geneous broadening.[7] In this case, there is negligible coupling between spins,[9] and we expect that the ratio of the peak absorption signal to the peak dispersion signal will be

$$\chi_{max}''/\chi_{max}' = 1.65/(1+\gamma^2 H_1^2 T_1^2)^{\frac{1}{2}}. \qquad (9)$$

The klystron employed for these measurements, a Varian VA-6315/V-153, delivered 130 mw to a matched load as measured with a microwave bolometer. The actual power absorbed by the cavity is

$$P_a = [4\beta_1/(1+\beta_1)^2]P_0. \qquad (10)$$

In this experiment we measured $\beta_1 = 0.16$ giving an absorbed power of 62 mw. The energy stored in the cavity may be calculated from the relation,

$$U = Q_0 P_a/\omega. \qquad (11)$$

Under the experimental conditions, this amounts to 0.050 erg or, taking the cavity volume to be 11.1 cm^3, the average energy density within the cavity is 4.5×10^{-3} erg/cm^3. The magnetic energy density within the sample

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[9] P. W. Anderson, Phys. Rev. **109**, 1492 (1958).

is larger than this by a factor of 9.8, as we have seen from the determination of the sample filling factor. Then, taking the energy density at the sample to be

$$(1/8\pi)(2H_1)^2 = 0.044 \text{ erg/cm}^3, \qquad (12)$$

we compute $H_1 = 0.53$ gauss. At this level of microwave power, the ratio of dispersion to absorption is observed to be 16. We thus calculate from (9) a spin-lattice relaxation time of 1.7 microseconds.

In computing the relaxation time from saturation measurements, we should have used the quantity,

$$\langle H_1^2/(1+\gamma^2 H_1^2 T_1^2)^{\frac{1}{2}}\rangle, \qquad (13)$$

where the average is taken over the sample. Instead, by introducing the filling factor, we have actually used the quantity,

$$\langle H_1^2\rangle/(1+\gamma^2\langle H_1^2\rangle T_1^2)^{\frac{1}{2}}. \qquad (14)$$

Normally, with only a slight variation in magnetic field intensity over the sample, there is very little difference between the two expressions, and this difference becomes smaller as the ratio χ'/χ'' becomes larger. For our measurements, taken in the region of high saturation, we neglect the effects of this approximation.

Relation Between X-Ray Coloration and Optical Bleaching of KCl Crystals*

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Changes in the absorption of KCl crystals in the spectral region of 200 mμ to 1000 mμ have been observed during room temperature x-ray irradiation and subsequent bleaching with F light. It is observed that both coloration and bleaching of the F band occurs in two stages. Secondary centers such as M, R, and V_3 centers grow primarily during the second stage of coloration, and the rate of growth of these centers during the second stage is enhanced by plastic deformation in a manner similar to that of the F band. It is found that the absorption change at the F band during the first stage of bleaching approximately equals that during the first stage of coloration. Furthermore, the initial rate of bleaching of the F band is proportional to the initial F band absorption in samples irradiated only into the first stage of coloration, but is essentially independent of the initial F-band absorption in samples irradiated into the second stage of colora-

tion. It is concluded from this and other evidence that the center responsible for the first stages of coloration and bleaching differs from the center responsible for the second stages of coloration and bleaching. A major point of difference is that the first stage centers are considered to be located in the bulk of the crystal, whereas the second stage centers are located in the vicinity of dislocations.

It is also observed that M centers which are formed from F centers during the first stage of bleaching can be bleached with F light. To explain the observations concerning this M-band bleaching, it is proposed that M as well as F centers are bleached when they are joined by mobile defects, possibly vacancy pairs Some of the second stage centers located in the vicinity of dislocations are thought to compete with the centers located in the bulk of the crystal for the mobile defects.

INTRODUCTION

IT has been known for some time that when NaCl and KCl crystals are irradiated with ionizing irradiation at room temperature the resultant growth of

the F band absorption occurs in two stages[1-3] During the first stage the increase in the absorption is rapid, while in the second stage the increase is much slower. (It has recently been shown[4,5] that when alkali halides

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[1] E. Goldstein, Z. Instrumenkunde **16**, 211 (1896).
[2] H. V. Harten, Z. Physik **126**, 619 (1949).
[3] K. Prizibram, *Irradiation Colours and Luminescence* (Pergamon Press, New York, 1956).
[4] H. W. Etzel and J. G. Allard, Phys. Rev. Letters, **2**, 452 (1959).
[5] P. V. Mitchell, D. A. Wiegand, and R. Smoluchowski, Phys. Rev. **117**, 442 (1960).

are irradiated with high-intensity ionizing irradiation a further, third state is observed during which the growth of the F band is again fairly rapid.) Gordon and Nowick[6,7] have suggested that the negative-ion vacancies involved in the formation of F centers during the first stage of coloration may be associated with the presence of impurities in the crystal. These vacancies are considered to exist in vacancy clusters which are located primarily in the bulk of the crystal and are dissolved through the action of the irradiation. Recently Rabin[8] has reported that the expansion of the crystal during the first stage of coloration is much less than that which would result if new vacancies were being formed. This result confirms the idea that during the first stage F centers are formed from vacancies already present in the crystal. Gordon and Nowick[6] also proposed that during the second stage vacancies are formed at dislocations. This proposal was substantiated by the fact that the rate of coloration during this stage is substantially increased by plastic deformation.[7] Seitz[9,10] has proposed that vacancies may be "evaporated" from dislocations when excitons, which are created by the irradiation, expend their energy at dislocation jogs. On the other hand, the process involved in the coloration of alkali halide crystals at low temperatures (e.g., liquid nitrogen or helium temperatures) is apparently different from the room temperature process, since the structure sensitivity and the impurity sensitivity characteristic of the room temperature coloration are not observed.[11,12]

It has also been known for some time that, when alkali halide crystals which have been exposed to ionizing irradiation or which have been additively colored are bleached with F light at room temperature, the F-band absorption decreases in two stages. During the first stage of bleaching the F-band absorption decreases rapidly, while during the second stage the decrease is much slower. Of the many experiments on the bleaching phenomenon, the work of Oberly[13] is particularly noteworthy. Oberly observed the photocurrent produced when x-irradiated KCl and KBr crystals were bleached with F light. He observed that during the first stage of bleaching the photocurrent decreased at a faster rate than the F-band absorption, while during the second stage of bleaching essentially no photocurrent is produced. Oberly proposed that the two stages of bleaching result from the presence of two types of centers whose absorption bands superimpose to yield the F band. One center may be bleached easily with a simultaneous production of a photocurrent, the other does not bleach easily and does not give rise to

photocurrent. Several other theories[10,14,15] have been advanced to account for the two stages of bleaching although no one theory has been able to account for all of the experimental observations.

It is striking that both the coloration and bleaching processes occur in two stages. However, the possibility of an interrelation between these stages has not as yet been explored. If a correspondence between the stages does indeed exist, it may yield further information as to the origin of the stages.

Finally, it has generally been observed that, as the F-band absorption decreases during the two stages of bleaching with F light, the M-band absorption first increases rapidly, and then goes through a maximum and decreases. The R- and N-band absorption are also observed to go through maxima, although these occur at times later than the maximum in the M-band absorption. It is, in fact, generally accepted that as a result of the room temperature bleaching of F centers M, R, and N centers are formed in some successive manner. However, no attempt has been made to find a correlation between the two stages of coloration and bleaching of the F band and the maxima in the growth of M, R, and N bands.

The present investigation attempts to determine whether or not interrelations exist between the stages of coloration and bleaching, and between these stages and the maxima in the growth of the M, R, and N bands. For this purpose a number of samples of KCl, both deformed and undeformed, have been irradiated into either the first or second stage of F-band coloration. Comparatively pure samples, as well as samples doped with divalent cation impurities, have been irradiated in this way. The changes in the absorption at the F, M, R, N, and V_3 bands have then been observed during subsequent bleaching with F light. The investigation is limited entirely to the room temperature coloration and bleaching processes.

EXPERIMENTAL METHODS

Undoped 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. Crystals of KCl with nominal additions to the melt of 0.006 at.% Ca, Cd, and Mn were grown in the laboratory from a reagent grade KCl by a modified Bridgman method. Samples were used either in the as-received condition or were plastically deformed by compressing large blocks of the Harshaw KCl between the jaws of a jeweler's vise, with the entire assembly submerged under water. Individual samples were then cleaved from the large blocks. In this way, samples were obtained with a nominal deformation of 2.5% and 3.2%. All samples were colored by irradiating them with x-rays from a

[6] R. B. Gordon and A. S. Nowick, Phys. Rev. 101, 177 (1956).
[7] A. S. Nowick, Phys. Rev. 111, 16 (1958).
[8] H. Rabin, Phys. Rev. 116, 1381 (1959).
[9] F. Seitz, Phys. Rev. 89, 1299 (1953).
[10] F. Seitz, Revs. Modern Phys. 26, 7 (1954).
[11] H. Rabin and C. C. Klick, Phys. Rev. 117, 1005 (1960).
[12] D. A. Wiegand and R. Smoluchowski, Bull. Am. Phys. Soc. 4, 148 (1959); Phys. Rev. 116, 1069 (1959).
[13] J. J. Oberly, Phys. Rev. 84, 1257 (1951).

[14] E. E. Schneider, Photographic Sensitivity (Butterworths Scientific Publications, Ltd., London, 1951), p. 13.
[15] M. Ueta and W. Känzig, Phys. Rev. 97, 1591 (1955).

copper target operated at 40 kv and 20 ma. The x-rays were filtered through 1.5-mm thick crystals of NaCl, so as to filter out the soft component. The x-ray unit contained voltage and current regulating circuits. In this manner an x-ray beam of approximately constant intensity was obtained, and a measurement of the duration of an irradiation was used to indicate the amount of x-ray exposure. 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. The irradiation was performed under ambient conditions in the dark. Actually the method of using the irradiation time as a measure of exposure gave rise to a small error in the determination of the rate of coloration of the crystals. This error comes about through the change in coloration rate with temperature fluctuations of the ambient. It was also found that the rate of coloration was influenced by the number of interruptions for absorption measurements. Apparently a small component of the coloration is thermally bleached during the room temperature absorption measurements. The total error in the absorption coefficient arising from these sources is estimated to be less than 0.01 mm^{-1}.

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 mμ to 1075 mμ. 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 ± 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 ± 0.05.

Optical bleaching was accomplished in the spectrophotometer with the variable slit set at 2 mm, and the wavelength set at 560 mμ (F light). Under these conditions the spectral band width of the bleaching light was approximately 100 mμ.

EXPERIMENTAL RESULTS

1. X-Ray Coloration

The x-ray irradiation of the various KCl crystals, as described in the previous section, was interrupted periodically and the optical absorption was measured over the spectral range of 200 mμ to 1075 mμ. The F band was the most prominent of the various absorption bands which were observed. On the red side of the F band the M, R_1, R_2, and N bands were observed with descending magnitudes in the order named. On the blue side of the F band, the K band was observed
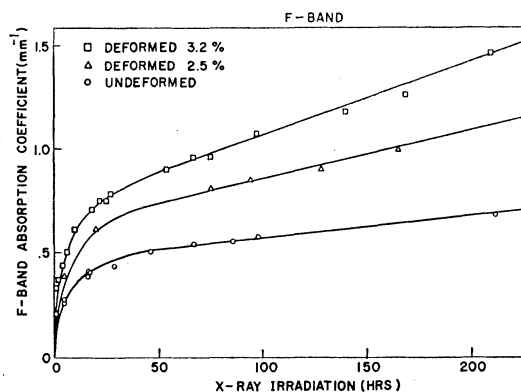

FIG. 1. Absorption at the peak of the F band ($\lambda=560$ mμ) as a function of irradiation with filtered x-rays, and as a function of plastic deformation.

usually only after prolonged periods of x-irradiation. In the ultraviolet a sharp, prominent band appeared with a maximum at 215 mμ. This coincides with the position of the usually observed V_3 band. As had been expected,[16] filtered x irradiation did not produce an observable V_2 band ($\lambda=230$ mμ). In addition to the V_3 band, two unidentified, minor absorption bands were observed at 260 mμ and at 330 mμ.

The growth of the F band during x irradiation in undeformed and deformed Harshaw KCl is shown in Fig. 1. The initial stage of rapid growth, in the undeformed samples, is assumed to cease at a value of 0.5 mm^{-1} for the F-band absorption coefficient. This absorption is equivalent to a F-center concentration of about 3×10^{16} cm^{-3} on the basis of Smakula's formula,[17] and an assumed value of 0.81 for the F-center oscillator strength. In the underformed samples the first stage is followed by a second stage during which a small, but finite, rate of growth is observed. The rate of growth of the F band during the first stage in deformed samples appears to be somewhat enhanced over that of the undeformed samples. However, during the second stage of irradiation, a considerably enhanced rate of growth occurs and no tendency toward a decrease in the growth rate is observed below 1.0×10^{17} cm^{-3}. It may be seen that 3.2% deformation increases the rate of growth of F centers during the second stage by a factor of 4 over that of undeformed crystals. These results agree qualitatively with those obtained for the growth of F centers during irradiation with γ rays.[7]

It was found that small additions of $CaCl_2$ to KCl markedly increases the amount of first stage coloration of the F band over that observed in Harshaw KCl. On the other hand, it was found that $CdCl_2$ and $MnCl_2$ are much less effective than $CaCl_2$ in enhancing the early coloration rate. In this respect the present results are in agreement with those of Etzel.[18] It should be

[16] R. Casler, P. Pringsheim, and P. Yuster, J. Chem. Phys. 18, 1564 (1950).
[17] A. Smakula, Z. Physik 59, 603 (1930).
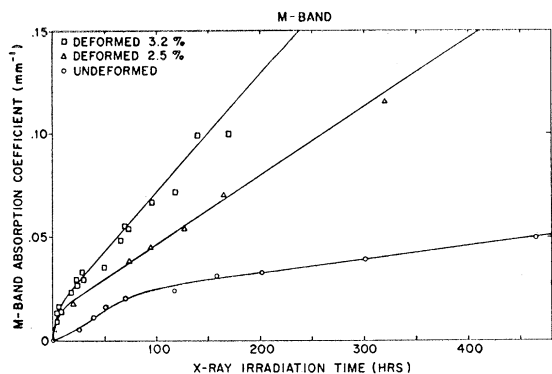[18] H. W. Etzel, Phys. Rev. 87, 906 (1952).

FIG. 2. Absorption at the peak of the M band ($\lambda = 830$ mμ) as a function of irradiation with filtered x-rays, and as a function of plastic deformation.

pointed out, however, that the concentration of impurity ions actually in the crystal varies depending on the particular impurity. This occurs because the fraction of impurity ions in the melt to that dissolved in the crystal is different for each impurity. Too much significance should not, therefore, be given to the relative enhancement of the first stage by the impurities. The transition period between the first and second stage of coloration in the doped samples (equivalent to the period of 10 hr to about 40 hr of irradiation in Fig. 1 for Harshaw KCl) occurs at longer times in the doped crystals than in the Harshaw crystals. After the

transition period, however, the rate of coloration of the F band is essentially the same for undoped and doped crystals. This is shown in Table I which lists the average rate of coloration of the various crystals in the interval between 100 hr and 300 hr of irradiation. It should be noted that the slopes of the growth curves during the second stage are the same for the Ca doped crystal and the Harshaw crystal, even though the F-band absorption, α_F, in the doped sample was about 2.5 mm^{-1} in contrast to about 0.6 mm^{-1} in the Harshaw crystal.

Apparently the addition to KCl of these divalent positive impurity ions primarily affects only the first stage of coloration. This result is in accord with the proposal of Schulman[19] that impurities influence the concentration of negative ion vacancies present in the crystal prior to irradiation, although how this is accomplished by divalent positive impurities is not clear.

Two stage coloration is also indicated in the growth of the M-, R_2-, and V_3-band absorptions. The general characteristics as well as the duration of the two stages correspond directly with the respective stages of the F-band coloration. The growth curves for the M band are shown in Fig. 2. It should be noted that the M-band absorption is approximately one order of magnitude less than that of the F absorption. This fact, plus the fact that the absorption measurements were conducted at room temperature, accounts for the larger scatter in the data. Figure 2 shows that the rate of growth of M
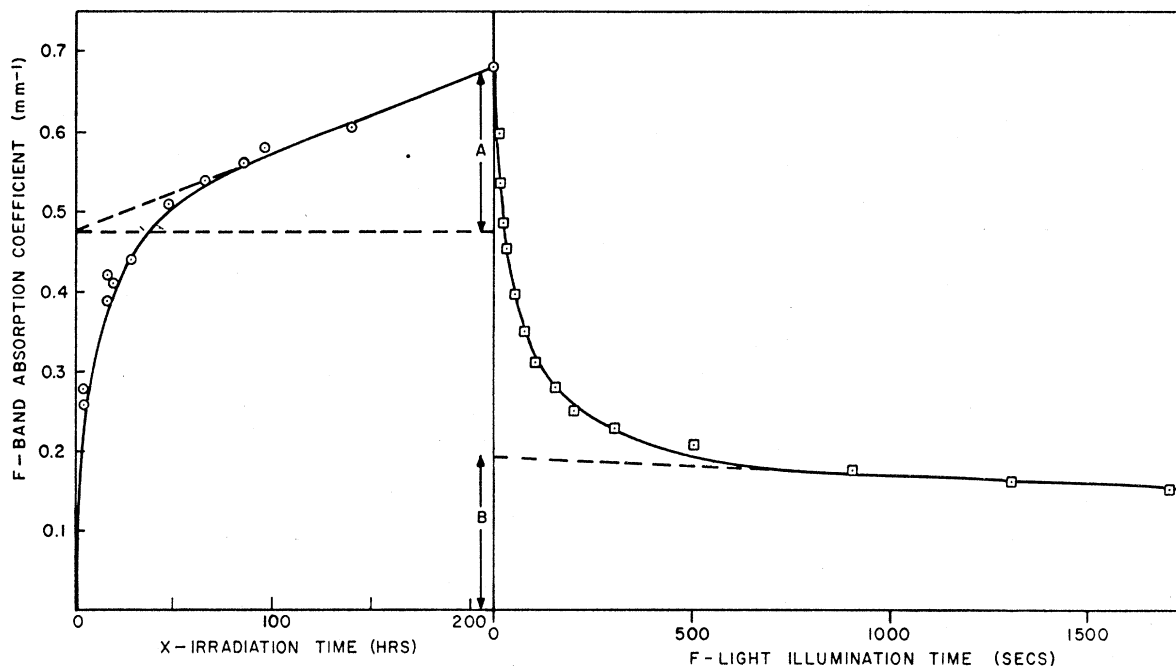

FIG. 3. Absorption at the peak of the F band for a typical crystal during x-ray irradiation and subsequent illumination with F light. The dotted lines indicate the method used to estimate the change in absorption during the second stage of coloration (A) and the second stage of bleaching (B).

[19] J. H. Schulman, J. Phys. Chem. **57**, 749 (1953).

centers during the first stage is somewhat less for the undeformed samples than for the deformed samples. Although the scatter in this region is considerable, the predominant number of data points (not all shown in Fig. 2) indicate that compared to F centers, M centers are formed very slowly during the first stage of irradiation in undeformed crystals. Plastic deformation greatly enhances the rate of second stage coloration to an even greater extent than for the F band. It may be seen that 3.2% deformation increases the rate of second stage growth of the M band by a factor of 8.5 over the rate in the undeformed crystal.

The scatter in the data makes it impossible to discern whether a difference exists between deformed and undeformed crystals in the first-stage growth rate for the R_2 and V_3 bands. However, a real difference is easily observed in these rates during the second stage of coloration. A deformation of 3.2% increases the second stage growth rate by factors of about 10 and 5.5, for the R_2 and V_3 band, respectively.

2. Correlation Between Stages of Coloration and Bleaching

The method used in the comparison between the growth and bleaching of the F band is most easily illustrated with the aid of Fig. 3. The left side of this figure shows the growth of the absorption at the maximum of the F band during irradiation of a typical Harshaw KCl crystal, and the right side of the figure indicates the decrease of the absorption during subsequent bleaching with F light. As a rough approximation, the growth of the F band during the second stage of coloration is assumed to be linear. The quantity A in Fig. 3 is the F-band absorption attributed to the second stage process and is the difference between the final absorption attained and a linear extrapolation of the long-time irradiation data backwards to zero time. Similarly, the absorption change during the second stage of bleaching is roughly obtained by linearly extrapolating backwards to zero time the long-time

TABLE I. Rate of increase of the F-band absorption coefficient during the second stage of coloration of Harshaw and doped KCl crystals.

Crystal	F band growth rate (mm^{-1}/hr of irradiation)
Undeformed Harshaw KCl	1.26×10^{-3}
KCl+0.006 at.% Ca	1.27×10^{-3}
KCl+0.006 at.% Cd	1.25×10^{-3}
KCl+0.006 at.% Mn	1.3×10^{-3}

bleaching data (the quantity B in Fig. 3). The absorption changes obtained in this way[20] for the two stages of coloration and for the two stages of bleaching are given in Table II for all of the Harshaw KCl crystals which were examined, deformed as well as undeformed.

It is apparent from Table II that a relationship does exist between the stages of coloration and bleaching. Namely, the change in the F-band absorption during the first stage of coloration approximately equals that during the first stage of bleaching, and consequently the absorption change during the second stage of coloration is of the same order as that during the second stage of bleaching. It is noteworthy, however, that when the second stage of coloration is very small then the second stage of bleaching is larger than it should be (see crystals 1, 2, 3, 4, and 7). This point will be discussed later.

Measurements were also made of the dependence of the initial bleaching rate on the F-band absorption prior to bleaching (α_{F0}). In Fig. 4 the results are shown for both the undeformed and deformed Harshaw KCl crystals. In this graph the average initial rate of bleaching is given in terms of the change in the F-band absorption during the first twenty seconds of bleaching. It will be observed that the initial bleaching rate increases proportionally to α_{F0} in crystals which have been irradiated only into the first stage of coloration ($\alpha_{F0} < 0.5$ mm^{-1}). However, the curve breaks sharply for samples irradiated into the second stage of coloration. From Fig. 4 it may be seen that the magnitude of

TABLE II. Changes in the F-band absorption during the stages of coloration and bleaching of Harshaw KCl crystals.

Crystal	Deformation	Irradiation stage	Prior to bleaching	1st stage coloration	1st stage bleaching	2nd stage coloration	2nd stage bleaching
				F-band absorption coefficient (mm^{-1})			
1	Undef.	First	0.25	0.25	0.24	0.002	0.01
2	Undef.	First	0.27	0.27	0.24	0.002	0.02
3	Undef.	First	0.42	0.42	0.38	0.004	0.04
4	Undef.	First	0.39	0.39	0.36	0.004	0.03
5	Undef.	Second	0.68	0.48	0.48	0.20	0.20
6	Undef.	Second	0.97	0.47	0.57	0.50	0.40
7	Def. 3.2%	First	0.38	0.38	0.35	0.002	0.03
8	Def. 2.5%	Second	0.90	0.64	0.60	0.26	0.30
9	Def. 3.2%	Second	1.46	0.75	0.70	0.71	0.76

[20] An exponential extrapolation of the long-time second stage data backwards to zero time was attempted, but it was found impossible to fit the second stage data to an exponential function. Since no other simple function could be found, it was decided to retain, as a first approximation, the method of linear extrapolation, even though it is doubtful that the second stage processes are exactly linear with time of irradiation and bleaching.

TABLE III. Changes in the F-band absorption during the stages of coloration and bleaching of KCl crystals doped with Ca.

Crystal	Nominal impurity content	Irrad. stage	F-band absorption coefficient (mm^{-1})				
			Prior to bleaching	1st stage coloration	1st stage bleaching	2nd stage coloration	2nd stage bleaching
10	0.006 at.% Ca	First	0.41	0.40	0.37	0.01	0.04
11	0.006 at.% Ca	First	0.66	0.64	0.58	0.02	0.08
12	0.006 at.% Ca	First	0.99	0.95	0.84	0.04	0.15
13	0.006 at.% Ca	Second	2.76	2.36	1.72	0.40	1.04

the bleaching rate for crystals irradiated well into the second stage is either equal to or slightly less than the bleaching rate for crystals which have been irradiated just to the end of the first stage of coloration. This result is observed in both undeformed and deformed crystals of Harshaw KCl, although the initial bleaching rate for the deformed crystals is consistently observed to be somewhat higher than that of the undeformed samples irradiated to the same α_{F0}.

It was necessary to check whether the decrease of the F band during the second stage of bleaching occurred as a primary result of the F light illumination, or merely represented the thermal bleaching of the F band. Accordingly, undeformed and deformed crystals were optically bleached to the beginning of the second stage, and then allowed to bleach thermally (in the dark) at room temperature. The observed rate of decrease of the F band was about one order of magnitude less than that during optical bleaching for the same standing time.

When the crystals, which had been doped with divalent positive ions were bleached with F light, the equalities which had been obtained for the Harshaw crystals between the stages of coloration and bleaching were no longer observed, when the same linear extrapolation used for the Harshaw crystals were applied. The observed deviations occur such that the absorption change of the F band during the second stage of bleaching is somewhat greater than that observed during the second stage of coloration. These deviations from equality are similar to those observed for lightly irradiated Harshaw crystals. The results for the Ca doped crystals are given in Table III.
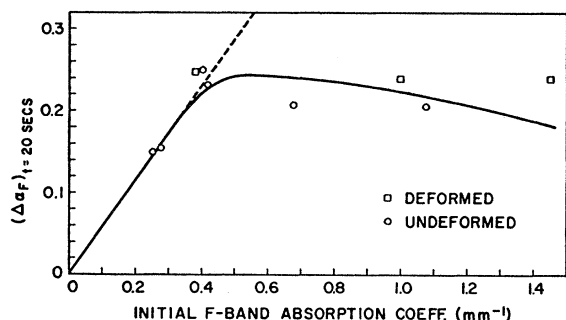

FIG. 4. The change in absorption at the peak of the F band during the first twenty seconds of illumination with F light as a function of the F band absorption prior to bleaching.

A second effect of additions of Ca is to increase the rate of initial bleaching over that of Harshaw KCl. This result is shown in Fig. 5 in which the change in the absorption at the F band $(\alpha_{F0}-\alpha_F)$ during bleaching is plotted for a Ca doped sample and a Harshaw sample each of which had been irradiated to about the same α_{F0} of 0.41 mm^{-1}. The initial bleaching rate for the sample doped with about 0.006 at.% Ca is approximately twice that of the Harshaw KCl. This result agrees with the observation by Kawamura and Okura[21] that in additively colored KCl the stability of the F band to bleaching with F light is increased when KCl crystals are purified by recrystallization. It is interesting to speculate that whatever is the phenomenon which makes Ca doped samples color more rapidly than purer crystals also makes them bleach more rapidly.

3. The Maximum in the M-Band Absorption

The maximum, which occurs in the absorption at the M band during the bleaching of the F band with F light, was observed in all of the samples. It is now found that the time to reach the maximum and the magnitude of the absorption at the maximum is related to the amount of prior x-ray irradiation. In Fig. 6 the absorption changes observed during bleaching at the F, M, R_2, and V_3 bands are plotted for three typical samples. The samples used for Fig. 6 had been x irradiated to either the saturation of the first stage of coloration $(\alpha_{F0}\approx0.5$ mm$^{-1})$ or well into the second stage. It can be observed that, as α_{F0} increases, the time to reach the maximum in the M-band absorption increases, and also the magnitude at the maximum increases. This variation in the maximum is replotted in greater detail in Fig. 7. Apparently the shape of the maximum also depends on α_{F0}. From Figs. 6 and 7 it can be seen that the time over which the maximum occurs increases with α_{F0}. After the period of relatively rapid decrease of the M band which occurs immediately after the maximum, a stage is reached during which the M band decreases at a very slow rate (see Fig. 6). The beginning of this stage corresponds roughly with the period during which the F band starts to decrease very slowly. In the following analysis of the data on the M band the period of the rapid growth and relatively rapid decrease of the M band is discussed first.

[21] H. Kawamura and H. Okura, J. Phys. Chem. Solids 8, 161 (1959).

The maximum in the M-band absorption can be discussed in terms of a competing M-band growth process and a concurrent M-band bleaching process. On the basis that M centers are formed from F centers during bleaching, and from the fact that the initial rate of F-band bleaching is essentially the same for all samples irradiated into the second stage (Fig. 4), a single monotonic growth function for the M band may be expected to exist. Confirmation of this prediction is given in Table IV which shows that, for samples irradiated to $\alpha_{F0} \geq 0.45$ mm^{-1}, the average rate of growth of the M band during the first 25 sec of bleaching is essentially independent of α_{F0} for second stage irradiated samples. As can readily be seen in Fig. 7, for bleaching times greater than 25 sec the net rate of growth of the M band differs between the three samples shown. This can, however, be understood in terms of the onset of the bleaching process for the M band.

If for all second stage samples the growth of the M band is essentially described by the same monotonically increasing function, then the change in the time of occurrence of the maximum with α_{F0} can only be explained if the bleaching rate of the M band, near the maximum, decreases with increasing coloration. It is now possible to successfully explain why the magnitude of the maximum in the M-band absorption increases with increasing irradiation. Namely, for highly irradiated samples the bleaching process does not set in until relatively later times and thereby gives the growth process a chance to reach higher levels.

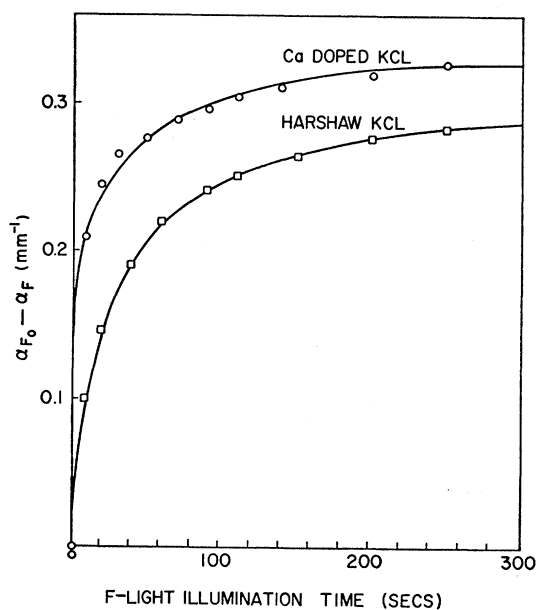Figures 8 and 9 show the effects of plastic deformation on the M-band bleaching rate. In Fig. 8 it is shown that

the M-band bleaching rate near the maximum is considerably greater in a deformed sample than in an undeformed sample irradiated to the same α_{F0}. However, if a comparison is made between the M-band bleaching
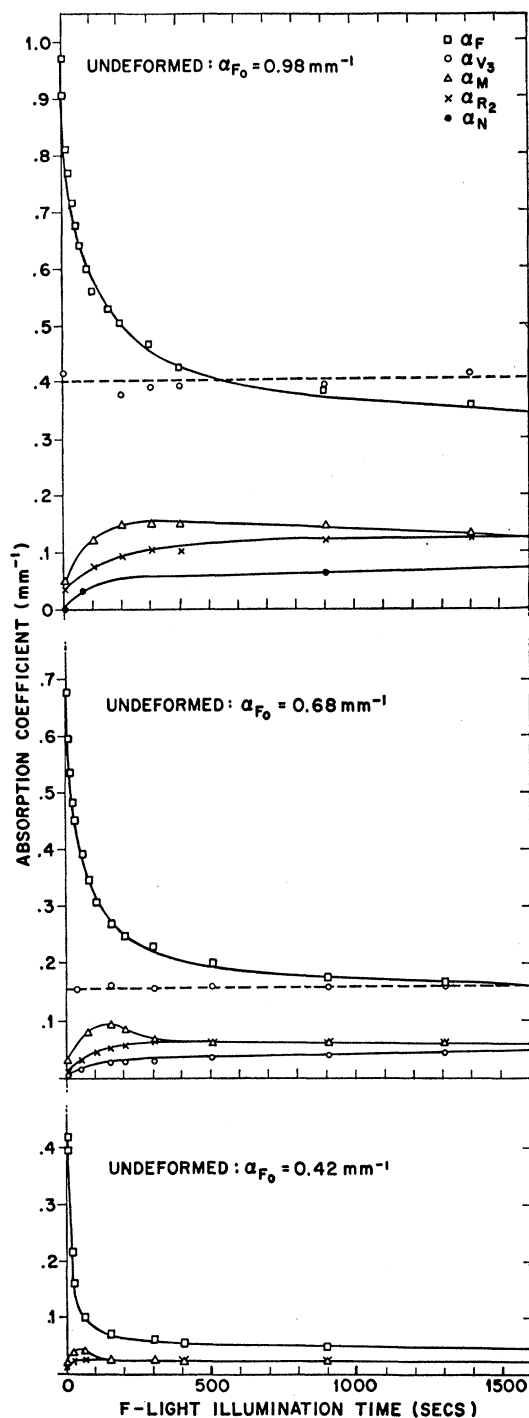

FIG. 5. Comparison of the initial bleaching rate between a Ca doped KCl sample and a Harshaw KCl sample which had been x irradiated to the same initial F band absorption (α_{F0}). The bleaching of F centers is given in terms of the difference between α_{F0} and the F band absorption α_F at any time during bleaching.

FIG. 6. Change in the peak absorption at F, M, R_2, N, and V_3 bands as a function of bleaching with F light. The bleaching behavior of these bands is shown for three undeformed samples of varying initial F band absorption (α_{F0}).
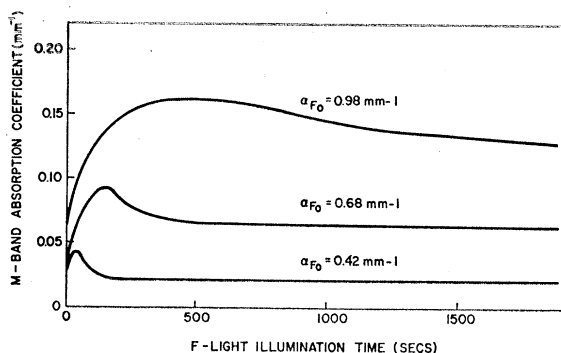
Fig. 7. Enlarged plot of the maximum in the M band absorption observed during bleaching in the three samples shown in Fig. 6.

rates in samples having the same total time of x-irradiation (see Fig. 9) then it is found that the bleaching rate in the vicinity of the maximum is greater for an undeformed sample than for a deformed sample.

Immediately after the relatively rapid rate of bleaching of the M band, that is, just at the beginning of the stage during which the M- and F-band bleach very slowly (see, e.g., Fig. 6, bottom curve, $t>150$ sec), the ratio of the F-band absorption to the M-band absorption is observed to be 2.5 ± 0.3 for all of the samples tested. This ratio is, however, not maintained during subsequent bleaching, and it reaches values as low as 2.0 in some samples after long periods of bleaching of the order of 4000 sec.

4. R, N, and V_3 Bands During Bleaching with F Light

The maxima in the R_1, R_2, and N band absorptions vary with α_{F0} in a way similar to that of the M band, that is, the maxima in the absorption of these bands occur at later bleaching times, and with a higher absorption, the greater the amount of coloration. This result may be observed, to some extent, in Fig. 7. In contrast, the absorption at the V_3 band (the only prominent V band observed) remained essentially constant or increased slightly during the bleaching process. Apparently, the room temperature, optical bleaching process in crystals irradiated with hard x rays does not involve the annihilation of holes at V centers. Instead bleaching occurs primarily through the formation of higher electron centers such as M, R, and N centers.[22]

DISCUSSION

1. The Two Stages of Coloration and Bleaching

The work of Nowick[7] has shown that during the second stage of coloration F centers are probably formed at dislocations, possibly by the Seitz[9] mechanism. This conclusion was based in part on the observa-

tion that the rate of formation of the F band during the second stage of coloration is enhanced by plastic deformation. In the present experiment it is observed that the secondary electron centers such as M, R, and N centers are formed primarily during the second stage of coloration. Furthermore, the rate of formation of these centers is substantially enhanced by plastic deformation. From this evidence one is led to conclude that the formation of vacancies at dislocations involves not only the generation of single vacancies, but also the generation of complex aggregates of vacancies so that M, R, and N centers are also formed. Seitz[10] has estimated that the most mobile vacancy configurations may migrate as far as 40 A away from their dislocation source during the x irradiation. Presumably, this applies to positive-ion vacancies (energy of migration, ϵ_m, of about 0.8 ev in KCl[23]), positive and negative ion pairs (ϵ_m of about 0.4 ev[24]), and to a limited extent to negative ion vacancies (ϵ_m of about 1.25 ev[25]). It is doubtful, however, that the more complex, relatively immobile centers such as M, R, and N possess sufficient energy to migrate over appreciable distances away from the source dislocation. It is then possible to construct the following tentative picture of the coloration process. F centers are the predominant centers which are formed during the first stage of coloration. The results of Gordon and Nowick[6,7] and of Rabin[8] suggest that during this stage F centers are formed in the bulk of the crystal through the dissolution of negative ion vacancies from vacancy clusters which existed in the crystal prior to irradiation. In contrast, during the second stage of coloration both single vacancies and vacancy aggregates are formed at dislocations. It is very likely that some of the F centers and most of the secondary electron centers which are formed remain in the vicinity of the dislocations.

If, indeed, the environment of the centers formed during the second stage of coloration differs from those formed during the first stage, then one might expect that their bleaching characteristics may be different. The most striking result of the present experiment is that in Harshaw KCl crystals the absorption change

Table IV. Average growth of the M band during the first twenty-five seconds of bleaching with F light as a function of the initial F-band absorption.

Crystal	Initial F-band absorption (mm⁻¹)	Change in M-band absorption in first 25 sec of bleaching (mm⁻¹)
3	0.42	0.023
4	0.39	0.023
5	0.68	0.025
6	0.97	0.022

[22] W. E. Bron and A. S. Nowick, Phys. Rev. 119, 114 (1960).

[23] H. Kelting and H. Witt, Z. Physik 126, 697 (1949).
[24] G. J. Dienes, J. Chem. Phys. 16, 620 (1948).
[25] J. A. Morrison and R. Rudham, J. Phys. Chem Solids 6, 402 (1958).

$(\Delta\alpha_F)$ at the F band during the rapid first stage of coloration approximately equals $\Delta\alpha_F$ during the rapid first stage of bleaching, and consequently that $\Delta\alpha_F$ during the relatively slow second stage of coloration is of the same order as $\Delta\alpha_F$ during the relatively slow second stage of bleaching. Furthermore, the initial rate of bleaching of the F band is proportional to the initial F-band absorption (α_{F0}) for crystals irradiated into the first stage of coloration, whereas for crystals irradiated into the second stage of coloration the initial rate of bleaching is essentially constant and about equal to the bleaching rate in crystals irradiated to the saturation of the first stage. These results strongly suggest that the F centers formed in the bulk of the crystal during the first stage of coloration are the centers which are eliminated during the first stage of bleaching, and that the centers formed at dislocations during the second stage of coloration are much more resistant to bleaching by F light. This interpretation is similar to the suggestion of Oberly[13] that the center responsible for the first stage of bleaching is different from that responsible for second stage of bleaching. The interpretation further suggests that the difference in the centers results from the difference in their environment. It will be convenient to refer to the centers produced during the second stage of coloration as "second stage centers", and to reserve the name "F center" for the center involved in the first stage of coloration and bleaching.

The results obtained with doped crystals seem at first hand to be contrary to those obtained from Harshaw crystals. In the doped samples (see Table III) the absorption change at the F band during the second stage of bleaching was observed to be somewhat greater than that during the second stage of coloration. Even in these crystals, however, the magnitude of the absorption change during the second stage of bleaching is more closely related to the amount of second stage coloration than to the total amount of coloration. This may be seen by comparing the four Ca doped crystals
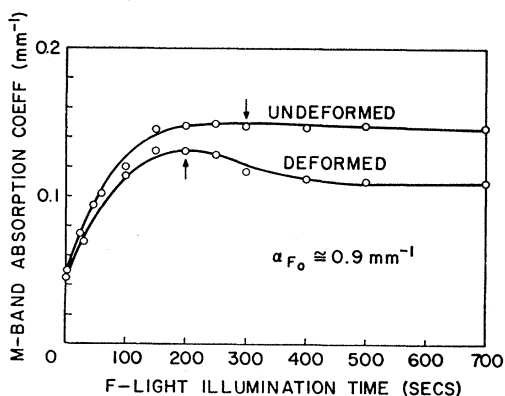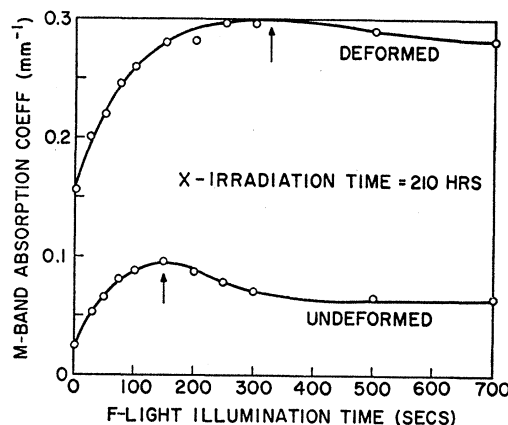

FIG. 9. A comparison of the maximum in the M band absorption observed during bleaching between an undeformed and a deformed sample which have been x irradiated for the same period of time. The arrows indicate the position of the maximum.

(10 through 13) in Table III. In these samples the initial absorption varies as roughly $2:3:5:14$, whereas the absorption change during the second stage of coloration varies as roughly $1:2:4:40$ and that during the second stage of bleaching as $1:2:4:26$. These results can be explained if it is assumed that during the first stage of bleaching a fraction of F centers (presumable those which are nearest to dislocations) are converted to second stage centers. Therefore, whenever the first stage of coloration is much greater than the second stage of coloration, the second stage centers formed from the conversion of F centers become a large percentage of the total number of second stage centers. It is, indeed, shown in Table III that as the ratio of the first to second stage coloration increases, the ratio of the absorption changes during the second stage of bleaching to that during the second stage of coloration also tends to increase. This explanation should also account for the presence of a second stage of bleaching in very lightly irradiated samples (see crystals 1, 2, 3, 4 and 7, Table II) and in additively colored samples (see for example reference 15 and Petroff[26]).

Further experimental results which show a difference in the bleaching behavior between the first and second stage centers have been obtained by observing the effect on the bleaching rate of the F band caused by varying the intensity of the bleaching light through a range from 1×10^{14} to 7.4×10^{14} photons/sec cm^2. It has recently been shown[27] that for samples irradiated to near the saturation of the first stage of coloration that the rate of bleaching of F centers during the first stage of bleaching is dependent on the intensity of the bleaching light. In the paper immediately following this one, it is shown that in contrast to the first stage of bleaching the bleaching rate during the second stage is con-

FIG. 8. A comparison of the maximum in the M band absorption observed during bleaching between an undeformed and a deformed sample which have been x irradiated to the same initial F band absorption. The arrows indicate the position of the maximum.

[26] St. Petroff, Z. Physik 127, 443 (1950).
[27] W. E. Bron and W. R. Heller, Bull. Am. Phys. Soc. 5, 185 (1960).

stant within the entire range of intensities. This last result is shown to be consistant with the idea that the centers formed during the second stage of coloration exist in close vicinity of each other.

If the second stage center is an F center, one would expect that its configuration and optical absorption would be modified relative to that of the first stage F center because of the marked difference in their environments. It is, of course, also possible that the absorption at the F band during the second stage is not due to F centers, but rather to one or more excited states of another center.

Several previous investigations have yielded evidence that absorption bands other than that of the normal F center may exist under the F band. Of these the earliest work is that of Petroff[26] who observed that a second absorption band (B band) appeared under the high-energy side of the F band when additively colored KCl crystals were optically bleached at room temperature. Petroff's experiment was repeated in greater detail by Konitzer and Markham[28] who confirm the earlier results and show that the B-band maximum occurs at about 2.33 ev while that of the F band occurs at 2.30 ev at liquid nitrogen temperature. Petroff, and more recently Lüty,[29] have shown that another band, the A band, exists on the lower energy side of the F band. The A band appeared during the optical bleaching of KCl at temperatures in the vicinity of $-30°C$, but was not easily observed at room temperature. Unfortunately, the room temperature absorption measurements of the present experiment were not able to resolve the B and F bands. It is, therefore, not possible to determine from the present results which, if any, of these bands is responsible for the absorption at 560 mμ during the second stage of bleaching.

Even more pertinent evidence for a submerged band under the F band is obtained from the recent series of experiments on the dichroism of alkali halide crystals.[30–34] Briefly, these experiments have shown that when samples containing only F centers are illuminated at liquid nitrogen temperatures with polarized F light the transmission and the luminescence of the sample remains isotropic. When samples containing both F and M centers are illuminated in the same way, both the F and M absorptions and emission become dichroic. Since the concentration of F and M centers does not change during the illumination, the observed dichroism of the M band must occur by an acutal reorientation of some of these centers at this low temperature.

Van Doorn[31] has proposed that the dichrosim of the

M band under F-light illumination can be explained if the M center possesses higher excited states whose absorption bands are underneath the F band. Pick[35] and van Doorn and Haven[31,36] have proposed that two such excited states of the M center should exist if the M center is composed of two F centers joined as nearest neighbors. This model of the M center is also shown to possess the required optical anisotropy. If the transitions to the two excited states are responsible for the absorption observed at the F-band region during the second stage of bleaching, then one would expect that the ratio of the absorption at the F band to that of the M band would be a constant. In the present experiment this ratio was observed to decrease from values near 2.5 to values near 2.0 during the second stage. It is possible, however, that a small component of the first stage F-center absorption exists during the second stage and that the measured absorption is the sum of this band plus that of the bands of the two excited M-center states. It is hoped that very careful absorption measurements at liquid nitrogen temperatures, which are capable of resolving these bands will help to decide this point.

Lambe and Compton[32] as a result of their experiments on dichroism proposed the following alternative interpretation. A mechanism exists by which excited F centers can transfer energy to M centers in such a way as to cause emission from the M center. This transfer mechanism may be a modified resonance transfer or a sensitized luminescence process. In addition, it is suggested that the observed dichroism of the F-band results from the ability of M centers to act on F centers located in their vicinity, in such a manner as to impart an anisotropy to the F center. This may be accomplished by interactions of nonisotropic electric or strain fields associated with M centers. It was pointed out that these interactions between F and M centers are possible only if these centers exist in very close proximity to each other. It has already been shown in the present paper that F centers modified in this way may be the source of the second stage of bleaching. Since the modified F centers should bleach essentially independently of M centers, a constant ratio of the F-band absorption to that at the M band need not be expected. It is, however, difficult to understand why the ratio of the absorptions should be so nearly the same in deformed and undeformed samples irradiated to greatly differing amounts. Furthermore, the model of Lambe and Compton does not explain how excitation with F light causes the necessary reorientation of M centers at low temperatures in order to produce dichroism. A possible *ad hoc* explanation is that the M center is able to reorientate by utilizing the energy that the F center loses through phonon emission, i.e., through a local heating of the lattice.[32]

[28] J. D. Konitzer and J. J. Markham, Phys. Rev. **107**, 685 (1957).

[29] F. Lüty, paper presented at the International Symposium on Color Centers in Alkali Halides, Oregon, 1959 (unpublished).

[30] C. Z. van Doorn and Y. Haven, Phys. Rev. **100**, 753 (1955).

[31] C. Z. van Doorn, Philips Research Repts. **12**, 309 (1957).

[32] S. Lambe and W. D. Compton, Phys. Rev. **106**, 684 (1957).

[33] H. Kansaki, Phys. Rev. **110**, 1063 (1958).

[34] G. Kuwabara and A. Misu, J. Phys. Soc. (Japan) **13**, 1066 (1958); **13**, 1038 (1958).

[35] H. Pick, Z. Physik **159**, 69 (1960).

[36] C. Z. van Doorn and Y. Haven, Philips Research Repts. **11**, 479 (1956).

In conclusion, the present experiment supports the ideas obtained from other investigations that there is a real difference between first stage and second stage centers. By relating the second stage of bleaching to the second stage of coloration, the present work shows that the second stage centers are located in the vicinity of dislocations and interact closely with one another.

2. The Maximum in α_M

In the section on Experimental Results it has been shown that the maximum in the absorption at the M band (α_M), which occurs during bleaching with F light, may be regarded as a superposition of a growth process and a bleaching process. The growth curve is shown to be the same for all samples irradiated into the second stage of coloration. In contrast, the bleaching behavior is shown to depend on the amount of irradiation. In a recent paper Bron and Nowick[22] have shown that the first stage of bleaching of the F band is itself a superposition of two bleaching processes, an initial rapidly decaying temperature-independent process[37] plus a temperature dependent process. The latter process is controlled by the motion of some mobile defect, possibly vacancy pairs and it is observed to occur with an activation energy of about 0.35 ev. The mobile defects are assumed to be produced through the dissolution of vacancy clusters which occurs when such a cluster captures photoelectrons. The bleaching of F centers is thought to occur when the mobile defects join F centers or negative-ion vacancies and form other electron centers such as M, R, and N centers. As the number of the secondary electron centers increases, the rate at which a mobile defect meets these centers should also increase. The eventual net bleaching of M centers can then be understood if such an encounter results in a permanent change in the M center to some higher electron center. Such a process can then account for the bleaching of the M center by F light. In a similar way R and N centers may also undergo bleaching. All of these centers, F, M, R, and N, which exist in the bulk of the crystal accordingly compete for the capture of the mobile defect. Vacancies and vacancy clusters formed at dislocations during the second stage of coloration also should compete with the first stage (bulk) centers for the available mobile defects. The

effect of the presence of secondary centers on the bleaching of M centers should best be observed when the number of F centers becomes relatively small. This should be the case after the maximum in α_M. On the basis of this argument one would then expect in heavily irradiated samples that the bleaching rate of the M band in the vicinity of the maximum should be relatively slow, since in these samples the concentration of second stage centers is high. As shown in Figs. 6 and 7 this prediction is indeed confirmed experimentally.

A further test of this hypothesis can be made by comparing the rate of bleaching of M centers in undeformed and deformed samples which have been irradiated for the same period of time (Fig. 9). In the deformed sample the concentration of second stage defects per unit volume of the crystal will be higher than in the undeformed sample. The rate of bleaching of M centers should, therefore, be lower in the deformed than in the undeformed samples. This prediction is in agreement with Fig. 9. A comparison cannot as easily be made for the bleaching rate of M centers in deformed and undeformed samples which have been given the same amount of second stage x irradiation. In this case the concentration of second stage defects should be approximately the same in each sample, and therefore the bleaching rate of M centers should be same. Actually, the bleaching rate is observed to be considerably lower in the undeformed sample which had to be irradiated for a longer period of time than the deformed sample (see Fig. 8). To be consistent with the present interpretation one is led to postulate that certain types of second stage defect configurations, obtained only after long periods of x irradiations, are more effective than others in trapping the mobile defects. The present experiment does not yield any further information on this last point. It is, however, interesting to note that Ingham[38] has reached a similar conclusion from the results of an experiment on changes in ionic conductivity during x irradiation.

[37] The paper immediately following this paper describes an experiment involving the temperature independent process.

[38] H. S. Ingham, Jr. and R. Smoluchowski, Phys. Rev. 117, 1207 (1960).