

Optical Properties of Some F -Aggregate Centers in LiF†

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Detailed studies have been made of the emission and associated excitation and absorption spectra of x-irradiated LiF. By studies of changes in the spectra during periods in the dark and during subsequent re-irradiation, and by use of the Mollwo-Ivey relationships, it has been possible to identify optical bands associated with the F_2^+ and the F_3^+ centers. The F_2^+ center has an absorption band at $645\text{ m}\mu$ and an emission band at $910\text{ m}\mu$, while the F_3^+ center has an absorption band at $458\text{ m}\mu$ and an emission band at $528\text{ m}\mu$. The F_3^+ absorption band ($458\text{ m}\mu$) is one of several bands underlying the M band ($441.2\text{ m}\mu$). It has been possible to induce transformations from the ionized F -aggregate centers to the F -aggregate centers, but it has not been possible to bring about the reverse transformations. The vibrational frequency as determined from the temperature dependence of the half-width of the pure M band was found to be close to the frequencies obtained from other bands. This result suggests that the centers associated with these bands are all interacting with the same normal lattice modes.

I. INTRODUCTION

THE coloration of LiF crystals by ionizing radiation has been extensively investigated by several authors¹⁻⁷ and a survey of coloration studies is given in Refs. 5 and 6. To some extent the identification of the various centers in LiF appears to be uncertain, and it is not possible to compare the F and F -aggregate centers to additively colored and irradiated samples because of the inability to additively color LiF.^{5,6} From the general behavior of the M and R bands in other alkali halides, the currently known assignments for the corresponding bands in LiF were, however, confirmed with a reasonable degree of certainty. Okuda⁴ has identified the R_1 and the R_2 bands as due to two transitions in the same centers. Still another band at $530\text{ m}\mu$ was observed in the present work to be directly related with the R_1 and R_2 bands. The fine structure exhibited for the first time in the R_2 band in LiF,¹ which was then supposed to be a peculiar property of LiF, has been recently found to be a general behavior of R_2 band in other alkali halides.⁸ A quadratic relationship was observed⁹ between the M and F bands in x-rayed LiF, and this seems to be in general agreement with the F_2 model of the M center.

Complications in the M -band absorption have however, been observed.⁵ In particular, the reported values of the position of the maximum of the M absorption

band range from 450 to $460\text{ m}\mu$ and at least two absorption bands were found⁵ to constitute the $450\text{ m}\mu$ band; it was suggested that only one of these is the M band. It is of interest that altogether three emission bands were observed^{4,10-14} due to excitation in the M -absorption region. Of these only one emission band was attributed to the M center. A tabulation summarizing the emission bands obtained by various authors under varying conditions of excitation is given in Ref. 14. The inability to correlate the various observed emission bands with absorption or excitation bands in the M absorption region is further complicated by the fact that the same emission bands can be stimulated by excitation in the R_1 , the R_2 , as well as in the F band.¹⁴ Similar behavior which has already been observed¹⁵⁻¹⁷ in other alkali halides seem to be associated with interactions between the various centers. In an effort to better understand not only the electronic properties of the various centers but also to gain some insight into the possible interactions between centers, a detailed study of x-irradiated LiF crystals has been undertaken. In the following, the emission bands due to excitation in the M region are presented along with their associated excitation and absorption spectra. In particular, the M -band region was analyzed in considerable detail. The results show that none of the emission bands can be directly connected to the M centers, but to other relatively weak absorption bands, usually masked by the stronger M -band absorption. Furthermore, an absorption band at about $458\text{ m}\mu$ underneath the M band and its associated emission band at $528\text{ m}\mu$ appears to be attributed to the F_3^+ center. Studies of the growth and

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decay of the various absorption and emission bands performed under varying conditions indicates simultaneous formation and destruction of some centers during irradiation.

In the course of this work, a pure M band was obtained. The vibrational frequency as determined from the temperature dependence of the half-width was found to be close to a theoretical normal lattice phonon frequency¹⁸ with an energy of 0.031 eV. Furthermore, about the same vibrational frequency was obtained from other excitation and emission bands. Pierce¹⁹ has concluded that in the case of the R_2 band in LiF, the transverse optical phonon with energy of 0.031 eV along [111] is strongly coupled to the R_2 center. Thus, the present results indicate that this may hold also for the M center and other bands in LiF.

II. EXPERIMENTAL

Single crystals of Harshaw LiF were cleaved into plates of dimensions about $1 \times 10 \times 10$ mm. This LiF cleaved very poorly, and was thus presumably very soft. The samples were exposed to x rays from a tungsten target tube operated at 35 kV and 30 mA. The samples were approximately 2.5 in. from the target and the sample temperature was in the vicinity of room temperature unless otherwise indicated. In some cases the irradiation passed through an aluminum window of thickness 0.025 cm. After irradiation absorption, emission and excitation spectra were taken.

Optical-absorption measurements were made at various temperatures between the temperature of liquid-nitrogen and room temperature with a Cary model 14R spectrophotometer. The resolution of the Cary in the range of 0.3 to 1.5 μ was increased by using a higher intensity tungsten lamp. After irradiation, care was taken to avoid exposure of the samples to radiation other than that of the measuring beam. The cryostat used for these measurements has been described elsewhere.²⁰ Temperature measurements were made with a copper-Constantan thermocouple mounted close to the sample on a copper sample holder. A heating coil was used to control the rate of warming.

The experimental arrangement used to obtain the excitation and emission spectra was similar to that described previously.²¹ For excitation measurement monochromatic light was obtained by the use of a Beckman DU monochromator used either with a tungsten lamp or a Hanovia xenon arch lamp for the spectral range below 400 $m\mu$. The radiation emitted from the sample was observed in a direction perpendicular to that of the incident beam. In all cases the monochromator was motor driven. The band pass of the mono-

chromator was approximately constant over any given excitation band and was less than 5 \AA throughout the region from 220 $m\mu$ up to 700 $m\mu$, and was about 50 \AA for the higher wavelength range. The excitation spectra were corrected for equal intensities of the light over the range of a given excitation band. For this purpose the spectral distribution of the intensities of the tungsten light in conjunction with the monochromator were calibrated by an Eppley Golay detector. In order to check the correction for the variation of the intensity of the excitations, spectra were taken point by point with the exciting intensity maintained constant by adjustment of the monochromator slit widths. In all cases appropriate filters were used to isolate a particular emission band while its excitation spectra was being measured.

For the emission measurements a Bausch and Lomb grating monochromator in conjunction with a Hanovia xenon compact 800 W arc lamp was used for excitation. The spectral width of the light beam from the monochromator was about 100 \AA . The emission was analyzed by the use of the Beckman model DU monochromator and the band pass was fixed for optimum resolution consistent with the emitted intensity and the detector sensitivity. The emission spectra were corrected for the spectral response of the detector and monochromator dispersion. Various detectors were used depending upon the spectral location of the emission. A DuMont photomultiplier with a S-13 response was used in the visible range while an RCA 7102 photomultiplier was used in the infrared up to a wavelength of 1 μ . An RCA germanium diode type SQ2516 served as the detector for emission up to 1.7 μ . This diode, however, has sufficient sensitivity in the 0.6 to 1.0 μ range to serve as a check on the RCA photomultiplier and identical results were obtained using both detectors in this wavelength range. In these measurements the detector was mounted at the usual entrance slit of the Beckman monochromator.

III. RESULTS

A. Absorption Measurements

Several weak absorption bands have been reported^{1,5} to decay following prolonged exposure of LiF crystals to x-ray (or electron) irradiation at room temperature. In contrast, the absorption in the M region (the M -band maximum is at about 446 $m\mu$) is increased. This is illustrated by the example of Fig. 1 curve (a), where the absorption spectrum immediately upon termination of the x-ray exposure is given. Curve b was taken 24 h after curve a and during this period, the crystal was held in complete darkness. No further change in the absorption could be detected after another 24-h period. The main change during the period of darkness is an enhancement on the M -absorption region while a broad band at about 630 $m\mu$ disappears. There is also a small decrease of a weak band at 530 $m\mu$ and a small reduction in absorption in the R_1 (315 $m\mu$) and R_2 (375 $m\mu$) bands.

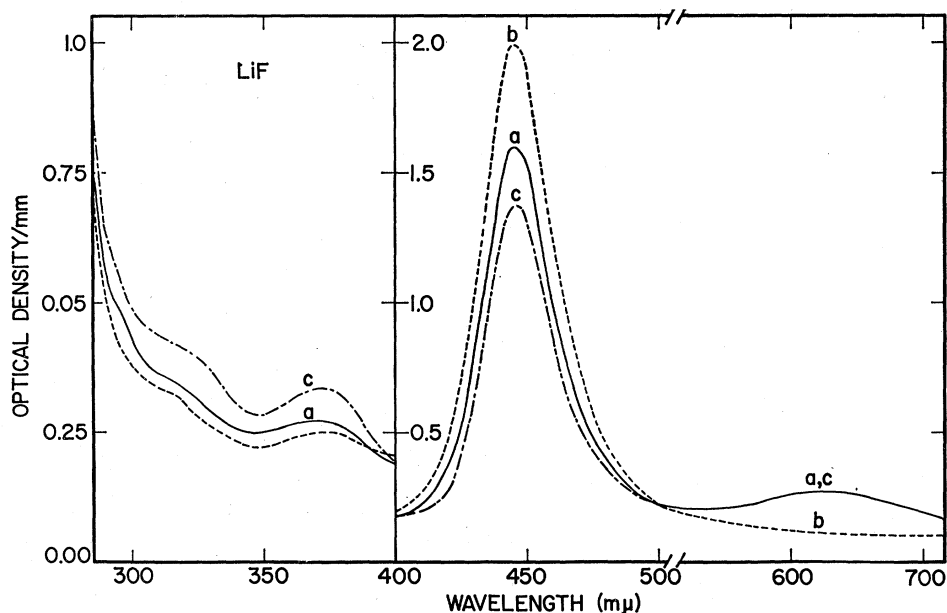
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FIG. 1. Absorption spectra of a LiF crystal x-irradiated at room temperature and recorded for various conditions. Curve (a) immediately after termination of the x-ray exposure; curve (b), after 24 h holding the crystal in the dark; curve (c), sample re-irradiated for 30 sec.

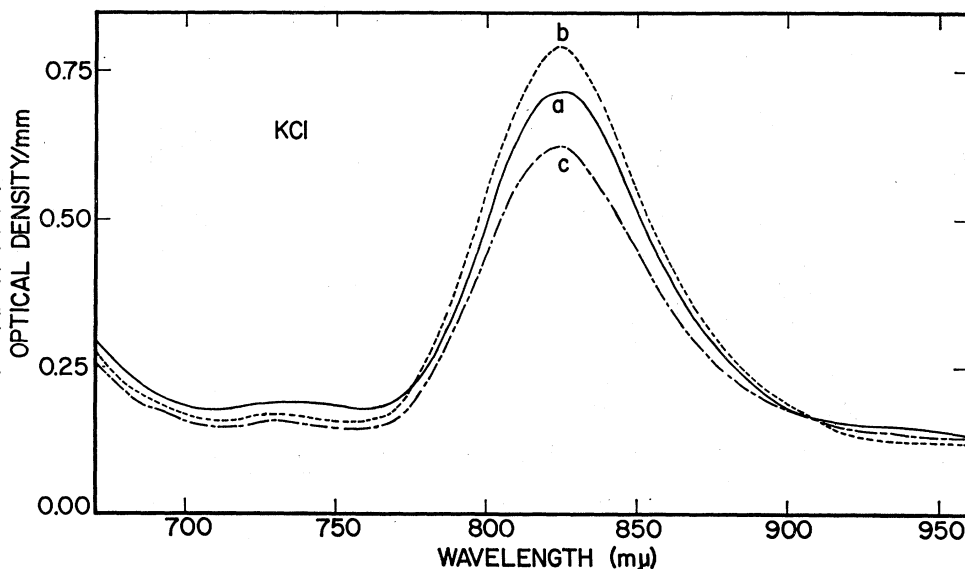


Because of the scale of Fig. 1 the weak bands (e.g., the band at $530\text{ m}\mu$) are not shown distinctly as in the original data. An appreciable decrease was also observed in the $290\text{ m}\mu$ region. Following this extended period in darkness at room temperature, the crystal was re-irradiated for 30 sec and the measured spectrum is given by curve (c) of Fig. 1. It seems that a short re-exposure to x irradiation is sufficient to produce a reversal of the decay during darkness. A considerable decrease in the M -absorption region was observed while the $630\text{ m}\mu$ band was essentially restored to the intensity immediately following cessation of the initial irradiation, curve (a), Fig. 1. The $530\text{-m}\mu$ band increases as did the absorption in the R region. This cycle of events

could be repeated several times and will be treated further and in more detail in connection with similar changes in emission intensities. For future reference it is important to note that the changes in absorption in the M -band region are always greater on the long-wavelength side than on the short wavelength side.

It is of interest that the absorption in the M region of a KCl crystal x irradiated at room temperature was also observed to increase in intensity while the crystal was held in the dark. As illustrated in Fig. 2 curves (a), (b), and (c) show the corresponding spectra as in Fig. 1 but for KCl. In this case however, curve (b) was recorded 4 days after that of curve (a). Enhancement in the M region occurred rather slowly and was accom-

FIG. 2. Absorption spectra of a KCl crystal x-irradiated at room temperature and recorded for various conditions. Curve (a), immediately after termination of the x-ray exposure; curve (b), after four days holding the crystal in the dark; curve (c), sample re-irradiated for 30 sec.



panied by small decreases in the *R* and the *F* band. A broad and weak band at longer wavelengths than the *M* band was also observed to disappear. As for LiF a short irradiation produces a large decrease of the *M* band and a small increase in the bands at longer wavelengths as shown by curve (b). The absorption in the *R* bands, however, decreased with the re-irradiation of the KCl crystals in contrast to the considerable increase observed in the *R* bands of LiF samples.

A detailed study of the differences of absorption spectra in the region of the *M* band due to enhancement in the dark and changes due to the short re-x-irradiation of LiF, indicates a structure of overlapping bands underlying the stronger *M* band. Kaufman and Clark⁵ who took the differences of successive spectra at room temperature only during the growth of the *M* band in the dark have also shown the presence of at least two absorption bands in the *M* region. In an attempt to improve the resolution of the structure in the *M* absorption region, a fresh LiF crystal was irradiated at room temperature, quickly cooled to liquid-nitrogen temperature, so as to quench in the defects giving the absorption bands at room temperature. The absorption spectrum was then measured in the range 0.25–1.0 μ . The crystal was then warmed to room temperature, kept in the dark for several hours, then the absorption spectrum was remeasured at low temperature. The difference in the two spectra in the 400–800 μ is given in Fig. 3(a). The broad band at 630 $m\mu$ as indicated at room temperature (Fig. 1) appears now with a peak at 645 $m\mu$. This shift is probably due to less overlap with a broad band at about 530 $m\mu$. In the remainder of this paper, this absorption band will be called the 645 $m\mu$ band. The absorption difference, curve a of Fig. 3 in the region of the *M* band shows structure which indicates the presence of at least three bands at about 408, 430

and 458 $m\mu$ that do not coincide with the maximum of the *M* band at 441 $m\mu$. The *M*-band half-width and maximum are also given in Fig. 3. Clearly the enhancement in absorption is only in part due to an increase in the *M* band.

It is known that excitation in the *M* band produces a green emission with a peak at 525 $m\mu$ and a red band at about 670 $m\mu$.^{4,10,11} Both bands are treated in Sec. IV in more detail, but for the sake of comparison the excitation spectra are also given in Fig. 3. In each case, a suitable combination of interference and cutoff filters with the band pass covering about half the width of the corresponding emission, was selected for the excitation measurements. Curve *b* shows the excitation for the red emission and curve *c* the excitation for the green emission. The excitation for the green emission was taken in a sample lightly colored such that the optical density at the maximum in the *M* region was 0.05. Measurements indicate that the apparent excitation spectrum is affected by the presence of strong *M* absorption. Both curves were taken at liquid-nitrogen temperature. The main peak at 458 $m\mu$ for the 528- $m\mu$ emission [Fig. 3, curve (c)] is clearly not associated with the *M* band at 441 $m\mu$. In addition the peak at 446 $m\mu$ for the red excitation spectrum [curve (c), Fig. 3], although close to the *M*-band peak, occurs at a slightly longer wavelength. Furthermore, the entire red excitation spectrum does not coincide with the *M* band. This is more clearly shown in Fig. 4, in which curve *a* gives the *M* absorption band, while curves (b) and (c) show again the excitation for the red and green emission, respectively. A band half-width of 0.275 eV was obtained for the red excitation band compared with only 0.134 eV for the *M* band. Both were obtained at liquid-nitrogen temperature. The red excitation [curve (b), Fig. 3] seems to follow the enhancement of the absorp-

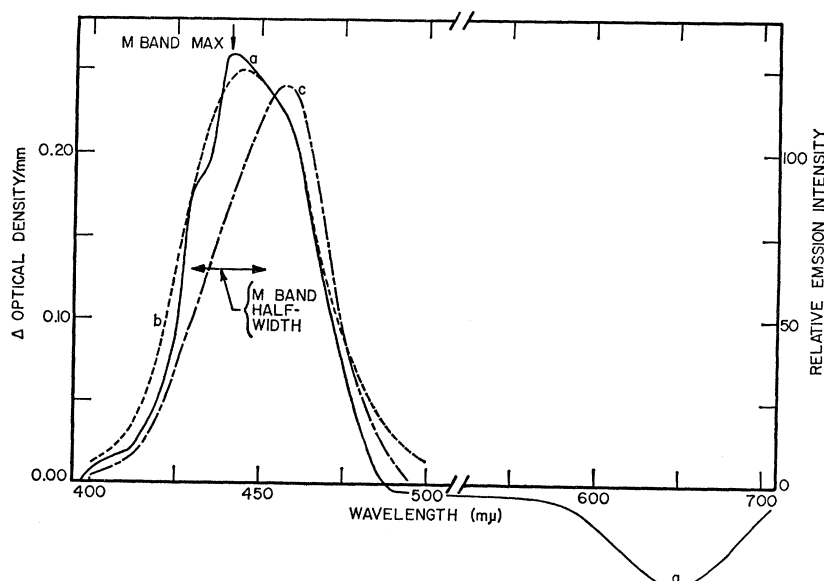


FIG. 3. Typical difference curve of the absorption spectra [curve (a)] as a result of holding the crystal in the dark for about ten hours following the x-ray exposure at room temperature; arrows indicate the peak and half-width of the *M* band. Curves (b) and (c) are the excitation spectra for the 670 and 528- $m\mu$ emission, respectively. All spectra were measured at 77°K.

tion [curve (a), Fig. 3] rather than the M band itself. The maximum at $458\text{ m}\mu$ in the excitation spectrum for the green emission [curve (c), Fig. 3] is observed to correspond in wavelength to an absorption band of the same peak wavelength in the M region.

An additional very weak blue emission (with a peak at about $490\text{ m}\mu$) was also observed upon excitation in the short wavelength tail of the M absorption. This band is very weak, possibly due to re-absorption in the M band. Its excitation spectrum, (not shown in Fig. 3) has a poorly resolved doublet with maxima at about 404 and $410\text{ m}\mu$ at liquid-nitrogen temperature. These two wavelengths are close to the peak wavelength of another absorption band at $408\text{ m}\mu$ in the M -absorption region [curve (a), Fig. 3]. Thus, it appears that the various emission bands obtained upon excitation in the M -absorption region are not directly related to M centers but rather are associated with bands underneath the strong M band. This is further supported by other observations that are presented in the next section.

B. Growth and Decay of the Green Emission and Associated Absorption Band

As expected, simultaneous increases in the green and red emission intensities (the latter will be dealt with elsewhere) due to excitation in the M region, were observed during the *dark enhancement* of the absorption in the M region. This is illustrated in Fig. 5. Curve (a) shows a typical increase in the M -absorption region at room temperature from the increase of the M -band maximum during time in the dark. The crystal in this experiment was exposed to light periodically only during the optical measurements. The decay of the

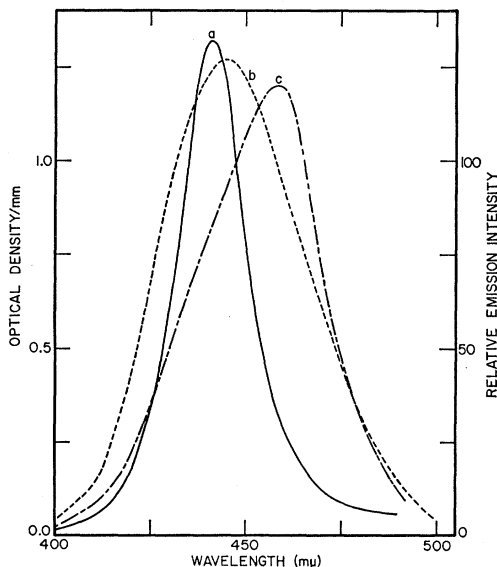


FIG. 4. Comparison of the M band (curve a) at 77°K with the excitation bands (curves b and c) also at 77°K for the 670 and $528\text{-m}\mu$ emission, respectively.

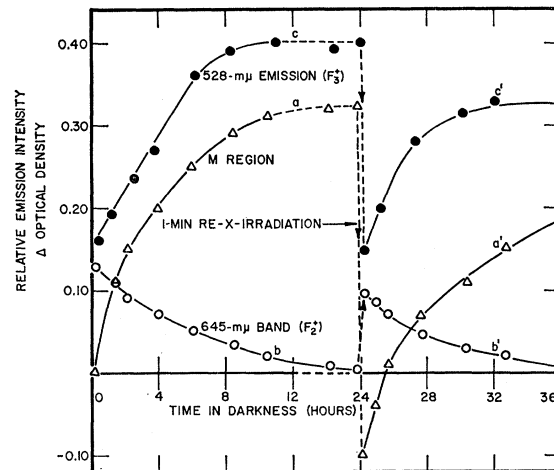


Figure 5

FIG. 5. Growth and decay curves of absorption and emission bands versus time in the dark. Curve (a), the enhancement of absorption in the M region as obtained from the M -band peak; initial optical density of the M band was 1.45 immediately after the x-ray exposure; Curve (b), the decay of the $645\text{-m}\mu$ band and curve c the growth of the green emission band due to excitation at $470\text{ m}\mu$. Curves (a'), (b'), and (c'), the respective regrowth and decay curves after re-irradiation for one minute. Measurements and x irradiation at room temperature.

$645\text{-m}\mu$ absorption band is given by curve (b) and it appears to vanish in the same period of about 16 h during which the enhancement in the M region reaches its saturated value. Curve (c) shows similarly the green emission intensities as a function of time in the dark. These were obtained from the excitation spectra by employing a weak light beam from a monochromator. In other measurements, however, the changes in intensity and the shape of the emission band during the dark period were examined by excitation with monochromatic light at $470\text{ m}\mu$ of higher intensity. No change in the shape of the green emission band was observed and similar variations in intensity as that given by curve (c) were found.

The green emission growth curve of Fig. 5 seems to follow, except at short times, the growth curve (a) for the enhancement in the M absorption. A remarkable increase over 200% of the green emission was obtained during the dark period as shown in Fig. 5, curve (c), compared to an enhancement of less than 20% in the M absorption. The green emission intensity appears, however, to increase with the enhancement of absorption in the M region rather than with the M band itself. This is illustrated by a reversal of the growth and decay processes by a re-irradiation for one minute at the end of a dark period of 24 h. The $645\text{-m}\mu$ band increases almost to its former value; in contrast, the absorption in the M region and the emission intensity reduces to less than their initial values obtained upon termination of the irradiation. The short re-exposure apparently causes a decrease of some of the absorption band produced during the initial x irradiation. The crystal is then

kept in the dark for an additional 22 h and the growth and decay curves (a'), (b'), and (c') are also given in Fig. 5. A second short re-irradiation reverses the growth and decay as at the end of the first dark period. It is clear from the data of the previous section that the enhancement of the absorption during the dark period is due to several bands in the M region and further that the percentage increase in the M band is much less than the percentage increase in these other bands. From Fig. 5, it is also apparent that the percentage increase in the green emission during the dark period and the pronounced reversal of the emission efficiency during re-irradiation are both much greater than the percentage change in the M absorption. These results coupled with the excitation spectra strongly suggest that the green emission is not associated with the M band but with other absorption band masked by the M band, e.g., band at 458 $m\mu$.

Re-irradiation appears to shed some light on the complicated processes involved in the formation and destruction of the various centers during x irradiation at room temperature. The re-irradiation apparently disturbs the static equilibrium existing among the centers after a prolonged period in the dark. This is partly illustrated in Fig. 6, where the effect of re-irradiation at room temperature on various bands is given. This sample is x rayed at room temperature and then kept in the dark for several days until the M band reaches a saturated optical density of 1.57. Curve a shows the change in absorption in the M region upon re-irradiation. Within the first minute, this absorption drops sharply due to the preferential bleaching of bands underneath the M band (See Fig. 12) and as it is evident also from curve (c) of Fig. 6 that a similar drop is observed in the green emission intensity. Further irradiation gives rise to an enhancement in the M -

absorption region. The enhancement in this case seems to be associated primarily with production of new M centers. This was verified by taking difference curves and comparing them with the pure M band. It is also important to note that the 528- $m\mu$ emission intensity remains almost constant during the growth of the M band (see in Fig. 6). This result further indicates that the 528- $m\mu$ emission band is not associated with the M center. It appears then that two processes are involved in the change of the absorption in the M region due to re-irradiation at room temperature. The initial irradiation gives primarily a rapid bleaching, probably by photo-ionization of bands underneath the M band. These bands are formed during the dark period. Longer re-irradiation gives rise to M -center formation. In contrast, the increase in the R_2 band (Fig. 6) within the first minutes is proportional to the decrease of the green emission [curve (b)]. The R_2 band decreases for longer times of re-irradiation. It is not clear whether or not this decrease of the R_2 band is connected directly with the formation of new M centers. Also curve (d) of Fig. 6 shows that the 645- $m\mu$ band increases rapidly within about three minutes to value (0.11 o.d.) found immediately after the previous irradiation and before the prolonged dark period. Further re-irradiation causes a slow increase in this band. Curve (e) of Fig. 6 gives the absorption of the broad band at about 530 $m\mu$. It appears to vary in direct proportion to the R_2 band [curve (c)]. Following the re-irradiation, 40 min in total, the crystal was held in the dark and the changes in each band of Fig. 6 are indicated by the arrows.

The effect of re-irradiation at low temperature on the various bands of a LiF crystal also initially x-rayed and kept at room temperature in the dark for several days is given in Fig. 7. The results appear to be less complicated than when the re-irradiation is performed at

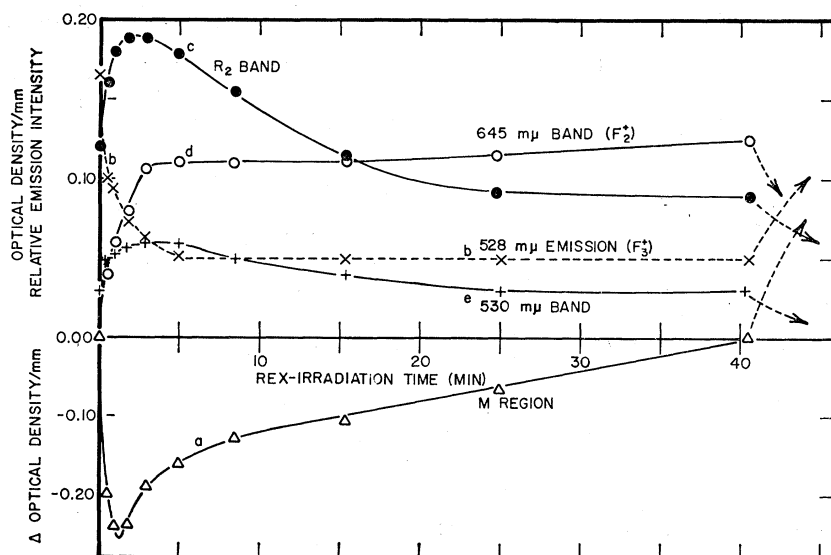


FIG. 6. Variation of various absorption and emission bands as a function of re-irradiation at room temperature of a LiF initially x-rayed and kept in the dark for several days at the same temperature. Curve (a), the change in absorption at the M -band maximum (initial optical density=1.57 after a prolonged dark period). Curve (b), the change of the intensity of the 528- $m\mu$ emission band due to excitation at 470 $m\mu$; curves (c), (d), and (e), the respective changes of the R_2 , 645- and 530- $m\mu$ absorption bands. Arrows indicate the direction of the change of each band in the dark following termination of the re-x exposure (sample thickness—1 mm.).

room temperature. (Fig. 6). The 645- $m\mu$ band is not produced during the re-irradiation at 77°K. Re-irradiation at 77°K resulted in relatively larger decrease in the M region (particularly on the long-wavelength side of the maximum (Fig. 12) than when the sample was re-irradiated at room temperature (Fig. 1). It turns out that this decrease is associated with a more effective bleaching of the 458- $m\mu$ band which lies underneath the M band. There is also a decrease of the 528- $m\mu$ emission band during the re-irradiation [curve (b), Fig. 7] which is proportional to the decrease of absorption in the M region [curve (a), Fig. 7]. Thus the emission disappears entirely and the changes in the M region saturates by irradiation for about 10 min. This suggests that the bleaching of the absorption band at 458 $m\mu$ is completed in this period of 10 min. The pure M band thus obtained,

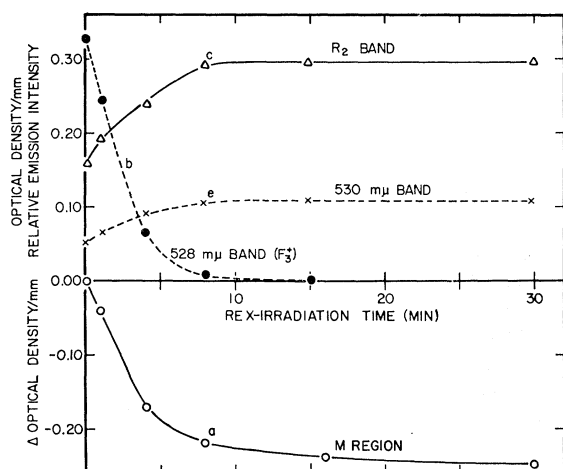


FIG. 7. Variation of various absorption and emission bands as a function of re-irradiation at 77°K. The sample was first x-rayed and kept in the dark for several days at room temperature. Curves (a), (b), (c), and (e) correspond, respectively to those of Fig. 6. The initial maximum optical density in the M -band region was 1.48 at 77°K (sample thickness—1.1 mm).

is treated in the last section of this paper. The decreases of the 458- $m\mu$ absorption band is proportional to the growth of the R_2 band [curve (c), Fig. 7]. From the close relationship between the R_2 band and the 458 $m\mu$ as depicted here and in the foregoing section, it is suggested that the 458- $m\mu$ is due to the F_3^+ center. Further discussion of this is presented in the discussion section.

Whereas longer times of re-irradiation at room temperature gives rise to the formation of new M centers [Fig. 6, curve (a)], probably by conversion from R centers, no similar change in the absorption in the M region was observed at 77°K. The formation of M centers from R centers is not expected to take place at 77°K. The broad band at 530 $m\mu$ [curve (e), Fig. 7] seems again to vary in proportion to the R_2 band [curve (c)].

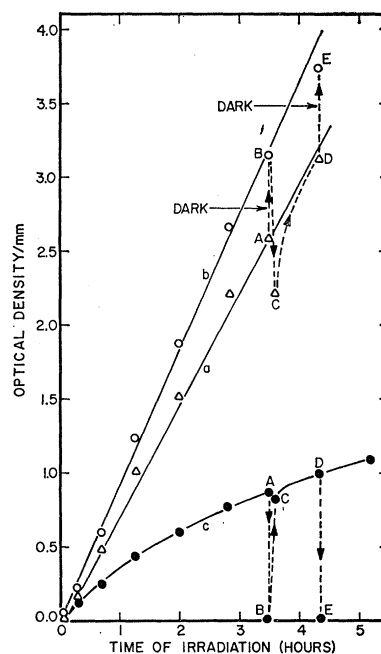


FIG. 8. Growth of maximum absorption in the M region versus time of x irradiation for LiF at room temperature. Δ curve (a) obtained each time immediately upon termination of the irradiation; \odot curve (b) obtained from the corresponding Δ underneath it by holding the crystal in the dark until no change in the peak absorption was observed (48 h). The repeated cycle of passing from one curve to the other is depicted by the path $A \rightarrow B \rightarrow C \rightarrow D \rightarrow E$. In $A \rightarrow B$, enhancement of the absorption occurred during the dark, after which a short x exposure (1 min) gives C . D is obtained after a longer irradiation period and lies on the growth curve (a); E was obtained from D by keeping the specimen in the dark again. Curve (c), the corresponding growth etc. of the 645- $m\mu$ absorption band.

C. M -Band and Green-Emission Formation

Some additional information pertaining to the enhancement of absorption in the M region and the M -band formation can be derived from the growth of the M band and the intensity of the green emission versus time of x irradiation. The growth curves discussed in this section were determined for two different experimental conditions; (a) during x irradiation; and (b) the dark period after the irradiation. The data were obtained as follows: immediately upon termination of the first irradiation (of 5 min.) of a fresh LiF crystal, the absorption spectrum²² and the green emission intensity were recorded at room temperature. These were then remeasured but after holding the crystal in the dark for 48 h. The second irradiation was then per-

²² In the course of this work, the shape of the M band was observed to flatten at the top, when the optical densities of the M -band maxima were higher than 2.5. This flattening was caused by the luminescence stimulated in the crystal by the measuring beam. A Corning filter transmitting in the range of the M band was cut in two; one half was inserted between the sample and the detector to prevent luminescence from reaching the latter, while the other half was inserted in the reference beam. A satisfactory band shape was attained with this arrangement.

formed and the corresponding measurements were taken again in the same manner. The process, of course, was repeated for each additional x irradiation. Thus, two growth curves were obtained for each of the measured parameters, one upon termination of the x irradiation and the other after the dark period. This is illustrated in Fig. 8, in which are plotted the optical density maximum in the M region for the initial growth, curve (a), obtained upon termination of x irradiation and curve (b), after the dark period. Each circle on curve (b) was obtained from the corresponding triangle under it on curve (a), after the dark period. It is evident that upon resuming the x-ray exposure, the optical density in the M region after the dark period tends to reach a value characteristic of the x-irradiation condition prior to the dark period. See also Fig. 5. Likewise, there is an optical density in the M region characteristic of an extended dark period. The cycle of events is more fully demonstrated in the Fig. 8. Also shown in Fig. 8, curve (c) is the same sequence of events for the 645- $m\mu$ band (with an enlarged scale). This band as indicated previously decays entirely in the dark period and regrows upon resuming the irradiation as clearly shown in the curve (c) (see also Fig. 5).

In Fig. 9 are plotted the growth curves of the intensity of the green emission that were obtained for the same crystal and under the same conditions as those of Fig. 8. Curve (a) in Fig. 9 [corresponding to curve (a) in Fig. 8] shows the intensity immediately after stopping irradiation while curve (b) [corresponding to curve (b); Fig. 8] gives the intensity after 48 h in the dark. Thus, each circle on curve (b) represents the emitted intensity attained after the dark period from the corresponding triangle on curve (a) characterizing the intensity reached upon termination of the x irradiation. The path $A \rightarrow B \rightarrow C \rightarrow D \rightarrow E$ in Fig. 9 as in Fig. 8 again depicts a typical cycle. Of importance in Fig. 9 is the

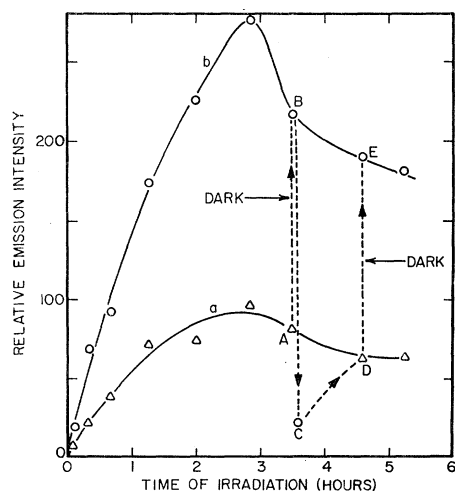


FIG. 9. As Fig. 8, but for the 528- $m\mu$ emission intensity. Data obtained for the same crystal by excitation at 470- $m\mu$ illumination.

considerable enhancement in the intensity of the green emission (over 200%; see also Fig. 5) attained in the dark after each irradiation. In the foregoing sections, it was indicated that this increase is directly associated with a corresponding growth of an absorption band in the M region, but which is masked by the M band. The relative intensities of this masked band can be, therefore, estimated from the corresponding emission intensities. It is evident from the growth of the emission [curve (a) of Fig. 9] that this band is also growing during x irradiation. The intensity of this emission upon termination of x irradiation seems to be less than half of that attained after the dark period. As has been shown (Fig. 5) a short re-irradiation leads to almost a complete quenching of the emission as indicated by $B \rightarrow C$ in Fig. 9. It appears then that during irradiation simultaneously the centers which are responsible for this emission are being created and destroyed. The role these centers play in connection with the production of other centers is discussed later in more detail. Under the particular conditions employed in this experiment the emission intensity reached a maximum after about 3 h of irradiation and decreased for longer exposure times as shown in Fig. 9. This maximum might be due to a saturation in the concentration of the emitting centers. In fact, the dark-period enhancement of the absorption in the M region [difference between curves (b) and (a) in Fig. 8] as well as that of the emission intensity [difference between curves (b) and (a) in Fig. 9] were found to be linear up to about two hours of irradiation where the enhancement in the M region also tends to saturate. The pronounced drop of the emission intensity for longer times of exposure is accounted for by the growth of the M band itself which strongly overlapping the absorption band associated with the emitting centers.

D. Emission and Excitation Spectra

As pointed out earlier, illumination in the M -band region gives rise to at least three emission bands that are associated with bands underlying the M band. Two of these bands are illustrated in Fig. 10, in which monochromatic excitation at 465- $m\mu$ curve a , gives primarily the green emission with a peak at about 528 $m\mu$ and only a small amount of red emission peaking at about 670 $m\mu$. The latter becomes the main emission when the excitation is altered to 445 $m\mu$ as shown by curve (b). Excitation by 380- $m\mu$ light gives only the third (blue) emission band at 495 $m\mu$. Excitation at 405 $m\mu$ gives, however, both the green and blue emission bands which overlap sufficiently so as to be unresolved. In fact, on decreasing the exciting wavelength from 405 $m\mu$, the green emission band maximum appears to shift to shorter wavelengths due to the increase of the relative intensity of the blue emission. The excitation band for the blue emission peaks at about 408 $m\mu$ (see Sec. IA). The low emission efficiency of this band might be

attributed to re-absorption in the M region. Both spectra in Fig. 10 were taken at 77°K with resolutions of less than 15 Å for the green emission and 70 Å for the red emission. Other runs taken with higher resolution have not detected any of the sharp lines that were found by Kaplyanskii.¹² The spectra in Fig. 10 was obtained from LiF sample previously x-rayed and kept in the dark for a long period.

It should be pointed out that the spectrum of the red emission recorded at 77°K immediately following the x irradiation at room temperature differs considerably from the spectrum plotted in Fig. 10, curve (b). Besides an increase in the emission intensity (as in the case of the green component) variations in the band shape and peak position were observed. The band peak shifted from 710 to 670 m μ in the course of holding the crystal in dark at room temperature after the x-ray exposure.

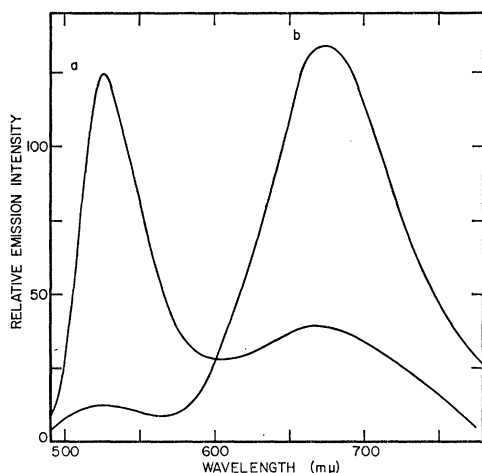


FIG. 10. Emission spectra due to excitation at two wavelengths in the M region; Curves (a) and (b) were obtained with excitation by monochromatic light at 465 and 445 m μ , respectively, at 77°K. This LiF sample was x-rayed and kept in the dark for several days at room temperature before measurements.

The shift in the peak position that occurred upon standing in the dark seems to explain the discrepancies in the peak of the red emission as reported by various authors.^{4,6,10} The variations observed in the red emission along with other emission bands at longer wavelengths will be reported elsewhere.

The temperature dependence of the green emission is illustrated in Fig. 11. Curve a and curve b show the spectra at 77°K and room temperature, respectively. At 77°K, the band peaks at about 528 m μ and the width at half-maximum is 0.242 eV compared to 0.328 eV at room temperature. The vibrational frequency that influences a luminescent center in the excited state is usually deduced from the temperature dependence of the half-width of the emission band. A reasonable estimate for the frequency can be obtained, from the half-width data as determined at 77°K and room temperature. The value obtained, thus, was found

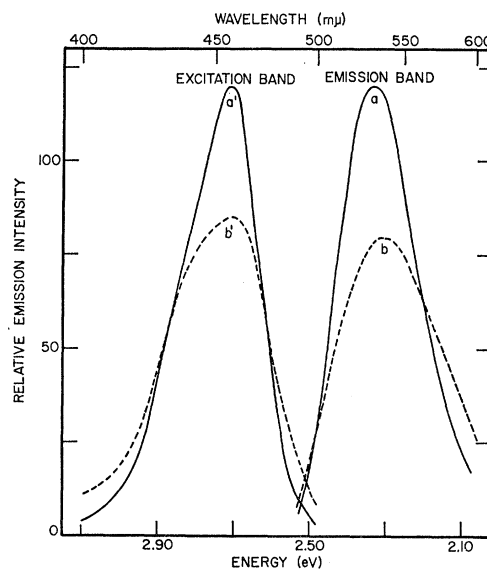


FIG. 11. The temperature dependence of the emission and excitation spectra for the green luminescence; curves (a) and (b) represent the emission spectra at 77°K and room temperature, respectively, due to 465-m μ excitation. Curves (a') and (b') are the excitation spectra at 77°K and room temperature.

to be $\omega = 2\pi \times 7.5 \times 10^{12} \text{ sec}^{-1}$. Also in Fig. 11, curve (a') and curve (b') are the excitation spectra for the green emission at 77°K and room temperature. As indicated earlier, the peak at about 458 m μ [curve (a')] agrees with a band underlying the M band. The half-widths as determined from the excitation curves in Fig. 11 were 0.237 eV at 77°K and 0.322 eV at room temperature. It is of interest that approximately the same half-widths are obtained as in the case of the emission spectra. Thus about the same vibrational frequency of $2\pi \times 7.4 \times 10^{12} \text{ sec}^{-1}$ is found for the ground state as for the excited state. In fact, the excitation and the emission curves are approximately mirror images of each other.

E. Pure M Band

As noted elsewhere in this paper (see Fig. 3), there are several absorption bands underneath the M band. A considerable enhancement of the intensities of these bands is attained if the crystal is kept in the dark for several hours following the x-ray exposure. It was also found, however, that a suitable re-irradiation appears to lead to an extensive bleaching in these bands, thus enabling the "pure" M band to be observed. In Fig. 12 is shown the absorption in the M region at 77°K of a crystal previously x-rayed and then kept in the dark for 6 h at room temperature. A short re-x irradiation at 77°K resulted in considerable bleaching of absorption particularly at longer wavelengths as shown by curve (b). The half-width of 0.152 eV obtained from curve (a) was reduced to 0.134 eV following the re-irradiation. In fact, samples treated in various ways always give the

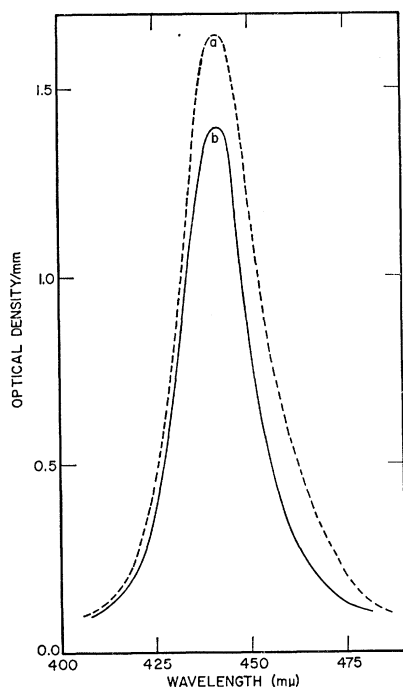


FIG. 12. Curve (a), the M band recorded at 77°K for a sample initially x rayed and kept for six hours in the dark at room temperature. Curve (b) the same as a but following a short re-x irradiation at 77°K .

same minimum value for the half-width when re-irradiated at 77°K . The peak of the band at $442\text{ m}\mu$ in curve (a) appears to shift slightly to $441.2\text{ m}\mu$ in curve (b). No further variation in the half-width of the M band [curve (b)] can be detected by additional re-irradiation. The M band thus obtained is approximately Gaussian in shape and as far as it can be determined, curve (b) of Fig. 12 seems to represent to a good approximation the absorption of the pure M band.

Further support for this is provided by detecting the presence of the bands underlying the M band by observing their respective emission intensities. This has been done and it was found that the green emission stimulated by excitation at $460\text{ m}\mu$ entirely disappeared after the re-irradiation [Fig. 7, curve (b)]. This indicates that the absorption band at $458\text{ m}\mu$ was bleached and this is evident also from the preferential bleaching (Fig. 12) on the long-wavelength side of the maximum due to the re-irradiation. On the other hand, there was no observable decrease (following the re-irradiation at 77°K) in the intensity of the red emission due to excitation at $445\text{ m}\mu$. This indicates then that the band responsible for the red emission is still present. However, in a separate experiment using a sample that was cooled to 77°K immediately after termination of the x-ray exposure, a relatively weak red emission was obtained. The half-width of the M band in this case following a short re-irradiation at 77°K was also about 0.134 eV . Thus the absorption band responsible for the

red emission is apparently very weak and can be neglected in determining the half-width of the M band. The absorption band at $458\text{ m}\mu$ (giving the green emission which had been bleached effectively by the re-irradiation) on the other hand, has a significant influence on the shape of the M band, in particular by distorting the long-wavelength tail. A half-width of 0.176 eV was obtained from the M band measured immediately after room temperature was reached. Several spectra of the M band were also recorded at intermediate temperatures while heating the crystal to room temperature. The crystal was then re-cooled back to 77°K and the M band was compared to curve (b). A small enhancement particularly in the longer wavelengths of the tail of the M band was observed. This is in agreement with the re-appearance of the green emission which was however, of very low intensity compared to that measured before the re-irradiation. Thus, almost the same half-width as that of curve (b) was obtained. This indicates that the half-widths obtained at the intermediate temperatures referred to above are also those of the pure M band. When the crystal was then kept in the dark at room temperature over a period of two days, the half-width measured at 77°K increased to 0.154 eV . A considerable enhancement of the absorption in the M region was also found, and the band shape was similar to that of curve a in Fig. 12. The green emission also returned to the intensity prior the re-irradiation. It should be pointed out that changes in other bands not in the M region were also observed due to the foregoing treatments. These will be dealt with elsewhere. Table I summarizes the changes in half-widths of the M band at 77°K and room temperature obtained under various conditions.

From the half-width data as determined from the pure M band at various temperatures between $77^\circ\text{--}300^\circ\text{K}$, an estimate of the vibrational frequency that influences the M center in its ground state was derived. Figure 13 gives a plot of the half-width of the pure M band versus the square root of the absolute temperature. The vibrational frequency turns out to be $\omega = 2\pi \times 8.12 \times 10^{12}\text{ sec}^{-1}$ which is not too different from those obtained in the present work from the green emission band and also its excitation band. An energy separation 0.031 eV was obtained^{8,19} from the zero-

TABLE I. M -Band half-width at 77°K and room temperature under various conditions.

No.	Condition	Half-width (eV) 77°K	Half-width (eV) room temperature
1.	Upon termination of x irradiation	0.141	0.186
2.	After in dark for several hours	0.152	0.190
3.	As 2 but after short x irradiation at 77°K	0.134	0.176

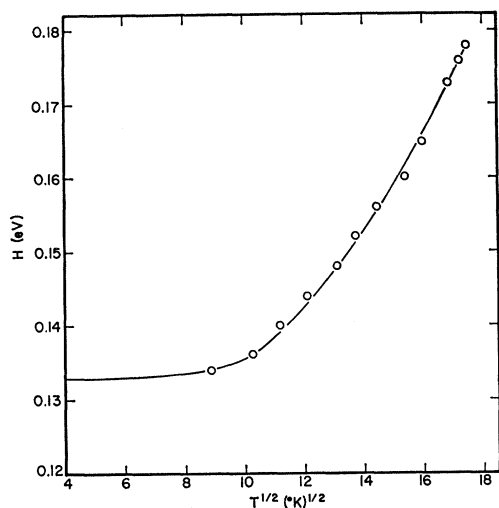


FIG. 13. Variation of the half-width H of the pure M band in LiF versus the square root of the absolute temperature. Experimental values are indicated together with the theoretical curve given by $H = C \coth^{1/2}(\hbar\omega/2kT)$ with $C = 0.133$ eV and $\omega = 2\pi \times 8.12 \times 10^{12}$ sec $^{-1}$.

phonon line and the associated subsidiary peaks on the higher energy side of the R_2 band in LiF. Thus, the frequency of the lattice modes involved is $2\pi \times 7.5 \times 10^{12}$ sec $^{-1}$, which is very close to the frequencies found in this work.

IV. DISCUSSION

A. Absorption in the M Region

Kaufman and Clark⁵ have reported a variation in the peak of the M band between 445 and 460 $m\mu$ in electron-irradiated LiF samples, and they deduced that the absorption in the M region consists of at least two bands having peaks close to 438 and 458 $m\mu$ at room temperature. They suggested that one of these is the M band. Detailed studies that included measurements of absorption spectra and excitation spectra for the various emission bands taken under varying conditions in the M band region revealed in the present work the presence of several bands not directly related to the M band. Thus, from the difference between absorption data taken immediately upon termination of x irradiation and that taken after holding the crystal in the dark at room temperature for long times, a complicated structure of poorly defined bands was obtained in the M region [Fig. 3, curve (a)]. Besides the M band with a peak at 441.2 $m\mu$, altogether four weaker bands were observed when the absorption measurements were made at low temperature.

Some of this multiplicity of absorption bands is also evident from the excitation spectra for emission. It is known^{4,10,14} that excitation in the M region yields green and red emission bands with peaks at about 528 and 670 $m\mu$, respectively. It has been shown in the present work, that the peak at 458 $m\mu$ in the excitation spec-

trum for the 528- $m\mu$ emission band corresponds with a bump in the difference of absorption spectra while the excitation band for the 670- $m\mu$ emission has about the same maximum and half-width as the absorption difference curve (Fig. 3). It should be pointed out that measurements^{4,17} of the polarization of the luminescence indicate that the 670- $m\mu$ emission could arise from centers having a $\langle 110 \rangle$ symmetry axis. These investigators thus concluded that the 670- $m\mu$ emission band is due to the M center. On the other hand, the half-width of the excitation spectrum for the red emission widely differs from that of the pure M band (Fig. 4) but seems to follow the enhancement in absorption as noted above. Measurements on the emission spectra also indicate²³ that the 670- $m\mu$ band is apparently a composite of at least two bands at about 650 and 700 $m\mu$. It is thus possible that one of these is the emission of the M center. An excitation peak at about 410 $m\mu$ for a comparatively weak emission at 490 $m\mu$ was also observed to coincide with an absorption band in the vicinity of the M band (see Sec. IIIA). Thus bands in the M region which are at best poorly resolved in absorption can be further studied in the excitation spectra.

B. Ionized F -Aggregate Centers

Further evidence that the green (528 $m\mu$) emission is unrelated to the M band is provided by the growth and the regrowth curves in Fig. 5 and the bleaching in the M region (Figs. 7 and 12). The variations in the tail on the long-wavelength side of the M band turns out to be directly related to changes in the green emission. Of interest is the remarkable growth of the green emission intensity in the first few hours after cessation of the x-ray exposure (Fig. 5). An additional observation regarding the 458- $m\mu$ band is that it can be bleached by a short re-irradiation and is always accompanied by a considerable increase in the R bands (Figs. 6 and 7). However, the correlation between the 458- $m\mu$ and the R bands can best be observed when the re-irradiation is performed at 77°K (Fig. 7). An analysis of the data reveals that the decay of the 458 $m\mu$ band is proportional to the growth of the R_2 band. The F , M and 645- $m\mu$ bands do not change during this time. These results suggest that the centers associated with the 458- $m\mu$ band are converted to R centers as a result of the re-irradiation at 77°K. It is suggested that the 458- $m\mu$ band arises from a transition of the F_3^+ center and further that the green emission at 528 $m\mu$ is also associated with this center.

It appears that the short re-irradiation provides free electrons which are captured by the F_3^+ centers and so converted to R centers. The suggestion that the 458- $m\mu$ band is due to a transition of the ionized R center is consistent with the newly reported²⁴ absorption bands

²³ J. Nahum and D. A. Wiegand, International Symposium on Color Centers in Alkali-Halides, abstract 140, 1965 (unpublished).

²⁴ I. Schneider and H. Rabin, Phys. Rev. Letters 13, 690 (1964).

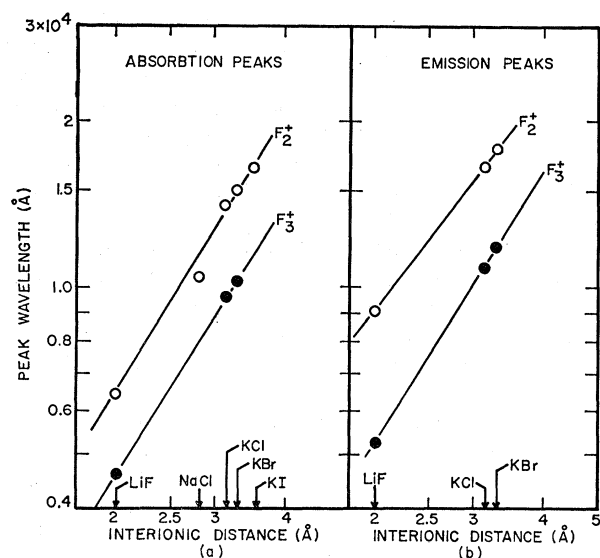


FIG. 14. A Mollwo-Ivey type plot for the various absorption and emission bands associated with ionized F -aggregate centers, F_2^+ and F_3^+ . Data for NaCl, KCl, KBr, and KI are taken from Refs. 25 and 26.

in KCl and KBr that have been attributed to ionized F -aggregate centers. In the course of writing the present paper, Schneider and Rabin²⁵ reported Mollwo-Ivey plots for absorption bands of ionized F -aggregate centers in several alkali halides. It appears, however, that the reported ionized R -center band at 1.02μ for KBr, was erroneously located at somewhat longer wavelengths in Fig. 1 of Ref. 25. A Mollwo-Ivey replot for the F_3^+ bands as reported²⁵ for KCl and KBr at 0.96 and 1.02μ , respectively together with the corresponding band at $458 m\mu$ for LiF is given in Fig. 14(a). Figure 14(b) shows also a Mollwo-Ivey type of relation for the associated emission bands of the F_3^+ centers as reported²⁶ recently for KCl at 1.08μ and KBr at 1.18μ together with the emission band at $528 m\mu$ as presently observed for LiF.

It is noteworthy that polarization measurements of the emission excited by light in the M region of LiF have shown a polarized emission of the green component⁴ that cannot be related to the M center. Recent measurements^{27,28} have in fact shown that the polarization of the $528\text{-}m\mu$ (green) emission is consistent with the symmetry of the F_3^+ model.

²⁵ I. Schneider and H. Rabin, Phys. Rev. **140**, A1983 (1965).

²⁶ I. Schneider and M. N. Kabler, International Symposium on Color Centers in Alkali-Halides, abstract 165, 1965.

²⁷ Y. Farge (private communication). Note added in proof: Since the preparation of this manuscript, the authors have become aware that others have come to similar conclusions regarding the emission and absorption associated with the F_2^+ and F_3^+ centers. Our results and interpretations are given in Atomic Energy Commission Contract No. AT(30-1)-30.33 Report, January, 1966 (unpublished). Y. Farge, G. Toulouse, and M. Lambert, Compt. Rend. **B262**, 1012 (1966); J. Phys. Radium **27**, 287 (1966).

²⁸ J. Nahum (to be published).

Although the F_3^+ center was originally produced²⁴ in KCl and KBr by re-irradiation and bleaching at low temperature, Schneider and Rabin²⁵ have very recently reported that the ionized R center in KCl and KBr can be produced at room temperature. It has been possible to produce the F_3^+ center in LiF by irradiation in the vicinity of room temperature. In addition there is a considerable enhancement in the intensity of the F_3^+ absorption band when the crystal is allowed to remain in the dark for several hours after termination of the irradiation (Fig. 5). The enhancement of the F_3^+ band during the dark period was accompanied by only a small decrease in the R bands. It appears that this decrease in the R bands cannot solely account for the formation of the F_3^+ band. In the reverse process, i.e., the conversion of R centers to F_3^+ centers (Figs. 6 and 7), a much larger increase in the R band was observed for a comparable decrease in the F_3^+ band. It should be mentioned that a band at about $290 m\mu$ possibly associated³ with clustered vacancies and another band at $645 m\mu$ were observed to decay during the enhancement in the M region. As will be discussed later, the $645\text{-}m\mu$ band probably arises from a transition of the ionized M center. A possible explanation for the enhancement in the F_3^+ band following the cessation of the irradiation is that clustered vacancies produced by the x rays combine with the F_2^+ centers so as to be transformed to F_3^+ centers. That no electronic transitions occur in the dark during the formation of F_3^+ centers is supported to some extent by the fact that no detectable phosphorescence in the spectral range $0.25\text{--}2 \mu$ was observed during this period.

As indicated above, subsequent x raying at 77°K of a crystal initially x-rayed at room temperature resulted in $F_3^+ \rightarrow R$ conversion. All attempts to induce the reverse optical conversion $R \rightarrow F_3^+$ with intense R light at 77°K were unsuccessful and the R bands remained unchanged. In contrast to the behavior in KCl and KBr, excitation into the V_k band at $345 m\mu$ produced by the re-exposure to x rays at 77°K also fails to induce a detectable F_3^+ band.

It should be noted that when a sample which has been re-irradiated at 77°K , is warmed to the vicinity of room temperature, a relatively small number of F_3^+ centers are reformed (Sec. III E). In addition the $645\text{-}m\mu$ band is to a good approximation completely restored in the temperature range $260^\circ\text{--}290^\circ\text{K}$ to the value found after the initial irradiation at room temperature. Upon keeping the crystal in the dark at room temperature, changes in the absorption spectra occur which are the same as those that took place after the initial irradiation. Thus, the $645\text{-}m\mu$ and the $290\text{-}m\mu$ band decrease and the number of the F_3^+ band increases considerably (the $290\text{-}m\mu$ band is reproduced by the re-irradiation at 77°K).

It is noteworthy that others have reported^{1,7} a band at $630 m\mu$ which is formed in the vicinity of room

temperature upon warming a sample heavily x-irradiated at 77°K (It was noted in Sec. IIIA that the peak of this band is, in fact, at 645 m μ). In contrast, in the present experiments only a short re-exposure at 77°K of less than 5 min, was sufficient to reproduce upon warming the 645-m μ band in a crystal x-rayed and kept in the dark at room temperature. It was suggested⁷ that the band is possibly due to an intermediate configuration between the F center and the M center. As shown in Fig. 14(a), the band at 645 m μ in LiF appears to satisfy a Mollwo-Ivey plot for the ionized M bands as recently reported²⁵ for several alkali halides. The peak position at 1.03 μ for the F_2^+ band in NaCl²⁵ is somewhat low; the peak at 1.2 μ observed by Pierce²⁹ for NaCl seems, however, to give a better straight line. In Fig. 14(b) is given a Mollwo-Ivey plot for the emission bands at 1.65 μ in KCl and 1.80 μ in KBr attributed²⁶ to the F_2^+ centers, together with the emission band at 910 m μ associated²³ with absorption band at 645 m μ in LiF. These plots suggest that the 645-m μ band in LiF arises from a transition of the F_2^+ center. Recent measurements²⁸ have shown that the polarization properties of the emission at 910 m μ due to excitation in the 645-m μ band are consistent with the symmetry of the F_2^+ model.

C. Production and Transformation of Centers

As in the case of the F_3^+ band, it was not possible to recover the 645-m μ band after decay in the dark at room temperature by optical excitation in the M band, or V_k excitation following a re-exposure to x rays at 77°K. It is important to point out that the annealing⁷ of the volume expansion, induced in LiF by x rays at 77°K, indicates processes such as vacancy clustering or vacancy interstitial annihilation in the temperature range 260°–290°K. It appears that in this temperature range many complex processes are going on simultaneously. Thus the F_2^+ band at 645 m μ is formed possibly by the union of an anion vacancy and F center. The formation of a sizeable M band in the same temperature range can be due to the reaction $F_2^+ \rightarrow M$ by electron capture. Electrons are probably provided by thermal release from traps as indicated by the bursts of thermal luminescence and conductivity observed³⁰ at about 253°K.

As indicated earlier the F_3^+ band at 458 m μ was also observed to form in the temperature range 260°–290°K on warming from 77°K. In addition the formation of this band was considerable during the decay of the 645-m μ band while holding the crystal in the dark for several hours in the vicinity of room temperature. As the F_3^+ band is masked by the M band, it is difficult to determine directly the relative enhancements of these two bands during the decay of the 645-m μ band. How-

ever, from the growth and bleaching features in the absorption in the M region and from the variations of the emission intensities associated with the F_3^+ band as found in the present work, it appears that most of the increase in absorption in the M region is not due to the growth of the M band but is due to the growth of the F_3^+ band. The former is formed somewhat below room temperature probably from the F_2^+ center by electron capture, whereas the F_3^+ center is formed as suggested earlier from the F_2^+ center by vacancy capture (F center). The decay of the F_2^+ band can be described by first-order kinetics, whereas the growth of the F_3^+ band appears to take place with higher order kinetics.

Although in KCl and KBr, it was possible to induce the transformation of F aggregates to ionized F aggregates and vice versa,²⁵ the evidence of many experiments indicates that only the transformation of ionized F aggregates to F aggregates can be induced in LiF, that is, the ionized F aggregates are not produced significantly, if at all, from the F aggregates. In particular, it was not possible to induce variations at low temperature in the F aggregates and the ionized F -aggregates bands in LiF by optical excitation. However, a short re-exposure to x rays alone was effective in bleaching the ionized bands (originally produced at room temperature). For example, while the $F_3^+ \rightarrow R$ conversion is relatively easy to achieve, completely at 77°K (Fig. 7) and partially at room temperature (Fig. 6), all attempts to induce the reverse conversion of $R \rightarrow F_3^+$ were unsuccessful. Furthermore, it appears that the formation of the ionized R centers precede the formation of the R centers. Thus, it is possible to produce the F_3^+ band in the absence of the R band at room temperature in a sample that was initially x-rayed at 77°K and kept at room temperature for a long time. The F_3^+ band can also be produced in the absence of the R band by holding a sample at room temperature for several hours following a light x irradiation at room temperature. Thus, the data suggest that the M and R centers in LiF cannot be produced in significant amounts without the prior formation of the respective ionized centers.

Sonder and Sibley³¹ have demonstrated that the F and M centers in KCl are in dynamic equilibrium during irradiation at room temperature. Harrison³² has proposed that a dynamic equilibrium exists among the F and all F aggregates. The data of Figs. 5, 6, 8, and 9 indicate that this equilibrium exists among all the F aggregates centers in LiF including the F_2^+ and F_3^+ centers during irradiation at room temperature and further that a different equilibrium is established after holding the x-rayed crystal in the dark for several hours. That a dynamic equilibrium exists during irradiation is deduced from the observations (a) that a short re-irradiation returns the concentrations of the various

²⁹ C. B. Pierce, International Symposium on Color Centers in Alkali Halides, Abstract 148, 1965 (unpublished).

³⁰ C. J. Delbecq, P. Pringsheim, and P. H. Yuster, Z. Physik 138, 266 (1954).

³¹ E. Sonder and W. A. Sibley, Phys. Rev. 129, 1578 (1963).

³² P. G. Harrison, Phys. Rev. 131, 2505 (1963).

centers to approximately the values before the dark periods (Figs. 5, 8, and 9) and (b) that there appears to be simple relationships among the changes in the concentrations of the various centers during a short re-irradiation (Fig. 6). However, a careful analysis of the data reveals that the short re-irradiation does not completely reverse the processes which have occurred during the dark period. As indicated earlier, F_3^+ centers are formed but there is no significant decrease in the R bands during the decay of the 645-m μ band (F_2^+ band) (Fig. 5). This suggests the conversion $F_2^+ \rightarrow F_3^+$. In contrast during the re-irradiation [the sharp drops in curves (a) and (b) of Fig. 6] the conversion $F_3^+ \rightarrow R$ appears to take place in the first few minutes until the F_3^+ band is decreased to a somewhat lower value than that attained during the initial irradiation. The R centers are apparently transformed to M centers for longer exposure, possibly by interstitial capture (For detailed descriptions of Figs. 5 and 6, see Sec. IIIB). The net effect of the dark period and the re-irradiation is thus indirectly to convert F_2^+ centers to M centers. Presumably the transformations that take place during the dark period and during the short re-irradiation were also operating during the entire irradiation at room temperature. F_2^+ centers must then be created continuously during the irradiation.

As indicated earlier, the F_2^+ center is possibly formed by the union of an anion vacancy with an F center. Motion of negative ion vacancies has been suggested⁷ previously. It appears that the processes involved in the transformations among the various centers during a room-temperature irradiation require the motion of anion vacancies. This supports the proposal³¹ that the equilibrium between the F and M centers involves a mobile entity to account for the simultaneous creation and destruction of the F and M centers during radiation.

It should be noted that a broad band at about 530 m μ was observed to change in the same way as the R bands (Figs. 6 and 7) under varying experimental conditions. Thus it is possible that the 530-m μ band is associated with the same center as the R bands. This is consistent with Silsbee's³³ results for KCl that indicate the existence of several R -center transitions in the region between the F and M bands. It is difficult to determine whether the zero-phonon line at 523.5 m μ is to be associated with the 530-m μ band or with an underlying band which has not been identified. However, careful analysis of absorption spectra taken at 77°K under

various conditions suggest that this sharp band at 523.5 m μ is not associated with the broad 530-m μ band.

D. Vibrational Frequencies

Since it has been possible to obtain a pure M band it has also been possible by studies of the temperature dependence of this band to deduce the vibrational frequency associated with the ground state. This vibrational frequency is found to be approximately $\omega = 2\pi \times 8.12 \times 10^{12} \text{ sec}^{-1}$, which is in reasonable agreement with the value of $\omega = 2\pi \times 8.65 \times 10^{12} \text{ sec}^{-1}$ obtained for the F center³⁴ in LiF. Furthermore, the frequencies that influence the F_3^+ center in LiF in its ground state as well as in its excited state were derived, respectively from the associated excitation band at 458 m μ and from the emission band at 528 m μ . Both values turn out to be close (see text) to that obtained for the M center. It is also interesting that approximately the same values of the vibrational frequency²³ was also obtained from the emission band at 910 m μ and from its excitation band at 645 m μ associated with the F_2^+ center. This implies that all the centers associated with these bands in LiF interact with phonons of the same frequency in the ground states and in several cases also in the excited states. In addition, energies which are integer multiples of 0.031 eV were derived from the separation between the zero phonon line and the subsidiary peaks associated with the R_2 band^{8,19} in LiF. Other bands²⁸ in the 0.8 and 1- μ region which have zero-phonon lines at 833.5 m μ and 1.040 μ , respectively, also give this energy separation. The frequency of the lattice modes involved with these centers $\omega = 2\pi \times 7.5 \times 10^{12} \text{ sec}^{-1}$. All of these frequencies agree very well with a theoretical normal-lattice phonon frequency of $2\pi \times 7.5 \times 10^{12} \text{ sec}^{-1}$ in LiF as determined by Karo and Hardy.¹⁸ By comparing the energy separation between the zero-phonon lines and the associated peaks in the R and N bands in a variety of alkali-halide crystals with theoretical normal-lattice phonon energies, Pierce⁹ came to the conclusion that the broadening of at least the R_2 and N bands is due to lattice interactions involving normal lattice phonons. In support of Pierce's conclusion, the foregoing results indicate that the phonons involved in broadening other bands in LiF, e.g., F , M , and the ionized F aggregates, are also normal lattice phonons. The important lattice mode in LiF is a transverse optical phonon with the energy of 0.031 eV propagating along the $[111]$ direction.

³³ R. H. Silsbee, Phys. Rev. **138**, A180 (1965).

³⁴ H. Rabin and M. Reich, Phys. Rev. **135**, A101 (1964).