Conversion of F_3^+ Centers and Destruction of R Centers in LiF with R Light*†

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R_1 and R_2 bleaches of irradiated LiF near 300°K have revealed the existence of a new color center whose main absorption band covers the region of the R_1 and R_2 bands. The new center is not related to any of the known color centers, and facilitates the conversion of F_3^+ centers into R centers according to the mechanism $F_3^+ + e \rightarrow R$, where the electron is provided by the photo-ionization of the new color center by the R bleach. Simultaneously, but at a slower rate, the R bleach also destroys the R centers by two concurrent mechanisms: (a) decomposition of an R center into an M center and an F center, and (b) conversion of an R center into another color center whose absorption band (550 mμ) is in the N-band region. If an N band in LiF is to be identified with the 550-mμ band, the present work favors a rearranged F_3 model for the N center over the current Pick model of an F_4 complex.

I. INTRODUCTION

SINGLE crystals of LiF, when exposed to ionizing radiation at room temperature, develop stable F, M, F_3^+, and R (color) centers.[1-7] The peak of the large F-center band is near 245 mμ.[8] The van Doorn model of the R center consists of an equilateral triangular array of three nearest-neighbor F centers lying in a {111} plane.[9] Considerable support of this F_3 model of the R center has been reported, including studies on polarized luminescence,[10] polarized bleaching,[11] radiation equilibria,[12] and discrete phonon line absorption.[13,14] The R center possesses several electronic states, and thus its absorption spectrum displays several absorption bands corresponding to transitions to excited levels. In LiF, the peaks of the two principal bands, called the R_1 and R_2 bands, are at 313 and 378 mμ, respectively.[15] Another band (R_N) resulting from a lower energy transi-

tion of the R center has recently been reported by the present authors.[16]

The M center, consisting of a pair of adjacent F centers,[17] has its principal band near 445 mμ. Under the M band there is a weak band whose peak is almost coincident with that of the M band. This weaker band is ascribed to the F_3^+ center,[7,18] an ionized R center. Although the half-width of this band is 0.318 eV while that of the M band is 0.19 eV,[7] the weaker band is often masked by the more intense M band. However, the existence of F_3^+ centers in irradiated LiF can be demonstrated and investigated by measuring the luminescence induced with an M light excitation.[19] The observed spectrum of the luminescence exhibits two prominent emission bands. When the spectral response of the detector is linearized, the peak of one band is near 540 mμ and that of the other near 670 mμ.[4,18,20] The 540-mμ emission band has been assigned to the F_3^+ center,[7,18] while the 670-mμ emission band is tentatively assigned to the M center.[4] This latter assignment, however, does not seem to be well established, since there has been a claim that another weak band underlying the large M band may be responsible for all or part of the 670-mμ emission band.[7] In any case, the 540-mμ emission band facilitates the investigation of the F_3^+ center under the controlled optical treatments employed in this work.

The present paper presents experimental evidence indicating that F_3^+ centers can be transformed into R centers by means of R bleach, and that simultaneously, but at a slower rate, R bleach also destroys R centers. Therefore, the concentration of R centers with time of

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R bleach can be represented by a consecutive photo-chemical reaction of the form

$$F_3^+ + e \rightarrow R \rightarrow \text{products of destruction.} \quad (1)$$
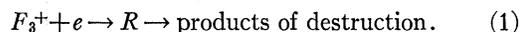
Section II contains the experimental procedure. The results and discussion pertaining to the transformation of F_3^+ centers into R centers, the first reaction of Eq. (1), are given in Sec. III. In Sec. IV the results of the optical destruction of R centers, the second reaction of Eq. (1), are given and then discussed. Finally, a conclusion is drawn in Sec. V.

II. EXPERIMENTAL PROCEDURE

Single crystals of LiF were purchased from Harshaw Chemical Co., Cleveland, Ohio. Samples approximately $10 \times 7 \times 1$ mm^3 were cleaved along the cubic axes and subsequently irradiated at room temperature with γ rays for doses of from 1 to 100 MR. The absorption spectra were recorded either with a Bausch & Lomb model 505 or a Cary model 14R spectrophotometer. For measurements above room temperature a high-temperature cell was constructed which could hold the sample at a constant temperature ($\pm 1°$K) of $300°$–$675°$K. For measurements down to $77°$K, a miniature Joule-Thomson refrigeration system (Cryo-Tip, model AC-1-110) purchased from Air Products and Chemical, Inc., Allentown, Pa., was used. Both cells could be rotated $90°$ such that the sample could be alternated between the bleaching light and the measuring beam of the spectrophotometer.

The concentration of R centers was conveniently measured by the peak height of the R_2 band for the following two reasons. First, the R_1 and R_2 bands arise from transitions of the same center and thus retain a constant relative peak-height ratio. Secondly, the R_1 band was somewhat masked by the low-energy side of the intense F band. Usually the F-center concentration was so large that accurate measurements of the F band could not be made.

As discussed in the Introduction, the concentration of F_3^+ centers was measured in terms of the emission band of the F_3^+ centers. The emission spectra were obtained using a Cary model 14 R in the transmission mode. The excitation source was a 150-W tungsten lamp in conjunction with an interference filter with λ_0 at 435 mμ and a bandwidth of 10 mμ.

In order to observe possible generation of free electrons by bleaching with R light, photoconductivity measurements were taken. These were made by placing the sample between two electrodes, one a small copper plate and the other a nickel screen, in series with a 300-V dc potential difference. The exciting light entered through the screen and produced a current of the order of 10^{-13} A. The current was measured with an electrometer (General Radio Company type 1230-A) using an input resistance of 10^{10} Ω.

The R light used for the bleaching was obtained from a 1000 W dc Hg-Xe arc in conjunction with a grating monochromator. For R_1 bleach the monochromator was set at 313 mμ with a slit width of 10 mμ. For R_2 bleach the monochromator was set at 365 mμ with a slit width of 20 mμ. The larger slit width in the latter case was used to gain intensity since the rates of the reactions induced by R_2 bleach were considerably slower than those induced by R_1 bleach.

III. CONVERSION OF F_3^+ CENTERS

Figure 1 illustrates the effect on both (a) the emission and (b) the absorption spectra of an irradiated sample of LiF with increasing time of R_1 bleach. It is seen that after a slight initial increase, the R bands (measured by the peak height of the R_2 band) slowly decrease and are completely destroyed after 25 min. The peak height of the M band increases slowly and saturates at about a 15% increase when the R centers are destroyed. It appears that the 670-mμ emission band increases slightly, but small changes in this band are difficult to measure accurately due to the overlap of the 540-mμ emission band. The early stages of R_2 bleach (365 mμ) also reveals a rapid partial decrease of the 540-mμ emission band and a slight increase of R centers. Thus using either R_1 or R_2 light, the behavior of the R bands and the 540-mμ emission band during the early stages of bleaching is the same: The R bands increase slightly and the 540-mμ emission band decreases to about half its initial intensity. Since the 540-mμ emission band is due to the F_3^+ center, this suggests that during the early stages of bleaching, F_3^+ centers are converted into R centers.

Concurrently with observing changes induced in the emission and absorption spectra, photoconductivity
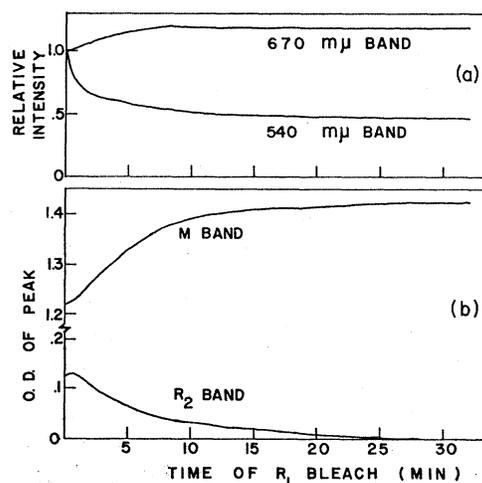
FIG. 1. Variation in emission and absorption peaks of a γ-irradiated (40 MR) sample of LiF with R_1 bleach near $300°$K: (a) emission due to M-light (435 mμ) excitation; (b) absorption.

measurements were taken. Using either R_1 or R_2 light as the source of excitation, a photocurrent was observed. Moreover, this photocurrent decreased rapidly with time of R bleach. The decay in the photocurrent followed the decrease of the 540-mμ emission band. It ceased when the 540-mμ emission band ceased decreasing. These measurements indicate the generation of free electrons by the R bleach, which participate in the conversion of F_3^+ centers into R centers during the early stages of R bleach. The fact that the photocurrent ceased early in the bleaching process while a considerable concentration of R centers still remained is consistent with the reported observation that R centers are not photo-ionized by R light.[7] Thus the free electrons must originate from the photo-ionization of a new kind of color centers (designated X for convenience), whose main absorption band (the X band) lies in the region covering the two R bands.

Additional supporting evidence on the conversion of F^{3+} centers into R centers by means of the X center can be obtained from studying the kinetics of the decrease of F_3^+ centers. The reaction, the first reaction of Eq. (1), would be expected to be governed by an equation for a second-order process:

$$d[F_3^+]/dt = -k[F_3^+][e],\qquad(2)$$

where $[F_3^+]$ and $[e]$ are the concentrations of F_3^+ centers and electrons, respectively, present at time t. If the electrons are furnished by the photo-ionization of the X centers, the concentration of X centers would be expected to be described by a first-order reaction:

$$[X] = [X]_0 e^{-k_2 t},\qquad(3)$$

where $[X_0]$ is the initial concentration. The concentration of electrons present at time t is then taken to be

$$[e] = \gamma[X] = \gamma[X]_0 e^{-k_2 t},\qquad(4)$$

where γ is a proportionality factor. From Eqs. (2) and (4) one obtains

$$\ln\frac{[F_3^+]}{[F_3^+]_0} = 2.303\ \log_{10}\frac{[F_3^+]}{[F_3^+]_0} = \frac{k_1}{k_2}(e^{-k_2 t}-1),\qquad(5)$$

where $k_1 \equiv k\gamma[X]_0$ and $[F_3^+]_0$ is the initial concentration of F^{3+} centers. Thus Eq. (5) indicates that a plot of $\log_{10}[F_3^+]$ against $e^{-k_2 t}$ should be linear, the slope being $k_1/2.303k_2$. Let $[F_3^+]_\infty$ be the concentration of F_{3+} centers in the limit as $t \to \infty$, or $e^{-k_2 t} \to 0$. In the sample used for R_1 bleach, 48% of the F_3^+ centers remained even after prolonged bleach, and thus $[F_3^+]_\infty/[F_3^+]_0 = 0.48$. For convenience, the initial concentration $[F_3^+]_0$ is normalized to unity. Then the concentration of F_3^+ centers decreased from 1 to 0.48. The "theoretical" plot (using the observed value of $[F_3^+]_\infty$) of Eq. (5) is shown by the straight line in Fig. 2(a). In the sample used for R_2 bleach, 37% of the F_3^+ centers remained for $t \to \infty$. The theoretical plot in this case is shown by
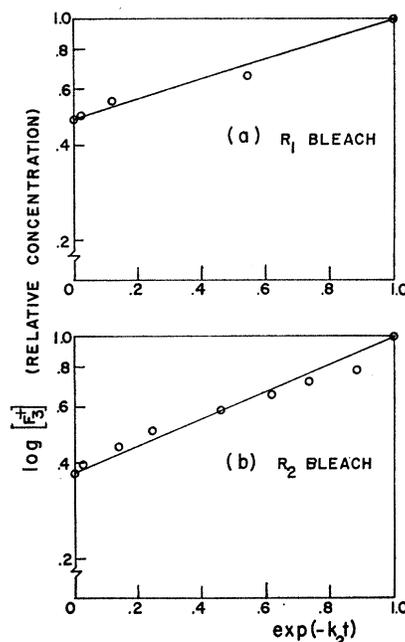
FIG. 2. Plot of $\log_{10}[F_3^+]$ against $e^{-k_2 t}$, where t is the time of R bleach. The straight lines represent a theoretical plot of Eq. (5), while the circles are experimental points for (a) R_1 bleach ($k_2 = 0.3$), and (b) R_2 bleach ($k_2 = 0.06$).

the straight line in Fig. 2(b). Since the experimental data on $\log_{10}[F_3^+]$ are taken as a function of time t, the comparison of the experimental data with the theoretical straight line can be made by searching for an optimum value of k_2. The best fit was obtained using $k_2 = 0.3$ for the case of R_1 bleach, and $k_2 = 0.06$ for the case of R_2 bleach. The results are illustrated by the circles of Fig. 2. Note that the above procedure is based on several simplifying assumptions: (a) The intensity of the 540-mμ emission band is proportional to the concentration of F_3^+ centers; (b) the intensity of the bleaching light is constant and uniform throughout the sample; (c) the proportionality factor γ remains constant; (d) the X center is destroyed by a first-order reaction; and (e) all the photoelectrons released are captured by F_3^+ centers. Considering these simplifications, the agreement between experiment and theory is considered satisfactory.

In order to consolidate further the existence of this new X band, changes in the absorption spectrum during the early stages of the bleaching were more carefully examined by means of a "difference" spectrum. This is obtained by placing an identical irradiated crystal in the reference beam of the spectrophotometer. Using this difference spectrum, small changes induced by short periods of bleaching are no longer masked by the large absorption bands, but appear as deviations from a "flat" spectrum of zero optical density. A difference spectrum obtained after 15 sec of R_1 bleach is illustrated by the solid curve in Fig. 3. Similar results have also been obtained by means of R_2 bleach. Three points of

interest should be mentioned in connection with the solid curve (difference spectrum) of Fig. 3. First, the relatively large dip below zero in the region 300–330 mμ indicates a decrease in the corresponding region of the absorption spectrum (not the difference spectrum) during the early stage of R_1 bleach. The maximum dip region does not belong properly to either the R_1 band or the R_2 band. Second, the region of the R_N band has increased, indicating an increase of the R center concentration. This should account for the two "peaks" near the centers of the R_1 and R_2 bands. Third, in the region of the M band, there is a positive peak and two negative dips. The former is located at the center of the M band. This pattern can be most easily accounted for as a result of two simultaneous, but distinct, changes: an increase in the M-band absorption, and a decrease in the F_3^+ absorption. These observations are consistent with the proposed mechanism for the participation of the X center in the conversion of F_3^+ centers into R centers. The broken curves in Fig. 3 represent a graphical decomposition of the solid curve consistent with the proposed conversion mechanism operating in the early stages of R bleach. It shows that the new X band is fairly broad.

The X band is not present in *unirradiated* samples, but appears when samples obtained from different manufacturers are irradiated with x rays, γ rays, or neutrons. This indicates that the X band is a general characteristic of LiF irradiated at room temperature and not something particular to a few samples. It is not a transition associated with either the M center or the R center, since these increase, not decrease, during the early stages of R bleach. It is unlikely that the X band is a transition associated with the F_3^+ center, since the conversion ceased while nearly half of the F_3^+ centers still remained. Thus the broad X band is ap-
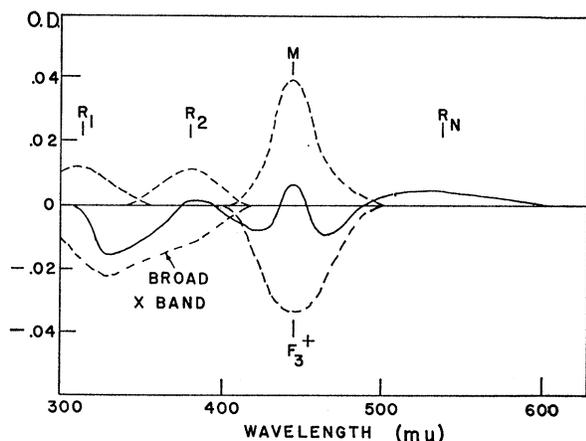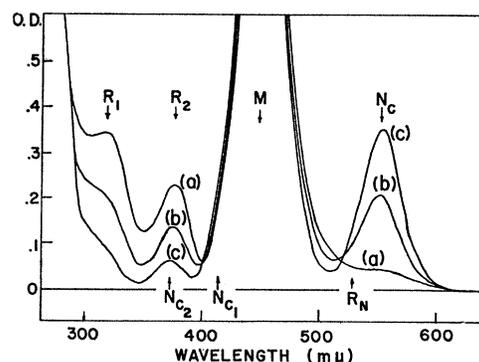
FIG. 4. Absorption spectrum of γ-irradiated (100 MR) LiF at room temperature (a) before R_2 bleach, (b) after 13 min of R_2 bleach, and (c) after 33 min of R_2 bleach.

parently not associated with any of these centers currently known to exist in the irradiated sample. However, no definitive model of the X center is easily available at the moment. This is mainly due to the very small concentration of the X center and its thermal instability above room temperature.

IV. DESTRUCTION OF R CENTERS

A. R_2 Bleach

Figure 4 illustrates the absorption spectrum of an irradiated sample of LiF (a) before R_2 bleach, (b) after 13 min of R_2 bleach, and (c) after 33 min of R_2 bleach. No further change was induced by additional bleaching. The decrease of R_1 and R_2 bands and the appearance of a band at 500 mμ are evident. Since the F-aggregate bands on the long-wavelength side of the M band are commonly referred to as N bands, the band at 550 mμ to be discussed in this paper will be designated as the N_c band for convenience and the color center responsible for it as the N_c center. This notation is consistent with that used in an earlier paper by the present authors.[16] This notation, however, does not necessarily imply that the N_c center actually corresponds to Pick's model of N centers. The decrease on the long-wavelength side of the M band (445 mμ) is due to a decrease of the R_N band.[16] This band is due to a low-lying transition of the R center and extends from approximately 480 to 600 mμ. Whenever the N_c band is produced, two smaller bands, one on the short-wavelength side of the M band and the other under the R_2 band, also increase. These are labeled N_{c1} and N_{c2}, respectively, and are tentatively ascribed to higher transitions of the N_c center. The N_{c1} band is masked by the larger M band, but the N_{c2} band was determined to have a peak height $\frac{1}{6}$ that of the N_c band. In contrast, when the R centers are destroyed without the accompanying creation of the N_c band (see Sec. V) neither the N_{c1} nor N_{c2} band appears. The peak of the M band in Fig. 4 extends to an optical density of 2.2. It changed only slightly during the bleaching process. The F band (235 mμ) was too large to observe accurately.

FIG. 3. Difference in the absorption spectrum of a γ-irradiated (100 MR) sample of LiF after 15 sec of R_1 bleach near 300°K. Solid curve is the observed change; broken curves are decompositions into R bands, an underlying broad band, the M band, and the F_3^+ band (see text).

To determine whether the N_c band increased in a direct relation to the decrease of the R bands, a plot of the increase in the optical density (o.d.) of the peak of the N_c band (ΔN_c) versus the decrease in the o.d. of the peak of the R_2 band (ΔR) is shown in Fig. 5. ΔR was measured at the peak of the R_2 band since the R_1 band is rather masked by the much larger F band. The graph is divided into two regions by a broken line: Region A is to the left and region B, as shown, is to the right. Region A represents the first few minutes of bleach. As discussed in Sec. III, during the early stages of bleach, R centers are created due to the conversion of F_3^+ centers as well as destroyed [see, e.g., Fig. 1(b)]. In region B, the creation process [the first reaction of Eq. (1)] has nearly ceased, and the destruction process dominates. It is seen that in region B the relation between ΔR and ΔN_c is linear. This indicates that the growth of the N_c band is directly related to the decay of the R bands. The slope of the linear region in Fig. 5 is 1.25.

When the R_2 bleach is applied at a controlled temperature, above or below room temperature, the N_c band is again produced. The resulting plots of ΔN_c versus ΔR are similar to Fig. 5; however, the slope of the linear portion (region B) decreases as the temperature is increased. This variation of slope with temperature is illustrated in Fig. 6.

The fact that the slope decreases as the temperature increases indicates that for a given number of R centers destroyed, more N_c centers are produced at lower temperatures than at higher temperatures. This suggests that in addition to the $R \rightarrow N_c$ conversion there is at least one other mechanism whereby R_2 bleach destroys R centers.

The existence of simultaneous modes of destruction is illustrated in Fig. 7, where the R_2 bleach is applied at 378°K. The F band was measured by means of a difference spectrum, with the reference sample necessarily at room temperature. The observed change in the F band was not as accurate as those in the R_2, M, or N_c bands and thus is shown by a broken curve. It is seen
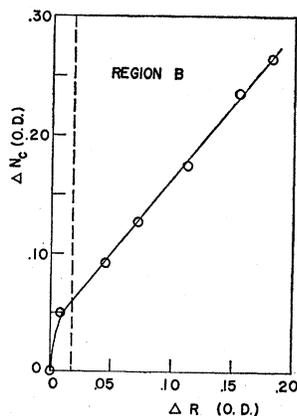
in Fig. 7 that the M, F, and N_c bands all increase in direct relation to the decrease of the R bands. The results therefore indicate that the destruction of R centers by R_2 bleach occurs by two concurrent mechanisms: Qualitatively speaking, (a) an individual R center is destroyed by decomposition into an F center and an M center or (b) it is destroyed by conversion into an N_c center. The latter mode is permanent, that is, no decrease in the N_c band occurs when a bleached sample is stored in the dark at room temperature for several months. The former mode, however, is not entirely permanent, for some regrowth of the R bands and decrease in the M and F bands are observed after storage in the dark for several months. Therefore, the second stage of Eq. (1) is replaced explicitly by a pair of concurrent processes:

$$R \rightarrow F + M, \qquad (6a)$$

$$R \rightarrow N_c. \qquad (6b)$$

The proposed mechanism of Eq. (6) is consistent with
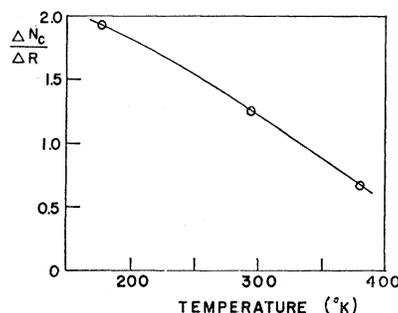
FIG. 6. Dependence of the ratio $\Delta N_c/\Delta R$ with temperature of sample.

the observed kinetics for the R_2 bleach. Let $[R]$ be the concentration of R centers present at time t. The decrease of R centers should be of the first order, since Eq. (6) implies that[21]

$$d[R]/dt = -k_a[R] - k_b[R] = -k[R], \qquad (7)$$

where the specific reaction rate k is the sum of the individual rates. Upon integration, it is seen that a plot of $\ln[R]$ against t should be linear, the slope being equal to $-k$. Using common logarithms, a plot of $\log_{10}[R]$ against t is also linear, the slope being $-k/2.303$.

Note that in studying the kinetics of the R bleach, care must be taken to insure that a constant intensity of light be incident on all parts of the sample. In all cases reported in this work, as the R bleach progresses, the optical density of the R bands gradually decreased since the R centers were gradually being destroyed. Therefore, as the bleach continued, the samples became

FIG. 5. Plot of the increase in the N_c band against the decrease in the R bands. Region B represents the destruction of the R centers.

[21] S. Glasstone, *Textbook of Physical Chemistry* (D. Van Nostrand Co., Inc., New York, 1946), p. 1086.

more transparent to R light, and the intensity of the bleaching light at any given depth in the sample (except the front face) gradually increased. This required a correction factor to be applied to the observed data. This correction factor is derived in the Appendix. In short, it amounts to using an effective time of bleach t', which, except for $t=0$, is slightly less than t. For accurate studies of the kinetics, $\log_{10}[R]$ should be plotted against t' rather than against t. The corrections are small unless the difference in the initial and final optical density at the wavelength of the bleaching light is more than 0.1.

The data, dots and circles, in Fig. 8 represent three sets (a), (b), and (c) of experimental plots of $\log_{10}[R]$ versus t' for R_2 bleach at room temperature. The (a)–(c) sets correspond to different intensities of R_2 light: 2×10^{15} photons/cm^2 sec for set (a) to 1×10^{16} photons/cm^2 sec for set (c). The initial R-center concentrations are normalized to unity, and the first few data points

FIG. 8. Plot of $\log_{10}[R]$ against t' for different intensities of R_2 bleach at room temperatures, where t' is the effective time of R_2 bleach for constant intensity (see text).

FIG. 7. Change in the absorption peaks when R_2 bleach is applied at 378°K.

(for small t') are omitted for reasons discussed following Fig. 5. The straight lines fitting the experimental points are each obtained from Eq. (7) with $k=0.0063$, 0.033, and 0.067, respectively, for the sets (a)–(c). In each case the data points are well represented by a straight line and are thus consistent with Eqs. (6) and (7).

B. R_1 Bleach

The changes induced in the absorption spectrum of an irradiated sample of LiF with time of R_1 bleach at room temperature are illustrated in Fig. 9. The initial o.d. at the peak of the R_2 band was 0.085. The R bands decrease steadily and are completely destroyed after 17 min of bleach for this sample. An experimental plot of $\log_{10}[R]$ against t' is well represented by a straight line, indicating that the destruction of R centers by R_1 bleach is also of the first order. Both the M band and the F band increase steadily until the R centers are destroyed, and then remain constant. The ratio of the increase in

the o.d. of the F band to that of the M band is 7/4, the same as for the case of R_2 bleach in Fig. 7. No formation of N_c centers is observed. This indicates that at room temperature R_1 bleach destroys R centers only by decomposition into F centers and M centers, Eq. (6a). However, when similar R_1 bleach is conducted at 77°K, a large N_c band is produced, and the increase in the F and M bands is small. These results indicate that the destruction of R centers by bleaching with either R_1 or R_2 light occurs by the same two concurrent mechanisms of Eq. (6). However, R_1 bleach differs from R_2 bleach in that the temperature range where each of the two mechanisms is effective differs. For the case of R_2 light (365 mμ) at room temperature, most of the R centers are converted into N_c centers. As the temperature is increased, more of the excited R centers have an energy sufficient to decompose. Using R_1 light (313 mμ), which is 0.56 eV higher in energy than R_2 light, the excited R centers possess sufficient energy to decompose at room temperature. At lower temperatures fewer R centers can decompose, and more are converted into N_c centers.
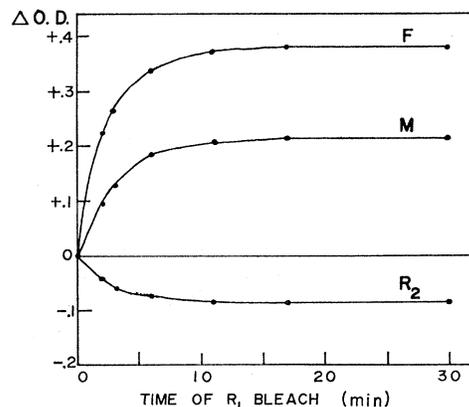
FIG. 9. Change in the absorption peaks when R_1 bleach is applied at room temperature.
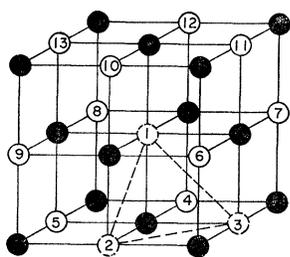
FIG. 10. Schematic diagram of the van Doorn model of the R center in LiF (see text).

The R-to-N_c conversion does not appear to involve any capture of one or more additional defects by the R center. Two major reasons in support of this reasoning may be given. First, such a capture conversion would not yield the observed first-order kinetics but a higher-order kinetics. Second, the location of the N_c band (550 mμ) differs definitely from the locations of known charged R-center configurations such as R^+(458 mμ)[7] or R'(820–960 mμ).[22] Thus, the feasibility of an R center being converted into an N_c center by a rearrangement mechanism is considered.

In order to facilitate the discussion of the rearrangement mechanism, Fig. 10 illustrates the van Doorn model of an R center in LiF. The closed circles represent cations (Li$^+$ ions) and the open circles represent anions (Fl$^-$ ions). The R center is represented by the three broken circles (numbered 1, 2, and 3) lying in a {111} plane and forming an equilateral triangle. Consider the anion sublattice and the F center at site 1. Its nearest neighbors (neglecting the cation sublattice) consist of 12 anion sites (sites 2–13). Of these, two sites (2 and 3) are also occupied by F centers. There are thus 10 sites available for a near-neighbor jump of the F center at 1. When, for example, the ion at site 7 and the F center at site 1 are interchanged, the F center at site 1 is said to jump to site 7.

If the F center at site 1 jumps to one of the sites 8, 10–13, the result is a decomposition of the R center into an M center (2 and 3) separated from an F center. If the F center at site 1 jumps to site 7, the result corresponds to merely another R center. However, if the F center jumps to sites 7 or 9, the result is a new configuration consisting of three F centers forming an isosceles triangle still in a {111} plane. If the F center jumps to sites 4 or 5, the result is a new configuration consisting of three F centers forming a right isosceles triangle in a {100} plane. Thus of the 10 sites available for the F center at site 1, jumping to five of them results in the destruction of the R center by decomposition, jumping to one results in a reorientation only, and jumping to the remaining four results in the destruction of the R center by rearrangement into a new configuration consisting of an isosceles triangle in either a {111} or {100} plane. The same division of possible jumps exists for all three of the F centers comprising the R center regardless of the original orientation of the R center.

[22] A. E. Hughes, Solid State Commun. 4, 337 (1966).

Now when an R center absorbs an "R" photon and is excited, there is a nonzero probability that one of the three F centers comprising the R center will jump to one of those five sites that lead to the destruction of the R center into an M center and an F center. Energy considerations indicate that, at a given temperature, this probability is higher for R_1 light (313 mμ) than for R_2 light (365 mμ) and increases in both cases as the temperature is raised. This is consistent with Eq. (6a) and its observed characteristics. If the energy of the excited R center is not sufficient for this type of jump to occur, it is still possible that the R center may be destroyed by having one of the three F centers jump to one of the four sites, thereby resulting in the rearrangement of the R center in a {111} or a {100} plane. Rearrangement is favored over decomposition at lower temperatures since the decomposition jump is more inhibited energywise at the lower temperatures. This rearrangement mechanism is consistent with the observed properties of Eq. (6b). Thus the N_c center is possibly a rearrangement of the R center into an isosceles triangle in either a {111} or {100} plane.

The N_c band observed in the present work is probably not related to the I band reported by Farge et al.,[23] whose peak absorption at 77°K is at 550 mμ, for at 77°K the peak of the N_c band is shifted to 542 mμ. Moreover, the I band is produced by neutron or heavy electron irradiation at low temperatures, while the N_c band is produced by optical bleach of R centers. The relation of the N_c band to the so-called N bands is uncertain. N bands in LiF have their absorption peaks near 550 mμ.[24–26] Models for these N centers have not been well established, though current Pick's models of the N centers consist of two distinct combinations of four closely associated F centers.[27] They are produced either by prolonged irradiation or by raising the temperature of a moderately colored sample to above 450°K. It is also known that N centers have higher absorption bands (N_R) in the region of the R_1 and R_2 bands,[28] as does the N_c center (see Fig. 4). If an N band near 550 mμ is to be identified with the N_c band observed in the present work, the present work would favor the rearranged F_3 model for the N center over Pick's F_4 model. Note that a similar proposal has recently been made for the N_1 center in KCl.[29]

V. CONCLUSION

R_1 and R_2 bleach of irradiated LiF near 300°K have revealed the existence of a new color center whose main absorption band covers the region of the R_1 and R_2

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[29] I. Schneider and M. N. Kabler, J. Phys. Chem. Solids **27**, 805 (1966).

bands. The new center is apparently not related with any of the known color centers, and facilitates the conversion of F_3^+ centers into R centers according to the mechanism

$$F_3^+ + e \rightarrow R,$$
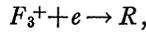
where the electron is provided by the photo-ionization of the new color center by the R bleach. Additional supporting evidence is provided by photoconductivity measurements and reaction-kinetics studies. In addition, the destruction of R centers in LiF by R_1 and R_2 bleach has been found to occur by two concurrent mechanisms: (a) decomposition of an R center into an M center and an F center, and (b) conversion of an R center into another color center whose absorption band (550 mμ) is in the N-band region. This mechanism is governed by a first-order kinetics. This rules out any capture process involving other defects. Relatively speaking, the conversion destruction is more predominant over the decomposition at lower temperatures. If an N band in LiF is to be identified with the 550-mμ band, the present work favors a rearranged F_3 model for the N center over the current Pick's model of an F_4 comples. A discussion based on the van Doorn model of the R center suggests that the color center responsible for the 550-mμ band is a rearrangement of the R center into an isosceles triangle configuration in either a {111} or a {100} plane.

APPENDIX

Equation (7) assumes a constant intensity of light incident on all parts of the system; however, in the experiments reported in this paper the intensity was not constant due to the decrease in the optical density as the reaction proceeded. To determine the necessary correction factor, consider a thin slab of sample at a depth x. Let the intensity of light at the depth x and at time t be $I_x(t)$. I_0 is the intensity incident on the front fact ($x = 0$). I_x is initially less than I_0, but gradually approaches I_0 as t increases, since the sample becomes more transparent as the bleach continues. An effective time of bleach (t'') is now defined for the slab by the relation

$$\text{total flux} = I_0 t'' = \int_0^t I_x(t) dt, \tag{A1}$$

so that the same total flux passes, but the intensity of light at the slab is considered constant and equal to I_0.

For any x, $I_x(t)$ is related to I_0 by the relation

$$I_x(t) = I_0 e^{-\alpha(t)x}, \tag{A2}$$

where $\alpha(t)$ is not constant, but decreases with time of bleach. The explicit form of $\alpha(t)$ is yet to be determined. After substitution, Eq. (A1) takes the form

$$t'' = \int_0^t e^{-\alpha(t)x} dt. \tag{A3}$$

This must be averaged over x and becomes

$$\langle t'' \rangle = t' = \frac{1}{l} \int_0^t \int_0^l e^{-\alpha(t)x} dx dt, \tag{A4}$$

where l is the thickness of the sample. To obtain t', the right side must be integrated, and so an analytic expression for $\alpha(t)$ is needed.

Experimentally, it was found that despite the changes in the internal intensity, a plot of $\log_{10}[R]$ against t was fairly well represented by a straight line. This is because the change in the optical density at the wavelength of the bleaching light was not great (typically 0.2) so that the correction is relatively small (typically 10%). It was therefore assumed that $\alpha(t)$ decayed by first order, so that

$$\alpha(t) = \alpha_0 e^{-\beta t}, \tag{A5}$$

where β is obtained from the best straight line drawn through the experimental points from the plot of $\log_{10}[R]$ against t. Equation (A4) then becomes

$$t' = \frac{1}{l} \int_0^t \int_0^l e^{-\alpha_0 x e^{-\beta t}} dx dt. \tag{A6}$$

For small $\alpha_0 x$ the integrand can be expanded, and integration yields

$$t' = t - \tfrac{1}{2}\alpha_0 l \left(\frac{e^{-\beta t} - 1}{-\beta} \right) + \tfrac{1}{6}\alpha_0^2 l^2 \left(\frac{e^{-2\beta t} - 1}{-2\beta} \right) + \cdots, \tag{A7}$$

where $\alpha_0 l = 2.303$ times the total decrease in the optical density of the sample at the wavelength of the bleaching light (the total decrease in the R bands at 313 or 365 mμ for R_1 and R_2 bleach, respectively). The magnitude of the higher-order terms decrease rapidly, and so only the first two need be retained. Using Eq. (A7), the effective time of bleach t' can easily be obtained from the experimental data.