

Thermal Production of F -Aggregate Centers in KCl

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The optical absorption spectrum of a KCl crystal x rayed at liquid nitrogen temperature has been followed during warming in the dark to about 320°K. This measurement not only provides a means for the study of M -center formation by the aggregation of separated F centers, but also the formation of other F -aggregate centers. The principal features of this measurement are as follows. A small initial M band appears superimposed on the F' band at liquid nitrogen temperature upon completion of x raying. Warming to about 207°K results in the disappearance of the F' band with the M band remaining essentially unchanged. At 207°K the onset of F -center migration is indicated by the initiation of growth of the M band and several longer wavelength bands. The M band shows continued growth with increasing temperature, increasing by over an order of magnitude upon

reaching room temperature. Owing to a particularly large M -center concentration (in the presence of few R centers), Okamoto's M_4 excited M -center band is directly observed. Absorption structure appearing to the long-wavelength side of the N bands at about 1350 $m\mu$ and other structure between the M and the N bands likewise show steady growth with increasing temperature above 207°K, but became unstable at higher temperature. The 1350- $m\mu$ structure, which shows a steady increase over the temperature range 207–248°K, declines above 248°K and disappears completely by 269°K. A possible fundamental role of luminescence in the production of F -aggregate centers by varied methods is mentioned, and the primary influence of local vibrations of the lattice in affecting the optical transition of the M center is discussed.

INTRODUCTION

THE discovery by Ottmer¹ of the optical absorption band that is known as the M band in alkali halide crystals marks the initial effort in the study of the family of optical absorptions appearing to the long-wavelength side of the F band designated as the R , M , and N bands. Molnar,² for whom the M band is named, and Petroff³ subsequently carried out systematic studies of these bands in various x rayed and additively colored alkali halides, and Seitz^{4,5} made tentative proposals for the models of the centers giving rise to these bands. The principal underlying basis for the assignment of the models to the R - M - N series was the fact that these absorption bands appeared to be products of F -center coagulation, created at the expense of the F band. It is for this reason they are referred to collectively as F -aggregate centers.

The current count of optical absorption bands associated with F -aggregate centers has grown considerably larger than the R_1 , R_2 , M , and N bands reported by the early investigators. Okamoto⁶ has recently made a careful investigation of the optical anisotropy of F -aggregate bands and he has been able to enumerate as many as four R -center absorptions, six M -center absorptions, and two N -center absorptions. Several of these bands are particularly weak in absorption strength and lie beneath a much larger F band.

In recent years the M center has been singled out for rather close scrutiny. Studies of the thermal equilibrium between F and M centers in additively colored crystals⁷ and also the nonequilibrium production of F and M

centers in x-rayed crystals⁸ supported the earlier contention of van Doorn and Haven⁹ and Pick¹⁰ that the M center is a simple aggregation of two F centers (F_2 model of the M center). This is the same model that Seitz⁴ anticipated earlier for the R_2 center. As of the present writing the M center appears to be the only F -aggregate center whose model is on a reasonably secure foundation.

There are two principal methods for the production of F -aggregate centers in alkali halide crystals. The first method is the exposure of a crystal to ionizing radiation (x rays, gamma rays, etc.) and F -aggregate centers appear together with F centers. The second method consists of irradiating a crystal that initially contains F centers with light at the wavelength of the F band; the F band decreases as a result of this irradiation and the R - M - N series appears. The latter process of photochemical or optical conversion as it is referred to, occurs if the F centers are initially present in the crystal either as a result of additive coloration with excess alkali metal or as a result of x-ray irradiation.

Both processes of F -aggregate production are strongly temperature dependent. In the case of optical conversion, F -center aggregation is negligible in the temperature range where $F \rightarrow F'$ conversion is appreciable. For KCl optical $F \rightarrow M$ conversion does not become important until temperatures somewhere in the vicinity of 200–230°K are reached.^{11,12} Above this temperature a number of investigators have reported on the temperature dependence.^{3,11–13} In the case of the production of F -aggregate centers by ionizing radiation, it had been generally thought that such production is inhibited at low temperatures.¹⁴ It has recently been demonstrated

¹ R. Ottmer, *Z. Physik* **46**, 798 (1928).

² J. P. Molnar, dissertation, Massachusetts Institute of Technology, 1940 (unpublished) and *Phys. Rev.* **59**, 944 (1941).

³ S. Petroff, *Z. Physik* **127**, 443 (1950).

⁴ F. Seitz, *Revs. Mod. Phys.* **18**, 384 (1946).

⁵ F. Seitz, *Revs. Mod. Phys.* **26**, 7 (1954).

⁶ F. Okamoto, *Phys. Rev.* **124**, 1090 (1961).

⁷ C. Z. van Doorn, *Phys. Rev. Letters* **4**, 236 (1960).

⁸ B. J. Faraday, H. Rabin, and W. D. Compton, *Phys. Rev. Letters* **7**, 57, 433 (1961).

⁹ C. Z. van Doorn and Y. Haven, *Phillips Research Repts.* **11**, 479 (1956), and C. Z. van Doorn, *ibid.* **12**, 309 (1957).

¹⁰ H. Pick, *Z. Physik* **159**, 69 (1960).

¹¹ F. Lüty, *Z. Physik* **165**, 17 (1961).

¹² T. Tomiki, *J. Phys. Soc. Japan* **15**, 488 (1960).

¹³ W. E. Bron and A. S. Nowick, *Phys. Rev.* **119**, 114 (1960).

¹⁴ W. H. Duerig and J. J. Markham, *Phys. Rev.* **88**, 1043 (1952).

that M centers are induced by x rays in the liquid-nitrogen and liquid-helium temperature range,⁸ although in significantly smaller quantity than is usually observed near room temperature.

The picture that is held is that M -center formation by x rays occurs at low temperature by the production of a pair of F centers at neighboring negative ion sites. F centers produced at isolated sites presumably do not aggregate to form M centers at low temperature. The observation that warming a crystal after x-ray irradiation at low temperature resulted in a much enhanced M -center concentration⁸ has provided evidence that isolated F centers can indeed be induced to aggregate at sufficiently high temperature. This process like the photochemical process emphasizes the essential role of thermal activation in the production of F -aggregate centers. It is the purpose of this paper to describe a series of experiments in which the optical properties of KCl to the low-energy side of the F band were examined during warming after an extended x-ray exposure at liquid-nitrogen temperature. These measurements reflect on the processes of F aggregation and at the same time provide a method for attaining particularly large concentrations of F -aggregate centers.

EXPERIMENTAL PROCEDURE

The experimental work deals with an extended series of measurements performed on a single KCl crystal obtained from the Harshaw Chemical Company. The crystal was cleaved along (100) planes into a flat plate, approximately 0.61 mm thick, and mounted in a Hofman low-temperature, double-walled Dewar. The Dewar was provided with a beryllium entrance window for the x-ray beam and calcium fluoride windows for optical measurement. These windows were mounted on a head that could be manually rotated in order that the crystal could be optically measured along the direction

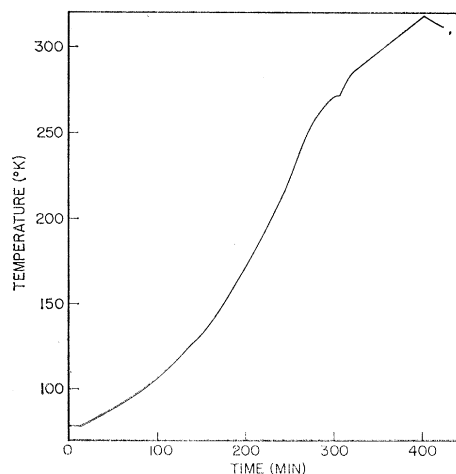


FIG. 1. The time sequence of warming of KCl following an extended x-ray exposure at liquid-nitrogen temperature.

of x raying. This direction was along the perpendicular to the face of the crystal plate.

The crystal was mounted on a copper block provided with an aperture for optical measurement. The junction of a copper-Constantan thermocouple was mounted against the crystal face, and the junction and a portion of the surrounding crystal were covered with Dow Corning 4 Compound to insure thermal contact at low temperature. The thermocouple was initially checked at the ice point and at liquid-nitrogen temperature and was found to agree closely with standard calibrations.

The crystal was kept in the dark during x raying and during subsequent warming, and was subjected to light only during periodic optical measurement and intervals of bleaching to be described. Optical measurements were made with a Cary, model 14MR, recording spectrophotometer, modified to accommodate the Dewar. The x-ray exposure was performed with a Machlett OEG-60, tungsten-target tube operated at 50 kV and 50 mA using a Bracke-Seib dc generator with an estimated output ripple of about 5%. The approximate distance of the crystal from the anode of the x-ray tube was 11.7 cm.

The x-ray exposure was performed at liquid-nitrogen temperature for a period of 61 h. The Dewar was refilled as required during irradiation and the crystal temperature was measured repeatedly to insure that liquid-nitrogen temperature was maintained throughout the exposure. Following the termination of x raying, the nitrogen was poured from the Dewar, and the Dewar and crystal within were allowed to warm under the action of ambient heating. The warming characteristic is shown in Fig. 1. Over an appreciable portion of time, the rate of warming was near 1 deg/min. In order to extend the measurements above room temperature, warm water was transferred to the Dewar at temperatures above about 270°K. This procedure accounted for the jog in the data of Fig. 1 and provided for an increase in temperature to about 318°K before the temperature declined.

During the warming sequence of Fig. 1 periodic optical absorption measurements were made by scanning the spectral range from 1700 to 700 $m\mu$, Figs. 2-5. The 700- $m\mu$ limit was chosen so as to avoid irradiating into the F band with the spectrophotometer beam. Upon reaching 312°K, the terminal point of Fig. 1, measure-

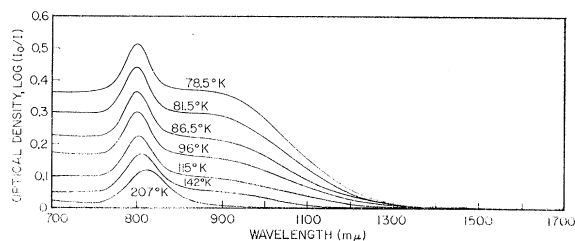


FIG. 2. The optical absorption spectra of KCl over the temperature range 78.5-207°K upon the termination of x raying at liquid-nitrogen temperature.

ments were extended to shorter wavelengths into the tail of the *F* band (Figs. 5-7).

RESULTS

The data as obtained in chronological order are shown sequentially in Figs. 2-7. Figure 2 shows the warming sequence from 78.5 to 207°K. Upon the termination of x raying, the *M* band is shown perched on top of a much broader *F'* band. As the temperature increases the *F'* band is observed to diminish while the *M* band remains essentially unchanged except for slight thermal shifting and broadening. At 207°K the *F'* band has fully disappeared and the *M* band appears to be the only band present in the spectral range 700-1700 μ .

Figure 3 shows the optical spectra in the range 207 to 248°K as the warming sequence continued. The 207°K data are the same as shown in Fig. 2. It is observed that there is a considerable enhancement of absorption structure. The most prominent change is roughly an order of magnitude increase in the *M* band. In addition longer wavelength structure makes its appearance in the vicinity of 930 and 1350 μ . The latter absorptions also increase in magnitude over the temperature range 207-248°K.

Figure 4 shows a continuation of the warming sequence over the temperature range 248 to 295°K. To avoid additional complication in the figure the spectra at 288 and 295°K are reproduced only over the range from the peak of the *M* band to the peak of the 930- μ structure. The magnitude of the *M* band and the structure at 930 μ continue to increase over this temperature range extending to 295°K, although at a decreasing rate, and the band at 1350 μ is simultaneously observed to vanish. At 269°K the 1350- μ band has fully disappeared. In Fig. 4 the spectral region between the *M* and 930- μ structure shows a general filling in, owing presumably to the growth of additional absorption.

Figure 5 shows the full 295°K spectrum from 700 and 1700 μ , and the spectrum taken at 312°K (the terminal point of Fig. 1) with the short-wavelength

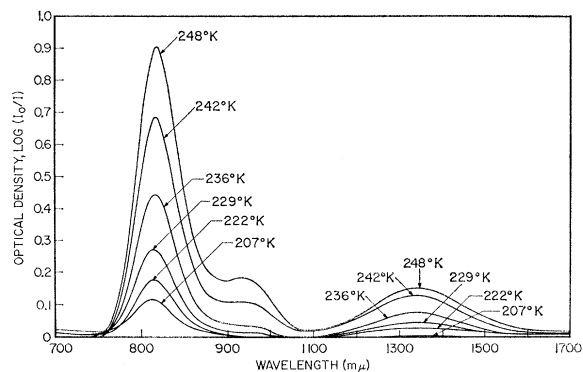


Fig. 3. The optical absorption spectra of x-rayed KCl over the temperature range 207-248°K in continuation of the data of Fig. 2.

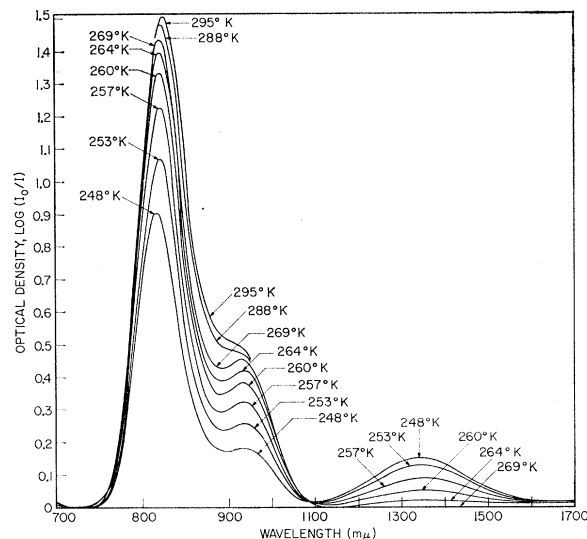


Fig. 4. The optical absorption spectra of x-rayed KCl over the temperature range 248-295°K in continuation of the data of Fig. 3. The data at 288 and 295°K are plotted only over a limited spectral range.

limit extended into the region of the *F* band. In addition to considerable growth in the *M* band, there appears to be a diminution of absorption structure in the vicinity of 930 μ in warming above 295°K.

Upon reaching 312°K the Dewar was evacuated and lowered to liquid-nitrogen temperature once again. During the evacuation the Dewar was pumped for a period of approximately 2 h during which time the crystal equilibrated near room temperature. The data taken at liquid-nitrogen temperature are also shown in Fig. 5. Absorption structure was observed to the short-

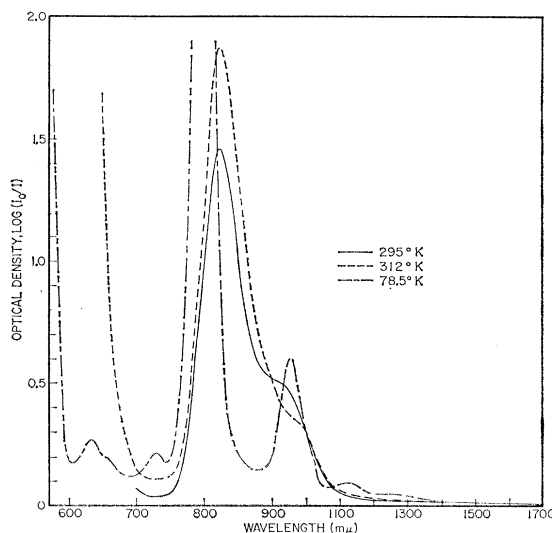


Fig. 5. The optical absorption spectra of x-rayed KCl at 295 and 312°K, and after subsequent cooling to liquid-nitrogen temperature in continuation of the data of Fig. 4.

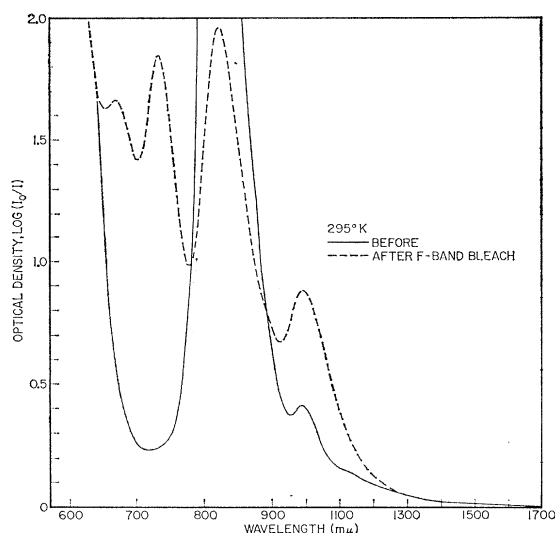


Fig. 6. The optical absorption spectra of x-rayed KCl at room temperature before and after bleaching with *F*-band light. These spectra were taken 5 days after the data of Fig. 5, during which time the crystal was kept in the dark at room temperature.

wavelength side of the *M* band at 634, 656, and 730 $m\mu$ and on the long-wavelength side at 958, 1130, and 1260 $m\mu$. The 656- and 730- $m\mu$ bands correspond with reported positions of the R_1 and R_2 bands, respectively, and the 958- $m\mu$ band appears to be in agreement with the position of the N_1 band. To the long-wavelength side of the N_1 band a shoulder at about 1020 $m\mu$ falls at the expected position of the N_2 band. In addition, a shoulder just to the long-wavelength side of the *M* band was further resolved into a weak band peaking at approximately 853 $m\mu$ upon adding liquid helium to the Dewar. The crystal was thereafter returned to room temperature where it was allowed to equilibrate for a 5-day period in the dark.

The absorption spectrum after this 5-day period at room temperature is shown in Fig. 6. The principal change noted is a considerable enhancement of the *M* band. There is also some smaller enhancement in the absorption spectrum in the *R*-band region (in the valley between the *F* and *M* bands), and the N_1 band appears to be partially resolved at 988 $m\mu$. At this point the crystal was given an extended bleach at the wavelength of the *F* band, using a tungsten lamp and an interference filter passing at a peak position of 560 $m\mu$. As shown in Fig. 6 there is a large enhancement in the R_1 and R_2 bands, the *M* band is considerably reduced, and the N_1 band and the region to longer wavelengths is enhanced.

Figure 7 shows the absorption spectrum 6 days following the optical bleach. During this period the crystal was still maintained at room temperature in the dark. It is clear that the changes induced by previous photochemical bleaching in the *F* band were not permanent. The R_1 and R_2 bands are reduced and the *M* and *N* bands are enhanced. Upon examination of this crystal

at liquid-nitrogen temperature the R_1 and R_2 bands are more fully resolved as are the N_1 and what is perhaps the N_2 band on the long-wavelength shoulder at about 1020 $m\mu$. Also the structure to longer wavelengths at 1130 and 1260 $m\mu$ (also seen in Fig. 5) is much enhanced.

DISCUSSION

It is clear from the data that considerable *F* aggregation is induced upon warming a KCl crystal x rayed at low temperature. This technique allows for the unique production of *M*-band absorptions well in excess of optical densities of 2 in the presence of insignificant *R*-center absorption (Fig. 5). When additional aggregation is allowed to take place upon standing at room temperature, the optical density is extrapolated to be approximately 3.5 at the peak position of the *M* band (Fig. 6). Upon bleaching in the *F* band after warming, large *R* and *N* absorptions may also be induced in the range of 1 to 2 in optical density (Figs. 6-7). Owing to a coloration gradient accentuated by the use of unfiltered x rays, Smakula's formula gives only a rough estimate of the average concentration of centers. The initial *M*-center concentration at liquid-nitrogen temperature after x raying is computed to be $6.7 \times 10^{15}/\text{cm}^3$ using an *M*-center oscillator strength of 0.38 for a Gaussian band shape.⁸ On the basis of a quadratic relation between *F* and *M* centers,⁸ $n_M = \text{const} \times n_F^2$, the initial *F*-center concentration is computed to be $4 \times 10^{18}/\text{cm}^3$. Upon warming from liquid-nitrogen temperature to the vicinity of 320°K the *M*-center concentration is approximately $1.4 \times 10^{17}/\text{cm}^3$, an increase of about a factor of 20. Presumably, the surface coloration is substantially larger than the average volume coloration.

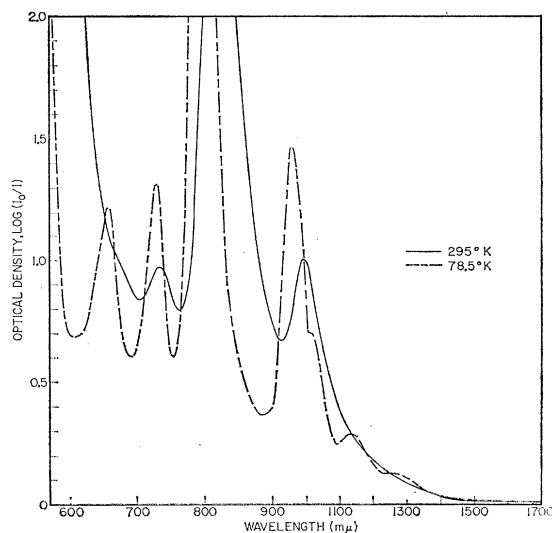


Fig. 7. The absorption spectra of x-rayed KCl at room temperature and liquid-nitrogen temperature. These data were taken 6 days after the data of Fig. 6, during which time the crystal was kept in the dark at room temperature.

The warming technique provides not only an added method for the production of the known *F* aggregates (*R*, *M*, and *N* centers), but also a means for the introduction of other centers. The structure at 1350 $m\mu$ appears to be stable only in the temperature range 207–269°K with maximum stability at 248°K (Figs. 3–4). Okamoto⁶ reports a band at 1380 $m\mu$ in KCl which is converted from a band peaking at 1460 $m\mu$ upon bleaching with *F*-band light at liquid-nitrogen temperature, and upon subsequent warming to room temperature the latter band is reformed at the expense of the absorption at 1380 $m\mu$. It is not clear that the 1380- and 1350- $m\mu$ bands are identical. The 1350- $m\mu$ absorption reported here does not appear to be interconvertible with a longer wavelength band which is stable in the vicinity of room temperature, and moreover, it appears to have a somewhat larger half-width than the 1380- $m\mu$ band.

At least three bands have been observed in this work that do not appear to have been reported earlier. Two of these bands are partially resolved at liquid-nitrogen temperature (Figs. 5 and 7), and are observed to peak at approximately 1130 and 1260 $m\mu$. A third band is only weakly indicated as a shoulder on the long-wavelength side of the *M* band at liquid-nitrogen temperature (Fig. 5). This band is partially resolved at liquid-helium temperature and falls at about 853 $m\mu$.

A most interesting consequence of the particularly large *M*-center to *R*-center concentration ratio in this work is the direct observation of Okamoto's *M*₄ band.⁶ This absorption which is presumably due to an excited state transition of the *M* center is shown in Fig. 5 at liquid-nitrogen temperature, peaking at about 634 $m\mu$, with a smaller *R*₁ band appearing as a long-wavelength shoulder. This band predicted to be in the ratio of 1:40 with the *M* band (Okamoto's *M*₁ band) can apparently be easily investigated with the high *M*-center concentrations produced by the technique herein described.

The situation in the spectral range between the peaks of the *M* and *N* bands seems to be complicated owing to the presence of unresolved band structure. As pointed out above in connection with Fig. 4 there appears to be a filling in of the absorption structure between the *M* band and the 930- $m\mu$ absorption structure. A subtraction of the spectra at 269°K from that at 295°K indicates the presence of at least one absorption band peaking in the neighborhood of 855 $m\mu$. This may be identical to the weak structure reported above at 853 $m\mu$ upon lowering the crystal to liquid-helium temperature. It is furthermore noted absorption structure which peaks in the neighborhood of 930 $m\mu$ (Figs. 3–4) is observed to disappear either in full or in part in warming between 295 and 312°K (Fig. 5). A subtraction of the absorption data at 312°K from those at 295°K after normalization of the *M* bands, shows that the absorption peak of the depleted structure occurs at approximately 940 $m\mu$. The absorption shoulder remaining to the long-

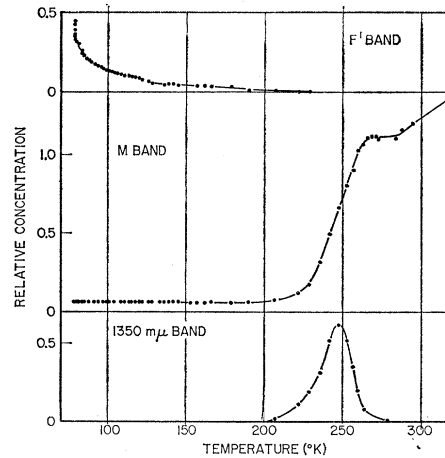


FIG. 8. Relative concentrations of centers arising from the *F'*, *M*, and 1350- $m\mu$ bands in KCl as a function of temperature following x-raying at liquid-nitrogen temperature.

wavelength side of the *M* band at 312°K (Fig. 5) appears to be *N*-band structure. This structure is fully resolved as shown at liquid-nitrogen temperature into a prominent *N*₁ band at 958 $m\mu$ and perhaps a weaker *N*₂ long-wavelength shoulder in the neighborhood of 1020 $m\mu$. The assignment of this structure is in agreement with the *N*-band structure in Figs. 6–7 at both room and liquid-nitrogen temperatures. In Fig. 7 the *N*₂ band at 1020 $m\mu$ appears to be more fully resolved. It is concluded therefore that the rather broad structure appearing in the range 900–1000 $m\mu$ in warming from liquid-nitrogen temperature (Figs. 3–4) is an admixture of both *N* bands and some other absorption peaking near 940 $m\mu$. The spectral region between the peak of the *M* band and the *N*₁ bands appears to be a most active spectral range in warming following x-ray irradiation. Measurements using polarized light in this spectral range might prove to be most fruitful for unraveling the overlapping structure which appears to be present.

Figure 8 shows the relative concentration of the centers giving rise to the *F'*, *M*, and 1350- $m\mu$ bands as a function of temperature. In the case of the *F'* band the relative peak height at 830 $m\mu$ (with the *M* band subtracted) is assumed to be proportional to the concentration of centers, taking the half-width of this band to be temperature independent, and in the case of the 1350- $m\mu$ band the relative peak height is also assumed proportional to the concentration since there does not appear to be any appreciable half-width change in the limited temperature range of this band. The data for the *M* band in Fig. 8 are proportional to the area under the absorption curve (peak height times half-width) and a unit of 1.0 of the ordinate corresponds to roughly 10^{17} centers/cm³. It is clear that the *F'* centers introduced by x raying are fully depleted before the onset of growth of the *M* bands. This disappearance of the *F'* band seems to fall at considerably lower temperature than

the 200°K point reported by other investigators.^{15,16} The onset of M -center formation is noted to occur at about 207°K and after a linear rise reaches a plateau at about 270°K and thereafter increases at a slower rate. The slower rate may be characteristic of aggregation of F centers over large distances while the initial rise and leveling off may be representative of the aggregation of F centers closely spaced to one another. In this regard it would be important to verify that the rate of warming was slow enough that equilibrium concentrations of centers were present continuously at each temperature. This point is deserving of further investigation particularly in light of the fact that M centers appear to continue to be formed upon standing in the dark over periods of days following the warmup (Figs. 5–6). It would not only be of interest to study the growth characteristic for different rates of heating following x raying but it would be most interesting to extend these measurements into the temperature range where F aggregates are reported to be disrupted.¹² Although there is little that can be said with respect to the nature of the 1350- $m\mu$ band, it appears from Fig. 8 to be unrelated to the M center owing to the fact that the M -center growth is almost perfectly linear in the temperature range over which the 1350- $m\mu$ band reaches a maximum and declines. Accordingly, two likely models whose existence might be anticipated, the M' center (M center plus an electron) and the singly ionized M center (Seitz R_1 model⁴) are unlikely for this reason (as well as others).

Figure 6 shows the typical enhancement of the R_1 , R_2 , and N bands upon bleaching with F -band light. It is noticed that the M band simultaneously undergoes a decline. Since the rates of growth of these bands were not followed as a detailed function of bleaching time, it is not known whether the decrease in the M band was preceded by some growth. The interesting observation was made that upon standing in the dark after the bleach there was considerable enhancement of the M band and decrease of the R_1 and R_2 bands (Fig. 7). At the same time the N band appeared also to increase by some small amount. It is apparently clear that optical conversion of F aggregates are not in all cases stable at room temperature.

The mechanism of F aggregation seems to be complicated by the fact that it can be activated thermally in addition to the methods of photochemical conversion and x raying in the dark. One point of view to take is that all three processes produce an effect in the crystal that leads to some identical chain process giving rise to F -aggregate centers. It is interesting to take note that there appears to be at least one factor which may be common to all of these processes, namely, F -band light. In the instance of warming following x-ray ex-

posure, the thermoluminescence of the warmed crystal may provide this light, and in x raying in the "dark," the x-ray-induced photoluminescence of the crystal may likewise promote the formation of F aggregates. Large differences in the ratio of M to F centers in different alkali halides x rayed at room temperature¹⁷ could perhaps be explained on the basis of varying luminescence efficiencies. These possibilities are certainly deserving of further attention in view of the fact that thermoluminescence of x-rayed crystals^{15,18} and x-ray-induced photoluminescence^{19,20} are appreciable in the alkali halides, and moreover, the warming characteristic of the M band in Fig. 8 bears marked similarities to the temperature dependence of photochemical $F \rightarrow M$ conversion.¹¹ If $F \rightarrow M$ conversion results from the Coulomb attraction of F' centers and anion vacancies created by optical photons as has been suggested,¹¹ the presence of F -band light in the various processes of M -center formation may prove to be significant. It should be mentioned that an optical photon does not appear to be absolutely necessary for this mechanism to be operative, since x rays presumably could act directly to produce F' and alpha centers in the dark, and the energy release in nonradiative recombinations during warming from low temperature after x raying may likewise promote the production of F' and alpha centers and thus eventually M centers.¹⁷

Figures 9–10 give peak position and half-width data, respectively, of the M band in KCl as extracted from this and earlier⁸ work. The half-width data at high temperature were based only on the short-wavelength side of the band owing to appreciable overlapping structure on the long-wavelength side. The thermal shift of the peak of the M band shows the same general behavior observed for the F band,²¹ except that the magnitude of this shift in the case of the M band appears to be considerably less than that observed for the F band. Figure 10 gives a plot of the half-width of the M band as a function of the square root of the absolute temperature in order to obtain an estimate of ν_0 , the vibrational frequency that influences the M center in its ground state. Analogous to similar treatments for the F center^{21,22} ν_0 turns out to be approximately 3.2×10^{12} cps for the M center in KCl, which is not grossly different for corresponding values obtained for the F center in KCl (2.6×10^{12} cps, reference 21, and 2.96×10^{12} cps, reference 22), but about a factor of 2 less than the value of 6.3×10^{12} cps, the longitudinal optical frequency of the

¹⁷ H. Rabin "Proceedings of International Conference of Crystal Lattice Defects, Kyoto, 1962" [Suppl. J. Phys. Soc. Japan (to be published)].

¹⁸ A. Halperin and N. Kristianpoller, J. Opt. Soc. Am. **48**, 996 (1958).

¹⁹ W. E. Spicer, Phys. Rev. **106**, 726 (1957).

²⁰ G. Bonissoni, P. Camagni and G. Chiarotti, *Proceedings International Conference on Color Centers and Crystal Luminescence Torino, Italy 1960* (Litografia E. Gili, Torino, 1961), p. 153.

²¹ G. A. Russell and C. C. Klick, Phys. Rev. **101**, 1473 (1956).

²² J. D. Konitzer and J. J. Markham, J. Chem. Phys. **32**, 843 (1960).

¹⁵ D. Dutton and R. Maurer, Phys. Rev. **90**, 126 (1953).

¹⁶ A. Halperin, A. A. Braner, M. Schlesinger, N. Kristianpoller, *Proceedings International Conference on Semiconductor Physics Prague 1960* (Czechoslovakian Academy of Sciences, Prague, 1961), p. 724.

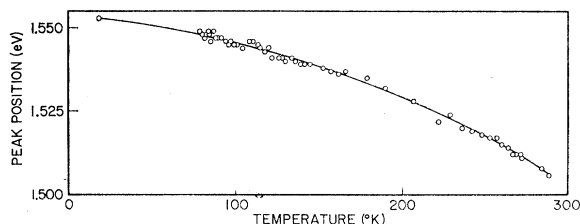


FIG. 9. Variation of the peak position of the *M* band as a function of temperature for KCl.

lattice. The latter fact leads one to conclude that the *M* center in the ground state is more strongly influenced by local vibrations than vibrations characteristic of the perfect lattice. Unlike NaCl,²³ however, in KCl the value of ν_0 for the *M* center is not appreciably larger than ν_0 for the *F* center.

SUMMARY

The principal results of this investigation may be summarized as follows:

(1) Warming a KCl crystal x rayed at liquid-nitrogen temperature results in the production of sizeable absorptions to the long-wavelength side of the *F* band.

(2) The principal growth upon warming occurs in the *M* band due presumably to the aggregation of isolated *F* centers that are immobile at low temperature. The critical temperature for this aggregation in KCl occurs at approximately 207°K.

(3) Other absorption structure peaking at approximately 1350 $m\mu$ disappears at about 269°K after reaching a maximum at about 248°K. This structure appears to be unrelated to the *M* center.

(4) New absorption bands are observed at approximately 1130 and 1260 $m\mu$ to the long-wavelength side of the *N*-band structure, and a variety of absorption changes are observed between the *M* and *N* bands. At least one band is present in the neighborhood 853–855 $m\mu$ which grows upon warming, and other absorption structure at about 940 $m\mu$ which also grows upon warming is unstable above about 295°K. There is apparently considerable absorption activity in the vicinity between the *M* and *N* bands that is deserving of further attention.

(5) The warming technique after x raying allows for

²³ W. D. Compton and C. C. Klick, Phys. Rev. **112**, 1620 (1958).

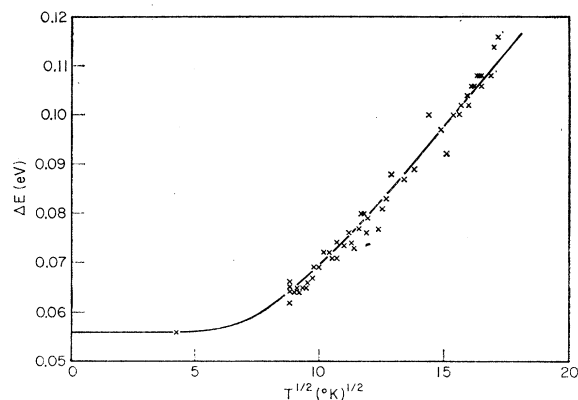


FIG. 10. Variation of the half-width (ΔE) of the *M* band in KCl as a function of the square root of the absolute temperature (T). Experimental points are indicated along with the theoretical curve given by $\Delta E = A[\coth(h\nu_0/2kT)]^{1/2}$ with $A = 0.056$ eV and $\nu_0 = 3.2 \times 10^{12}$ cps.

the production of considerable *M*-center concentrations in the presence of few *R* centers. The fact allows for the direct observation of one of the bands that have been attributed by Okamoto to be due to *M*-center excited states.

(6) The metastable character of *F*-aggregate centers induced by photochemical bleaching is demonstrated by a sizeable enhancement of the *M* band at the apparent expenses of the *R*₁ and *R*₂ bands upon standing at room temperature after the bleach.

(7) The production of *F*-aggregate centers by x raying in the dark in the vicinity of room temperature and by warming after x raying at low temperature may be strongly influenced by luminescence of the crystal itself. Accordingly, the same mechanism that is operative in optical *F* → *M* conversion may also play a role in these processes of *F* aggregation.

(8) An estimate of the vibrational frequency of the lattice which influences the *M* center in its ground state is not grossly different than similar values determined for the *F* center in KCl. These values are about half of the magnitude the longitudinal optical frequency of the lattice.

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