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# Formation of $N$ centers in pure NaCl

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The formation of color-center $N$ bands peaking at 828 and 903 nm in pure NaCl crystals was experimentally investigated. A photoaggregation process following coloration was employed for $N$-center formation. Both the method of coloration and the wavelength of the aggregating light were found to affect the specific color centers formed and their relative densities. It is argued that the observed differences are due to $F'$-center excitation during aggregation. The nature of the two $N$-center bands is discussed in view of band-growth characteristics and fluorescence data.

## I. INTRODUCTION

A pair of absorption bands, called the $N_1$ and $N_2$ bands, which belong to electrically neutral color centers and lie at longer wavelengths than the $F_2$ band, have been observed in several alkali halide hosts.[1-4] These $N$ bands have generally been thought to arise from transitions of $F_3$ or $F_4$ aggregate color-center configurations. Experimental data are still incomplete, and interpretations regarding the nature of the $N$ transitions sometimes appear contradictory. For example, the $N_1$ band in NaCl is believed by some researchers to arise from a planar $F_4$ configuration.[5] On the other hand, both $N$ bands in KCl—as well as the shorter-wavelength $R_1$ and $R_2$ bands—are believed to arise from the trigonal $F_3$ color center.[6] Other possibilities have not yet been unambiguously disproved by experiment.[7,8]

Recently, the $N_2$ center in KCl has been shown to be laser active.[9] The KCl $N_2$-center laser, operating between 1.23 and 1.35 $\mu$m, is presently the only color-center laser in the 1.3-$\mu$m region with infinite operational lifetime. It is also the first multielectron color-center laser demonstrating long-term operational stability. There is a strong possibility that this laser can also be created in other host lattices. To this purpose, the formation and optical properties of the $N$ centers must be better understood, and their structure positively identified. Hence, here we report on the formation of the $N$ centers in NaCl and discuss correlations among these and other color centers based on absorption and fluorescence data. We find that significant densities of $N$ centers can only be created in radiation-colored NaCl crystals, using a two-step photoaggregation procedure. Although the fluorescence bands corresponding to some of the $R$ and $N$ absorption bands in NaCl are identical, our data show that a single-defect model cannot account for all these bands.

## II. SAMPLE PREPARATION

Pure NaCl crystals were grown, using the Kyropoulos technique, under an inert Ar atmosphere at the Crystal Growth Facility of Cornell University. The ultrapure NaCl material was chlorine pretreated in order to remove anionic impurities, and the residual OH$^-$ content of the grown crystals was measured by uv-absorption spectroscopy to be less than 1 ppm. Also, cation analysis previously performed on similar NaCl crystals grown from the same stock material has shown trace impurity concentrations below 1 ppm. Results quoted in this work have shown no systematic sample dependence among several different NaCl boules.

3-mm-thick samples were cleaved out of the grown boules and colored either additively or by $\gamma$-radiation damage. Additive coloration was done in a heat pipe at 20 Torr Na vapor pressure and 970 K for 40 min. Coloration by $^{60}$Co $\gamma$ irradiation was done either at room temperature or at dry-ice temperature (195 K) for a total exposure of $10^7$ rad. Following coloration the additively colored crystals were polished and kept in the dark at room temperature, while the $\gamma$-irradiated crystals were promptly frozen to 77 K in the dark to prevent color-center aggregation. The $\gamma$-irradiated crystals were warmed up to room temperature immediately preceding the experiments and briefly handled under weak red light. In all the experiments described below, photoaggregation processes were carried out at approximately 260 K. This temperature, where vacancy mobility in NaCl is activated,[10,11] allows controlled but sufficiently fast photoaggregation rates. All spectra were taken at 77 K, unless otherwise noted.

## III. PHOTOAGGREGATION EXPERIMENTS

Following coloration the absorption spectra of the additively colored and $\gamma$-irradiated pure NaCl crystals were similar. Both showed a very pronounced $F$-band absorption (peak at 458 nm) and an $F_2$ band (peak at 718 nm). A broad $F'$ absorption band extending from 700 nm to shorter wavelengths was evident in the $\gamma$-irradiated crystals. This band peaks in the 460–520-nm region.[12,13] The identification of $F'$ centers was confirmed from the strong temporary bleaching of this absorption under 530–700-nm broadband illumination. The $F'$ band could be regenerated by $F$-band light illumination (light in the

400–500-nm region, for NaCl). It should be noted that the initial $\gamma$-irradiation temperature had no effect on the color-center formation. In all cases, no significant $F_2{}^+$ absorption band was observable in the ir, irrespective of the coloration procedure.

In order to optically form $N$ centers and other $F$-center aggregates in colored alkali halides, the usual technique is illumination of the crystal with $F$-band light at temperatures close to room temperature.[14–17] This photoaggregation process is thought to cause $F$ centers to migrate and combine to create higher aggregates. However, we noticed significant differences in the aggregate center formation when different illumination wavelengths, ranging from 400 to 633 nm, were used. For our experiments, light in the $F$-band region (specifically, 405 and 436 nm lines) was obtained from a focused 100-W high-pressure Hg lamp with a combination of 5-56 (blue) and 1-75 (ir-absorbing) Corning filters. Green light (546- and 579-nm lines) was obtained from the same lamp with GG 500 (long-pass) and KG-3 (heat-absorbing) Schott filters. Red light was obtained from a 5-mW, 633-nm He-Ne laser. In all cases the source light was unpolarized.

In the following, we first describe the results of our photoaggregation experiments. Our argument for the observed differences is subsequently given.

In the additively colored crystals, $F$-band light aggregation reduced the optical density of the $F$ band and caused the appearance of broadband structureless colloidal absorptions, accompanied by a decrease and broadening of the $F_2$ band [Fig. 1(b)]. However, use of green light for the aggregation enhanced the $F_2$ band and produced less colloidal absorption [Fig. 1(c)]. In either case only trace $N$- and $R$-band absorptions were observed to form. Attempts to increase these absorptions by increasing the total color-center population (by using higher coloration pressures) were unsatisfactory, due to the tendency towards colloidal center formation in pure NaCl under these conditions.

In the $\gamma$-irradiated crystals, $F$-band photoaggregation enhanced the $F_2$ band and created well-resolved $R_1$, $R_2$, $N_1$, and $N_2$ color-center absorptions [Fig. 2(b)]. The $R_1$, $R_2$, $N_1$, and $N_2$ bands peaked at 544, 601, 828, and 903 nm, respectively. Aggregation using $F$-band (blue) light favored the production of $N_2$ centers relative to $N_1$.

When $\gamma$-irradiated crystals were photoaggregated using green light, the results differed depending on whether or not the crystal has been previously exposed to blue ($F$-band) light. If this preexposure had been avoided, photoaggregation with green light caused the formation of $F_2$ centers alone [Fig. 2(c)], for illumination periods up to a few hours that we tried. The $N$-band absorptions produced with this method were negligible. Short time exposure to blue light, however, followed by photoaggregation with green light led to formation of strong $R$ and $N$ bands as well as enhancement of the $F_2$ band [Fig. 2(d)]. We have not attempted detailed measurements of the minimum time of blue-light preexposure that is necessary to alter the products of green-light aggregation, however, it is on the order of 1 min or less. This two-step aggregation procedure produced a much greater population of $N$ centers compared to using $F$-band light alone. In contrast to blue-light aggregation, green-light processing favored the formation of $N_1$ centers relative to $N_2$.

Red-light photoaggregation in $\gamma$-irradiated crystals led to the formation of the $N_2$ band without any simultaneous $N_1$-band formation [Fig. 2(e)]. This result is remarkable, since in other host lattices that we have studied (KCl, KBr) it has proven impossible to create the $N_2$ absorption band without simultaneous formation of the $N_1$ band. In the NaCl case described here the $N_2$-band formation quickly saturated to a maximum value [shown in Fig. 2(e)], with no further absorbance increase under prolonged red-light illumination.

In higher-resolution spectral scans (not shown) we resolved a zero-phonon line on the long-wavelength side

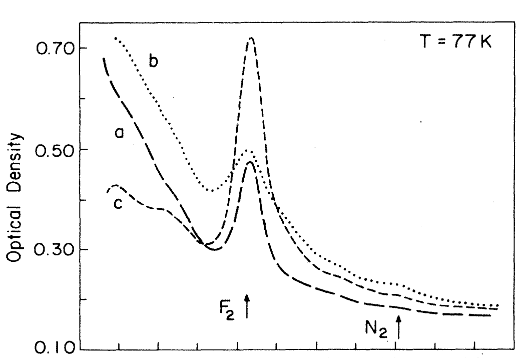

FIG. 1. Absorption spectra of 3-mm-thick, additively colored, pure NaCl crystals at 77 K. *a*, after coloration at 20 Torr. *b*, after 80-min $F$-band (blue) light photoaggregation at 260 K. *c*, after 150-min green-light photoaggregation at 260 K. Curves *b* and *c* belong to different samples.

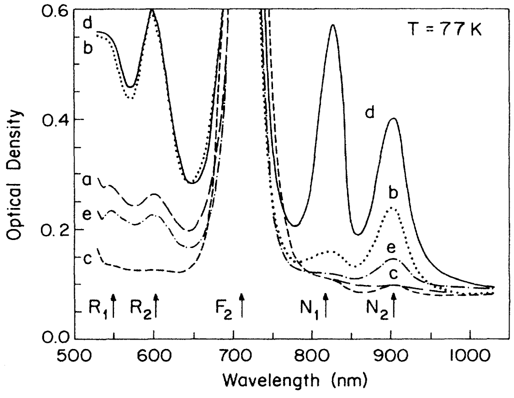

FIG. 2. Absorption spectra (at 77 K) of pure NaCl crystals colored by $\gamma$-radiation damage. *a*, after coloration. *b*, after 30-min $F$-band (blue) light photoaggregation at 260 K. *c*, after 80-min green-light photoaggregation at 260 K. *d*, after 30-min exposure to blue light and subsequent 80-min photoaggregation with green light at 260 K. *e*, after 60-min red-light photoaggregation at 260 K. Curves belong to different samples, colored simultaneously and having the same thickness.

of the $N_1$ band (840 nm) at 77 K; this line has been previously observed at 4 K.[5] Earlier piezospectroscopic studies of this line have indicated a planar $F_4$ model as best describing the structure of the $N_1$ center in NaCl.[5] No line structure associated with the $N_2$ band was observed in our experiments.

The results of the aggregation experiments are summarized in Table I. To explain the observed differences, we propose a model of aggregate-formation kinetics which involves direct $F'$-center excitation. We suggest that optical excitation of the $F'$ centers leads to aggregation processes that can account for the variation of results obtained with different illumination wavelengths or with different coloration methods. If only $F$-center excitation was responsible for the aggregation process, then the various illumination wavelengths should only lead to formation of the same centers (with possibly different aggregation rates). Since the $F$ and $F'$ bands do not coincide in peak and width, each wavelength excites a different proportion of $F$ and $F'$ centers, leading to different color-center kinetics. Also, the only apparent difference produced by the two coloration methods was the abundance of $F'$ centers in the irradiated crystals (presumably an equal amount of $\alpha$ centers also exists in these crystals to preserve macroscopic charge neutrality). Therefore, the different photoaggregation products that result from the two coloration methods must be attributed to the excitation of $F'$ centers.

Due to the large width of the $F'$ band and its partial overlap with the $F$ band, the specific aggregation kinetics resulting from the excitation of the $F'$ centers alone should be a subset of those occurring during excitation at the $F$-band wavelengths. In this latter case well-known additional processes occur, including $F$-center ionization and formation of mobile $\alpha$ centers ($2F \rightarrow \alpha + F'$),[10,14,16,18–23] as well as migration of $F_2$ centers[24] due to excitation of higher transitions (which overlap with the $F$ band very closely). These additional processes enhance the aggregation rates and lead to more complicated reactions. In these, the $F'$ centers are thought to serve merely as vacancy recombination sites ($\alpha + F' \rightarrow F_2$) (Refs. 14 and 16–18) or temporary reservoirs of thermally released electrons (for example, $F' + F_2{}^+ \rightarrow F + F_2$).[10,16,18,19,21,23]

According to our hypothesis, *optical* excitation of the NaCl $F'$ centers alone, at longer wavelengths where the $F$-band absorption is negligible, allows fewer aggregation mechanisms and supports some previously proposed aggregation models[23,25,26] that have not received particular attention. The reason is that long-wavelength illumination avoids the direct excitation of $F$ and $F_2$ centers and the accompanying kinetics described in the preceding paragraph. Although there is not yet sufficient evidence to state unambiguously the specific reactions that accompany the $F'$ excitation (and yield apparently different products from $F$-center excitation), we consider two possible routes: either that the $F'$ center itself is a mobile defect,[25] or that optical excitation of the $F'$ band causes the formation of another mobile species.

There is no experimental data on the mobility of the $F'$ center, but one might expect it to be on the same order as the mobility of other elementary point defects,[18,25,27] like the $F$ or $\alpha$ centers. One reason that the $F'$ center has not been seriously considered as a key mobile defect in aggregation processes is the very short lifetime of this center at temperatures around 273 K in many alkali halides.[22] Although the situation in NaCl is quite different, as will be explained below, the fact that the $F'$ center ionizes upon optical excitation makes it hard to conceive simple scenarios that would lead to migration of the $F'$ center itself.

The other possibility is that the ionization of the $F'$ center and ejection of one electron into the conduction band will lead to formation of a mobile center, when this electron recombines later with an electron trap. The most obvious case is capturing of the electron by an $\alpha$ center resulting in the formation of an $F$ center in its relaxed excited state (called $F^*$).[26,28,29] This state has been shown to have such high mobility in the lattice that it can be responsible for aggregation phenomena observed at temperatures as low as 80 K.[26] The $F^*$ can subsequently reionize thermally[30,31] at high temperatures, creating again an $\alpha$ center and a free electron capable of repeating this cycle, or the $F^*$ can decay to the $F$ ground state. The probability of nonradiative transition is very high at room temperature.[32] In this last case, the release of phonon energy ("thermal spike"[16]) of a few eV might also be sufficient to cause migration of the resulting $F$ center by one or more lattice sites.[23] It is not yet known which of the described possible mechanisms dominates.

In support of the $F'$-excitation models, the following facts should be considered. First, the $F'$ lifetime in NaCl at 293 K is approximately 20 min,[11,33] and much longer at the 260-K aggregation temperature due to the exponential thermal activation of the $F'$ decay process. This lifetime is orders of magnitude longer than the corresponding $F'$ lifetime in the extensively studied KCl host. Second, the quantum yield of the $F' \rightarrow F$ conversion under optical excitation of the $F'$ band at room temperature is very low.[30] The combination of these facts should allow a sufficient population of $F'$ centers to exist in NaCl during the photoaggregation time periods we employed in our experiments, even if the $F'$ band is not regenerated by $F$-center ionization. In this context the dramatic change in the results of green-light photoaggregation following $F$-band light preexposure may be due to an increase of the initial $F'$ population in the crystal (the short length of necessary preexposure indicates that its primary effect is color-center ionization, and, hence, formation of $F'$ centers, rather than photoaggregation).

TABLE I. Color-center formation in NaCl as a function of photoaggregating light. An asterisk indicates "no data obtained."

| Aggregating light | Additively colored crystals | $\gamma$-irradiated crystals |
|---|---|---|
| Blue | colloids | $F_2$, $R_1$, $R_2$, $N_1$, $N_2$ |
| Green | $F_2$ | $F_2$ |
| Blue+green | colloids | $N_1$, $N_2$, $R_1$, $R_2$, $F_2$ |
| Red | * | $N_2$ |

## IV. FLUORESCENCE EXPERIMENTS AND DISCUSSION

Fluorescence spectra of $\gamma$-irradiated NaCl crystals, aggregated using $F$-band light, are shown in Fig. 3. Here the 546- and 579-nm Hg-lamp lines, and a 831-nm laser-diode line were used to pump the $R_1$, $R_2$, and $N_1$ absorption bands, respectively. We did not have a monochromatic source of sufficient intensity to pump the NaCl $N_2$ band. The emission bands obtained from the $R_1$, $R_2$, and $N_1$ absorption bands were identical, to the accuracy of our measurements, and peaked at approximately 1.19 $\mu$m. Due to the low available power of our monochromatic sources, the smoothed scans of Fig. 3 were initially very noisy and it was not possible to rigorously test the findings of Ref. 2, where the authors report a disagreement of 0.03 $\mu$m between the peaks of the $R$- and $N_1$-center emissions. The half-widths of the $R_1$, $R_2$, and $N_1$ emission bands at 77 K were all approximately 0.14 eV in our experiments; here we disagree with the findings of Ref. 2, where the authors reported a 0.21-eV half-width for the $R$ emission and 0.28 eV for the $N_1$ emission at the same temperature (the smaller bandwidths observed in our samples, however, indicate fewer spurious effects from potential trace impurities).

The fluorescence experiments described here and in other work[6,34] show that in both NaCl and KCl host lattices the emission bands of $R$ and $N$ centers coincide. This has been traditionally one of the strongest arguments supporting the trigonal $F_3$ model for all $R_1$, $R_2$, $N_1$, and $N_2$ transitions in KCl.[6] However, it appears that, at least in NaCl, the $N_1$ band arises from a different defect than the $N_2$ band. The data of Fig. 2 show an unambiguous discrepancy between the growth rates of the $N_1$ and $N_2$ bands under various wavelengths of photoaggregating light. The absorbances of these bands should always grow proportionally if they originate from the same center. The two bands are separated well enough, so that the possibility that other absorptions are hidden under them is very small. Similar discrepancy appears between the $N_1$- and $R$-band growth rates. In view of these facts, it is rather striking that experiments yield the coincidence of fluorescence bands shown in Fig. 3. This casts doubt on the validity of fluorescence arguments used in discussing relations between $R$ and $N$ centers in other hosts.

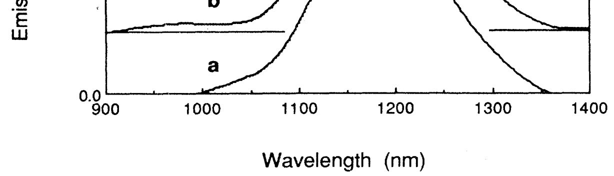

FIG. 3. Fluorescence spectra (at 77 K) of pure NaCl crystals colored by $\gamma$-radiation damage. *a*, $R_1$-band fluorescence (546-nm pump). *b*, $R_2$-band fluorescence (579-nm pump). *c*, $N_1$-band fluorescence (831-nm pump). Curves have been normalized to same height and vertically offset for clarity.

The possibility that the $N_1$ band in NaCl is due to an $F_3{}^+$ transition (an assumption based on the exact overlap of $N_1$ and $F_3{}^+$ absorption bands in KCl (Ref. 35) is unlikely for the following reason. We have been able to create a significant $F_3{}^+$ absorption in oxygen-doped NaCl, with a peak at 859 nm and a 0.078-eV (±0.008 eV) half-width. The formation of the $F_3{}^+$ band in crystals containing $O^{2-}$ ions results from the electron-trapping ability of such oxygen defects (a fact that also assists in the formation of $F_2{}^+$ centers[36]). This $F_3{}^+$ band formed in the absence of both $N$ bands during 300-K photoaggregation and bleached at 77 K under $F$-band light illumination (in ~1 h). Despite the fact that it was formed in a doped crystal, the 859-nm band was identified as belonging to an unperturbed center, due to the absence of peak shift during photoaggregation steps which caused shifts in the $F$, $F_2$, and $F_2{}^+$ bands.[36] The $F_3{}^+$ band in NaCl was clearly distinct from the $N_1$ and $N_2$ bands, due to the good peak-wavelength separation.

There may be significant differences between the NaCl system and the well-studied KCl, regarding the nature of the $R$ and $N$ bands. Our recent experiments in additively colored KCl support the $F_3$ model for the $R_1$, $R_2$, and $N_2$ bands.[37] There exists no evidence that the same model should not also apply to NaCl. However, it is impossible at this point to relate the $R$ and $N_2$ bands in NaCl based on the band-growth data presented here. One reason is the difficulty of accurately separating the change in the $R$ bands from potential concurrent changes in the overlapping $F'$ absorption, even when we attempted to bleach the $F'$ band before spectra were taken. More experimental data are needed, both in NaCl and in other hosts, in order to unambiguously relate the $R$ and $N$ bands, and explain the differences between the $N_1$ and $N_2$ bands.

In conclusion, specific aggregation procedures lead to more efficient $N$-band formation in NaCl than the usual method of plain $F$-light illumination. The observed differences in photoaggregation between additively colored and irradiated crystals, as well as the different results obtained with different wavelengths of aggregating light, can be attributed to excitation of color-center transitions other than the $F$ band. $F'$ centers especially seem to play an important role in the formation of higher aggregates, such as $R$ and $N$ centers. Despite the coincidence of the emission bands corresponding to several $R$ and $N$ absorptions, it is doubtful that all of them originate from the same defect.

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