

tion, it is necessary to correct for refraction at the surface of the crystal to obtain a picture of the internal distribution of the secondaries. This correction involves the choice of a refractive index for the crystal. For each crystal studied it was possible to find by trial a unique value of the refractive index for each energy group of secondaries which gave consistent internal angular distributions for all primary energies and angles of incidence employed. The distribution so obtained gave peaks whose positions and widths are in agreement with the theory for interzone transitions. The values of the refractive indices obtained in this manner differ markedly from free-electron refractive indices in the range of low and medium secondary energies. The implication is plainly that electrons of these energies in nickel and copper are not free, or nearly free,<sup>12</sup> and with refinement the study of angular distributions may be used as a tool

to study in detail departures from the free electron approximation in the excited states of many solids. Since the refractive index is proportional to  $\nabla_{\mathbf{k}}E(\mathbf{k})$ , it is possible in principle to determine the shape of the  $E(\mathbf{k})$  curve for these excited states, given sufficiently detailed information about the index of refraction.

## V. ACKNOWLEDGMENTS

The author is pleased to thank Professor Robert Gomer, Professor Andrew Lawson, and Professor Morrel Cohen of the Institute for Study of Metals and Dr. Foster Rieke of Chicago Midway Laboratories for many helpful discussions and suggestions during the course of this work. Thanks is also due Mr. Paul Dolon and Mr. Paul Husted for their help in fabricating parts of the apparatus.

## Temperature Dependence of Optical Bleaching of KCl Crystals near 0°C\*

W. E. BRON AND A. S. NOWICK

*International Business Machines Research Center, Yorktown Heights, New York*

(Received February 12, 1960)

Further insight has been sought into the mechanism of optical bleaching in the vicinity of room temperature by studying the temperature dependence of the bleaching curves for KCl crystals which had been initially irradiated with hard (filtered) x-rays. The absorptions at the maxima of the  $F$ ,  $M$ ,  $R_1$ , and  $R_2$  bands were observed to change during illumination with  $F$ -light and to be strongly temperature dependent in the range of  $-30^\circ\text{C}$  to  $+10^\circ\text{C}$ , whereas the absorption at the  $V_3$  band was essentially unchanged. For comparison an analysis was made of the data of Petroff on the early growth of the  $M$  band during bleaching with  $F$ -light in additively colored KCl crystals. In this case a unique activation energy,  $\epsilon$ , of  $0.35 \pm 0.05$  eV and a number of defect jumps  $N_j \approx 10^{10}$

are indicated by the data. It appears that the bleaching curves of the x-irradiated samples are composed of a temperature independent and a temperature dependent part. The temperature dependent part probably is the same as that responsible for bleaching in additively colored crystals. The above results for  $\epsilon$  and  $N_j$  suggest that the temperature dependent bleaching process results from the trapping of photoelectrons at vacancy clusters which are formed during bleaching through the migration of mobile defects, possibly vacancy pairs. This conclusion is supported by the observations by others that the  $\alpha$  band is not observed during bleaching at room temperature.

## INTRODUCTION

A NUMBER of mechanisms have been proposed to account for experimental results obtained when  $F$  centers in alkali halides are bleached with light in the  $F$  band in the vicinity of room temperature. Among the mechanisms proposed are the following: Bleaching occurs when (i) the photoelectrons produced through the ionization of  $F$  centers are annihilated at holes associated with  $V$  centers<sup>1-3</sup> (ii) photoelectrons are captured by clusters of vacancies, which results in the

production of secondary color centers either immediately or after a suitable ejection of surplus vacancies from the cluster,<sup>4</sup> and (iii) negative-ion vacancies obtained through the ionization of  $F$  centers combine with other vacancies and migrate to form aggregates, which upon the proper acquisition of photoelectrons form  $R$ ,  $M$ , and  $N$  centers.<sup>5</sup> The bleaching of  $F$  centers through the formation of  $F'$  centers need not be considered as a possible mechanism, since in alkali halides such as NaCl and KCl the  $F'$  center is not stable in the vicinity of room temperature.<sup>6</sup>

It will be convenient to refer to the bleaching mechanisms which involve diffusion of defects as "defect-migration" mechanisms, and to refer to the mechanisms which involve only the motion of electrons from  $F$  centers to existing electron trapping centers as "elec-

\* Part of a thesis submitted by W. E. Bron in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, 1959. This paper was originally presented at the International Symposium on Color Centers in Alkali Halides, at Oregon State College, September, 1959.

<sup>1</sup> E. E. Schneider, *Photographic Sensitivity* (Butterworths Scientific Publications, London, 1951), p. 13.

<sup>2</sup> I. L. Mador, R. F. Wallis, M. C. Williams, and R. C. Herman, *Phys. Rev.* **96**, 617 (1954).

<sup>3</sup> F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954).

<sup>4</sup> M. Ueta and W. Kanzig, *Phys. Rev.* **97**, 1591 (1955).

<sup>5</sup> F. Seitz, *Revs. Modern Phys.* **18**, 384 (1946).

<sup>6</sup> H. Pick, *Ann. Physik* **31**, 365 (1938).

tron-transfer" mechanisms. One way of distinguishing these two types of mechanisms is in terms of the temperature dependence of the bleaching process. A "defect-migration" mechanism, such as mechanism (iii), should lead to a strongly temperature dependent bleaching process, the activation energy of which is equal to the motion energy of the defect that controls the migration process. On the other hand, one may anticipate that the simple "electron-transfer" mechanism gives rise to an essentially temperature independent bleaching process. This may be seen as follows: Pick<sup>6</sup> has shown that above  $-80^{\circ}\text{C}$  photoelectrons are produced at  $F$  centers in KCl with a quantum efficiency of unity by light lying in the  $F$  band. In other words, above  $-80^{\circ}\text{C}$  when an electron is raised into its excited state by  $F$ -light, there is sufficient thermal energy available to carry the  $F$  center electron into the conduction band from the excited state. This step of the electron-transfer process is, therefore, temperature independent. A classical calculation<sup>7</sup> has shown that the capture cross section for photoelectrons of charged and uncharged potential secondary centers<sup>8</sup> and of  $V$  centers should not be strongly temperature dependent. A possible exception is the trapping of photoelectrons at  $V_3$  centers, which is thought to involve a thermally activated step of the order of 0.25 ev.<sup>3</sup>

Unlike the simple "electron-transfer" mechanism as defined above, a modified electron-transfer mechanism proposed by Ueta and Känzig<sup>4</sup> can be expected to produce temperature dependence. Ueta and Känzig consider the early stage of optical bleaching to involve the transfer of a photoelectron from an  $F$  center to a neutral quartet of vacancies. The quartet may capture the electron to produce an  $M$  center and a positive-ion vacancy. The later must then be ejected from the cluster. Ejection of a positive-ion vacancy from the quartet might be anticipated to involve an activation energy similar to that for the migration of a positive-ion vacancy (about 0.8 ev).<sup>3,5</sup>

It should, therefore, be possible to learn more about which of the proposed mechanisms controls optical bleaching by determining the kinetics of the process. Accordingly, it was decided in the present experiment to investigate the temperature dependence of the bleaching process in x-irradiated crystals. In this connection it should be noted that Schneider and co-workers<sup>1,9,10</sup> have conducted optical bleaching experiments from room temperature to  $160^{\circ}\text{C}$  and found the initial, or first stage<sup>11</sup> of bleaching to be temperature

independent. In the present experiment measurements of the kinetics of bleaching of  $F$  centers were made in the range of temperatures from  $+10^{\circ}\text{C}$  to  $-30^{\circ}\text{C}$ . It was further decided to extend the previous work by observing the effect of bleaching with  $F$ -light on the absorption of all observable prominent color bands ( $F$ ,  $M$ ,  $R$ ,  $N$ , and  $V_3$  bands). The investigation has been restricted primarily to the first stage of optical bleaching.

## EXPERIMENTAL METHODS

Crystals of potassium chloride approximately  $10\times 10\times 1$  mm in size were cleaved from a large single crystal of KCl obtained from the Harshaw Chemical Company. Samples were used in the as-received condition. All samples were colored by subjecting them to x rays from a copper target operated at 40 kv and 20 ma. The x ray unit contained voltage and current regulating circuits. X rays were filtered through 1.5-mm thick crystals of NaCl so as to filter out the soft components. During the irradiation the sample was mounted at a distance of 3 inches from the x ray port with the large face perpendicular to the x ray beam. In this way the sample was irradiated uniformly over the area of observation, which was a square of dimensions 4 mm $\times$ 4 mm. Each sample was irradiated for a period of three days under ambient conditions in the dark, which was sufficient to bring the crystal to within 90% of the saturation of the first stage of  $F$  center coloration.

Optical absorption measurements were made in a Beckman Model DU spectrophotometer equipped with a stabilized ac power supply. Absorption measurements were made over the spectral range of 200 m $\mu$  to 1075 m $\mu$ . The major absorption bands which were observed were the  $F$ ,  $M$ ,  $R_1$ ,  $R_2$ ,  $N$ , and  $V_3$  bands. In general the accuracy in the measurements of the optical density were highest for the  $F$  band and are accurate to about  $\pm 0.01$ . This estimate of the error does not apply to optical densities of less than 0.6 or at wavelengths in the vicinity of the  $V_3$  band. Because of the reduced sensitivity of the spectrophotometer in these cases, the estimated error in the optical density increases to  $\pm 0.05$ .

Optical bleaching was accomplished in the spectrophotometer with the variable slit set at 2 mm, and the wavelength set at 560 m $\mu$  ( $F$ -light). Under these conditions the spectral band-width of the bleaching light was approximately 100 m $\mu$ . The integrated light intensity with the slit set at 2 mm was 0.13 lumens/cm<sup>2</sup> at the 560 m $\mu$  setting. Rough light intensity measurements were made with a Photovolt Model 200 photometer which had a special selenium photocell as the sensing unit. The calibration supplied by the manufacturer was applied to these measurements. The measuring light

bleaching of alkali halides occurs in two stages [see, e.g., J. J. Oberly, Phys. Rev. **84**, 1257 (1951); and A. S. Nowick, Phys. Rev. **111**, 16 (1958)]. In each case, an initial rapid stage is followed by a second stage during which events occur much more slowly.

<sup>7</sup> S. I. Pekar, *Untersuchungen über die Elektronentheorie der Kristalle*, (Akademie-Verlag, Berlin, 1954).

<sup>8</sup> A "potential color center" is here defined as having the vacancy configuration of the color center without the electrons or holes of the color center.

<sup>9</sup> D. F. Grant, thesis, University of Durham, April, 1950 (unpublished).

<sup>10</sup> R. V. Hesketh, thesis, University of Durham, October, 1953 (unpublished).

<sup>11</sup> It has been known for some time that in the vicinity of room temperature coloration with ionizing irradiation as well as optical

had a bandwidth of approximately  $1\text{ m}\mu$  and a total energy flux of at least two orders of magnitude less than that of the bleaching light. Bleaching by the measuring light was negligible and was, therefore, neglected in all of the present experiments.

For the low-temperature observations a cryostat was constructed which was designed to be an integral part of the spectrophotometer. The construction of this cryostat is similar to that described by Dorendorf.<sup>12</sup> Uniformity in the temperature of the specimen was obtained by mounting it in the cavity of a copper block. This unit was in turn mounted on a second copper block which was suspended from the bottom of the inner tube of the cryostat. The second copper block contained two square holes of exactly the same dimensions. One of these ports was used as the optical reference, while the specimen was mounted in front of the other port. Light passed through the cryostat through optical-grade quartz windows. It was possible to place either of the ports in the path of the light beam of the spectrophotometer by a simple, fixed translation of the cryostat. Temperature at the specimen was measured with a copper-constantan thermocouple attached to the copper block containing the specimen. Temperatures in the range from  $+10^\circ\text{C}$  to  $-40^\circ\text{C}$  were obtained by filling the inner tube of the cryostat with a mixture of dry-ice and trichlorethylene. It was possible to vary the temperature by heating a small carbon resistor, one lead of which was soldered to the copper block holding the specimen. The current through the resistor was regulated with an electronic proportioning temperature controller, and the temperature was maintained to  $\pm 0.2^\circ\text{C}$ . Absorption measurements were made at temperature.

Measurements were also made of the total quantum efficiency of the room temperature bleaching process using  $F$ -light. For this experiment the slit width of the spectrophotometer was reduced to  $0.6\text{ mm}$ . At this setting the intensity of the  $560\text{ m}\mu$  light incident on the center of the sample was estimated to be about  $2.2 \times 10^{14}$  photons/sec  $\text{cm}^2$ . This estimate is based on the assumption made by various previous investigators, that the light intensity is constant for all the wavelengths of light which pass through the slit. Some doubt of the validity of this assumption is raised by the intensity distribution supplied by the manufacturer of the spectrophotometer, according to which the light intensity decreases approximately linearly from the center wavelength of the band pass, and reaches zero intensity at the edges of the slit of the spectrophotometer. It seems doubtful that this "triangular" distribution can be correct. It is obvious that the light intensity at  $560\text{ m}\mu$  calculated in terms of this "triangular" distribution would be twice as great as that calculated from the present assumption of a "rectangular" distribution.

## EXPERIMENTAL RESULTS

The x ray irradiation as described in the previous section leads to an absorption of the  $F$  band of approximately  $0.45\text{ mm}^{-1}$  at room temperature. In terms of Smakula's<sup>13</sup> equation and an oscillator strength of 0.81 this absorption corresponds to an  $F$  center concentration of approximately  $3 \times 10^{16}\text{ cm}^{-3}$ . On the low-energy side of the  $F$  band only slight absorptions were observed at the  $M$  ( $\lambda = 830\text{ m}\mu$ ),  $R_1$  ( $\lambda = 680\text{ m}\mu$ ),  $R_2$  ( $\lambda = 740\text{ m}\mu$ ), and  $N$  ( $\lambda = 975\text{ m}\mu$ ) bands, when absorption measurements were made at room temperature. In the ultraviolet a sharp, prominent band appeared with a maximum at  $215\text{ m}\mu$ . This coincides with the position of the usually observed  $V_3$  band. As had been reported elsewhere,<sup>14</sup> filtered x-irradiation did not produce an observable  $V_2$  band ( $\lambda = 230\text{ m}\mu$ ). In addition to the  $V_3$  band, two minor absorption bands were observed at  $260\text{ m}\mu$  and  $320\text{ m}\mu$ .

A preliminary bleaching experiment was conducted to determine the effect of the intensity of the bleaching light on the initial rate of bleaching of the  $F$  band. Samples of KCl were irradiated to the same extent as the crystals which were used for the study of the temperature dependence of the bleaching process, and then bleached with  $F$ -light of various intensities from about  $1 \times 10^{14}$  to a maximum of about  $7.4 \times 10^{14}$  photons/sec  $\text{cm}^2$  at the center of the sample. These intensities were obtained by setting the spectrophotometer wavelength indicator to  $560\text{ m}\mu$  with the slit opened to  $2\text{ mm}$ , and placing between the slit and the specimen a series of Kodak neutral filters.

The results of the experiment are shown in Fig. 1.

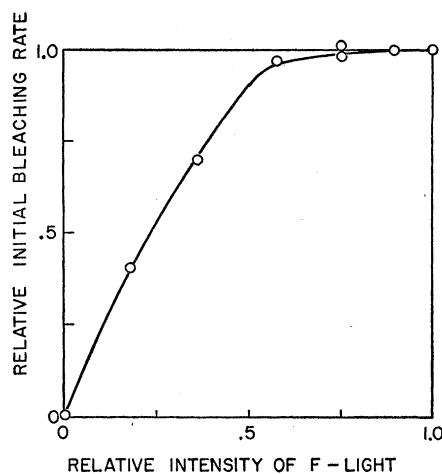


FIG. 1. Initial rate of bleaching as a function of the intensity of the light incident on the sample. In this graph the ordinate is the ratio of the initial rate of bleaching of  $F$  centers with light of reduced intensity to the rate of bleaching using light of maximum intensity. The abscissa is the relative intensity of incident  $F$ -light. The maximum intensity of  $F$ -light used was  $7 \times 10^{14}$  photons/sec  $\text{cm}^2$ .

<sup>13</sup> A. Smakula, Z. Physik **59**, 603 (1930).

<sup>14</sup> R. Casler, P. Pringsheim, and P. Yuster, J. Chem. Phys. **18**, 1564 (1950).

<sup>12</sup> H. Dorendorf, Z. Physik **129**, 317 (1951).

In this figure the initial rate of bleaching of  $F$  centers with filtered light relative to that with unfiltered light is plotted against the relative amount of incident light. It can be seen that the initial rate of bleaching is approximately proportional to the light intensity up to approximately 50% of maximum light intensity. However, the initial rate of bleaching is found to be independent of light intensity for intensities greater than 75% of maximum, i.e., greater than about  $5.1 \times 10^{14}$  photons/sec cm<sup>2</sup>.<sup>15</sup> It can readily be shown, for the range where the bleaching rate is independent of light intensity, that bleaching will not alter any gradients in  $F$  center concentration present in the crystal prior to bleaching. In accordance with this result, only  $F$ -light with a maximum intensity ( $7.4 \times 10^{14}$  photons/sec cm<sup>2</sup>) was used throughout the study of the bleaching of the  $F$  band, except for the determination of the quantum efficiency of the bleaching process when  $F$ -light with the intensity of  $2.2 \times 10^{14}$  photons/sec cm<sup>2</sup> was used.

Since it had been previously observed that re-irradiation after complete optical bleaching does not bring a sample to the same state as after the first irradiation, each sample could be irradiated and bleached only once. Accordingly, a number of samples irradiated to exactly the same initial  $F$  band absorption ( $\alpha_{F0}$ ) are required in order to investigate the bleaching process over a range of temperatures. Because of fluctuations in the room temperature during x-irradiation, it was found possible to obtain only three such samples. These were used for bleaching runs at  $-30.7^\circ\text{C}$ ,  $-20.5^\circ\text{C}$ , and  $-10.7^\circ\text{C}$ . For experiments at  $-0.9^\circ\text{C}$  and  $+10.6^\circ\text{C}$  specimens were used for which  $\alpha_{F0}$  varied by  $\pm 5\%$  from the standard value of  $0.45 \text{ mm}^{-1}$ . It was observed from experiments at several temperatures that the bleaching curves of a number of such samples differing slightly in  $\alpha_{F0}$  could be superimposed by a shift along the absorption scale. It was, therefore, possible to interpolate, point for point, the bleaching curves of these samples and obtain, to a high degree of accuracy, the corresponding bleaching curve for a sample with the standard value of  $\alpha_{F0}$ .

Since the absorption measurements were performed at the temperature of the sample during bleaching, an additional correction is required because of the shift in wavelength and the change in the absorption at the maxima of the various absorption bands as a function of temperature. Accordingly, the shifts in the position and magnitude of the maximum absorption of each of the prominent bands was measured in one sample over the range of temperatures employed. The at-temperature bleaching measurements were then always made at the wavelength of maximum absorption for the temperature of the run. In order that the results for different temperatures be comparable, the magnitude

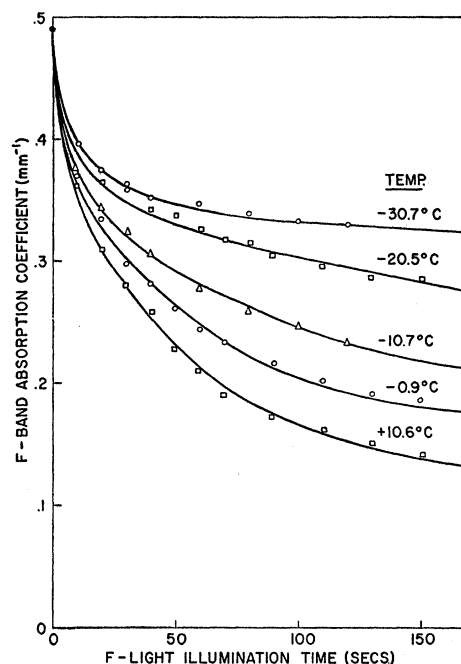


Fig. 2. Changes in the absorption at the  $F$  band during bleaching with  $F$ -light at various temperature ranging from  $-30.7^\circ\text{C}$  to  $+10.6^\circ\text{C}$ . Absorption measurements were made at the maximum of the  $F$  band at each of the temperatures shown. The magnitude of the initial absorption was arbitrarily corrected to the absorption at  $-30.7^\circ\text{C}$ .

of the initial absorption was arbitrarily corrected to the absorption at  $-30.7^\circ\text{C}$ , i.e.,  $\alpha_{F0} = 0.49 \text{ mm}^{-1}$ .

The results for the initial stage of bleaching of the  $F$  band are given in Fig. 2. These measurements show that this stage of bleaching is strongly temperature dependent. Observations were also made on the  $M$  and  $R$  band absorption during bleaching with  $F$ -light. Since the optical density at these bands was often less than 0.6, the accuracy in the absorption measurements were, as noted earlier, somewhat less than that for the  $F$  band. As has been repeatedly observed by others, it was found that during the time the  $F$  band bleaches, the  $M$  band rises rapidly to a maximum and then decreases slowly. It was also observed, as previously reported by Petroff<sup>16</sup> for additively colored KCl, that the time of occurrence of the maximum of the  $M$  band was shorter and the magnitude at the maximum was smaller the higher the temperature of the sample during optical bleaching. The rate of growth of the  $M$  band during the initial period of bleaching with  $F$ -light was found to be strongly temperature dependent. During room temperature optical bleaching, the  $R$  band also goes through a maximum, though at a later time than the  $M$  band. A strong temperature dependence was also found for the growth of  $R$  centers. This temperature dependence had the following features. The growth curves of the  $R$  band for the  $+10.6^\circ\text{C}$ ,  $-0.9^\circ\text{C}$  and

<sup>15</sup> The significance of this independence of the bleaching rate on light intensity is to be discussed in a later paper.

<sup>16</sup> S. Petroff, Z. Physik **127**, 443 (1950).

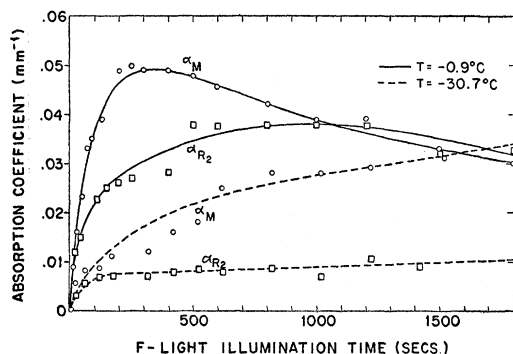


FIG. 3. Comparison of the changes in the  $M$  and  $R_2$  band absorption during bleaching with  $F$ -light with the crystal held at  $-0.9^\circ\text{C}$  and  $-30.7^\circ\text{C}$ . Absorption measurements were made at temperature.

$-10.7^\circ\text{C}$  runs were similar in character to that observed during room temperature bleaching except that the growth rate was successively slower the lower the temperature during bleaching. In contrast, it was found that for the two lowest temperatures,  $-20.5^\circ\text{C}$  and  $-30.7^\circ\text{C}$ , the growth of the  $R$  band essentially ceased after 100 sec of illumination with  $F$ -light. This effect is shown in Fig. 3, where a comparison is made between the  $-0.9^\circ\text{C}$  and  $-30.7^\circ\text{C}$  runs for the  $M$  and  $R$  band absorptions.

The absorption at the  $N$  band is very weak throughout the bleaching process. Therefore, no attempt was made to observe the change in  $N$  band absorption. In each sample tested, the  $V_3$  absorption remained constant throughout the bleaching phase, while the absorption of the two minor  $V$  bands mentioned earlier decreased slightly during the first fifty seconds of bleaching and then remained constant.

Schneider and co-workers in their analysis of the optical bleaching process were able to subtract out the second stage of bleaching by considering that bleaching during this stage follows the equation  $n = n_0 \exp(-\nu t)$  where  $t$  is the bleaching time,  $\nu$  a frequency parameter, and  $n$  and  $n_0$  are respectively the instantaneous and initial concentration of  $F$  centers. It may be argued, therefore, that the difference between the present result, that the first stage is temperature dependent, and Schneider's result that it is temperature independent<sup>1,9</sup> occurs because in the present analysis the second stage was not subtracted out. In the analysis of the data of the present experiment, however, it was found impossible to fit the results for the second stage to an exponential form or to any other simple analytical expression, therefore making it impossible to subtract out the second stage from the total bleaching curve.

If a single activation energy controlled the bleaching of  $F$  centers, it would be possible to superimpose the  $F$  band bleaching curves for the various temperatures by making an appropriate change in the time scale for each temperature. It is observed, however, that no such superposition can be achieved, in that the curves for the

various temperatures diverge rapidly from each other, after adjustment of the time scales to produce coincidence at the early part of the curves. The strongest divergence occurs in the curves for the  $-20.5^\circ\text{C}$  and  $-30.7^\circ\text{C}$  runs relative to those obtained at the three highest temperatures. It is generally considered that the bleaching rate of  $F$  centers depends on the growth of the secondary centers such as  $M$  and  $R$  centers. It is, therefore, probable that the strong divergence of the  $F$  band bleaching curves at  $-30.7^\circ\text{C}$  and  $-20.5^\circ\text{C}$  from the higher temperature curves is related to the fact that for these lowest two temperatures the growth of the  $R$  center essentially ceases after a short period of time (Fig. 3).

As in the case of the  $F$  band it, was found that the curves for the growth of the  $M$  band at various temperatures during bleaching with  $F$ -light could not be superimposed by a change in the time scale, because these curves diverged too rapidly from each other. However, the divergence of the  $M$  band curves from each other appeared to be less than that of the  $F$  band curves. No unique activation energy could, therefore, be determined for the growth of the  $M$  band during bleaching.

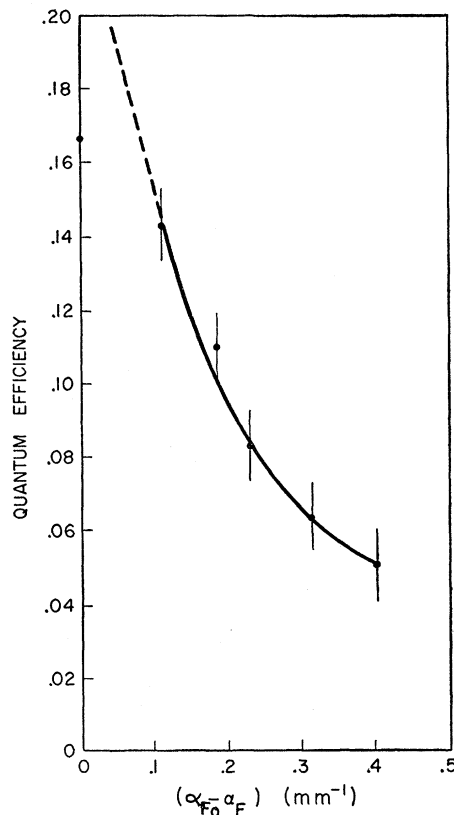


FIG. 4. The total quantum efficiency ( $F$  centers bleached per absorbed quantum of  $F$ -light) as a function of the change in absorption at the  $F$  band as bleaching at room temperature progresses. The change in the absorption is measured as the difference in the  $F$  band absorption at the start of bleaching ( $\alpha_{F0}$ ) and the instantaneous absorption at the  $F$  band ( $\alpha_F$ ).

The main conclusion to be drawn from the data of the present experiment is that the initial stage of optical bleaching of crystals colored by x rays is temperature dependent, although the temperature dependence cannot be described in terms of a unique activation energy.

The total quantum efficiency ( $F$  centers bleached per absorbed quantum of  $F$ -light) was determined at room temperature during the first stage of bleaching of the  $F$  band, in crystals initially irradiated to  $\alpha_{F0}=0.45 \text{ mm}^{-1}$ . The results are given in Fig. 4, where the quantum efficiency is plotted against the decrease in the  $F$  band absorption during bleaching. Unfortunately, accurate measurements could not be made at the beginning of the bleaching process where the rate of bleaching is very high. The results are not inconsistent with a value of unity at the start of bleaching, but thereafter the quantum efficiency decreases rapidly to values in the vicinity of 0.1. This result also differs from that found by Schneider,<sup>1</sup> who reports that the entire first stage of bleaching proceeds with a quantum efficiency of unity. The value of 0.1 is to be compared with the value of 0.3 reported by Mador *et al.*,<sup>2</sup> and 0.23 reported by Camagni and Chiarotti,<sup>17</sup> both for NaCl.

It seemed interesting to compare the present results on x-irradiated crystals with data for the bleaching process in additively colored crystals. Accordingly, an analysis was made by the present authors of the data reported by Petroff<sup>16</sup> on the temperature dependence of the growth of the  $M$  band in additively colored crystals during bleaching with  $F$ -light, in the range of temperatures from 0°C to 76°C. Petroff apparently made absorption measurements with a highly sensitive spectrophotometer, which was able to measure very small absorptions at the  $M$  band to an unusual degree

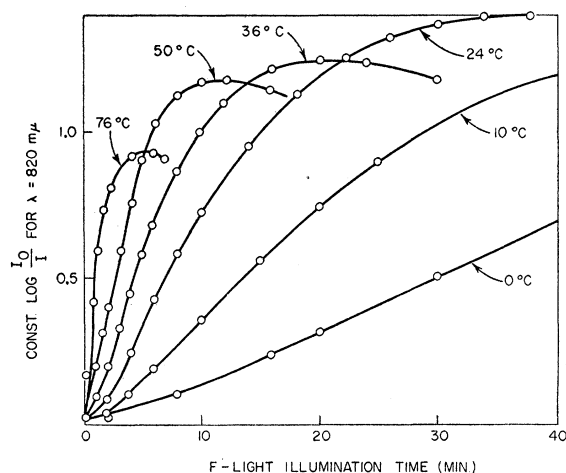


FIG. 5. Optical absorption at the maximum of the  $M$  band in additively colored KCl during bleaching with  $F$ -light at various temperatures. Absorption measurements were made at temperature (after reference 16).

<sup>17</sup> P. Camagni and G. Chiarotti, *Nuovo cimento* **11**, 1 (1954).

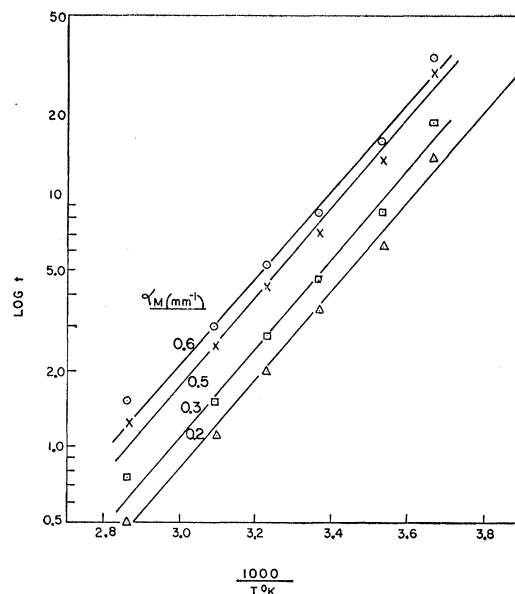


FIG. 6. Variation of the  $\log t$  with reciprocal absolute temperature, where  $t$  is the time to attain a given level,  $\alpha_M$  of absorption in the  $M$  band during bleaching with  $F$ -light. The various curves, for different values of  $\alpha_M$ , are obtained from the data of Petroff (Fig. 5).

of precision. The growth curves of the  $M$  band, which exhibit a strong temperature dependence, are replotted in Fig. 5. Although Petroff does not report any concurrent measurements on the  $F$  band, the same temperature dependence can be expected for the bleaching of  $F$  centers in the additively colored crystals if the formation of  $M$  centers in the early stage of bleaching occurs by the simple reaction:  $F \rightarrow M$ .

A unique activation energy can be obtained from a plot of the logarithm of the time for the  $M$  band to grow to a fixed absorption vs the reciprocal of the absolute temperature. Such plots are presented in Fig. 6, for absorption levels ranging from 13% to 40% of the maximum absorption at room temperature. It has already been pointed out that the  $M$  band absorption goes through a maximum during bleaching of the  $F$  band. This maximum in the  $M$  band absorption undoubtedly results from a superposition of competing growth and bleaching processes. Accordingly, only the early part of the  $M$  band growth curve, which is considerably removed from the maximum, can be expected to be representative of the growth process. In view of the fact that the magnitude at the maximum in the  $M$  band curve is considerably smaller for the 76°C curve than for the lower temperature curves, the least weight should probably be given to the points from the 76°C curve when drawing the best straight line through the points in Fig. 6. The value of the activation energy obtained from the lines drawn in this way is  $0.35 \pm 0.05$  ev. The constancy of the activation energy up to 40% of the maximum absorption suggests that at least in

this range of absorption there exists a unique activation energy.

### DISCUSSION

In the Introduction three mechanisms have been outlined which have been proposed in the literature to account for optical bleaching of  $F$  centers in alkali halides in the vicinity of room temperature. In mechanism (i) bleaching is considered to occur through the annihilation of photoelectrons from  $F$  centers at holes associated with  $V$  centers. One should, therefore, observe during the bleaching of  $F$  centers a corresponding bleaching of  $V$  centers. In the present experiment the only prominent  $V$  band which was observed, the  $V_3$  band, was found to be resistant to bleaching. Only a small amount of bleaching was observed at the two minor  $V$ -type bands, however the duration of bleaching of these bands was much shorter than that observed at the  $F$  band. Thus, bleaching by annihilation of electrons at  $V$  centers, although possibly present to a small extent, can be ruled out as the dominant mechanism. Apparently, the dominant optical bleaching of crystals colored with hard x-rays is similar to that of additively colored crystals, since in both cases bleaching consists primarily of the formation of secondary electron centers.

In the Introduction it has also been noted that one distinguishing feature between the proposed mechanisms of optical bleaching is the temperature dependence of the process to be expected from each mechanism. In the present experiment it has been observed that the first stage of bleaching of the  $F$  band in x-irradiated crystals is temperature *dependent*, although the process is not governed by a unique activation energy. A strong temperature dependent process has also been observed by Petroff<sup>16</sup> in the growth of the  $M$  band during optical bleaching of additively colored crystals. Annihilation of photoelectrons at  $V_3$  centers is the only simple electron transfer mechanism which can lead to a strongly temperature dependent bleaching process. The bleaching of  $V_3$  centers was not, however, observed in the present experiment. The observed temperature dependence of the bleaching process, therefore, most probably results from the motion of defects such as proposed in mechanism (iii) or in the mechanism proposed by Ueta and Känzig.

There are two results from Petroff's data which tend to eliminate the Ueta and Känzig mechanism. First, the value of the activation energy obtained, 0.35 eV, is substantially lower than the value (near 0.8 eV) expected to control this mechanism. Second, the number of defect jumps calculated from Petroff's data is inconsistent with this mechanism. If bleaching is controlled by the migration of defects to form potential secondary centers, then the time constant ( $\tau$ ) for the process may be described as

$$\tau = (N_j/\nu_0) \exp(\epsilon/kT), \quad (1)$$

where  $N_j$  is the number of jumps of the migrating defect before it combines with other defect,  $\nu_0$  the frequency factor for the individual jumps of the particular defect,  $\epsilon$  the activation energy, and  $T$  the absolute temperature. In the case of the ejection of vacancies from vacancy clusters as envisioned by Ueta and Känzig, the same equation ought to apply, and one should expect it to yield a value for  $N_j$  of the order of unity. Inserting into the above equation the following values obtained from Petroff's data:  $\epsilon = 0.35 \pm 0.05$  eV,  $\tau = 10^{2.5}$  sec at  $T = 300^\circ\text{K}$ , and assuming that  $\nu_0 = 10^{14}$  sec<sup>-1</sup> (in accordance with results for other defect migration processes), one obtains a value for  $N_j$  of  $5 \times 10^{10 \pm 1}$  jumps. It can be concluded, therefore, that the mechanism proposed by Ueta and Känzig is not compatible with the information obtained from Petroff's results, but rather that migration over a considerable distance is involved. We are then led to focus attention on mechanism (iii) presented in the Introduction.

Mechanism (iii) supposes that the negative-ion vacancies obtained through the ionization of  $F$  centers enter into combination with other defects during the bleaching process. The temperature dependence of the process is then controlled by the slowest moving defect which is involved. In favor of this mechanism is the recent observation<sup>18</sup> that during room temperature optical bleaching of KI the  $\alpha$  band is not observed after partial bleaching of  $F$  centers. On the other hand, the  $\alpha$  band is observed to grow during bleaching at liquid nitrogen temperatures.<sup>19</sup> When a crystal is warmed-up to room temperature after bleaching at liquid nitrogen temperatures, however, the  $\alpha$  band is again observed to disappear. Added confirmation of mechanism (iii) is obtained from the recent work of Hesketh<sup>20</sup> on the variation of the quantum efficiency during the optical bleaching of  $F$  centers in KCl. Hesketh concludes from his results that in the vicinity of room temperature the vacancies generated during irradiation with x rays are only stable when occupied by electrons.

The question then arises as to which defect controls the bleaching process. In the particular defect-migration process proposed by Seitz,<sup>5</sup> bleaching is considered to occur as follows. Negative-ion vacancies, formed by the ionization of  $F$  centers are joined by positive-ion vacancies to form pairs, which are considerably more mobile than the negative-ion vacancies. These pairs meet other vacancies to form, upon the proper acquisition of electrons,  $M$ ,  $R$ , and  $N$  centers. The bleaching process is, therefore, dependent on the rate of formation of the secondary centers, the latter being formed through a migration process. In the model proposed by Seitz, the rate controlling process should be the migration of the lower mobility defect, viz., the positive-ion vacancies, involving an activation energy of about 0.8

<sup>18</sup> H. Hersh (private communication).

<sup>19</sup> C. J. Delbecq, P. Pringsheim, and P. Yuster, *J. Chem. Phys.* **19**, 574 (1951).

<sup>20</sup> R. V. Hesketh, *Phil. Mag.* **4**, 114 (1959).

ev. It is difficult to reconcile the Seitz mechanism with the considerably lower activation energy of 0.35 ev determined from Petroff's data. Alternatively, the controlling defect may be vacancy pairs already present in the crystal during bleaching which combine with the ionized  $F$  centers immediately to form potential  $M$  centers. The controlling process could then have a unique activation energy as low as about 0.4 ev,<sup>21</sup> in agreement with the value obtained from Petroff's data.

The results of the present experiment on the bleaching of x-irradiated crystals seem at first hand to be in contradiction to mechanism (iii), in the sense that although a temperature dependent bleaching process is observed it is not found to be controlled by a unique activation energy. This result can, however, be explained if it is assumed that in crystals colored by hard x rays the first stage bleaching of  $F$  centers occurs by a combination of the defect-migration and electron-transfer mechanisms. Bleaching then occurs as the superposition of the two processes, one of which is independent of temperature and the other of which is controlled by an activated step. In this experiment, the observed parameter of the process, the  $F$  band absorption coefficient,  $\alpha_F$ , can be expressed as the sum of two functions,

$$\alpha_F = f(t) + g(t, T), \quad (2)$$

where  $t$  is time, and  $T$  the absolute temperature. It is, however, impossible to obtain an activation energy from data at different temperatures unless the functions  $f$  and  $g$  are explicitly known. A very rough estimate of the activation energy can be obtained if it is assumed that in the lowest temperature run of the experiment, the  $-30.7^\circ\text{C}$  run, the temperature dependent part of bleaching is very small compared to the temperature independent part, i.e., the data over the time interval of Fig. 2 represent only  $f(t)$ . An estimate of the temperature dependent part of bleaching,  $g(t, T)$ , is then obtained when the bleaching curve for the  $-30.7^\circ\text{C}$  run is subtracted from the curves of each of the higher temperature runs. The value of the activation energy found in this way is approximately 0.3 ev. It, therefore, appears that the temperature dependent part  $g(t, T)$ , of the bleaching process in x ray irradiated crystals may be the same as that observed in additively colored crystals, since it is controlled by an activation energy in the same range as that obtained from Petroff's results. The temperature independent part of bleaching may be due to the transfer of photoelectrons either to potential secondary electron centers present in the crystal prior to bleaching, or to annihilation of photoelectrons at holes associated with the two minor  $V$  bands.

<sup>21</sup> G. J. Dienes, J. Chem. Phys. **16**, 620 (1948).

The observed variation in the quantum efficiency (Fig. 4) can now also be explained. The transfer of electrons from  $F$  centers to some pre-existing traps present only in x-irradiated crystals is considered to occur during the initial, very rapid, part of the first stage of bleaching with a quantum efficiency near unity. As the traps become fully occupied, and the electron-transfer mechanism subsides, bleaching becomes increasingly dependent on the rate of formation of secondary centers. During this period, photoelectrons can be retrapped several times by negative-ion vacancies before they are finally trapped at secondary centers. The retrapping of photoelectrons accounts for the observed low value of the quantum efficiency during the later period of the first stage of bleaching.

It remains to discuss the significance of the observed value of 0.3 to 0.4 ev for the activation energy for defect migration during bleaching. As has been pointed out above, this value suggests that the controlling process involves the migration of vacancy pairs or some other highly mobile unit. It may be argued, however, because of the inherent mobility of vacancy pairs, that it is hardly likely that more than an equilibrium number of isolated pairs can exist in KCl crystals at room temperature. Assuming an energy of formation of vacancy pairs of about 1.5 ev<sup>22</sup> one may anticipate at room temperature an equilibrium concentration of about  $10^{-2} \text{ cm}^{-3}$ . Obviously, this concentration is too small to account for any of the observed bleaching of  $F$  centers (which are present to the extent of at least  $10^{16} \text{ cm}^{-3}$ ). As an alternative possibility, it is conceivable that vacancy pairs can be produced in relatively large numbers during bleaching from vacancy aggregates which exist in the crystal prior to bleaching. For example, a simple aggregate such as a quartet of vacancies might, upon the capture of a photoelectron, split into two vacancy pairs one of which contains a trapped electron. Presumably, both types of vacancy pairs can migrate rapidly through the lattice and complete the bleaching process by combining with the available negative-ion vacancies. It is interesting to note that recent work of Lüty<sup>23</sup> has furnished evidence for a center consisting of an electron trapped in a vacancy pair which may be observed during bleaching near  $-30^\circ\text{C}$ .

#### ACKNOWLEDGMENTS

The authors are grateful to F. G. Fumi and W. R. Heller for their helpful discussions.

<sup>22</sup> F. G. Fumi and M. P. Tosi, Discussions Faraday Soc. **23**, 94 (1957).

<sup>23</sup> F. Lüty, paper presented at International Symposium on Color Centers in Alkali Halides, Oregon, 1959 (unpublished).