.50	
x rays, 78°K (reference 5)	0.77	0.65	-	0.25	
KBr, x rays, 78°K (reference 4)	1.0	0.77	0.03	0.13	

an additively colored crystal, as a function of the relative intensity of the bleaching light for three different monitoring light intensities. Similar results were obtained for crystals x rayed at 80°K and 300°K. ΔD_q increases with increasing saturation light intensity at a diminishing rate, but the dependence of optical density change on the monitoring light intensity is the inverse of the case with " F saturation light," Fig. 3. Noting that the extent of F -band bleaching reaches a

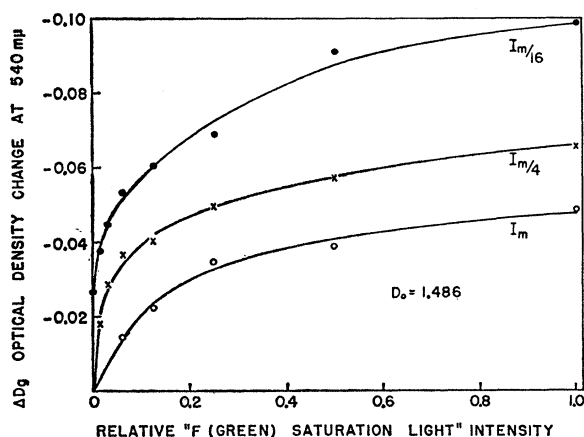


FIG. 6. The extent of F -band optical density change due to " F saturation light" at various monitoring light intensities, for additively colored KCl.

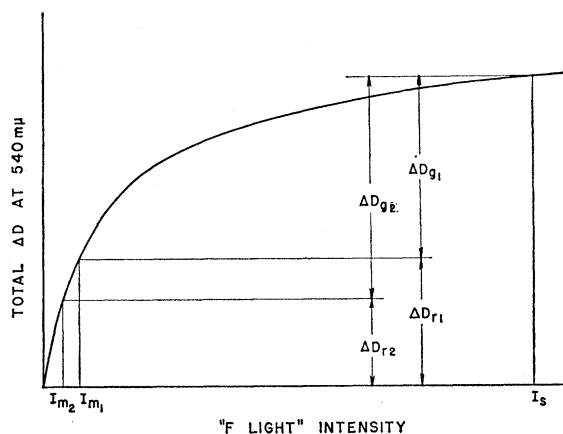


FIG. 7. The dependence of total F -band optical density change on the total incident " F light" intensity-schematic; I_m and I_s are monitoring and saturation light intensities respectively.^a

^a The light intensities in this figure are not to scale; I_s is about 50 times larger than I_m .

saturation value that is much smaller than the total F band, Reinberg and Grossweiner⁶ concluded that only a fraction of the F band is "bleachable" and put this forth as an argument in favor of tunneling. However, Fig. 6 shows that the measured extent of bleaching can be appreciable at high total light intensities. To explain the variation of the apparent bleaching with the monitoring light intensity, we refer to Fig. 7, which shows qualitatively the dependence of the total F -band optical density change on the total " F -light" intensity. It is assumed that the spectral distribution of the monitoring and saturation light is identical in the narrow-wavelength band considered, so that their intensities are additive. Figure 7 shows the expected changes ΔD_r and ΔD_q for two different monitoring light intensities and it is clear that the predicted variations correspond to the results of Figs. 3 and 6. This analysis suggests that if to each value of ΔD_q in Fig. 6 is added the value of ΔD_r for the corresponding monitoring light intensity from Fig. 3, the quantitative curve for the light-intensity dependence of the " F light" bleaching will be obtained and the results should fall on a line for the three different monitoring light intensities. Furthermore, the measured values of ΔD_r for different monitoring light intensities should fit the same bleaching curve. This plot is shown in Fig. 8 for the best data obtained from an additively colored crystal. The filled circles show the contribution of various monitoring light intensities to total F -band bleaching (as measured from the effect of high intensity " F' light") and the crosses show the corrected F -band bleaching due to " F saturation light." The equilibrium extent of " F light" bleaching varies approximately with the logarithm of the incident light intensity for the range of light intensity used. The kinetic model proposed by Reinberg and Grossweiner⁶ indicates that the equilibrium constant should be independent of the light intensity, in the range where dark

processes do not compete. The more detailed kinetic model proposed below leads to the same conclusion. Possible explanations for the observed light-intensity dependence are given in the discussion.

Transient Processes

The rate data, as shown in Fig. 2, provide further information about the mechanism of the F - to F' -center conversions during transitions between equilibrium conditions. Figure 9 shows representative data for the return to equilibrium under the monitoring light following the removal of saturation light, plotted as exponential functions of time. The recovery after bleaching F' centers with " F' saturation light" follows closely first-order kinetics, Fig. 9(a). However, the return to equilibrium when " F saturation light" is removed deviates markedly from exponential, Fig. 9(b). These results are in agreement with decay curves obtained in

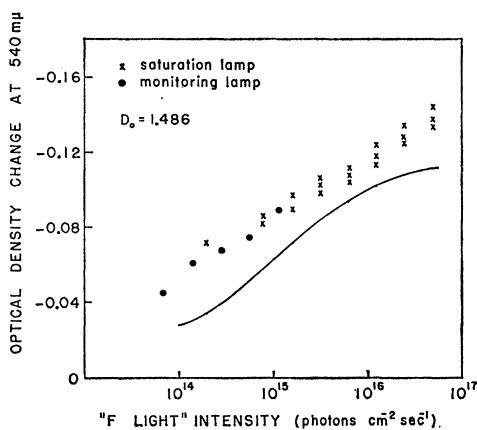


FIG. 8. The F -band optical density change shown as a logarithmic function of the total incident " F light" intensity, for additively colored KCl. The solid line is calculated from Eq. (27).

previous work⁶ where the displacement from equilibrium was induced by high-intensity light pulses. The kinetics of the buildup of optical density change upon illumination with saturation light are shown in Fig. 10. Here the difference between the final equilibrium value and the instantaneous value is plotted as an exponential function of time. Although first-order kinetics are not followed exactly, the deviations are not large. The rate-constant for buildup is linear in the light intensity, as shown in Fig. 11, where the reciprocal of the time required for the optical density change to reach one-half of the final value is plotted as a function of the relative light intensity for the case of " F' saturation light". Similar results are obtained for the case of " F saturation light". It should be pointed out that the slow dependence of the final optical density change on light intensity (4:1000) does not modify the interpretation of Fig. 11, since the linear dependence in the exponent is controlling. The results on buildup (approach to equilibrium from low- to high-light intensity) and

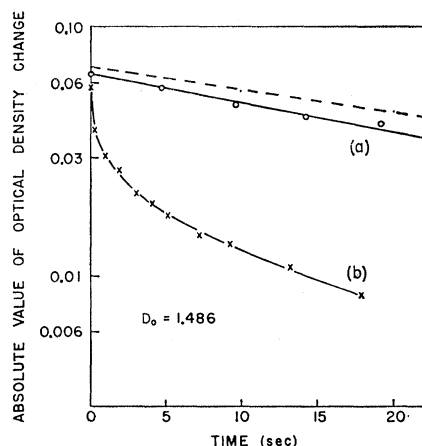


FIG. 9. Kinetics of return to equilibrium after removal of saturation light. Plot (a) is for " F saturation light" and plot (b) is for " F saturation light." The dashed line is calculated from Eq. (30).

decay (approach to equilibrium from high- to low-light intensity) show that the transformations are controlled by the rate of light absorption in the F and F' bands and that the competing processes are pseudo-first order under the experimental conditions. The kinetic equations proposed below are consistent with these conclusions.

DISCUSSION

The experimental results show that the extent of reversible F - to F' -center conversion at 80°K does not vary appreciably with the method of coloration. If it is assumed that the F centers in additively colored KCl are uniformly distributed, then the average distance between F centers for a concentration of 10^{17} cm^{-3} is about 200 Å, which makes a tunneling mechanism very improbable. Although previous results on x rayed

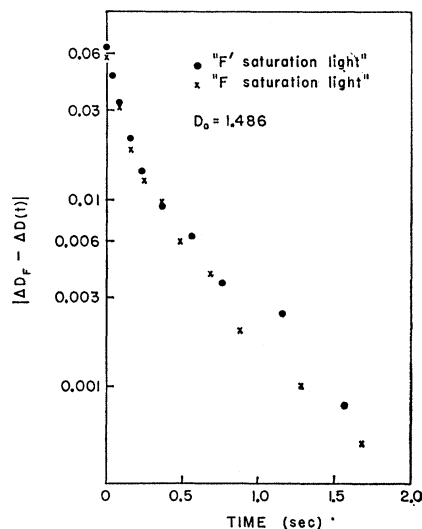


FIG. 10. Kinetics of approach to equilibrium under " F " and " F' saturation light."

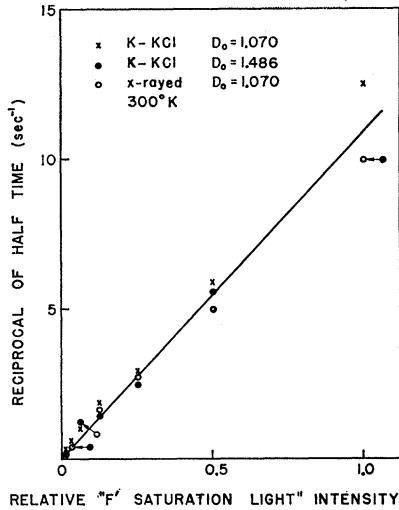


FIG. 11. The rate constant for approach to equilibrium under "F saturation light" as a function of light intensity.

crystals were interpreted by tunneling,^{4,6} the agreement between x-rayed and additively colored crystals in the present work strongly suggests that tunneling is not significant. The controlling factors are taken to be the spectral overlap of the F and F' bands, the photoionization efficiencies of F and F' centers, and the electron-capture cross sections of the F center and chloride-ion vacancy. It is possible to fit the experimental results by a set of kinetic equations formulated on this basis, and to calculate the photoionization efficiency of the F center and the relative electron-capture cross sections.

To account for the light intensity gradient and the change in spectral distribution through the crystal, the rate equations are written for a slice of crystal of incremental thickness located at a distance x from the illuminated face. If $i(0, \lambda)$ is the spectral intensity of incident light per unit wavelength at $x=0$ and $i(x, \lambda)$ is the spectral intensity at a distance x from the illuminated face, then

$$i(x, \lambda) = i(0, \lambda) \exp[-2.3D(x, \lambda)], \quad (1)$$

where $D(x, \lambda)$ is the optical density of the portion of the crystal from 0 to x .

The following assumptions are the basis for the kinetic equations:

(a) The F - to F' -center conversion proceeds through photoionization of the F center and subsequent capture of the electron at another F center.

(b) The concentrations of F centers, F' centers, and negative-ion vacancies are uniform in a slice of incremental thickness.

(c) Diffusion between neighboring slices can be neglected.

(d) The photoionization efficiency of the F' center is unity at 80°K.¹ The resulting equations are:

$$\frac{dn_F}{dt} = -\eta I_F + I_{F'} + k_V n_V n_E - k_F n_F n_E, \quad (2)$$

$$\frac{dn_V}{dt} = \eta I_F - k_V n_V n_E, \quad (3)$$

$$\frac{dn_{F'}}{dt} = k_F n_F n_E - I_{F'}, \quad (4)$$

$$\frac{dn_E}{dt} = -k_F n_F n_E - k_V n_V n_E + I_{F'} + \eta I_F, \quad (5)$$

where n_F , $n_{F'}$, n_V , n_E , are the volume concentrations of F centers, F' centers, negative-ion vacancies, and conduction electrons respectively, I_F and $I_{F'}$ are the differential rate of light absorption (photons-sec⁻¹ cm⁻³) in the F and F' band respectively as defined in the Appendix, k_F (cm³-sec⁻¹) is the capture coefficient for the F center, k_V (cm³-sec⁻¹) is the capture coefficient for a negative-ion vacancy, and η is the quantum efficiency for photoionization of the F center. Similar equations have been applied by Hesketh,¹⁰ Mador *et al.*,¹¹ and Bron and Heller¹² to room-temperature bleaching of F centers.

Two additional equations are obtained from the requirements of conservation of the number of negative-ion vacancies and of the total charge:

$$n_F + n_{F'} + n_V = \text{const}, \quad (6)$$

$$n_F + 2n_{F'} + n_E = \text{const}. \quad (7)$$

Equations (6) and (7) are not independent of Eqs. (2) to (5); any four of Eqs. (2) to (7) may be used.

The solution can be simplified by noting that the lifetime of a conduction electron against trapping by F centers is about 10⁻⁹ sec,¹³ so that for the conditions of our measurements (dn_E/dt) ≈ 0 giving:

$$n_E = (\eta I_F + I_{F'}) / (k_V n_V + k_F n_F). \quad (8)$$

Furthermore, the value of n_E for the maximum light intensity used during irradiation is about 10⁸ cm⁻³,¹⁴ which is much smaller than either n_F , $n_{F'}$, or n_V and may be neglected in Eq. (7). With this approximation:

$$\frac{dn_F}{dt} = 2(k_V n_V I_{F'} - k_F n_F \eta I_F) / (k_V n_V + k_F n_F). \quad (9)$$

The light absorption rates can be related to the color center concentrations by

$$I_F = 2.3\alpha n_F g_F, \quad (10)$$

$$I_{F'} = 2.3\alpha n_{F'} g_{F'}, \quad (11)$$

where g_F and $g_{F'}$ are absorption factors which are calculated from the F and F' band-absorption spectra and the spectral distribution of the incident light, as discussed in the Appendix and α is a parameter which

¹⁰ R. V. Hesketh, thesis, University of Durham, Durham England, 1953 (unpublished).

¹¹ I. L. Mador, R. F. Wallis, M. C. Williams, and R. C. Herman, *Phys. Rev.* **96**, 617 (1954).

¹² W. E. Bron and W. R. Heller, *Phys. Rev.* **119**, 1864 (1960).

¹³ A. G. Redfield, *Phys. Rev.* **94**, 537 (1954).

¹⁴ An estimate of an upper limit of n_E for the experimental conditions is obtained from Eq. (8) using values $n_F = 2 \times 10^{17}$ cm⁻³, $n_V = n_{F'} = 2 \times 10^{15}$ cm⁻³, $I_F = 4 \times 10^{18}$ photons-sec⁻¹-cm⁻³ and $I_{F'} = 10^{16}$ photons-sec⁻¹-cm⁻³ calculated from Eq. (10) and Eq. (11), $k_F = 3 \times 10^{-9}$ cm³-sec⁻¹, $k_V = 4 \times 10^{-7}$ from a classical calculation by Pekar which is discussed in more detail later, and $\eta \leq 0.1$.

is proportional to the total intensity of the incident bleaching light. Substitution of Eqs. (10) and (11) into Eq. (9) gives

$$\begin{aligned} (dn_F/dt) &= 4.6\alpha(k_V n_V n_{F'} g_{F'} - k_F \eta n_F^2 g_F) / (k_V n_V + k_F n_F). \quad (12) \end{aligned}$$

The quantities $n_{F'}$ and n_V can be eliminated with Eq. (6) and Eq. (7). If n_{F^0} and n_{V^0} are the concentrations of F centers and negative-ion vacancies when all of the F' centers are transformed into F centers (under strong red saturation light), then

$$n_{F'} = \frac{1}{2}(n_{F^0} - n_F), \quad (13)$$

$$n_V = n_{V^0} + \frac{1}{2}(n_{F^0} - n_F). \quad (14)$$

Substitution into Eq. (12) gives

$$\begin{aligned} (dn_F/dt) &= 2.3\alpha \frac{g_{F'}(2n_{V^0} + n_{F^0} - n_F)(n_{F^0} - n_F) - 4q\eta g_F n_F^2}{2n_{V^0} + n_{F^0} - (1 - 2q)n_F}, \quad (15) \end{aligned}$$

where q is the ratio of the electron-capture coefficient of the F center to that of the negative-ion vacancy. Equation (15) forms the basis for a discussion of the experimental results. It should be noted that it pertains only to local concentrations and that an integration over the thickness of the crystal is necessary before comparisons can be made. The absence of the alpha band in crystals which are additively colored or x rayed at 300°K suggests that $n_{V^0} \approx 0$ in these cases. For low-temperature x rayed crystals, n_{V^0} may be the order of n_{F^0} .¹⁵

Photoionization Efficiency

The initial rate of recovery in an additively colored crystal immediately after the " F' saturation light" is turned off corresponds to the value obtained from Eq. (15) for $n_F = n_{F^0}$ and $n_{V^0} = 0$, noting that the F' centers in this case have been completely converted to F centers:

$$(dn_F/dt)_{t=0} = -4.6\alpha\eta g_F n_F. \quad (16)$$

The optical density of a crystal block of thickness x and 1 cm² area at a wavelength λ and at a time t is related to the concentration of F centers by

$$D(x, \lambda, t) = \epsilon_F(\lambda) \int_0^x n_F(x, t) dx, \quad (17)$$

where $\epsilon_F(\lambda)$ is a coefficient which may be calculated from the F -band absorption spectrum. We consider in the following the optical density at the peak wavelength of the F band. The local F -center concentration is obtained from Eq. (17):

$$n_F(x, t) = \frac{1}{\epsilon_F(\lambda)} \left(\frac{\partial D}{\partial x} \right). \quad (18)$$

Substitution of Eq. (18) into Eq. (16) gives

$$\left[\frac{d}{dt} \left(\frac{\partial D}{\partial x} \right) \right]_{t=0} = -4.6\alpha\eta g_F \left(\frac{\partial D}{\partial x} \right)_{t=0}. \quad (19)$$

Integrating over the thickness of the crystal from $x=0$ to $x=L$, noting that $dD/dt = d\Delta D/dt$, and solving for η gives

$$\eta = - \frac{d\Delta D_L}{dt} / \left(4.6\alpha \int_0^{D_L} g_F dD \right), \quad (20)$$

where D_L and ΔD_L are the total optical density and optical density change respectively. The integral was calculated numerically from the values of g_F obtained from Eq. (A3) in the Appendix. The initial bleaching efficiency (number of F centers bleached per photon absorbed) is 2η . The initial rate of optical density change was measured directly from the oscillograms. The average result obtained from two additively colored crystals with initial concentrations of 1.2×10^{17} and 1.8×10^{17} cm⁻³ F centers and for several values of the monitoring light intensity is $\eta = 0.020 \pm 0.003$. For comparison, an estimate of the photoionization efficiency can be obtained from the photoconductivity experiments of Pohl and co-workers.^{2,3} The product of the photoionization efficiency and range per unit field for additively colored KCl with 2.7×10^{16} F centers per cm³ is about 10^{-10} cm²/v at 90°K. This is equal to $\eta\mu\tau$, where μ is the mobility and τ is the lifetime of a photoelectron against capture by an F center. Assuming that τ does not vary strongly with temperature, we can obtain its value from the photoelectric yield at 273°K where η is almost unity. For $n_F = 2.7 \times 10^{16}$ the range per unit field is about 10^{-8} cm²/v and taking $\mu = 25$ cm²/v-sec at 273°K and $\mu = 100$ cm²/v-sec at 90°K, estimated from the data of Redfield,¹³ we obtain $\tau = 4 \times 10^{-10}$ sec and $\eta = 0.0025$. A recent calculation of the thermal ionization efficiency of the excited KCl F center was made by Swank and Brown¹⁶ based on measurements of the fluorescent and photoconductive lifetimes. Assuming that this quantity is equivalent to the low-temperature photoionization efficiency, their results give $\eta = 0.00014$ at 80°K. On the other hand, the initial quantum efficiency for the conversion of F to F' centers can be estimated by extrapolating Pick's bleaching data¹ to 80°K giving $\eta \approx 0.05$, in fair agreement with our result. The photoconductivity methods give ionization efficiencies that are considerably lower than from optical bleaching measurements. A possible explanation is that a small extent of F -band bleaching can markedly reduce the range of photoelectrons, because of the high-capture cross section of negative-ion vacancies. Some F -band bleaching is unavoidable under " F light" except when the crystal is illuminated with strong " F' light" at the instant before measurement, such as was done in the work reported here.

¹⁵ F. Seitz, Revs. Modern Phys. **26**, 7 (1954).

¹⁶ R. K. Swank and F. C. Brown, Phys. Rev. Letters **8**, 10 (1962).

Equilibrium of F and F' Centers

To discuss the equilibrium measurements we set $(dn_F/dt)=0$ in Eq. (15) and obtain:

$$n_F^{-2}(2n_V^0+n_F^0-n_F)(n_F^0-n_F)=4\eta q(g_F/g_{F'}). \quad (21)$$

The discussion is limited to the case $n_V^0=0$; we again introduce the optical density and integrate over the thickness of the crystal, obtaining

$$\Delta D=2(\eta q)^{\frac{1}{2}} \int_0^{D_q} (g_F/g_{F'})^{\frac{1}{2}} dD, \quad (22)$$

where ΔD is the change in optical density at the peak of the F band (corresponding to the number of F centers transformed into F' centers) and D_q is the equilibrium optical density of the crystal at the peak wavelength of the F band. From Eq. (A5) derived in the Appendix, we obtain by integrating Eq. (22):

$$\Delta D = \frac{4K^{1.5}(\eta q)^{\frac{1}{2}}}{3L} \left[1 - \left(1 - \frac{LD_q}{K} \right)^{1.5} \right]. \quad (23)$$

A "least-squares" fit of this equation to the results of Fig. 4 gives for $(\eta q)^{\frac{1}{2}}$ the values 0.015 and 0.020 for filtered and unfiltered x rays respectively. The value of $(\eta q)^{\frac{1}{2}}$ from the data of Fig. 5, excluding the crystals colored at 80°K, is 0.018. The value of q calculated from the average $(\eta q)^{\frac{1}{2}}$ and the photoionization efficiency given above is 0.016 ± 0.005 .

The value for $(\eta q)^{\frac{1}{2}}$ was calculated on the assumptions that the rate-controlling processes are the capture of electrons at F centers and at negative-ion vacancies, and that the negative-ion vacancies are due only to ionized F centers. For crystals x rayed at 80°K, the presence of the alpha band suggests that the number of negative-ion vacancies may be comparable to the number of F centers. However, the data of Fig. 5 for such crystals shows that the extent of F - to F' -center conversion is only 50% smaller than for additively colored crystals, which is inconsistent with the capture-cross-section ratio calculated above. Possible reasons for the disagreement are: (a) the number of negative-ion vacancies in KCl after x raying at 80°K is actually at least an order of magnitude smaller than the number of F centers, or (b) the optical bleaching processes in crystals x rayed at 80°K differ from those in crystals additively colored or x rayed at 300°K. It is pointed out below that a high concentration of negative-ion vacancies can enhance the capture cross section of the F center and alter the value of q . In view of this, the data obtained from crystals x rayed at 80°K have not been utilized for numerical calculation.

Our experimental value of q can be compared with an estimate given by Pekar¹⁷ on the basis of a classical calculation. He considers two limiting cases, where the

¹⁷ S. I. Pekar, *Untersuchungen über die Electronentheorie der Kristalle* (Akademie Verlag, Berlin, 1954), p. 154 ff.

recombination rate is limited either by the transition of the electron to the ground state of the center, or by the diffusive motion of the electron in the attractive field of the center. The large interaction of electrons with the lattice polarization and the low mobility in polar crystals suggest that the latter case is more likely to be applicable for KCl. This assumption is supported also by the agreement obtained with values of capture cross sections from photoconductivity experiments. The expressions given by Pekar are:

$$k_F = 1.1(4\pi\mu)(kT)^{\frac{1}{2}}(\gamma/2\kappa^2e^2)^{\frac{1}{2}}, \quad (24)$$

$$k_V = 4\pi e\mu/\kappa, \quad (25)$$

where μ is the mobility, κ is the dielectric constant, and γ is the polarizability of the F center. Taking $\gamma = 2 \times 10^{-23}$ cm³, as estimated from the F -center volume for a mean radius of 1.6 Å,¹⁵ and $\kappa = 5$, gives

$$q = 0.925(kT)^{\frac{1}{2}} \left(\frac{\gamma\kappa^2}{e^6} \right)^{\frac{1}{2}} \approx 0.01, \text{ at } 80^\circ\text{K}. \quad (26)$$

Considering the approximations of the calculation, the agreement with the experimental value of 0.016 is satisfactory.

Although the above kinetic equations account satisfactorily for the main features of the equilibrium, they do not explain the logarithmic dependence on the light intensity shown in Fig. 8, noting that the light intensity parameter α does not appear in Eq. (21). It is clear that the model must either be supplemented by an additional electronic process or that the rate constants k_V and k_F must vary with the light intensity. The conditions for which trapping centers can assume abnormally high cross sections have been suggested by Bron and Heller.¹² Under high light intensities, the concentration of vacancies will be sufficiently large so that the attractive fields of the vacancies and F centers overlap, thus enhancing the capture cross section of the F center. (An isolated F center captures from electron plane waves to a bound state, whereas the initial state for capture by the perturbed F center has a partial Coulombic character.) Alternatively, the model can be supplemented by the addition of a dark decay of the F' band, due to thermal ionization of the F' center. If this process is included, the solution of the kinetic equations leads to the modified equilibrium relation:

$$\Delta D = 2(\eta q)^{\frac{1}{2}} \int_0^{D_q} \left[\frac{g_F}{g_{F'} + 1/\alpha\tau} \right]^{\frac{1}{2}} dD, \quad (27)$$

where τ is the lifetime of the F' center. The solid line in Fig. 8 was calculated from Eq. (27) with the value of $(\eta q)^{\frac{1}{2}}$ previously given, g_F and $g_{F'}$ for the "F saturation light," and assuming $\tau = 60$ sec. The functional dependence is similar to the experimental results although the numerical values are about 30% lower. However, this value of τ is many orders of magnitude

smaller than experimental observations of the dark decay time of the F' band at 80°K,^{1,4} so that this argument is not satisfactory. On the basis of the equilibrium results, it is not possible to show conclusively that the first explanation applies.

Kinetics of Transitions Between Equilibrium States

For a discussion of the rate of transition between equilibrium states, Eq. (15) must be integrated with respect to time and over the thickness of the crystal. Taking again $n_{V^0}=0$ and setting $\Delta n_F = n_F - n_{F^0}$ gives

$$(d\Delta n_F/dt) = 2.3\alpha \frac{g_{F'}(\Delta n_F)^2 - 4qg_F\eta(n_{F^0} + \Delta n_F)^2}{2qn_{F^0} - (1-2q)\Delta n_F}. \quad (28)$$

Equation (26) can be integrated exactly:

$$\left(\frac{1-2qb}{1+2qb}\right)\left(\frac{b+1}{b-1}\right) \log_e \left| \Delta n_F - \frac{n_{F^0}}{b-1} \right| + \log_e \left| \Delta n_F + \frac{n_{F^0}}{b+1} \right| = \log_e G - mt, \quad (29)$$

where

$$m = 9.2\alpha(\eta q g_F g_{F'})^{\frac{1}{2}} \left(\frac{b+1}{1+2qb}\right), \quad b = \left(\frac{g_{F'}}{4q\eta g_F}\right)^{\frac{1}{2}},$$

and G is a constant of integration to be determined from the initial conditions. The final value of Δn_F given by Eq. (29) is $-n_{F^0}/(b+1)$, corresponding to the local equilibrium concentration. For values of Δn_F close to equilibrium, the time dependence is determined mainly by the second term on the left hand side of Eq. (29), and the optical density change is an approximate exponential function of time. The approximate rate constant m is linear in the light intensity, in agreement with the experimental results, Fig. (11).

The complete calculation has been carried out for the case of return to equilibrium after the " F' saturation light" is turned off. The initial condition for this case is $\Delta n_F=0$ and with the appropriate value of G , Eq. (29) gives

$$\left(\frac{1-2qb}{1+2qb}\right)\left(\frac{b+1}{b-1}\right) \log_e \left| \frac{\Delta n_F}{n_{F^0}/(b-1)} - 1 \right| + \log_e \left| \frac{\Delta n_F}{n_{F^0}/(b+1)} + 1 \right| = -mt. \quad (30)$$

Equation (30) gives $\Delta n_F/n_{F^0}$ as a function of time and position in the crystal. Introducing again the incremental optical density and integrating numerically over the thickness of the crystal we obtain the change in optical density as a function of time. The result of this calculation is shown by the dashed line in Fig. 9. Although the agreement is satisfactory it should be pointed out that the value of the photoionization effi-

ciency has been calculated from this data, so that this comparison does not constitute a completely independent check of the kinetic equations. A similar calculation for the return to equilibrium after bleaching with " F saturation light" was made by assuming an initial condition $\Delta n_F = -2n_{F^0}/(b+1)$. The calculated difference of the integrated optical density change from the equilibrium value is again very nearly exponential in time, with a rate approximately equal to that of the first case. This result differs considerably from the experimentally observed shape, Fig. 9(b). An enhanced F -center capture cross section at high " F light" intensity, as discussed above, would explain qualitatively the increased rate of F' -center bleaching shortly after the " F light" is removed. Examination of the decay data shows that for the same monitoring light intensity, the initial rate of return to equilibrium is faster at higher " F saturation light" intensity. However, the effect is not sufficiently pronounced to definitely establish the mechanism. For an additional check on the applicability of Eq. (29) to the two buildup processes, the rate constant m was calculated using average values of the light absorption factors g_F and $g_{F'}$ over the thickness of the crystal. The values obtained for m are 2 sec⁻¹ and 30 sec⁻¹ at the maximum intensities of the " F " and " F' " saturation light" respectively, which is in fair agreement with the experimental values of about 10 sec⁻¹ for both processes, Fig. 11.

CONCLUSIONS

1. Irradiation of colored KCl at 80°K with steady " F light" establishes an equilibrium between the concentrations of F' and F centers. For additively colored KCl, all bleached F centers are reversibly converted into F' centers. For x rayed crystals, only a fraction of the F centers initially bleached are converted into F' centers depending on the conditions of coloration and the F -center concentration.

2. For the range of light intensity investigated, 10¹⁴ to 10¹⁷ photons-cm⁻² sec⁻¹, the extent of equilibrium F -center conversion to F' centers varies approximately with the logarithm of the incident light intensity. This dependence can be explained qualitatively by assuming that the electron-capture coefficients of the F center and negative-ion vacancy vary with light intensity because of an overlap of the attractive fields at high-trapping center concentrations.

3. For a fixed-bleaching-light intensity, the extent of F - to F' -center conversion is a constant fraction of the F -center concentration. Since the rate of light absorption is exponential in the F -center concentration, it is concluded that the photoequilibrium is established in local regions of the crystal.

4. The transition from equilibrium at a low to a high light intensity (buildup) is an approximate exponential function of time with a first-order rate constant which is linear in the light intensity. The transi-

tion from equilibrium at a high to a low light intensity (decay) is exponential in time when F centers transform into F' centers, but deviates markedly when F' centers transform into F centers. The rate constant for the former case is linear in the light intensity. The latter case can be explained qualitatively by the consideration in item 2. The exponential time-dependence is consistent with transitions controlled by the rate of light absorption in competition with pseudo-first-order processes.

5. The above considerations and the insensitivity of the extent of equilibrium transformation to the method of coloration indicate that electron transport processes predominate, leading to a kinetic model based on photoionization of F and F' centers and electron capture at F centers and negative-ion vacancies. An analysis of the initial F -band bleaching rate for an additively colored crystal, under conditions where all F' centers are converted to F centers, leads to 0.020 ± 0.003 for the photoionization quantum efficiency of the KCl F center at 80°K ; this quantity is one-half of the photo-bleaching quantum efficiency. The equilibrium ratio of F' to F centers for additively colored KCl and crystals x rayed at 300°K gives 0.016 ± 0.005 for the electron-capture cross section ratio of the F center to the chloride-ion vacancy at 80°K .

Note added in proof. F. Lüty has measured q by similar methods from -80° to -160°C [*Halbleiterprobleme Band VI* (Vierweg u. Sohn, Braunschweig, Germany, to be published)]; extrapolation of his results to 80°K gives $q=0.05$. A recent calculation by J. Markham from published photoconductivity data gives $q=0.005$ (private communication). A weighted average of all available information, including the authors' result, gives 0.02 ± 0.01 for the ratio of the electron-capture cross section of the KCl F center of the chloride-ion vacancy at 80°K .

APPENDIX

We outline here the derivation of the light absorption relations. The light intensity at a distance x from the illuminated face is given by Eq. (1). The differential rate of light absorption at x and at a wavelength λ is:

$$-\frac{\partial i(x,\lambda)}{\partial x} = 2.3i(0,\lambda) \frac{\partial D}{\partial x} \exp[-2.3D(x,\lambda)]. \quad (\text{A1})$$

Introducing Eq. (18) and integrating over wavelength gives the differential rate of light absorption in the entire F band at x :

$$I_F(x) = 2.3n_F(x) \int_{\lambda_1}^{\lambda_2} i(0,\lambda) \epsilon_F(\lambda) \times \exp[-2.3D(x,\lambda)] d\lambda. \quad (\text{A2})$$

The integral,

$$\alpha g_F(x) = \int_{\lambda_1}^{\lambda_2} i(0,\lambda) \epsilon_F(\lambda) \exp[-2.3D(x,\lambda)] d\lambda, \quad (\text{A3})$$

can be calculated for selected values of x from the F -band absorption spectrum, or equivalently as a function of the optical density at the peak wavelength of the F band by means of Eq. (17). With this latter representation it is not necessary to make detailed assumptions for the distribution of F centers. Similarly for the F' band:

$$\alpha g_{F'}(x) = \int_{\lambda_1}^{\lambda_2} i(0,\lambda) \epsilon_{F'}(\lambda) \exp[-2.3D(x,\lambda)] d\lambda. \quad (\text{A4})$$

To calculate the coefficients $\epsilon_F(\lambda)$ and $\epsilon_{F'}(\lambda)$ it was necessary to obtain absorption spectra corresponding to a known number of color centers. The number of F centers was calculated by Smakula's formula for an oscillator strength of 0.81. The F' -band spectrum was obtained by optically bleaching an additively colored crystal at a temperature at which a large conversion of F to F' centers occurs and calculating the corresponding number of F' centers from the difference in the number of F centers before and after bleaching.

The function $g_F/g_{F'}$ for the monitoring light was found to be linear in optical density at the F -band peak to a good approximation:

$$g_F/g_{F'} = K - LD, \quad (0 \leq D \leq 2.0), \quad (\text{A5})$$

where K and L are constants determined by the filters used: $K=3.20$, $L=1.03$ for the Corning filter CS 4-64; $K=3.40$, $L=1.28$ for the combination of filters Corning CS 3-71 and B. & L. interference 540 $m\mu$.