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Optical Properties and Mechanism of Formation of Some F-Aggregate Centers in LiF†

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A study of positively charged, neutral, and negatively charged centers in LiF has been made. Effects observed include the induced transformations of ionized centers to F-aggregate centers, and reformation of the ionized centers in the dark, when samples reirradiated at low temperatures are warmed up. Polarization properties of the luminescence from various centers have also been studied. From the temperature dependence of the emission bands and the associated excitation bands for the M^+ and R^+ centers, vibrational frequencies were determined and were found to be close to a theoretical normal-lattice phonon frequency. From detailed studies of transformations among the various centers observed under varying conditions, it was possible to propose a mechanism of formation of the M and R centers and other complex centers. M- and R-center formation seems to occur through diffusion of α and M^+ centers, respectively, towards F centers ($\alpha+F\rightarrow M^+$ and $M^++F\rightarrow R^+$) followed by capture of a single electron. Experiments indicated that M' and R' centers are produced from the corresponding M^+ and R^+ centers apparently by a process involving two-electron capture.

I. INTRODUCTION

In a previous paper,[1] which will be referred to as I, the absorption bands at 645 and 458 mμ in LiF were ascribed to optical transitions of the ionized M and R centers, respectively. Additional experiments were carried out in the present work to study the polarization properties of the emission from M^+ and R^+ centers, as well as the $M^+\rightarrow M$ and $R^+\rightarrow R$ transformations and the reformation of the M^+ and R^+ centers when samples reirradiated at liquid-nitrogen temperature (LNT) are warmed up to room temperature (RT). The findings provide additional support for the proposed assignment of the 645- and 458-mμ bands as M^+ and R^+, respectively.

The luminescence arising from excitation in the M (or M^+) band in the presence or absence of M^+ and/or M' centers has been analyzed. It turns out that an optical excitation in the M band in crystals containing M^+ centers yields an emission characteristic of M^+ centers, while the efficiency of the emission from the M centers decreases and the spectrum shifts to longer wavelengths. When both M^+ and M' centers are present, luminescence characteristic of both these charged centers is emitted. Furthermore, optical excitation of the M^+ band yields M' as well as M^+ luminescence.

Similar effects occurring among various trapped-electron centers (F, M, R centers) have been reported[2–4] in other alkali halides. Lamb and Compton suggested that the luminescence characteristic of M and R centers stimulated by F light is due to an energy transfer occurring between the F center and the M and R centers. The observations of the present work, which were, however, confined only to the same center in its different charged forms, suggest that in this case, too, processes of energy transfer are involved.

A considerable amount of information regarding the formation of ionized M and R centers was obtained in *I*. It appears that these ionized centers play an essential role in the formation of neutral M and R centers. It was believed that a study concentrated on positively charged, neutral, and negatively charged centers should lead to deeper insight into the mechanism of formation of these centers.

Lüty,[5] in his study of the optical $F\rightarrow M$ conversion, was the first to propose that M-center formation is accomplished by a Coulomb interaction between F' and α centers. Delbecq[6] further considered the possibility that coagulation of F centers involves the motion of an α center towards an F center; upon electron capture the α-F pair transforms to an M center. Our results regarding M-center formation in LiF seem to fit in with Delbecq's proposal. The experiments further indicated that in the absence of electrons, the M^+ center transforms to an R^+ center by the aggregation $M^++F\rightarrow R^+$, where now apparently the M^+ center moves towards an F center. An R center is then produced eventually by an electron capture. This process of aggregation occurs even when electrons are available, for instance, during x irradiation at RT, but its probability is apparently much less due to the competing $M^++e\rightarrow M$ conversion.

It should be pointed out that regarding transformations among the various centers, LiF appears in general to behave differently from other alkali halides. For instance, no evidence has been reported that F-aggregate centers can be produced in appreciable amounts by F light illumination. According to Delbecq and Pringsheim,[7] only exposure to uv light beyond the

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spectral range of the *F* band enhanced the *M* and *R* bands. It is known[8] that formation of complex centers (for instance in KCl), at least during RT irradiation, is accompanied by a reverse process of destruction of the complex centers. Results with LiF indicate that the forward reactions proposed in the present work for the formation of the neutral centers are not reversible, and there is no evidence for destruction of the *M* or *R* centers during irradiation. In view of these results, formation of the aggregate centers in LiF seems to be considerably less complicated than in other alkali halides.

A study of formation of the negatively charged M' and R' centers is also included in the present work. These centers in KCl and KBr were first reported by Hirai *et al.*,[9] who found that a bleach in the *F* band leads to $M \rightarrow M'$ and $R \rightarrow R'$ transformations. In the case of LiF, it was not possible to induce these transformations. The M' and R' centers in LiF seem to form, as do the *M* and *R* centers, from the corresponding ionized *M* and *R* centers, apparently by a process involving a capture of two electrons.

II. EXPERIMENTAL

Experimental arrangements were similar to those described in I. Crystals obtained from the Harshaw Chemical Company were colored by x-raying them at RT. x irradiation, optical-bleaching, optical-absorption, and optical-emission measurements were carried out at various temperatures in a cryostat with a rotating head.

Optical-absorption measurements were made with a Cary model 14R spectrophotometer. A Bausch and Lomb grating monochromator in conjunction with a 800-W Hanovia zenon arc lamp was used for exciting the emission. A Beckman DU monochromator was placed perpendicular to the exciting beam to analyze the emitted radiation. A Du Mont photomultiplier with S-13 response, an RCA 7102 photomultiplier, and an RCA germanium diode (SQ2516) served as detectors for the spectral range 0.2–1.7 μ. The recorded spectra were corrected for the spectral response of the detector employed and for the dispersion of the monochromator. These corrections were included in one calibration factor which was determined as follows. The spectral intensities of a tungsten lamp in conjunction with the Bausch and Lomb monochromator were first measured by an Eppley Golay detector and then with the same system employed for analyzing the luminescence. The ratio of the intensities thus obtained gave the calibration factor as a function of wavelength. Care was taken in the calibration to use the same slit widths in the analyzing monochromator as those used in the emission measurements. Since the theoretical band shapes are given with respect of constant energy interval rather than constant wavelength interval, the curves of the emission bands should be corrected by a factor of $(1/h\nu)^2$. Thus to obtain a relative measure of the emission spectra in terms of the number of photons per sec and per energy interval, the recorded spectra were multiplied by an over-all factor of $(1/h\nu)^3$.

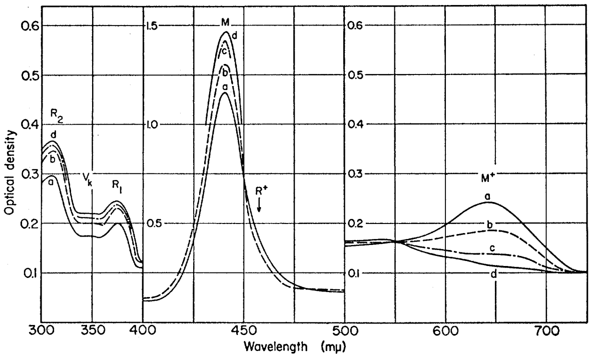

FIG. 1. $M^+ \rightarrow M$ conversion due to re-exposure to x-rays at. LNT, after quick cooling following RT irradiation. Absorption spectra at various exposure times : curve (a)—none; curve (b)—1 min; curve (c)—3 min; curve (d)—7 min (Vibronic structure in the R_2 band is omitted.)

In measurements of the polarization of the emission, crystals were excited by monochromatic light falling at normal incidence and the luminescence emitted normally from the opposite surface was examined. Suitable filters were inserted in the optical path to isolate the emission. For the polarization measurements, HN and HR polaroid sheets were used, depending upon the spectral range of the exciting and emitted light.

III. RESULTS

A. Ionized *M* Center, M^+

1. $M^+ \rightarrow M$ *Transformation*

In I it was suggested that the absorption band at 645 mμ arises from a transition of the M^+ center, and that the emission band at 910 mμ, produced by excitation in the 645-mμ absorption band, arises from an M^+ center. Support for the above is provided herein from the following additional observations: (a) $M^+ \rightarrow M$ conversion takes place after short reirradiation at low temperature; (b) the polarization properties of the 910-mμ emission are consistent with this assignment.

The M^+ band at 645-mμ is produced by prolonged x-ray irradiation in the vicinity of room temperature. The correlation between this band and the *M* band can be observed by reexposure to x-rays at low temperature. This is illustrated in Fig. 1. Curve (a) gives the absorption spectrum of a crystal cooled to LNT immediately after the termination of the x-irradiation at RT. Curve (b), taken after a short reirradiation at LNT, shows a

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[8] See W. D. Compton and H. Rabin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964) Vol. 16] for a review of processes of formation and destruction of *F*-aggregate centers.

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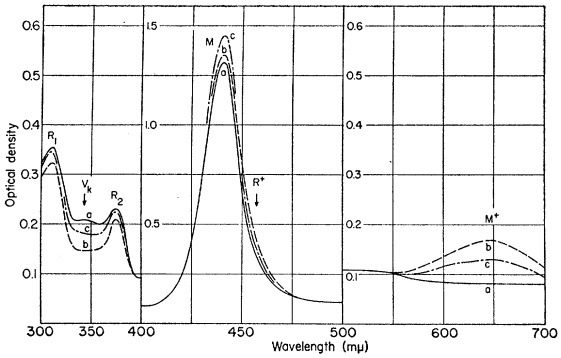

FIG. 2. Reformation of M^+ centers upon warming specimen to the vicinity of room temperature following a short reirradiation at LNT: curve (a)—LNT absorption spectrum of specimen x-rayed at RT, kept in the dark for 2 days, and then x-rayed for 8 min at LNT; curve (b)—absorption spectrum also at LNT but following warming to the vicinity of RT; curve (c)—LNT absorption spectrum of the same specimen after a 1-min second re-exposure to x-rays at LNT. (Vibronic structure in the R_2 band is omitted.)

decrease in the 645-mμ band and an increase in the M band at 441.2 mμ. Curves (c) and (d) show the spectra after longer reirradiations at LNT. It is seen that once the 645-mμ band has disappeared, no further increase in the M band occurs with longer exposure times. Half-width data of the M band show that the enhancement of absorption observed in the M region as a result of the reirradiation is due to an increase in the pure M band, and not to an increase in the weak R^+ band at 458 mμ produced by the initial irradiation at RT (see I). In fact, the short reirradiation at LNT even causes a small reduction in the tail on the longer-wavelength side of the M-band peak [compare curves (a) and (b) in Fig. 1], as a result of x-ray bleaching of the R^+ band. As will be shown later, this bleaching of the R^+ band results in an increase in the R bands. The growth of the M band during the LNT reirradiation is proportional to the decrease in the 645-mμ band. The ratio of the changes in the absorption coefficients at the peaks of the respective bands was found to be $|\Delta\alpha_M/\Delta\alpha_{M^+}|=2.5$. From the half-widths of the pure M band (see I) and M^+ band (Table I), the relative oscillator strengths of the M and M^+ transitions turn out to be $f_M/f_{M^+}=1.1$.

It should be mentioned that the 645-mμ absorption band decays within several hours at RT, and thus for the above measurements it is essential to cool the crystal quickly following the x-ray exposure. In an attempt to bring about the reverse $M\rightarrow M^+$ transformation, the crystal was illuminated with monochromatic V_k light. The V_k band at 345 mμ produced by the reirradiation at LNT almost vanished, but no 645-mμ band could be detected.

TABLE. I. Spectral characteristics of the absorption bands associated with the M^+ and R^+ centers in LiF.

Proposed model	Peak position (LNT) (mμ)	Half-width (LNT) (eV)	Vibrational frequency ν_a ($\times10^{12}$/sec)
M^+	645	0.308	6.8
R^+	458	0.238	7.6

The 645-mμ band did appear, however, when samples initially x-rayed and kept in the dark for a long time at RT (until no absorption at 645 mμ is observed) were subjected to a short reirradiation at LNT and then warmed up to the vicinity of room temperature. This is exemplified in Fig. 2. A reirradiated sample at LNT gives the absorption spectrum, curve (a), showing no absorption at 645 mμ since it decays in the dark period at RT. If the band had still been present, however, it would have been bleached by the reirradiation at LNT (see Fig. 1). The 645-mμ band makes its appearance in the temperature range 260°–290°K. When the reirradiated sample was kept at 290°K for about an hour, until a sizeable absortpion in the 645-mμ region was attained, and then recooled to LNT, the spectrum shown in curve (b) of Fig. 2 was obtained. The absorption difference of curves (a) and (b) indicates that the enhancement in the M region is due not only to an increase in the M band but also to the formation of a weak R^+ band at 458 mμ. The absorption difference in the 645-mμ region gives a band with the same peak position and half-width as in Fig. 1. In other words, the 645-mμ absorption band produced by irradiation at RT is the same as that formed by warming the sample irradiated at LNT to the vicinity of room temperature. As in the foregiong case (Fig. 1), one expects that a short re-exposure to x-rays should cause a reduction in the 645-mμ band and an enhancement of the M band. This indeed occurs, as shown by curve (c), Fig. 2. It was observed that the weak R^+ band at 458 mμ formed by the warming was also bleached, and a corresponding increase occurs in the R bands.

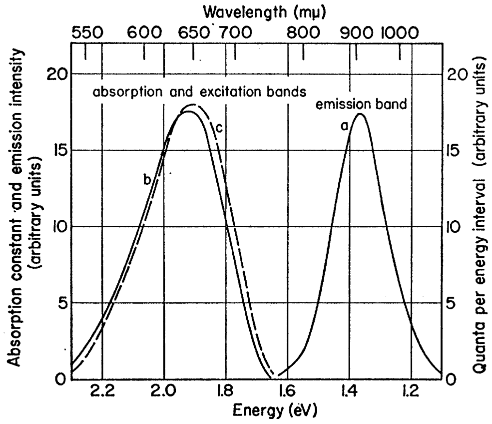

FIG. 3. Optical spectra associated with the M^+ center in LiF: curve (a)—emission spectrum resulting from M^+ light illumination at 645 mμ; curve (b)—absorption spectrum for the M^+ center; Curve (c)—excitation spectrum for M^+-center emission. All spectra measured at LNT.

2. *Emission*

In crystals showing the 645-mμ absorption band, luminescence has been observed as a result of monochromatic illumination. Curve (a) of Fig. 3 shows the emission spectrum at LNT due to excitation in the 645-mμ absorption band. The emission consists of a symmetric band peaking at 910 mμ and having a width at half-maximum of 0.215 eV. The emission intensity decreases with temperature and drops by a factor of about 3 when the crystal is warmed from LNT to the vicinity of room temperature. Also shown in Fig. 3 is the 645-mμ band absorption, curve (b). The band was determined from the difference in absorption spectra measured at LNT [such as from curves (a) and (b) in Fig. 1). As shown by curve (c), the excitation spectrum at LNT for the 910-mμ emission closely follows the 645-mμ absorption band, indicating that this emission at 910 mμ is associated with the 645-mμ band.

The decay and regrowth features of the 645-mμ absorption band have been described in I in connection with other bands. As pointed out, the 645-mμ absorption band produced by x-irradiation at RT decresaes and disappears almost completely within several hours. The intensity of the 910-mμ emission produced by excitation in the 645-mμ band was observed to follow the decay and regrowth of the 645-mμ absorption band. Curves (a) and (b) of Fig. 4 show, respectively, the decay of the 645-mμ absorption and 910-mμ emission bands, when the sample is kept in the dark at RT following a prolonged irradiation. The decay curves can be fitted by first-order kinetics. Within 10 min after reirradiation, both intensities are rapidly restored to their initial values (as indicated in Fig. 4) and the cycle of the decay and regrowth can be repeated, as shown by curves (a′) and (b′) of Fig. 4. These results provide further evidence that the emission at 910 mμ is associated with the 645-mμ absorption band. For future reference, the growth and decay of the emission from R^+ centers (treated in more detail in I are also included in Fig. 4 [curve (c)].

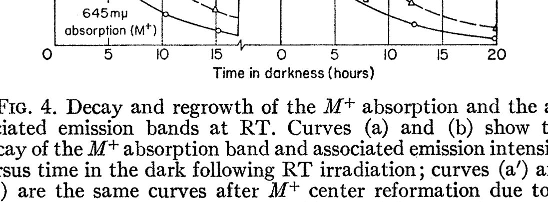

FIG. 4. Decay and regrowth of the M^+ absorption and the associated emission bands at RT. Curves (a) and (b) show the decay of the M^+ absorption band and associated emission intensity versus time in the dark following RT irradiation; curves (a′) and (b′) are the same curves after M^+ center reformation due to a short 10-min reirradiation; curves (c) and (c′) show the growth of the emission intensity from R^+ centers prior to and following the reirradiation.

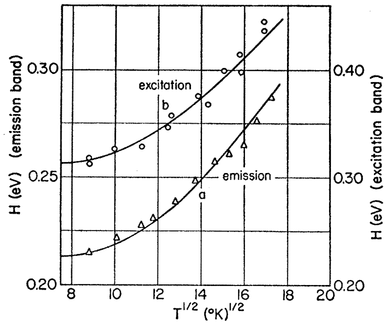

FIG. 5. The half-width H versus the square root of the absolute temperature for the emission and excitation bands of the M^+ center; experimental values △ and ○ shown with theoretical curves given by $H=C\coth^{1/2}(\hbar\omega/2kT)$; for curve (a)—$C=0.213$ eV and $\omega=2\pi\times7.4\times10^{12}$ sec^{-1}; for curve (b)—$C=0.304$ eV and $\omega=2\pi\times6.8\times10^{12}$ sec^{-1}.

The shape of the emission band at 910 mμ can be fitted by a Gaussian function, while the 645-mμ absorption band can be approximated by a double Gaussian. The emission band was measured at various temperatures up to RT. By plotting the width of the emission band against the square root of the absolute temperature [curve (a), Fig. 5, left-hand ordinate scale], an estimate of the characteristic lattice frequency for the excited state was derived. The shape of each emission band was corrected for the spectral response of the photomultiplier and analyzing monochromator, and the intensity was converted to number of photons per sec and per energy interval as indicated in Sec. II. It was difficult to obtain the width of the 645-mμ absorption band accurately at temperatures higher than 200°K, since overlap of a band at 530 mμ (see Fig. 1) becomes appreciable. The widths at various temperatures were obtained, however, from the associated excitation spectra of the emission at 910 mμ. The full widths at half-maximum are plotted against the square root of the absolute temperature in Fig. 5 [curve (b), right-hand ordinate scale]. Within the accuracy of the determination of the half-width, the vibrational frequency characteristic of the ground state of the M^+ center turns out to be about the same as that for the excited state. The peak positions, half-widths, and vibrational frequencies obtained for the absorption and emission bands of the M^+ center are listed in Tables I and II.

TABLE II. Spectral characteristics of the emission bands associated with the M^+ and R^+ centers in LiF.

Proposed model	Peak position (LNT) (mμ)	Half-width (LNT) (eV)	Vibrational frequency ν_e ($\times10^{12}$/sec)
M^+	910	0.215	7.4
R^+	528	0.218	7.0

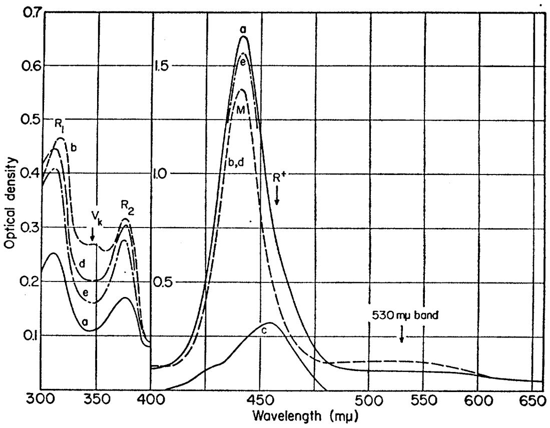

FIG. 6. $R^+ \rightarrow R$ conversion due to re-exposure to x-rays at LNT and subsequent reformation of R^+ centers upon keeping the sample in the dark at RT: curve (a)—optical absorption of specimen given RT irradiation and then kept in the dark at RT for one day; curve (b)—optical absorption of specimen of curve (a) after re-exposure to x-rays for 10 min at LNT; curve (c)—absorption difference in the M region [difference of curves (a) and (b)]; curve (d)—same as (b) but after 5-min illumination with 345-mμ light; curve (e)—optical absorption after sample was kept in the dark for 18 h following warming to RT; all spectra measured at LNT (Vibronic structure in the R_2 band is omitted).

3. Polarization of the Luminescence

The degree of polarization of the luminescence associated with the M^+ center provides additional support for the proposed model. The degree of polarization of the luminescence P is conventionally defined as $P = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$, where $I_{\parallel}$ and $I_{\perp}$ are the emission intensities measured with polarization parallel and perpendicular to the direction of polarization of the exciting light respectively. For comparison with the theory, the degree of polarization was measured for exciting light, polarized first in the [011] direction and then in the [001] direction.

The polarization of the emission was measured at LNT in specimens showing the 645-mμ absorption band. Results for the 910-mμ emission produced by excitation in the 645-mμ band are given in Table III for the case in which the direction of excitation and observation are the same. The measurements indicate that the center associated with the 645-mμ absorption band is anisotropic. Also shown in Table III (bottom line) is the degree of polarization of the luminescence that would be expected for dipoles oriented along ⟨110⟩. These values are not grossly different from the observed ones, indicating that the anisotropic center involved can be represented, with a reasonable degree of certainty, as an optical dipole oriented along a face diagonal. On the basis of the assignment of the 645-mμ absorption band to a transition of an M^+ center, it is expected that this center also possesses the same ⟨110⟩ symmetry axis as that of the M center. Thus the polarization properties of the emission associated with the 645-mμ absorption band are consistent with the proposed M^+ assignment for the 645-mμ band.

TABLE III. Degree of polarization of the luminescence in LiF crystals excited by polarized M^+ light. The computed values show the degree of polarization expected from the optical dipole along ⟨110⟩.

	P[011]	P[001]
Observed (LNT)	0.58	0.31
Computed	0.667	0.333

B. Ionized R Center, R^+

1. $R^+ \rightarrow R$ Transformation

An absorption band at 458 mμ, masked by the stronger M band, has been observed in LiF and was attributed to a transition of the ionized R^+ center. In addition, an emission band at 528 mμ produced by excitation in the 458-mμ band was ascribed to the luminescence of the R^+ center (see I). Further support for the proposed model along with observations regarding the absorption and emission bands of the R^+ center are described below.

Like the M^+ center, the R^+ center is produced in crystals x-irradiated at RT. In contrast to the decay observed in the M^+ band when the crystals are kept in the dark at RT following the x-irradiation [curves (a) and (b) Fig. 4], a considerable growth in the R^+ band at 458 mμ takes place during this period [curve (c), Fig. 4]. This growth of the R^+ band at 458 mμ causes an increase in the absorption on the longer-wavelength side of the M-band peak. The essential features of the $R^+ \rightarrow R$ conversion and the reformation of the R^+ band are summarized in Fig. 6. Curve (a) gives the absorption spectrum at LNT of a crystal that was subjected to a prolonged irradiation at RT, and then kept in the dark at RT for a long time to allow a maximum increase in the R^+ band. As shown by curve (b), subsequent re-exposure to x-rays, still at LNT, causes a decrease in the absorption in the M

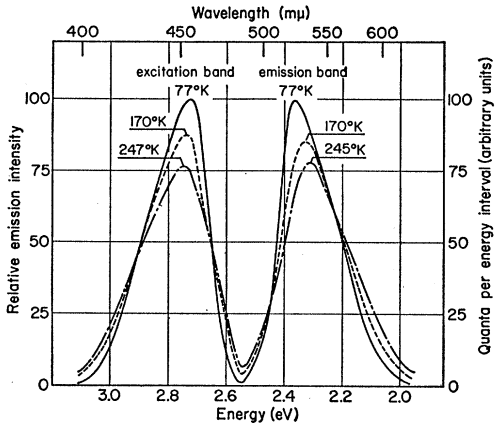

FIG. 7. Temperature dependence of the emission bands resulting from R^+ light illumination at 465 mμ and the corresponding excitation bands for R^+-center emission.

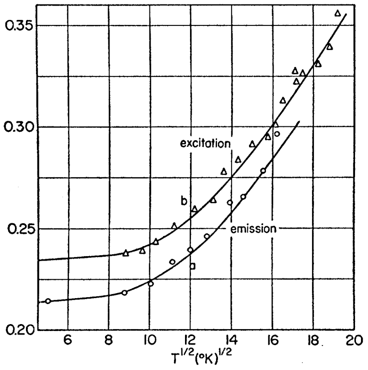

FIG. 8. The half-width H versus the square root of the absolute temperature for the emission and the excitation bands of the R^+ center; experimental values ○ and △ shown with theoretical curves given by $H=C\coth^{1/2}(\hbar\omega/2kT)$; for curve (a)—$C=0.213$ eV and $\omega=2\pi\times7.0\times10^{12}$ sec^{-1}; for curve (b)—$C=0.234$ eV and $\omega=2\pi\times7.6\times10^{12}$ sec^{-1}.

region and an increase in the R bands. In fact, the decreases observed in the M region due to reirradiation at LNT were proportional to the corresponding increases in the R_2 band [see curves (a), (b), and (c) of Fig. 7 in I]. The conversion ratio $|\Delta\alpha_{R_2}/\Delta\alpha_{R^+}|$ was found to be 0.5. $\Delta\alpha_{R^+}$ was estimated from absorption differences in the M region at 458 mμ. However, due to overlap with the strong M band, it is difficult to determine $\Delta\alpha_{R^+}$ accurately, especially since changes may also occur in the M band itself during the reirradiation. Nevertheless, the absorption difference in the M region as exemplified by curve (c) [difference of curves (a) and (b)] in Fig. 6 indicates that most of the reduction is due to the R^+ band 458 mμ.

The R^+ band produced at RT, like the M^+ band, can be completely bleached by a suitable reirradiation at LNT. In the latter case the bleaching is accompanied by an enhancement in the pure M band (Fig. 1), whereas in the former case there is a decrease in the M region (Fig. 6) due to x-ray bleaching of the R^+ band. In an effort to induce the $R\rightarrow R^+$ transformation, the crystal was excited in the V_k band produced by the reirradiation at LNT. As shown by curve (d), the V_k band decreased but no change could be observed in the M region. Like the M^+ band, [curve (b), Fig. 2] the R^+ band reappears when the crystal reirradiated at LNT is warmed to the vicinity of RT. Unlike the M^+ band, however, the R^+ band grows considerably if, after warming, the specimen is maintained at RT in the dark for several hours. (The M^+ band decays under these circumstances). This increase in the R^+ band appears (as in the case following a RT irradiation) as an enhancement on the longer-wavelength side of the peak of the M band [see curve (e) in Fig. 6].

The intensity of the emission at 528 mμ excited by R^+ light follows the changes that occur in the R^+ band. Thus the emission disappears entirely in the reirradiation at LNT, and grows together with the enhancement of the R^+ band observed in the period in the dark. This further indicates that the emission at 528 mμ is from the R^+ center.

It is noteworthy that formation of the R^+ band during warming and during the period in the dark is not accompanied by any significant change in the R bands [curve (e) Fig. 6] that can account for a possible $R\rightarrow R^+$ conversion. Similarly, the M^+ band produced in the process of warming to the vicinity of RT [curve (b), Fig. 2] is apparently not due to conversion of M centers to M^+ centers. In fact, instead of a decrease, an enhancement was observed in the M band while the M^+ band increases (Fig. 2). As pointed out, it was not possible to induce either the $M\rightarrow M^+$ or the $R\rightarrow R^+$ transformation by optical excitation in the V_k band. These results strongly suggest that ionized F-aggregate centers can not be produced in LiF from the corresponding F-aggregate centers.

2. *Emission*

Previous and present experiments related to the emission band at 528 mμ have shown that this emission is associated with the R^+ center. The temperature dependence of the emission band will now be reported in more detail. In Fig. 7 the emission band produced by excitation in the R^+ band is shown for various temperatures. Due to overlap with the M band, the R^+ band can best be studied via the excitation spectra of the 528-mμ emission. An excitation spectrum that follows the R^+ band faithfully can only be obtained, however, if the M band is weak. Since other emission bands are also produced by excitation in the M region, it is essential to use adequate filtration so that only light emitted from R^+ centers is measured. The excitation spectra taken in this way at various temperatures are also shown in Fig. 7.

The shape of the emission and excitation bands are nonsymmetrical. Each of the bands can be approximated by two Gaussians. Whereas the width at half-height on the violet side of the excitation band is

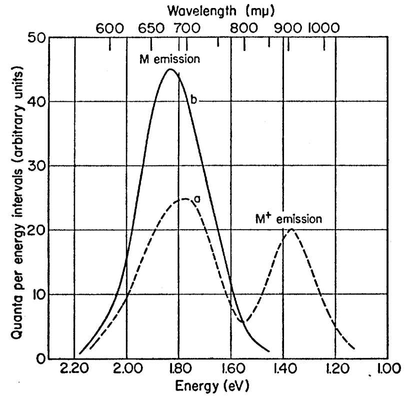

FIG 9. Emission spectra at LNT due to excitation in the M band at 445 mμ. Curve (a)—specimen contains M and M^+ centers; curve (b)—same specimen containing M but no M^+ centers.

larger than that on the red side, the emission band shows the opposite asymmetry. Peak positions and half-widths of the excitation and emission bands are listed in Tables I and II respectively. The widths of the emission and excitation bands versus the square root of the absolute temperature are given in Fig. 8 [curves (a) and (b), respectively]. Due to overlap with the violet side of an emission band at 670 mμ (also produced by excitation in the M band, see Fig. 9) which becomes appreciable at high temperatures, it was difficult to obtain accurate widths for the emission bands at temperatures above 200°K. These data have therefore been excluded from curve (a) of Fig. 8. The emission band was also measured at 25°K. The vibrational frequencies as determined from curves (a) and (b) of Fig. 8 are listed in Tables I and II. These frequencies are approximately the same as those obtained from an earlier estimate based on less extensive data.

3. Polarization of the Emission

Polarization measurements for the R^+ center were taken as in the case of the M^+ center. The values of the degree of polarization at LNT that are shown in Table IV for the R^+ center are not too different from those obtained recently by others [10].These values are approximately the same as those reported[4] for the R centers in NaCl and KCl. Although polarization properties of the emission associated with the R center are, in general, uncertain, the present results provide further support for the proposed R^+ center.

C. Interaction Between Different Centers

1. M and M^+ Center Interaction

It is known that excitation in the M band yields a red emission; the position of the peak as reported by various authors[11–13] ranges from 650–710 mμ. In the present work it was observed that the spectral distribution and intensity of this emission vary considerably in crystals containing M^+ centers. This is exemplified in Fig. 9. As shown by curve (a), excitation in the M band of a crystal containing M^+ centers gives rise to an emission band at 910 mμ in addition to the red emission at 710 mμ. Curve (a) was taken at LNT in a crystal that was immediately cooled to this temperature after a prolonged irradiation at RT. The crystal was then maintained in the dark at RT for several hours until no M^+ band could be detected [Fig. 4, curve (a)] and the emission spectrum was measured again at LNT. As shown by curve (b) of Fig. 9, the peak at 710 mμ shifts to 670 mμ and increases considerably in intensity, while the M^+ center emission completely disappears. Since the M^+ band can be restored again by short reirradiation at RT (Fig. 4), one expects such a reirradiation to reverse the changes that occurred in the emission spectra following the period in the dark. Following a short reirradiation, the M^+-center emission did indeed reappear as a result of excitation in the M band, while the intensity of the emission at 670 mμ decreased considerably and the peak shifted to 720 mμ. These variations in the red emission indicate that this emission is apparently a composite of at least two bands at approximately 670 and 725 mμ. Possibly the emission band at 670 mμ is associated with the M center. Indeed, polarization measurements seem to point to this. When emission was stimulated by M-band excitation, and a narrow spectral range of 620–670 mμ was selected by suitable filtration, the degree of polarization found at LNT was $P[011]=0.64$ and $P[001]=0.33$. These values are in good agreement with those reported by Lamb and Compton,[4] and are consistent with dipoles oriented along $\langle 110\rangle$. As for the 725-mμ emission, it was observed that excitation in the R_1 band gives a mixture of 725 mμ and M^+-center emission, even in the absence of M^+ center. It is possible that the emission at 725 mμ is from an R_1 center.

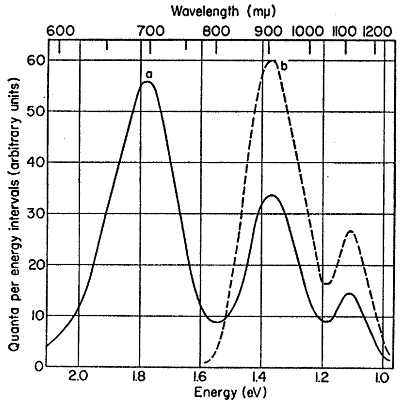

FIG. 10. Emission spectra at LNT in sample containing M^+, M, and M' centers: cruve (a)—excitation by M light at 445 mμ; curve (b)— excitation by M^+ light at 645 mμ.

TABLE IV. Degree of polarization of the luminescence in LiF crystals excited by polarized R^+ light. The bottom line shows the degree of polarization observed in NaCl and KCl by R_1 or R_2 light.

Material	$P[011]$	$P[001]$
LiF (LNT)[a]	0.24	0.03
NaCl, KCl (LNT)[a]	0.20	0.02

[a] Values taken from Ref. 4.

No significant changes in the M band were observed to accompany either the enhancement of the emission at 670 mμ occurring upon standing in the dark or the decrease in this emission following the reirradiation. In view of the overlap of M^+-center emission (at 670 mμ) with the M$^+$ band, it is possible that a cascade process may occur, giving rise to M^+-center emission. It appears,

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[10] Y. Farge, G. Toulouse, and M. Lambert, J. Phys. Radium **24**, 287 (1966).

[11] C. C. Klick, Phys. Rev. **79**, 894 (1950).

[12] A. Okuda, J. Phys. Soc. Japan **16**, 1746 (1961).

[13] P. Görlich, H. Karras, and G. Kotitz, Phys. Status Solidi, **3**, 1803 (1963).

however, that partial absorption of the 670-mμ emission by a weak M^+ band can not, on its own account for the considerable reduction observed in this emission when M^+ centers are present. A possible explanation for the reduction is that optical excitation energy is transferred from the *M* center to the M^+ center, by means of a resonance process of a type well known[14] in luminescent systems.

2. *M*, M^+, *and* M' *Center Interaction*

Besides the two emission bands produced by *M*-band excitation in specimens containing M^+ centers [curve (a), Fig. 9], an additional emission band at 1.12 μ was observed in specimens that had been very heavily x-irradiated at RT. This is shown in Fig. 10; curve (a) gives the emission spectrum at LNT due to excitation in the *M* band of a crystal x rayed at RT and immediately cooled to LNT. Curve (b) shows that the emission at 1.12 μ is produced along with the M^+-center emission by an M^+ light illumination. As reported previously,[15] the emission band at 1.12 μ is associated with an absorption band at 980 mμ. The absorption band shows a structure at LNT, with a zero-phonon line at 1.0406 μ (see I). The absorption band and the associated emission band produced by excitation in the 980-mμ band are given in Fig. 11. Very recently, Fitchen *et al.*[16] attributed this absorption band to a transition of an M' center. It appears, however, that the absorption at 980 mμ (Fig. 11) consists of two overlapping systems of bands, one with a zero-phonon line at 1.0406 μ and the other with a zero-phonon line at 1.012 μ. At least five bands at shorter wavelengths are apparently associated with the stronger line at 1.0406 μ, and two with the weaker line at 1.012 μ. In each case, the peaks are separated from the corresponding zero-phonon line by integer multiples of approximately 0.031 eV. Since the relative intensities of the bands in the two systems keep constant ratios irrespective of irradiation conditions, it seems that both systems arise from transitions of the same center.

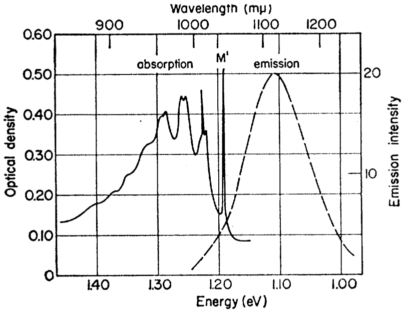

FIG. 11. M' absorption spectrum and the emission spectrum resulting from M' light excitation at 980 mμ; measurements at LNT.

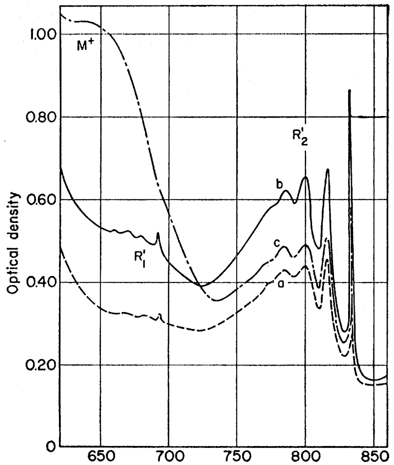

FIG. 12. Formation of R' centers due to reirradiation at LNT: curve (a)—optical absorption at LNT in the R_1' and R_2' region of a sample (2.2-mm thick) heavily x-rayed at RT; curve (b)—after 15-min reexposure to x-rays at LNT; curve (c)—optical absorption also at LNT but after warming to the vicinity of RT.

The appearance of M^+ and M' center luminescence as a result of *M*-band excitation suggests that interaction occurs between these centers. It should be noted that in the absence of M^+ centers, neither M^+ nor M' center emission can be observed due to *M* light illumination, even in the presence of M' centers. Possibly the energy from the excited *M* center is not effectively transferred to M' centers.

D. Negatively Charged *M'* and R' Centers

Along with the M' band (Fig. 11), two absorption bands at 680 and 790 mμ were also produced in samples heavily x irradiated at RT. As shown in Fig. 12, the band at 790 mμ exhibits a fine structure at LNT with a zero-phonon transition at 833.5 mμ (see I). The band at 790 mμ has been attributed[16] recently to a transition of an R' center. As in the case of the R_2 band, the peaks in this case are also regularly spaced with approximately 0.031 eV between successive peaks. It was observed that the ratio of the intensities of the bands at 680 and 790 mμ, like that of the R_1 and R_2 bands, is essentially constant under varying conditions. Also, the ratio of the wavelengths of the maxima of these two bands is approximately the same as that for the R_1 and R_2 bands. These results suggest that the bands are the R_1' and R_2' bands, respectively. In fact, the peaks at 680 and 790 mμ in LiF satisfy Mollwo-Ivey plots for the corresponding R_1' and R_2' peaks as reported[9] in KCl and KBr. It should be noted that a weak line at 693 mμ and at least two broad bands at shorter wave-

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[14] See C. C. Klick and J. H. Schulman [in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5] for a review of energy transfer involved in luminescence processes.

[15] J. Nahum and D. A. Wiegand, International Symposium on Color Centers in Alkali Halides, Urbana, Illinois, Abstract No. 140, 1965 (unpublished).

[16] D. B. Fitchen, H. R. Fetterman, and C. B. Pierce, Solid State Commun. 4, 205 (1966).

lengths with a separation between successive peaks of approximately 0.031 eV were observed at LNT. It is difficult to determine if this structure overlapping the R_1' band is associated with it.

In the production and transformation of the negatively charged M' and R' centers, it was observed that the absorption bands were bleached completely at RT by infrared illumination, and that a short reirradiation at RT restored the M' and R' bands to their values measured after the initial irradiation. The R' bands, like the R bands, were also observed to increase if the re-exposure to x rays was performed at LNT. This is shown in Fig. 12; curve (a) is the LNT absorption spectrum of a specimen kept a day in the dark following the irradiation at RT. It will be recalled that during this period in the dark an enhancement occurred in the R^+ band and that subsequent irradiation at LNT resulted in the $R^+ \rightarrow R$ transformation by electron capture. As shown by curve (b) in Fig. 12, an increase in the R' bands also occurred due to reirradiation at LNT. It is possible that R^+ centers can transform not only to R centers but also to R' centers. In contrast to the case of KCl and KBr,[9] all attempts to induce $M \rightarrow M'$ or $R \rightarrow R'$ conversions by exposure to F light were unsuccessful. These observations suggest that at least R' centers are not produced from R centers. As shown by curve (c) of Fig. 12, most of the enhanced portion in the R_2' band [curve (b)] resulting from the reirradiation at LNT disappears when the crystal is warmed to the vicinity of RT. It is possible that the R' centers transformed to R centers by a thermal release of their trapped electrons. The R_1' band could not be observed in curve (c), since it is masked by a stronger M^+ band formed by warming to RT (see also Fig. 2).

IV. DISCUSSION

A. Optical Absorption and Emission

The successful identification[17,18] of the ionized F-aggregate centers in KCl and KBr hinged on the fact that it was possible to produce these centers by inducing $M \rightarrow M^+$ or $R \rightarrow R^+$ conversions after which the reverse $M^+ \rightarrow M$ or $R^+ \rightarrow R$ transformations could be brought about by optical excitation. The former conversions are produced by illuminating the spectral region of hole centers, while the reverse conversions are produced by F light illumination. Attempts to employ this procedure to produce ionized centers in LiF were unsuccessful. Nevertheless, it has been possible to identify an absorption band at 645 mμ as being due to a transition of the M^+ center, and a band at 458 mμ (underneath the M band) as coming from a transition of the R^+ center on the basis of the following observations: (a) the 645- and 458-mμ bands transform with fixed ratio to M and R bands, respectively, as a result of short exposure only to x rays; (b) polarization properties of the emission associated with the 645 and 458 mμ absorption bands are consistent with the proposed models for these centers; (c) the peaks of the 645- and 458-mμ absorption bands and their associated emission bands fit the Mollwo-Ivey plots (Fig. 14 in I) of the corresponding peaks of the absorption and emission bands associated with the M^+ and R^+ centers in various alkali halides.[18,19]

Several authors[13,20,21] have observed an emission in the vicinity of 900 mμ along with other emission bands produced by excitation at various wavelengths. However, the source of this emission remains unknown. Farge *et al*[21] reported recently that the emission at 910 mμ is from a center comprising a Li atom in the interstitial position ($\frac{1}{4}$, $\frac{1}{4}$; 0).[22] In disagreement with this, our previous reports[1,15] and present results indicate that the emission at 910 mμ is from an M^+ center. Fig. 3, curve (c), shows that the excitation spectrum for this emission follows the M^+ band, and Fig. 4, curves (a) and (b), shows that the intensity of the emission varies with that of the M^+ band under various conditions. In addition, it is questionable whether an interstitial Li can be produced by x irradiation at RT. The prominent absorption band at 550 mμ which, according to Farge *et al.*, was also associated with a Li interstitial,[22] was produced in crystals by neutron irradiation, but this band has not been observed in crystals irradiated by x rays.

Within the accuracy of the half-width determinations the data for the absorption and emission of the ionized M^+ and R^+ centers (Tables I and II indicate that the effective phonon frequencies associated with the M^+ and R^+ centers are the same in their ground states as in their excited states. It turns out that these frequencies associated with the ionized centers are not grossly different from the frequencies associated with the F center[23] and the M center (see I). In addition, the vibronic structure in the R_2 band as well as in the R_2' and M' bands shows an approximately regular spacing, with an energy separation of about 0.031 eV between successive peaks. Thus these centers in LiF appear to be coupled to a single phonon mode with a frequency of about $\omega = 2\pi \times 7.5 \times 10^{12}$ sec^{-1}, which is not too different from the frequencies determined above for the M^+ and R^+ centers. It appears that the excited

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[17] I. Schneider and H. Rabin, Phys. Rev. Letters **13**, 690 (1964).

[18] I. Schneider and H. Rabin, Phys. Rev. **140**, A1983 (1965).

[19] I. Schneider and M. N. Kabler, International Symposium on Color Centers in Alkali Halides, Urbana, Illinois, Abstract No. 165, 1965 (unpublished).

[20] I. A. Ghormley and H. A. Levy, J. Phys. Chem. **56**, 548 (1952).

[21] Y. Farge, M. Lambert, and A. Guinier, J. Phys. Chem. Solids **27**, 499 (1966).

[22] Y. Farge, G. Toulouse, and M. Lambert, Compt. Rend. **262B**, 1012 (1966). More recently these authors have reported that an emission at 9000 mμ is due to an M^+. This agrees very well with our results. It is not clear, however, whether this emission differs from the emission that was initially attributed to an interstitial Li.

[23] H. Rabin and M. Reich, Phys. Rev. **135**, A101 (1964).

states of the M' center, like those of the ionized centers, are also coupled to a single mode with the frequency of the ground state. According to a very recent report of Fitchen *et al.*,[16] the emission spectrum of the M' center at 4°K shows the resonance line and mirror emission. The emission at 1.12 μ produced by excitation in the M' center, as previously reported,[15] does not show a vibronic structure at LNT (Fig. 11). All these frequencies, as derived previously and in the present work, agree very well with a theoretical normal lattice phonon frequency of $2\pi\times 7.5\times 10^{12}$ sec^{-1} for the transverse optical $\langle 111\rangle$ mode, as determined by Karo and Hardy.[24] These results further support our previous conclusions (I) that the electron-phonon interaction involved in these centers is a normal lattice phonon. The transverse optical $\langle 111\rangle$ phonon with energy 0.031 eV seems to be the predominant phonon that is coupled to these centers in LiF.

B. Mechanism of F-Aggregate Center Formation

The production of F-aggregate centers in LiF has been discussed in some detail in I. The present study, which concentrates particularly on the positively and negatively charged centers, provides more information on the mechanism of formation of these centers. This will now be discussed also in the light of our previous work. It was concluded in I that the ionized M and R centers cannot be produced in significant amounts from the neutral M and R centers. This conclusion is further supported by the following observations: (a) It was not possible to induce $M\rightarrow M^+$ or $R\rightarrow R^+$ conversions for instance by illuminating the V_k band; (b) the reformation of the M^+ centers during the warming up of a crystal that had been subjected to a short reexposure at LNT was not accompanied by any reduction in the M band. On the contrary, an increase occurred in the M band [Fig. 2, curve (b)]. Similarly, the considerable formation of R^+ centers when the specimen was kept in the dark at RT following warming [Fig. 6, curve (e)] or following RT irradiation (Fig. 4, curve (c)], was not accompanied by a significant decrease in the R bands. In any case, formation of R^+ centers during the period in the dark, in the vicinity of RT, was always accompanied by a decay in the concentration of M^+ centers (Fig. 4). In fact, it was possible to produce R^+ centers in the absence of R centers, in specimens lightly x rayed at RT. These observations further indicate that the formation of ionized M and R centers precedes the formation of the corresponding M and R centers.

It was proposed in I that the M^+ center is formed by the union of an anion vacancy and an F center ($\alpha+F\rightarrow M^+$) possibly accomplished by a motion of the anion vacancy. This seems to agree with Delbecq's proposal[6] that the α center is the mobile unit leading to M-center formation. Link and Lüty[25] have recently reported a high mobility of the anion vacancy and immobility of the F' center in the process of F_A-center formation. When electrons are available, the M^+ center eventually captures an electron and transforms to an M center. For instance, the $M^+\rightarrow M$ conversion observed when a specimen reirradiated at LNT is warmed to the vicinity of RT (Fig. 2) may be accounted for by the thermal release of electrons from traps during the warming. The electrons may also be supplied directly by the action of x rays. This is shown in Fig. 1 in which a short re-exposure to x rays resulted in $M^+\rightarrow M$ conversion at LNT. As pointed out, the conversion to M centers terminated when no more M^+ centers were present. Since further irradiation at LNT did not result in the production of new M centers, it seems that only electronic rearrangement is involved in the $M^+\rightarrow M$ conversion. It should be noted that in RT irradiation, as in LNT, the M^+ centers also transform to M centers, apparently by capturing electrons supplied by the exposure to x rays. In this case, however, the converted M^+ centers are rapidly replaced by new M^+ centers formed by the $\alpha+F\rightarrow M^+$ reaction. Since M^+ centers in LiF are not produced in appreciable amounts below 250°K, one expects M centers to be produced in large amounts only at higher temperatures.

It is of interest that very recently Farge, Lambert, and Smoluchowski[26] have also concluded from their study of M-center formation at RT and above that formation of M centers in LiF occurs through the reaction $\alpha+F\rightarrow M^+$, where an α center diffuses toward an F center, after which the M center is formed by electron capture.

Farge *et al.*[26] have also suggested that an R center is produced, in a similar way, by the $\alpha+M\rightarrow R^+$ reaction followed by capture of an electron. Our results, however, lead to the proposal that an R^+ center is formed through the union of an M^+ and an F center; the evidence for this is the following. There is considerable formation of R^+ centers when the crystal is kept in the dark for 8 h following the termination of the irradiation. This formation of R^+ centers is accompanied by the decay of the M^+ band, and terminates when no more M^+ centers are present (Fig. 4). It will be recalled that no change occurs in the M band during the decay of the M^+ band during the period in the dark. The $M^+\rightarrow M$ conversion can be expected only when electrons are supplied. A decrease in the F band was also observed during this formation of R^+ centers. These observations point to the occurrence of the reaction $M^++F\rightarrow R^+$. By analogy with M^+-center formation, it is suggested that the F center is immobile and that the M^+ center

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[24] A. M. Karo and J. R. Hardy, Phys. Rev. **129**, 2024 (1963).

[25] E. Link and F. Lüty, International Symposium on Color Centers in Alkali Halides, Urbana, Illinois, Abstract No. 120, 1965 (unpublished).

[26] Y. Farge, M. Lambert, and R. Smoluchowski, Solid State Commun. 4, 333 (1966).

diffuses towards it. When electrons are supplied, for instance by the action of x rays (Fig. 6), the R^+ center captures an electron and transforms to an R center. When the irradiation is performed at LNT, R-center formation ceases when all the R^+ centers present have been transformed (because R^+ centers are not produced at LNT). However, when the irradiation takes place at RT, the R^+ centers converted to R centers are continuously replaced by the reaction $M^+ + F \rightarrow R^+$ proposed above for R^+-center formation in the dark. That this process also occurs during the irradiation is plausible in view of the experimental evidence that transformations among the various centers, observed to occur at RT in periods of dark followed by re-exposures to x rays, also occur during the irradiation itself. For instance, Harrison[27] has concluded that in KCl and KBr the aggregation to M centers occurs by the same mechanism whether it results from continuous irradiation or from pulse irradiation and decay in the dark.

It is possible that the complex F_4 center is produced by an analogous process of diffusion of an R^+ center toward an F center, followed by electron capture. It appears that the R^+ center is immobile in the vicinity of RT, since no decay was observed in this band over an extended period in the dark [Fig. 4, curve (c)]. However, when a specimen containing R^+ centers is warmed to above 350°K, a decay occurs in the R^+ band, accompanied by a considerable formation of absorption bands at 520 mμ (possibly the N_1 band[28]) and at 550 mμ. Further studies concerning the processes involved are under way.

The positively charged α and M^+ centers seem to control the formation of the neutral M and R centers by diffusion. Since it was not possible to bring about the back reactions ($M \rightarrow M^+ \rightarrow \alpha + F$, or $R \rightarrow R^+ \rightarrow M^+ + F$), it appears that once M or R centers are produced in LiF, it is difficult to induce reduction[29] in their concentrations. In this respect LiF differs from other alkali halides. Schnatterly and Compton,[30] for example, have demonstrated that if KCl crystals initially x rayed at RT are reirradiated at LNT, exponential decay of the concentrations of M and R centers occurs. In contrast, the only change observed to occur in the M or R bands of LiF upon re-exposure at LNT was enhancement of these bands when M^+ or R^+ centers were present (Figs. 1 and 6). Sonder and Sibley[31] have reported that in KCl cycling of the irradiated intensity between low and high values produces reversible shifts in the relative density of the F and M centers in KCl. Harrison[32] has further demonstrated the occurrence of such shifts between the F and complex centers. In the course of the present work, it was observed that in LiF lowering the irradiation intensity during a room-temperature irradiation caused only a retardation in the F-center formation accompanied by an acceleration of the M-center formation, but no destruction of either of the centers. Conversely, raising the irradiation intensity was observed to cause only a retardation in the M-center formation and an acceleration of the F-center production.

The inability to induce reductions in the M and R centers in LiF by reirradiation at LNT or by altering the rate of irradiation strongly suggests that only the forward reactions proposed for the formation of these centers operate during irradiation at RT. The lack of back reactions in this unique case considerably simplifies the reaction kinetics relating to F-aggregate formation in LiF. The kinetics of aggregation to complex centers will be dealt with elsewhere in the light of the mechanism proposed for their formation.

It appears that, like the positively charged M^+ and R^+ centers, the negatively charged M' and R' centers cannot be produced from the corresponding M and R centers in LiF, for instance by optical bleach in the F band.[9] However, a short re-exposure of a specimen containing R^+ centers to x rays at LNT results in an increase in the R' bands [curve (b) of Fig. 12]. That this increase in the R' bands is not due to a $R \rightarrow R'$ transformation is evident from the fact that the R bands themselves are increased by this reirradiation (Fig. 6), due to $R^+ \rightarrow R$ transformation by electron capture. Since electronic rearrangement takes place as a result of this short reirradiation at LNT, it is concluded that the R^+ center can capture not only a single electron to form an R center but can transform to an R' center, apparently by some process of two-electron capture. Since the occurrence of two-electron capture by an R^+ or an M^+ center (see below) is much less probable than one-electron capture, one cannot expect strong M' or R' bands, as are obtained for M and R centers (Fig. 12). It was found that formation of both R and R' centers at LNT terminated when there were no more R^+ centers left. This similarity in this formation of the R and R' centers provides further support for the assignments of the bands at 690 and 790 mμ as R_1' and R_2'.

It should be pointed out that if the M' band was partially bleached by infrared light at RT, an enhancement in this band occurred as a result of subsequent irradiation at LNT. However, the M' band, unlike the

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[27] P. G. Harrison, International Symposium on Color Centers in Alkali Halides, Urbana, Illinois, Abstract No. 74, 1965 (unpublished).

[28] K. Kubo, J. Phys. Soc. Japan **16**, 2294 (1961).

[29] This does not imply that a temporary reduction cannot be induced in the M or R bands. For instance, Okuda (Ref. 12) has reported that a bleach in the R_1 band at RT reduced the R bands and increased the M band. This transformation was not permanent but was followed after an extended period in the dark by a restoration of the M and R bands to their initial values prior to the bleach.

[30] S. Schnatterly and W. D. Compton, Phys. Rev. **135**, A227 (1964).

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

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

R' bands, never exceeded the maximum value attained as a result of the initial irradiation at RT. Furthermore, without bleaching this M' band following the irradiation at RT, there was no significant change in it as a result of a reirradiation at LNT, although the crystal contained M^+ centers. The concentration of M' centers apparently attains a maximum value as a result of the initial irradiation at RT. It is possible, however, that during the initial irradiation at RT, M^+ centers, analogous to the case of R^+ centers, transform mostly to M centers but also partially to M' centers.

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Effects of Ordering on the Transport Properties of Sodium Tungsten Bronze*

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The electrical resistivities, Hall coefficients, and Seebeck coefficients of metallic Na_xWO_3 have been measured as functions of the sodium concentration (x value) from $x=0.4$ to $x=0.9$ and also a function of the temperature from 4 to 300°K. The resistivity, Hall coefficient, and Seebeck coefficient each showed an anomaly at $x=0.75$ where the sodium atoms are ordered. These results are the first demonstration of ordering effects in any transport property of any tungsten bronze. A careful selection of crystals that were homogeneous in electrical resistivity was necessary in order to see these ordering effects. For homogeneous crystals, the Hall coefficients were different from those previously reported and do not predict the exact number of free electrons.

INTRODUCTION

THE nonstoichiometric compounds M_xWO_3 (where M represents an alkali metal) are commonly referred to as the alkali tungsten bronzes, and, since their discovery,[1] their properties have stimulated the interest of many investigators. Although other bronzes have been prepared and investigated, the alkali tungsten bronzes have received the most attention. In particular, extensive data exist on sodium tungsten bronze, Na_xWO_3.

The resistivity data[2–5] of cubic $Na_xWO_3(1.0>x>0.48)$, together with the Hall coefficients,[5] indicated that cubic Na_xWO_3 exhibited metallic behavior and that each sodium atom contributes one electron to the conduction band. However, the resistivity which was measured by Brown and Banks[4] and by Gardner and Danielson[5] showed a definite minimum in the resistivity versus the sodium concentration at $x=0.75$. Brown and Banks interpreted the minimum in the resistivity in terms of an equilibrium between the undissociated sodium atoms and the sodium ions plus free electrons, while Gardner and Danielson suggested that the minimum was due to the ordering of the sodium atoms. However, Ellerbeck *et al.*[6] showed that the minimum in the resistivity was due to the inhomogeneous crystals which were used by the previous investigators and that when homogeneous single crystals were used for measurements, there was no minimum in the resistivity-versus–sodium-concentration curve. In fact, Ellerbeck *et al.* found no evidence of any anomaly at $x=0.75$ even though partial ordering of the sodium atoms had been seen at $x=0.75$ by Atoji and Rundle[7] in their neutron-diffraction work. However, Mackintosh[8] pointed out that the experimental evidence did not necessarily rule out the possibility of a maximum in the conductivity at $x=0.75$ and suggested that further measurements be made in the region of the superlattice structure.

Thus, in regard to the electrical properties of Na_xWO_3, there still exist two important questions. First, if greater care were taken in the preparation of the Na_xWO_3 single crystals and if more samples were used near the region of the superlattice structure, would it be possible to detect in the electrical transport prop-

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† U. S. Atomic Energy Commission Postdoctoral Fellow.

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