discussions concerning the relationship of the observed data with theory. I wish to express my gratitude to R. R. August of Autonetics for his assistance and direction, and to Mrs. D. A. George and J. Carlson for help in the preparation and mounting of the very thin specimens of gallium arsenide. The partial support of this work by the U. S. Air Force Office of Scientific Research is also gratefully acknowledged.

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Optical Properties and Formation Kinetics of M^+ Centers in NaF

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It is shown that the M^+ center in NaF has an absorption band at 740 mμ and an emission band at 943 mμ. M^+ centers in NaF can be produced by prolonged x irradiation at room temperature, or by irradiation at low temperature followed by annealing to near room temperature. From a study of the production and transformation of the M and M^+ centers it is concluded that the formation of an M center is preceded by the intermediate formation of an M^+ center. It is suggested that M centers in NaF, as in LiF, are formed through the reaction $\alpha+F \rightarrow M^+$, followed by electron capture. The kinetics of aggregation to M^+ centers in NaF and LiF are also studied in the present work.

INTRODUCTION

In recent years, a number of studies have been reported[1–5] on absorption bands associated with ionized F-aggregate centers in several alkali halides. Specifically, the existence of the ionized M and R centers, which will be referred to as M^+ and R^+ centers, respectively, has been established with a reasonable degree of certainty.

In this paper, the absorption and emission bands for the M^+ center in NaF are reported, along with a study of M^+-center formation by a thermally activated process. It was observed that formation of an M center in NaF, as in LiF, is preceded by the intermediate formation of an M^+ center. The kinetics of the aggregation to an M^+ center, apparently through the reaction $\alpha+F \rightarrow M^+$, has been studied in the present work. In general, the formation and transformation behavior of the M^+ and M bands in NaF resemble those reported previously[4,5] for the M^+ and M bands in LiF.

EXPERIMENTAL

Crystals obtained from Harshaw were cleaved into plates of dimensions $1\times10\times10$ mm. Low-temperature irradiations and measurements of absorption spectra, emission spectra, and optical bleaching were carried out with equipment and techniques similar to those described previously.[4,5]

The samples were mounted in a variable-temperature cryostat fitted with a rotatable head. Temperature measurements were made with a copper-constantan thermocouple mounted close to the sample on a copper sample holder. An electrical heating element was used to achieve a controlled rate of warming. A given temperature could be maintained within $\frac{1}{4}$°K. Optical-absorption measurements were made with a Beckman DK-1A spectrophotometer. To obtain greater accuracy, weak absorption bands were recorded in the 90–110 transmittance range of the spectrophotometer.

RESULTS

$M^+ \rightarrow M$ Transformation

An absorption band at 740 mμ, most probably arising from a transition of the M^+ center, is produced together with the stronger F and M bands by prolonged x irradiation at room temperature (RT). Support for this M^+ assignment is provided by the following observations: (a) During F-band illumination at low temperatures, the band at 740 mμ decreases in constant proportion to the growth of the M band; (b) as in LiF, crystals containing M^+ centers can undergo $M^+ \rightarrow M$ conversion under a short reexposure to x rays alone at low temperature. The conversion 740 m$\mu \rightarrow M$ is depicted in Fig. 1. Curve a shows the absorption spectrum of a crystal cooled to liquid-nitrogen temperature (LNT) immediately after the termination of the RT x irradiation. Curve b, taken after a short reirradiation at LNT, shows a decrease in the 740-mμ band and an increase in the M band at 499 mμ. Curves c and d show the spectra after longer reirradiations at LNT. The growth of the M band during the LNT reirradiation is proportional to the decrease in the 740-mμ band. The conversion ratio $|\Delta\alpha_M/\Delta\alpha_{M^+}|$ expressing the change in the absorption coefficients at the peaks of the respective bands is 3.6. From the half-widths of the M band ($W_M=0.105$ eV)

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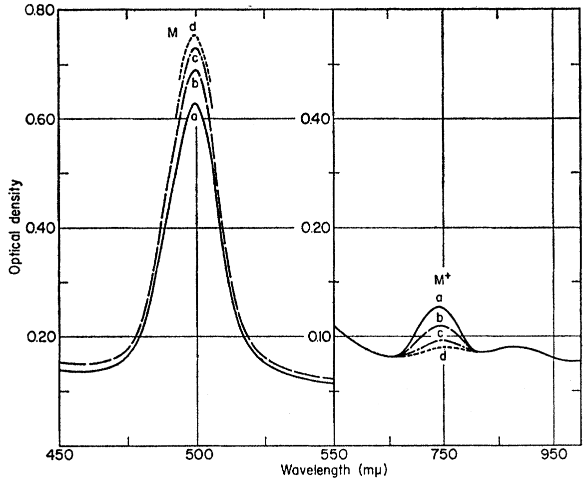

FIG. 1. $M^+ \rightarrow M$ conversion produced by reexposure to x rays at 77°K after quick cooling following prolonged irradiation at 295°K. Absorption spectra at various reexposure times; curve a, none; curve b, 1 min; curve c, 3 min; and curve d, 9 min.

and the 740-mμ band ($W_{M^+}=0.167$ eV) at LNT, the relative oscillator strengths of the M band and M^+ transitions are found to be $f_M/f_{M^+}=2.2$. Since the 740-mμ band decays if the crystal is kept in the dark at RT, it is essential for the above measurements to cool the crystal quickly following the x irradiation.

M^+ Generation

If an NaF sample is subjected to prolonged x irradiation below 260°K and then gradually warmed up, formation of the 740-mμ band is observed over a limited temperature range near RT. This is exemplified in Fig. 2. Curve a shows the absorption spectrum at LNT immediately after irradiation. Besides the strong F band at 335 mμ, a broad band[6] of unknown origin is observed at about 460 mμ, but no 740-mμ band. Spectra recorded during the warming up (Fig. 3, curve a) show the appearance and growth of the 740-mμ band in the temperature range 260–290°K. This behavior is similar to that of the M^+ band at 645 mμ in LiF, as shown in curve b of Fig. 3. As regards the absorption in the 460-mμ region, it almost disappears by the time the temperature reaches 270°K, while the F band decreases markedly. Curve b of Fig. 2 shows the spectrum obtained when the sample is recooled to LNT after being warmed to 290°K. This spectrum indicates that only a weak M band is produced during the considerable formation of the 740-mμ band near RT. After this production of the 740-mμ band, one would expect that exposure to F light would induce the transformation 740 mμ → M. This indeed occurs, as shown by curve c of Fig. 2. This result is consistent with the assignment of the 740-mμ band to an M^+ transition.

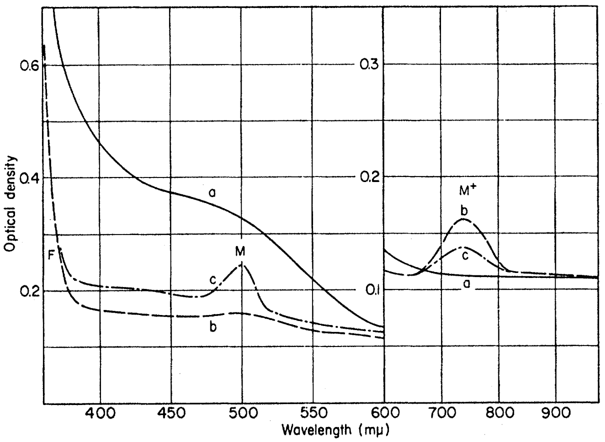

FIG. 2. Formation of M^+ centers upon warming crystal to 295°K following prolonged x irradiation at 77°K. Curve a, absorption spectrum at 77°K following x irradiation at 77°K; curve b, spectrum at 77°K but following slow warming to 295°K; curve c, after illuminating for 20 min with F light (335 mμ).

Note that, as in the case of the M^+ band in LiF (see Fig. 2 of Ref. 5), the M^+ band in NaF decays if the sample is kept in the dark for a long time at RT, but is reformed if the crystal is subjected to a short reirradiation below 260°K followed by warming. As in the foregoing case (Fig. 2), the M^+ band reappears at temperatures near RT.

Kinetics of M^+-Center Formation

Previous investigations have led to the proposal that M^+ centers in LiF are formed by the reaction $\alpha+F \rightarrow M^+$, apparently by the diffusion of an α center towards an F center. This conclusion is supported by the fact that the M^+ centers are not produced directly during the low-temperature x irradiation of the crystal, but are formed in a limited temperature range near RT,

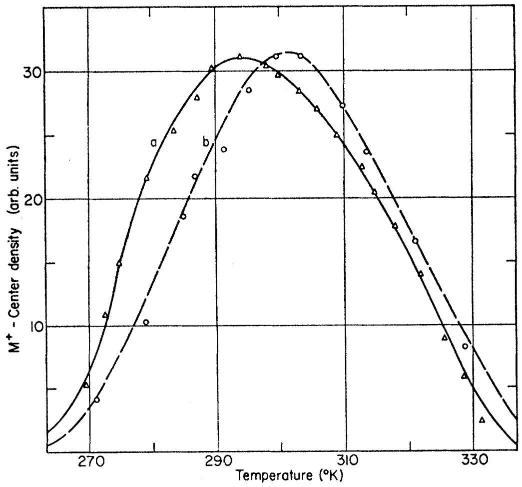

FIG. 3. Concentration of M^+ centers as a function of temperature following x irradiation at 77°K. Constant rate of heating, about 2°K per min. Curve a, NaF; curve b, LiF.

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[6] R. Fieschi, R. Oggioni, and P. Podini, Acta Phys. Polon. **26**, 633 (1964).

during the annealing of the crystal (Fig. 3). The present studies indicate that M^+ centers in NaF are also formed by the reaction $\alpha + F \rightarrow M^+$. Isothermal measurements of the generation of M^+ centers near RT were performed in the present work to determine the activation energies for the diffusion of the α centers in NaF and LiF. These measurements indicate that formation of the M^+ band can be described by first-order kinetics: $dn/dt = B(n_\infty - n)$, where n is the concentration of M^+ centers at time t, n_∞ is the maximum concentration reached, and B is a rate constant given by $B = B_0 \exp(-E/kT)$, where B_0 is a frequency factor and E is the activation energy for the reaction.

The method used to obtain the isothermal measurements was based on the fact that if M^+ centers have been formed and allowed to decay, they can be reformed rapidly by short reirradiation below 260°, followed by rewarming. The procedure adopted was as follows: (a) A fresh crystal was subjected to prolonged x irradiation at RT to produce a sizeable M^+ band; (b) the sample was then warmed to about 330°K until no M^+ band could be detected (Fig. 3); (c) the sample was then reirradiated for a short time (10 min) at 250°K and warmed rapidly to the control temperature, where the formation of M^+ centers was followed by recording the M^+ band as a function of time. Steps (b) and (c) were then successively repeated to obtain measuerments at different temperatures.

The results are summarized in Fig. 4, which shows semilog plots of the rate constant B versus $1/T$ for the formation of M^+ bands in NaF and LiF. From these data, the activation energies for M^+-center formation were found to be $E = 0.73$ eV for NaF and $E = 0.74$ eV for LiF. The corresponding frequency factors turn out to have about the same value, namely, $B_0 = 1.1 \times 10^{10}$ sec^{-1}. However, B_0 seems to depend on the amount of coloration of the sample; a larger value, $B_0 = 1.5 \times 10^{10}$ sec^{-1}, was obtained for a different NaF sample that was given a lower irradiation dose. This variation in the frequency factor could lead to a considerable uncertainty in the value obtained for the activation energy, unless care is taken to produce the same amount of coloration in the samples used for the isothermal measurements. Our method of performing the measurements on a single sample ensures the same initial irradiation in all cases, while the successive reirradiations are too short to change the total coloration produced by the prolonged initial irradiation. The uncertainty in the activation energies thus obtained is ±0.01 eV.

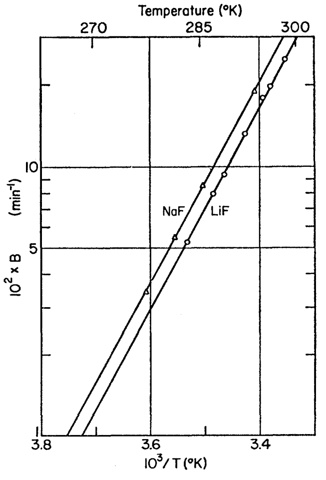

FIG. 4. Semilogarithmic plots of the rate constant for the formation of M^+ centers in NaF and LiF versus the reciprocal temperature.

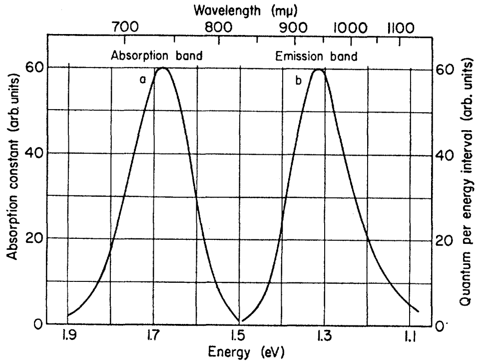

FIG. 5. Optical spectra of the M^+ center in NaF at 77°K; curve a, absorption spectrum; curve b, emission spectrum resulting from M^+ light illumination at 730 mμ.

M^+ Emission

Monochromatic stimulation in the 740-mμ absorption band yields an emission band peaking at 934 mμ at LNT. The emission and absorption spectra taken at LNT for the M^+ center in NaF are shown in Fig. 5. The shape of the emission band was corrected[5] for the spectral response of the photomultiplier and analyzing monochromator, and the intensity was converted to the number of photons per second per energy interval. The band thus obtained has a half-width of 0.163 eV, which is approximately the same half-width as the associated absorption band. In fact, the absorption and emission bands are approximately mirror images of each other.

It is known[6] that excitation in the M band produces an emission band at about 640 mμ. It was observed in the present work that in specimens containing M^+ centers the characteristic M^+ emission at 943 mμ is stimulated along with the M emission at 640 mμ by optical excitation in the M band. This appearance of M^+ emission may be due to partial absorption of the M emission by the M^+ band. Similar observations in LiF have been reported previously.[5]

On the basis of the assignment of the 740-mμ band to a transition of the M^+ center, it is expected that the center possesses the same $\langle 110 \rangle$ symmetry axes as the M center. The polarization properties of the emission produced by excitation in the 740-mμ band were measured as previously described.[5] The results indicate that the associated center is anisotropic. The degree of polarization obtained at LNT for exciting light polarized first in the [011] direction and then in the [001] direction are $P[011]=0.60$ and $P[001]=0.30$ when the directions of excitation and observation are the same. These values are not grossly different from the degree of polarization[7] that would be expected for dipoles directed along $\langle 110 \rangle$. Thus the polarization properties of the 943-mμ emission provide further support for the proposed M^+ assignment of the 740-mμ band.

CONCLUSIONS

In the present work, evidence has been presented to show that the 740-mμ absorption band in NaF arises from a transition of the M^+ center. The associated emission band is at 943 mμ.

In general, the formation of M and M^+ centers in NaF resembles that already reported for LiF. From kinetic studies of M^+-center formation it was possible to derive the activation energies for the diffusion of α centers in NaF and LiF. The values obtained in the present work are 0.73 ± 0.01 and 0.74 ± 0.01 eV, respectively, which are somewhat higher than the value 0.67 ± 0.04 eV reported by Farge, Lambert, and Smoluchowski[8] for M^+-center formation in LiF. It should be mentioned that the latter authors have recently shown[9] that a covalent bond between the α and F centers provides the attractive force leading to coagulation to an M^+ center.

As shown in Fig. 3, the M^+ band produced in NaF and LiF decays when the crystal is kept in the dark in the temperature range 290–340°K. During this decay there is only a slight increase in the M band. The conversion ratio $|\Delta\alpha_M/\Delta\alpha_{M^+}|$ for the transformation $M^+ \rightarrow M$ measured during the decay in the dark is considerably smaller than the ratios of 3.6 and 2.2 obtained for NaF (see above) and LiF (Ref. 5), respectively, when the conversion is induced by reirradiation at low temperature. The $M^+ \rightarrow M$ conversion can be expected when electrons are supplied. It was shown for LiF that the disappearance of the M^+ band near RT is accompanied by the formation of the R^+ band (Fig. 4 of Ref. 5), apparently according to the reaction $M^+ + F \rightarrow R^+$. Isothermal measurements performed in the present work for LiF indicate that the decay of the M^+ band and the growth of the R^+ band can be described by first-order kinetics. The activation energies derived from the isothermal decay of the M^+ band and from the growth of the R^+ band turn out to have about the same value of 0.82 eV. These results further support our previous conclusion that R^+ centers are formed by the reaction $M^+ + F \rightarrow R^+$. It is probable that R^+ centers in NaF are formed by an analogous reaction. Further studies in NaF are under way.

Note added in proof. While this paper was in press, the author became aware that absorption measurements on NaF were published by K. Konrad and T. J. Neubert [J. Chem. Phys. **47**, 4946 (1967)]. The conclusions of these authors regarding the absorption band associated with M^+ center are in agreement with this paper; preliminary results of this paper were given in Israel AEC Annual Report No. IA-1168, 1967 (unpublished).

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