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Ionized Electron Centers in Alkali Halide Crystals†

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New optical-absorption bands in alkali halide crystals are attributed to transitions of ionized F-aggregate centers. These bands are produced by cooling crystals containing F-aggregate centers to liquid-helium temperature and exposing them first to x rays and then to near-ultraviolet light. The x-ray exposure introduces trapped-hole centers, namely, V_K and H. Optical excitation at the spectral region of the overlapping V_K and H bands results in a decrease of both F-aggregate center and V_K-H absorption, and the production of the new bands in the near infrared. In KCl and KBr containing M centers, the M band transforms with a fixed ratio to bands at 1.40 and 1.49 μ, respectively. This ratio is also maintained in the restoration of the M band with subsequent F-light exposure. When optical dichroism is initially present in the M bands, the same dichroism appears in the new bands following the transformation process. These bands have been identified as transitions of the F_2^+ center. For crystals containing R centers, a one-to-one correspondence of R bands with a new near-infrared band attributed to the F_3^+ center is similarly observed. In KCl this band strongly overlaps the spectral position of the N_1 band at 0.96 μ. In KBr the F_3^+ transition lies at 1.02 μ and is clearly resolved from the N_1 band which apparently peaks at 1.07 μ. There is evidence to indicate that F_3^+ centers are also produced at room temperature as a result of either x-ray exposure of a virgin crystal or bleaching with F light of an additively colored crystal. For KCl and KBr crystals containing relatively large R and N bands, x-ray and near-uv exposure also results in the production of additional bands. First, a new absorption band is superimposed on the F_2^+ transition. The origin of this band is not known. Second, a band forms at 1.67 μ in KCl and 1.80 μ in KBr in crystals containing an N_1 band enhanced by annealing an additively colored crystal at 85°C. This band is tentatively ascribed to the singly ionized N_1 center, N_1^+.

INTRODUCTION

In recent years considerable work has been done to determine the nature of the centers which give rise to the R, M, and N optical-absorption bands in alkali halide crystals. The principal result of this effort has been increasing support for models which describe these centers as an aggregation of F centers. Van Doorn and Haven[1] first suggested that the M center is composed of the simplest F-center aggregation: two nearest-neighbor F centers lying along a ⟨110⟩ lattice direction. Studies of F- and M-center equilibria in both additively[2] and x-ray[3] colored crystals, as well as the results of magnetic-resonance[4] investigations, have supported this so-called F_2 model of the M center. Likewise, the proposal by van Doorn[5] and Pick[6] that the R center corresponds to an equilateral triangular array of three nearest-neighbor F centers forming a (111) lattice plane (F_3 model) has also received experimental confirmation.[7–9] The N_2 center, described by Pick[6] as arising from a tetrahedral configuration of four associated F centers has received some experimental support.[7] Since the F center is an electron trapped at an anion vacancy, these F-aggregate centers all have the property of being electrically neutral clusters of anion vacancies with trapped electrons.

It is reasonable to expect that various charged varieties of the F-aggregate centers can be produced, and indeed this has been shown to be the case for M and R centers which trap electrons[10] forming negatively charged M' and R' centers, respectively. Ionized forms of the F aggregates, which would have a net positive charge, have been predicted[11] but their existence has never been established. Although recent optical studies involving the temporary bleaching of the M center at low temperatures had a possible interpretation in terms of F_2^+-center formation,[12,13] the suggestion that the effect could be explained by the formation of a metastable M-center state[13] was confirmed by spin resonance.[4]

There are three basic considerations which may contribute to the successful production of ionized F-aggregate centers when combined in a single experiment. First, it is reasonable to initially introduce into the crystal the F-aggregate centers to be ionized. It is probably simpler to remove an electron from an existing F-aggregate center than to synthesize the desired center from its electronic and vacancy components. Second, in the event that ionized centers are thermally unstable, the greatest chance of success would be expected at low temperatures. Finally, the F-aggregate electron must be removed at least long enough for the observation of the ionized center. Specifically, this

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† A preliminary account of this work was given at the New York meeting of the American Physical Society, January 1965 [Bull. Am. Phys. Soc. 10, 77 (1965)].

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could involve using another center which traps an electron from an aggregate center.

Trapped-hole centers offer a particularly attractive defect to employ in the production of stable ionized F-aggregate centers. An electron in an aggregate center will be irreversibly removed if it can be induced to recombine with the hole. The V_K center,[14] or the self-trapped hole, is a likely center for this use. It is normally produced at low temperature and can be annihilated by electron capture as evidenced by its recombination luminescence.[15] The H center[16] is also a possible electron-annihilation center at low temperature.

X-ray exposure of virgin alkali halide crystals at liquid-helium temperature results in the simultaneous formation of both V_K and H centers.[17] Since both F-aggregate centers and hole-trapping centers can be independently introduced into a crystal, the possibility exists of producing and identifying ionized F aggregates. It would be expected that this process can be stimulated by optical means. First the absorption bands associated with trapped holes should decrease. In the case of the V_K center the perfect lattice would be restored, and in the case of the H center, an interstitial ion would probably form. Second, the F-aggregate bands should simultaneously transform to new bands associated with the ionized F aggregates.

A preliminary account of a series of experiments employing this technique has previously been given.[18] These studies pointed to the existence of the F_2^+ and F_3^+ centers. A full account of this work is herein described.

EXPERIMENTAL PROCEDURE

Crystals obtained from the Harshaw Chemical Company were colored either additively or by x raying at room temperature. Additive coloration of KCl, KBr, and KI in potassium vapor was carried out at roughly 550–670°C using either a sealed copper tube or a nitrogen pressurized system similar to that described by Van Doorn.[19] Prior to use, crystals were cleaved to appropriate size, wrapped in aluminum foil, and heated to about 550°C for several minutes. After quenching to room temperature the crystals contained primarily F centers. Initial F-center concentrations used in these studies ranged from about 5×10^{17} to $10^{18}/\text{cm}^3$.

Crystals were x rayed at room temperature or low temperatures using a 50-kV dc supply operating at approximately 40 mA. The x-ray tube (Machlett OEG-60) had a tungsten target, and the Be exit window of the tube was located 10 to 15 cm from the crystal. X-ray exposure times normally ranged from about 30 to 90 min, and x rays were either unfiltered or filtered with $\frac{1}{2}$ mm Al. Crystals were always shielded from room light during the x-ray exposure.

TABLE I. Peak positions at LHeT of optical-absorption bands in KCl and KBr given in mμ.

	H	V_K	F	R_1	R_2	M	N_1	N_2
KCl	335[a]	365[a]	537	658	729	798	960	1030
KBr	380[a]	385[a]	599	735	790	884	1070	1130

[a] Values taken from Ref. (17).

Selective optical bleaching, e.g., at the wavelengths of the F band or of the V_K-H band absorption, was accomplished with standard tungsten sources and appropriate optical filters. Both glass filters (Corning Glass Company) and interference filters (Farrand Optical Company) were employed. A Polaroid sheet (type HR or HN) or a Glan-Thompson prism was used for bleaching and absorption measurements with polarized light.

Low-temperature measurements were carried out in a stainless-steel Dewar with a rotating head for optical and x-ray work. Thus x raying, optical bleaching, and absorption measurements could be accomplished without warming to higher temperature. Temperatures cited in this work [room (RT), liquid nitrogen (LNT), and liquid helium (LHeT)] are nominal in that precision temperature determinations were not made. In warming experiments, in which optical spectra were obtained as a function of temperature, measurements were carried out in a second Dewar capable of maintaining a fixed arbitrary temperature from LHeT to about 80°K. This Dewar utilized the temperature-control technique described by Swenson and Stahl.[20] Both Dewars were designed for use in a Cary model 14 MR spectrophotometer, in which all optical-absorption measurements were made.

In addition to the various broad-band spectra observed during absorption measurements, a number of sharp-line absorptions were also recorded. Normally no special attempt was made to resolve the sharp absorptions shown in figures of this text.

EXPERIMENTAL RESULTS AND DISCUSSION

Centers attributed to ionized forms of the F aggregates were produced by the following procedure. Additively colored or RT x-ray colored crystals containing F-aggregate centers produced at RT by exposure to F light, were cooled to LHeT and exposed to x rays. This x-ray exposure resulted in absorption structure in the near ultraviolet, similar to that obtained in virgin crystals, which has been shown to be associated with V_K

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and H centers.[17] In addition, x-ray treatment enhanced the F band, caused a redistribution of the F-aggregate bands (usually a partial bleaching), and resulted in the formation of new bands in the near infrared. Through subsequent near-ultraviolet excitation at the spectral region of the overlapping V_K and H bands at LHeT, the V_K-H, the F, and the F-aggregate absorptions all decreased while the new near-infrared bands were enhanced. These infrared bands have been assigned to transitions of ionized F-aggregate centers.[18]

Several of these new bands were directly correlated with specific F-aggregate bands by their dichroism, and their fixed conversion ratios during V_K-H bleaching. Similar correlations were established by promoting a back reaction, i.e., by the conversion of new bands back to the F-aggregate bands, by subsequent F-light excitation. It was believed that in the latter process, the F-aggregate bands reappeared as a result of electron transfer from the excited F centers to the ionized F aggregates. In the former case, V_K-H excitation presumably induced recombination of the holes with electrons from F-aggregate centers.

These processes were studied primarily in KCl. Less extensive measurements were made in KBr and several other alkali halide crystals. Table I lists the approximate peak positions of the principal absorption bands arising from the V_K-, H-, and F-aggregate centers in KCl and KBr, while Table II gives the peak positions and half-widths of the new near-infrared bands in KCl and KBr. Specific evidence for the assignment of models in Table II will be given later in this section. Although comparatively large M bands were produced in both LiF (with x rays at RT) and NaF (with x rays and F-band bleaching at RT), subsequent x raying and optical excitation at LHeT did not result in the formation of bands that could be associated with F_2^+ centers.

The formation of the near-infrared bands was affected when the above experimental steps in the production process were modified. First, if a crystal containing F-aggregate centers was exposed to near-ultraviolet light corresponding to the trapped-hole bands at LHeT without prior LHeT x raying, the near-infrared bands did not form. Second, if the x-ray treatment at LHeT was carried out, but only F centers were initially present, the near-infrared bands also did not form upon subsequent near-uv exposure. Thus, the hole and F-aggregate centers were apparently both essential for the production of the near-infrared bands. There is an important qualifying comment which may be made with respect to the second point. Long x-ray exposures of virgin KCl crystals at LHeT did result in a very weak 1.40-μ band (see Table II) comparable in magnitude to the weak M band which simultaneously forms. This was not an unexpected result. Royce[21] has pointed out that F_2^+ centers could be expected to be produced directly under x rays by a statistical production of neighboring F and alpha centers, similar in nature to the formation of M centers by a pair of neighboring F centers.[3] Alternatively, it is possible that F_2^+ formation occurred in a virgin crystal as a result of x-ray ionization of M centers produced in the same x-ray exposure. This could be related to the earlier mentioned observation, that x-ray exposure at LHeT of a crystal containing F-aggregate centers resulted in the production of ionized centers. Several possible mechanisms for x-ray ionization of the M center are available: (1) direct photoionization by an incident x-ray photon, (2) capture of a hole generated during x raying, (3) ionization by the decay of an x-ray produced exciton, and (4) photoionization by optical photons generated during x raying.

TABLE II. Principal optical-absorption bands associated with ionized F-aggregate centers in KCl and KBr at LHeT; peak wavelength, $\alpha_{\max}(\mu)$; half-width, W(eV); and direction of dichroic absorption induced in band, D.

	$\alpha_{\max}$	W	D	$\alpha_{\max}$	W	D	$\alpha_{\max}$	D
KCl	1.40	0.086	⟨100⟩ ⟨110⟩	0.96	0.094	⟨110⟩	1.67	⟨100⟩ ⟨110⟩
KBr	1.49	0.073	⟨110⟩[a]	1.02	0.082	⟨110⟩	1.80	[b]
Proposed model	F_2^+			F_3^+			N_1^+	

[a] The experiment of producing ⟨100⟩ dichroism in the 1.49-μ band of KBr was not carried out. This dichroic absorption is anticipated in addition to ⟨110⟩.

[b] Dichroic-absorption experiments were not carried out for the 1.80-μ band in KBr; however, identical results to that obtained for the 1.67-μ band in KCl are expected.

Exposure to light in the M and R bands in KCl after LHeT x raying had the same effect as near-ultraviolet exposure. The V_K-H absorption bleached, and F-aggregate centers were partially converted to their ionized forms. It was of particular interest, however, to note that in the absence of R centers and with only M centers present, optical excitation with *R-band light* was effective in the $M \rightarrow F_2^+$ conversion. This was taken as evidence that long wave excitation did not act on the excess-electron centers, but probably was acting on the broad transition of the V_K center peaking near 750 mμ in KCl.[14] In the absence of information concerning an H-center transition in this region this result indicated that at least the V_K center was involved in the process of formation of ionized aggregates. Exposure to light near the maximum of the F band, on the other hand, was not effective in producing the near-infrared bands although the F band and V_K-H absorption both decreased. Since the 750-mμ V_K transition is very broad, and probably overlies the F band, the lack of production of near-infrared bands by F-light exposure was probably due to the fact that this light also resulted in a transfer of electrons to any ionized F-aggregate centers that might have been formed causing them to bleach instantaneously.

There were several ways in which the infrared bands produced at LHeT could be partially destroyed. In

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[21] B. S. H. Royce, Am. Soc. Testing Mater. Spec. Tech. Publ. **359**, 98 (1964).

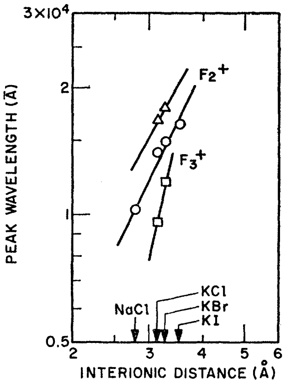

FIG. 1. A Mollwo-Ivey type plot for the various bands associated with ionized F-aggregate centers, F_2^+, F_3^+, and bands that may be associated with the ionized N_1 center (uppermost curve in the figure.)

certain instances this destruction resulted in a restoration of the original F-aggregate bands. These reverse conversions could be accomplished by optical or x-ray exposures or by warming the crystal above LHeT. As mentioned above, if the crystal was exposed to light at the wavelength of the F band following ionized-center formation, partial bleaching of the near-infrared bands, the F band, and part of the remaining V_K-H overlapping structure occurred. At the same time the initial F-aggregate bands reappeared. Second, a short x irradiation at LHeT after ionized F-aggregate formation with ultraviolet light quickly restored the F-aggregate bands and bleached the ionized F-aggregate bands. Finally, if a crystal containing ionized centers was warmed from LHeT, over 75% of the infrared bands bleached upon reaching 42°K, while the F-aggregate bands increased by approximately 50%. In this temperature range the V_K-H absorption decreased while the F band increased. Further warming from 42 to 75°K resulted in additional bleaching of both the F-aggregate and near-infrared bands. All three processes probably involved electron capture by ionized F-aggregate centers. In the first instance the electrons were produced from F centers upon F-light exposure. In the second case the electrons were produced by the action of x rays. In the warming experiment, electrons were probably produced by a process of thermal release, typical of this temperature range.[22]

A discussion follows of the photochemical transformations leading to the production and identification of the individual ionized aggregate bands presented above in Table II.

Ionized M Center, F_2^+

When M centers were present in KCl and KBr crystals, x raying and V_K-H optical excitation at LHeT resulted in the formation of bands at 1.40 and 1.49 μ, respectively. As indicated above these bands have been interpreted as arising from optical transitions of the F_2^+ center (Table II). This assignment was supported by an observed one-to-one correspondence in (a) the optical conversion $M \rightarrow F_2^+$, with V_K-H light (335-mμ excitation), (b) the reverse optical conversion $F_2^+ \rightarrow M$, with F light, and (c) the transfer of optical dichroism present in the M band to the band associated with the F_2^+ center. The conversion ratios for processes (a) and (b) were the same. These ratios are tabulated in Table III along with the relative oscillator strengths of the M and F_2^+ bands in KCl and KBr. The change in absorption coefficient ($\Delta\alpha$) was measured at the peak of the absorption bands. Oscillator strengths were obtained using the approximate formula

TABLE III. $M \rightleftarrows F_2^+$ and $R \rightleftarrows F_3^+$ optical-conversion ratios ($\Delta\alpha$=change in absorption peak height) and relative oscillator strengths (f) of M and F_2^+ transitions in KCl and KBr at LHeT, calculated from Eq. 1.

	$-\Delta\alpha_M/\Delta\alpha_{F_2^+}$	$f_M/f_{F_2^+}$	$-\Delta\alpha_{R_2}/\Delta\alpha_{F_3^+}$
KCl	3.7[a]	2.4	1.0
KBr	3.2	2.2	0.67

[a] This value is a downward revision (by about 12%) of an earlier estimate based on less extensive data (Ref. 18).

$$f_M/f_{F_2^+} \simeq -(\Delta\alpha_M/\Delta\alpha_{F_2^+})(W_M/W_{F_2^+}), \qquad (1)$$

where the W's are the appropriate absorption-band half-widths.

Figure 1 shows a Mollwo-Ivey plot of the F_2^+ bands in KCl and KBr together with bands for KI at 1.65 μ and NaCl at 1.03 μ. The latter bands were observed in additively colored KI and RT x-ray colored NaCl crystals treated in the same manner as described above for KCl and KBr; however, no similar correlation was established with the M band owing to the relative weakness of the bands. On this basis the F_2^+ assignments in KI and NaCl must be considered very preliminary.

There were two instances in which variation in the $M \rightarrow F_2^+$ conversion ratios occurred. First, an apparent variation was noted in those cases in which additional overlapping structure appeared in the region of the F_2^+

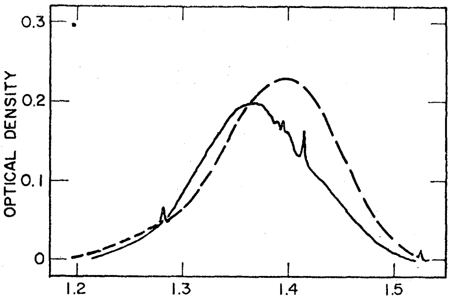

FIG. 2. Absorption spectra of two additively colored KCl crystals measured at LHeT. The absorption of one crystal (1.9 mm thick) is shown after the following treatments: first bleaching with F light for 40 min at RT, then annealing at 85°C for 10 min, followed by x raying for 1 h and 335-mμ exposure for 20 min at LHeT (solid curve). The absorption of the second crystal (1.1 mm thick) is shown after the following: first bleaching with F light for 3 min at RT, then annealing at 85°C for 60 min, followed by x raying for 50 min and 335-mμ exposure for 80 min at LHeT (dashed curve).

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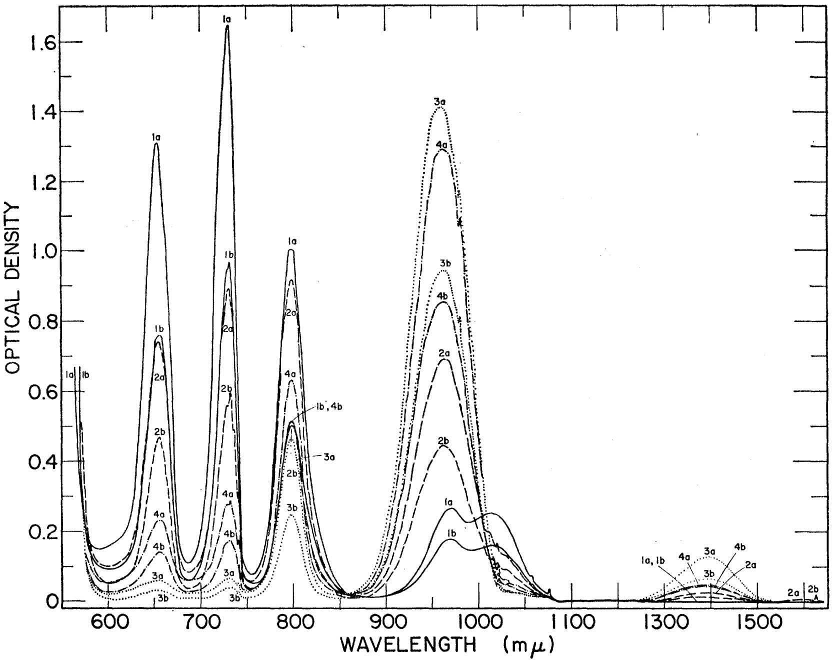

FIG. 3. Absorption spectra of an additively colored KCl crystal (0.8 mm thick) measured with polarized light at LHeT [(a) indicates $[0\bar{1}1]$ polarization direction, (b) indicates $[011]$ direction]; solid curves (1*a*,1*b*) after 90-min illumination with $[0\bar{1}1]$ *F* light at RT; dashed curves (2*a*,2*b*) after 75-min x-ray exposure at LHeT; dotted curves (3*a*,3*b*) after 90-min illumination with 335-mμ-light at LHeT; dash-dot curves (4*a*,4*b*) after 4-h illumination with unpolarized *F* light at LHeT.

band, as shown in Fig. 2 for two KCl crystals prepared in different ways. Second, the optical conversion ratios following x-ray exposure at LHeT given in Table III for the processes $M \rightarrow F_2^+$ was different from the corresponding $M \rightarrow F_2^+$ conversion observed during the x raying. This difference generally depended both on the state of the crystal prior to the x-ray exposure and the manner in which *F*-aggregate centers were initially introduced. For additively colored crystals initially containing *F* and *M* centers predominantly, the ratio obtained under x irradiation exceeded the ratio obtained by optical bleaching by about 20%. In crystals initially colored with x rays at room temperature and containing *F* and *M* centers predominantly, the ratio during LHeT x raying was approximately twice that obtained for optical conversion. In additively colored crystals containing rather large *R*-center concentrations, the ratio upon x raying was usually smaller than during subsequent optical conversion. In fact, in certain crystals the *M* band actually increased with x-ray exposure at LHeT [see Fig. 2, Ref. (18)]. The reason for this variation during the x-ray treatment is not clear. One possible explanation is that interstitial anions created by the x rays combine with *F*-aggregate centers. Thus, for example, the observation that the *M*-center concentration increases during x raying in crystals containing large *R*-center concentrations may indicate that *R* centers were transformed to *M* centers by interstitial capture.

As indicated above, the nature of the optical dichroism induced in the infrared transitions associated with the ionized centers provided additional support for the proposed models. It was shown that both ⟨110⟩ and ⟨100⟩ dichroism could be induced in the 1.40-μ band in KCl when produced in crystals initially containing similarly dichroic *M* bands. This is shown in Fig. 3 for an additively colored KCl crystal in which the *F*-aggregate bands were produced with ⟨110⟩ *F* light at RT. It is noted that ⟨110⟩ dichroism was simultaneously exhibited in the *R*, *M*, and *N* bands, i.e., the absorption coefficients for the band maxima are greater when measured with light polarized in the $[0\bar{1}1]$ direction than that measured with $[011]$-polarized light. X-ray and 335-mμ-light exposure at LHeT resulted in the production of the 1.40-μ band with approximately the same relative dichroism exhibited by the original *M* band. Figure 3 shows, however, that after prolonged *F*-light bleaching, following 335-mμ light exposure at LHeT, some reorientation of the 1.40-μ band did occur. Results similar to that shown in Fig. 3 for KCl were also obtained for KBr; in this case ⟨110⟩ dichroism was produced in the F_2^+ transition at 1.49 μ. A corresponding ⟨100⟩ dichroism experiment was not performed in KBr. The results of optical-dichroism experiments are summarized in Table II.

Since the *M* center is relatively simple, there is a severe limitation on the number of alternate models to the F_2^+ configuration which can account for the near-infrared transitions. This is particularly true since the production process is carried out at LHeT where ionic processes are restricted. Moreover the most obvious decomposition products of the *M* center (*F*, α, and *F'*) give rise to known transitions which are distinct from the near-infrared absorption bands that were observed. If a new ionic constituent is added to the *M* center it would be difficult to understand the almost complete transfer of M-center dichroism to the new center. Alternative models to the F_2^+ center in purely electronic conversion of the M center are also greatly restricted. It would be difficult, for example, to attribute the new bands to M centers which have captured an additional electron to form an M' center. Aside from the fact that the optical transitions of this center have been identified[10] and are distinct from the near-infrared bands reported here, this interpretation would have additional objections. For one, it would be hard to explain M' formation by excitation of the excess-hole centers which bleach during the exposure, and M' destruction (and M growth) by subsequent bleaching directly into the F band. Moreover, the necessity of prior x-ray exposure at LHeT for the formation of M' centers, in crystals initially containing F and F-aggregate centers, would likewise be difficult to understand. Another possible model to consider is the doubly ionized M center, the F_2^{++} center. Aside from the doubtful stability of an F_2^{++} center, this defect, like the α center, would not be expected to give rise to a near-infrared optical transition, but rather a perturbed exciton absorption in the ultraviolet.

A recent calculation by Wang[23] of the electronic states of the F_2^+ center gives additional support to the present assignment. Wang finds an energy of 0.93 eV for the $1s\sigma$-$2p\sigma$ transition of the F_2^+ center in KCl. This is in good agreement with the observed value of 0.89 eV (1.40 μ). An earlier calculation of Herman *et al.*[24] gave a somewhat smaller value of 0.64 eV for the same transition.

It should be pointed out that additional absorption bands in the vicinity of 1.40 μ have previously been reported in KCl. Okamoto[25] has shown that a band at 1.46 μ forms at RT in very lightly colored crystals. This band apparently transforms to a band at 1.38 μ with F-light bleaching at LNT. Rabin[26] has shown that by warming a crystal colored at LNT with x rays, a band at 1.35 μ forms in the temperature range 207–269°K. The relation of these bands, if any, to the 1.40-μ band reported here, is not known.

Several attempts were made to produce F_2^+ centers at higher temperatures. Although relatively large F_2^+-center concentrations were produced at LHeT, only a very weak F_2^+ band could be stably produced in KCl by both x raying and V_K stimulation at LNT. In addition to V_K-center formation, x-ray exposure at LNT produced a sizable F' band which readily bleached by subsequent exposure to ultraviolet light. It was also pointed out above that F_2^+ centers produced at LHeT were largely destroyed on subsequent warming to LNT. These experiments do not necessarily imply that the F_2^+ center is intrinsically stable only at low temperature. It is more likely that the formation of the F_2^+ center is limited by electron capture both during production at higher temperature (e.g., electron release from F' centers) and in warming.

Ionized *R* Center, F_3^+

When R centers were present in crystals, LHeT x-ray and 335-mμ light exposure resulted in bleaching of the R_1 and R_2 bands and the simultaneous formation of a single band at 0.96 μ in KCl and 1.02 μ in KBr. These new absorption bands were ascribed to transitions of the singly ionized R center. Assuming the F_3 model of the R center, this defect was the F_3^+ center. The arguments favoring such an interpretation are similar to those described above for the $M \rightarrow F_2^+$ conversion: (a) $R \rightarrow F_3^+$ conversion occurred in a fixed ratio during 335-mμ exposure, (b) the reverse $F_3^+ \rightarrow R$ conversion ratio likewise remained fixed under subsequent F-light excitation, (c) $\langle 110 \rangle$ dichroism, initially present in the R bands, was transferred to the band associated with the F_3^+ center. The conversion ratio $\Delta\alpha_{R_2}/\Delta\alpha_{F_3^+}$ was the same in processes (a) and (b); in KCl the value was 1.0 and in KBr, 0.67. (Since the R_1 and R_2 bands arise from the same center, the above ratio was arbitrarily taken with respect to R_2.) The above results are summarized in Tables II and III. Figure 1 shows a preliminary Mollwo-Ivey curve for the F_3^+ center. The slope clearly differs from that of the F_2^+ center.

As indicated in Table II, only anisotropic absorption in the $\langle 110 \rangle$ direction was observed for the F_3^+ bands. This dichroism could only be induced by producing F_3^+ centers from initially oriented R centers. The F_3^+ bands showed the same dichroic absorption as the R_1 and R_2 bands.[25] This result is consistent with the assignment of these bands as F_3^+ transitions. All attempts to induce dichroism directly into the F_3^+ bands by polarized bleaching with light at the wavelength of both the F_3^+ and F bands were unsuccessful.

The arguments for the assignment of the F_3^+ model to the center giving rise to the 0.96- and 1.02-μ bands in KCl and KBr, respectively, are parallel to corresponding arguments made earlier for the F_2^+ center and need not be repeated. In the present case one must consider the additional possibility of an F_3^{++} configuration. (The F_3^{+++} is excluded for the same reasons cited for the F_2^{++} center above.) Although the experiments performed in the present work cannot distinguish between the F_3^+ and F_3^{++} configurations, there are several reasons for favoring the former assignment. First, the probability of producing a single ionization as opposed to a double ionization is much more likely. Second, if the single observed band is to be attributed to the F_3^{++} center, it would be likely that a second band due to the F_3^+ center would also be observed during the conversion processes. No such intermediary product has been observed.

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The overlap of the 0.96-μ band ascribed to the F_3^+ center and the N_1 band is apparent in Fig. 3. This spectral region is considered in greater detail in Figure 4 for two additively colored crystals at LHeT. One crystal was thermally annealed at 85°C for 10 min following F-light exposure at RT. This annealing is known to result in a decrease in the R bands and an enhancement of the N_1 band.[27] The remaining data for the second crystal show the N-band absorption before and after x raying, and then after 335-mμ exposure; all at LHeT. The 0.96-μ band associated with the F_3^+ center is broader than the thermally enhanced N_1 band, while the peak positions are not appreciably different.

Corresponding data for additively colored KBr crystals in the general vicinity of the N bands are shown in Fig. 5. The thermally enhanced N_1 band, produced by annealing for 10 min at 85°C lies at 1.07 μ. In a second crystal initially containing an appreciable number of R centers, the N_1 band also lies near 1.07 μ. X-ray and 335-mμ exposure results in a decrease of the N_1 and N_2 bands while the band associated with the ionized R centers grows at 1.02 μ. In KBr the resolution of the F_3^+ and N_1 bands is clear.

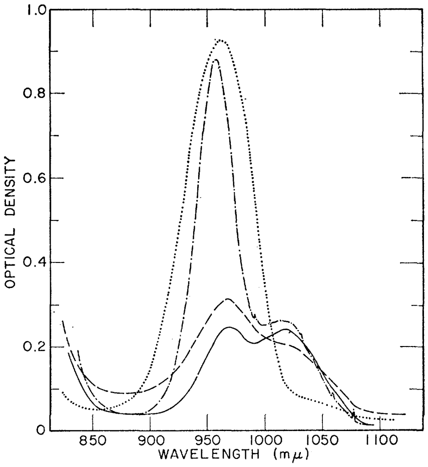

FIG. 4. Absorption spectra of two additively colored KCl crystals measured at LHeT. The absorption of one crystal (0.7 mm thick) is shown after exposure to F light for 60 min at RT (solid curve), after x raying for 75 min at LHeT (dashed curve), and after 335-mμ-light exposure for 21 min (dotted curve). The absorption of the second crystal (1.2 mm thick) is shown after exposure to F light at RT for 60 min and subsequent annealing at 85°C for 10 min (dash-dot curve).

Unlike F_2^+ centers, F_3^+ centers could apparently be produced at room temperature in either additively colored crystals exposed to F light or crystals x-ray colored in the dark at room temperature. In either case the reaction $F_3^+ \rightarrow R$ could be induced by subsequent optical excitation of the F center upon lowering to LHeT or LNT. The reverse process $R \rightarrow F_3^+$ could then be induced with intense R-light exposure. These processes are pictured in Figs. 6 and 7 for additively colored KCl and KBr, respectively. Crystals containing F aggregates produced at RT were cooled and exposed to F light. (F' centers produced by F-light exposure were easily bleached by exposure to light of longer wavelength.) The absorption at 0.96 μ in KCl and 1.02 μ in KBr decreased while the corresponding R bands increased. Subsequent exposure to R light produced the reverse effect. A difference curve (see inset in Fig. 7) for KBr shows that the absorption changes occur at approximately 1.02 μ, coinciding with the band associated with the F_3^+ center. Both the forward and reverse processes occurred with exactly the same conversion ratio in KCl and KBr as that given in Table III for

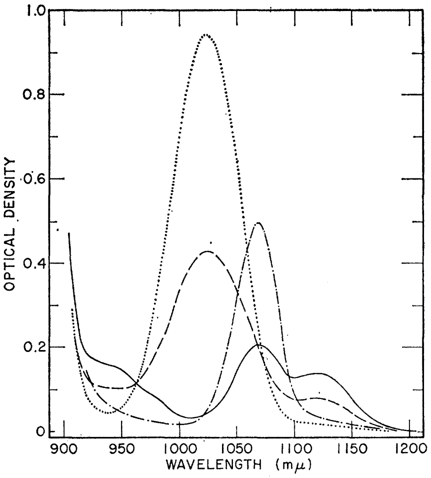

FIG. 5. Absorption spectra of two additively colored KBr crystals measured at LHeT. The absorption of one crystal is shown after exposure to 3-h F light at RT (solid curve), after x raying 1 h at LHeT (dashed curve), and after 3-min 335-mμ-light exposure (dotted curve). The absorption of the second crystal (1.5 mm thick) is shown after exposure to F light at RT for 3 h and subsequent annealing at 85°C for 10 min (dash-dot curve).

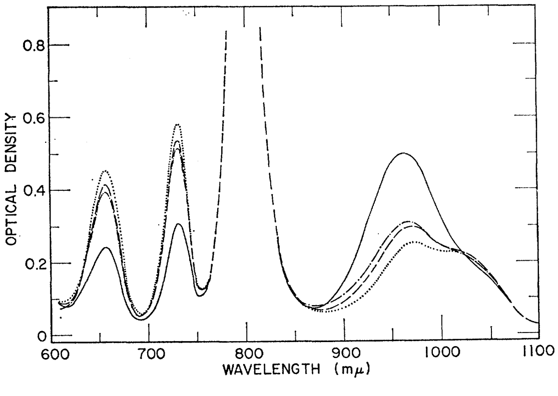

FIG. 6. Absorption spectra of an additively colored KCl crystal (2.8 mm thick) measured at LNT; solid curve, after 4-min illumination with F light at RT; dashed curve, after 6-min illumination with F light and 10-min of F' (780-mμ) light; dotted curve, after an additional 5-min illumination with F light and 10-min of F' light; dash-dot curve, after 20-min illumination with R light (654 mμ).

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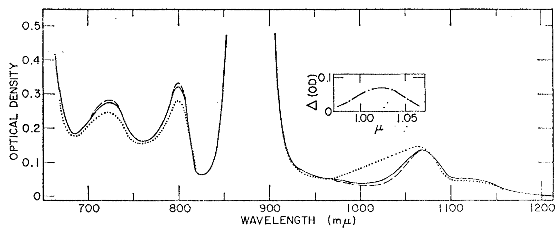

FIG. 7. Absorption spectra of an additively colored KBr crystal (2.0 mm thick) measured at LHeT; solid curve, after 10-min illumination with F light at RT; dashed curve, after 3-min illumination with F light and 10 min of F' (830 mμ) light; dotted curve, after 15-min illumination with R_2 light (804 mμ). The difference curve, given in the inset, gives the absorption difference occurring in the 1.02-μ region for the last two curves above.

F_3^+ centers created by the LHeT process described earlier.

Other Near-Infrared Absorption Bands

For crystals containing N bands (N_1 and N_2) produced by bleaching with F light at RT it is clearly seen that the N_2 band diminishes on both LHeT x-ray and 335-mμ exposure of KCl and KBr (Figs. 4 and 5). While it was generally difficult to follow the behavior of the N_1 band during these low-temperature processes in KCl since the F_3^+ band simultaneously grows at roughly the same spectral location, in KBr the N_1 band clearly shows some bleaching. Except for very weak bands of unknown origin, bands did not form at longer wavelengths (out to 2.5 μ) which could easily be associated with the ionized product of these N bands. One such weak band formed in crystals initially containing relatively large R bands upon exposure to x rays at LHeT. It appeared at approximately 1.60 μ with apparently an associated zero-phonon line at 1.63 μ; see, e.g., Fig. 3. This band disappeared on 335-mμ exposure following LHeT x raying, quite unlike the behavior of the F_2^+ and F_3^+ transitions.

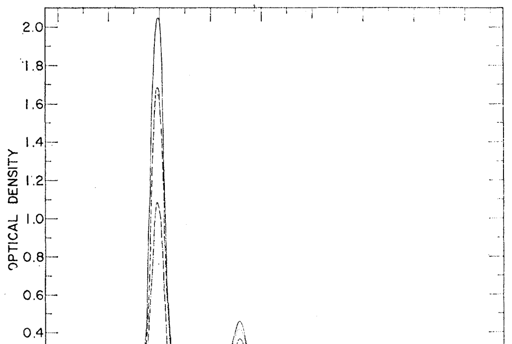

FIG. 8. Absorption spectra of an additively colored KCl crystal (0.8 mm thick) measured at LHeT; solid curve, after bleaching for 10 min with F light at RT and thermal annealing at 85°C for 35 min; dashed curve, after 50-min x-ray exposure at LHeT; dotted curve, after 80-sec illumination with 335-mμ light at LHeT; dash-dot curve, after an additional 45 min illumination with 335-mμ light at LHeT.

It may also be observed in Figs. 8 and 9 that an additional absorption with sharp-line structure overlaps the F_2^+ bands. An enlarged plot of this spectral region, Fig. 2, shows two KCl crystals annealed for different lengths of time. The crystal annealed for 10 min at 85°C shows a sharp line at 1.414 μ and several weaker lines at shorter wavelengths. These lines were absent in the crystal annealed for 1 h at 85°C, although sharp lines lying at 1.278 and 1.525 μ appeared. Other sharp lines, in the region from approximately 0.95 to 1.15 μ are also apparent in several of the figures. In KBr the structure which overlaps the F_2^+ band has a sharp absorption line peaking at 1.547 μ.

Additional bands also appeared during LHeT x raying and optical excitation at 335 mμ in crystals which were thermally treated following F-aggregate center formation at RT. The absorption changes which occurred, for example, in a crystal annealed for 35 min at 85°C prior to the LHeT treatments are shown in Fig. 8. It will be recalled that this particular thermal treatment resulted in both R-band bleaching and an enhancement of the N_1 band. A broad-band peaking near 1.67 μ, with an apparent associated zero-phonon line at 1.733 μ, grew as a result of x raying and 335-mμ exposures. In a similarly treated KBr crystal, shown in Fig. 9, the thermally enhanced N_1 band at 1.07 μ bleached, while a new band grew at 1.80 μ (with an apparent associated zero-phonon line at 1.868 μ).

In KCl crystals containing dichroic N_1 bands, the long wavelength band formed with corresponding dichroism (see Table II). Figure 10 shows dichroic spectra obtained for an additively colored crystal containing F-aggregate bands which was thermally annealed (10 min at 85°C) to enhance the N_1 region and subsequently exposed to ⟨110⟩ N_1 light at RT. This exposure induced dichroism in not only the N_1-band region but also the M band and the R bands. Subsequent x raying and 335 mμ-light exposure at LHeT resulted in the formation of a 1.67-μ band with ⟨110⟩ dichroism.

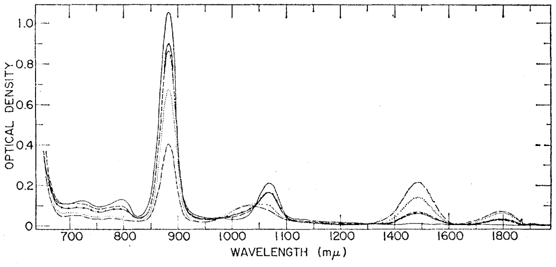

FIG. 9. Absorption spectra of an additively colored KBr crystal measured at LHeT; solid curve, after bleaching with F light at RT and thermal annealing at 85°C for 10 min; dashed curve, after after 40-min x-ray exposure at LHeT; dotted curve, after 7.5-min illumination with 335-mμ light at LHeT; dash-dot curve, after an additional 70-min illumination with 335-mμ light at LHeT; dash-circle curve, after 65-min illumination with F light at LHeT.

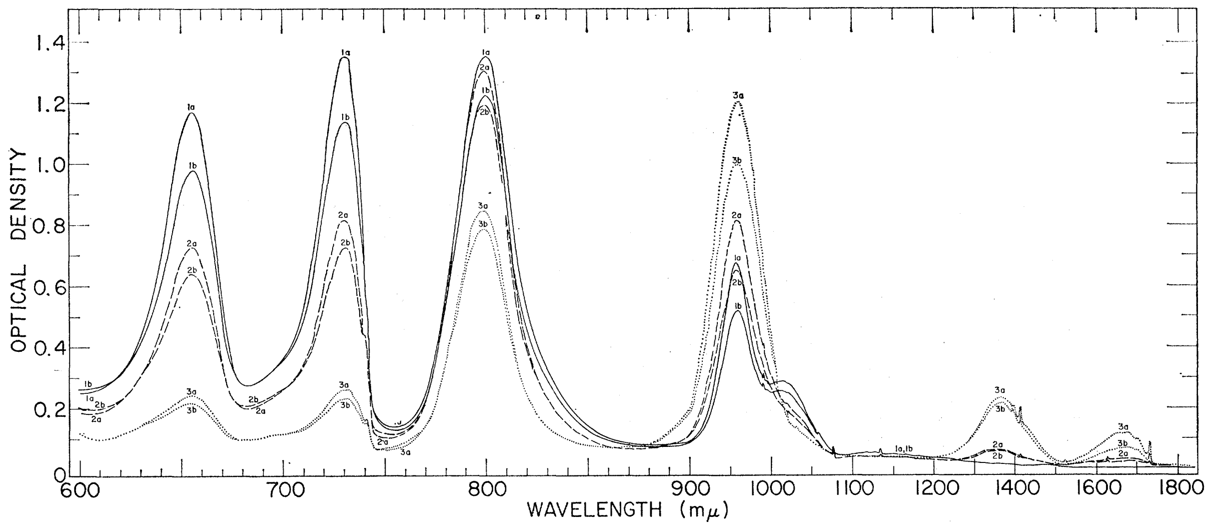

FIG. 10. Absorption spectra of an additively colored KCl crystal (1.9 mm thick) measured with polarized light at LHeT [(a) indicates [0$\bar{1}$1] polarization direction, (b) indicates [011] direction]. F-aggregate centers were produced initially by bleaching with unpolarized F light for 40 min at RT. The LHeT spectra were obtained as follows: solid curves (1a,1b), after thermal annealing for 10 min at 85°C and exposure to [011] polarized N_1 light for 3 h at RT; dashed curves (2a,2b) after 60-min x-ray exposure at LHeT; dotted curves (3a,3b) after 30-min illumination with 335-mμ light at LHeT.

The 1.67-μ band in KCl and the 1.80-μ band in KBr are possibly due to the ionized N_1 center as indicated in Table II. (The singly ionized form N_1^+ is made by analogy to corresponding assignments for ionized M and R centers described above.) For one, the induced dichroism of the 1.67-μ band is the same as that known to occur in the N_1 band.[25,27] Although a good one-to-one correspondence was not established between the decrease of the N_1 band and the growth of the long wavelength bands, the latter bands depended on the presence of sufficiently enhanced N_1 absorption. The fact that only a very weak 1.67 μ occasionally appears in unannealed crystals suggests the possibility that the presence of R centers reduces the conversion efficiency for ionizing N_1 centers. Alternatively, the N_1 transition only makes a small contribution to the total absorption in the N_1 region; it is possible that in crystals with relatively large R-center concentrations, the absorption in the N-band region is largely due to R-center transitions.[8]

CONCLUSIONS

New near-infrared bands have been produced by cooling additively colored crystals containing F-aggregate centers to the liquid-helium temperature and exposing them to x rays and near-ultraviolet light. Based primarily upon the results of absorption measurements made during the formation and destruction of the new bands and the F-aggregate bands in KCl and KBr, the new bands have been attributed to transitions of ionized F-aggregate centers, F_2^+, F_3^+, and N_1^+. The assignments, as well as the nature of the processes themselves, are tentative in the sense that complete confirmation must await the results of auxiliary experiments, e.g., electron spin resonance. Moreover, it is clear that while one can discuss the mechanism of production of the ionized center in a general way, the details of the electronic processes require further work. For example, the transformation of F-aggregate to ionized F-aggregate centers presumably occurs as a result of an electron-hole recombination process but questions relating to the manner in which charge is transferred remain unanswered.

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