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Photoionization and photochemical production of color centers in Ce^{3+}- and Ce^{3+}:Na^{+}-doped CaF_2

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The photoionization of Ce^{3+} in CaF_2 has been reinvestigated with CaF_2:Ce^{3+} and CaF_2:Ce^{3+}, Na^{+}. Irradiation of the singly doped crystals with 308-nm light at room temperature produces Ce^{2+}. However, at 80 K, we found no Ce^{2+} and observed only that the F^- interstitial charge compensator moved from the (001) site to the (111) site. (Units are $a/2$, the unit cell dimension.) In the doubly doped crystals, we observed the production of Ce^{2+} at 80 K. Diffusion processes at higher temperatures lead to formation of other color centers. A mechanism that accounts for these observations is proposed.

As part of an ongoing investigation into the processes of photoionization and electron transfer in ionic crystals, we have been studying the photochemical production and spectroscopy of color centers in CaF_2 doped with Ce^{3+} either alone or with Na^{+}. Pogatshnik and Hamilton[1] reported on the photoionization of Ce^{3+} in CaF_2 with ultraviolet irradiation and showed that the photoproduction of certain visible absorption bands is a two-step, two-photon process. In their study, they noted that bleaching of these absorption bands occurs within the first laser pulse. It was not stated that Ce^{4+} is formed, but neither was it made clear what the products of irradiation were. In this study, we have attempted to identify the products of the "photoionization," and to provide a mechanism for the changes observed in the absorption spectrum following irradiation.

The trivalent cerium ions occupy Ca^{2+} sites and so require some type of charge compensator for the extra positive charge. In singly doped crystals grown in the absence of oxygen, charge compensation is provided by an interstitial fluoride. Several charge compensation sites have been identified. Two common sites are the tetragonal center, C_{4v} F^- (100), and the trigonal center, C_{3v} F^- (111). (The coordinates of the charge compensator are expressed in the (hkl) notation in units of $\frac{1}{2}$ the unit-cell dimension.) Figure 1(a) presents model pictures of these sites. In both of these sites, the charge compensation is local. Charge compensation may also be achieved by a remote interstitial fluoride with the cerium ion in a cubic environment.

Both the C_{4v} site and the C_{3v} site have been studied by a variety of techniques.[2-9] Kaplyanskii and co-workers have studied the optical absorption and emission of Ce^{3+} in CaF_2.[2-4] Their work shows that the sharp line seen in absorption at 313.2 nm is due to the $4f \rightarrow 5d$ transition of Ce^{3+} in the C_{4v} F^- (100) site. Manthey[8,9] showed by stress experiments that the sharp line at 311.8 nm is due to Ce^{3+} in the trigonal site. Thus, we have a simple and direct spectroscopic method for distinguishing these sites.

For the doubly doped crystals, different types of charge-compensation sites are created by the introduction of monovalent impurity ions along with the trivalent rare earth.[10] In these crystals, both the rare-earth and the monovalent ion occupy divalent calcium sites. There are a number of possible orientations for these ion pairs. Model pictures of two of these sites are shown in Fig. 1(b).

The charge-compensation sites of the doubly doped crystals have also been the subject of several studies.[10-12] In a recent report from this laboratory, the optical-absorption and fluorescence excitation spectra of these sites were presented.[12] It must be pointed out that this paper contains a significant error. What appeared to be a spectral hole in the excitation spectrum has been shown

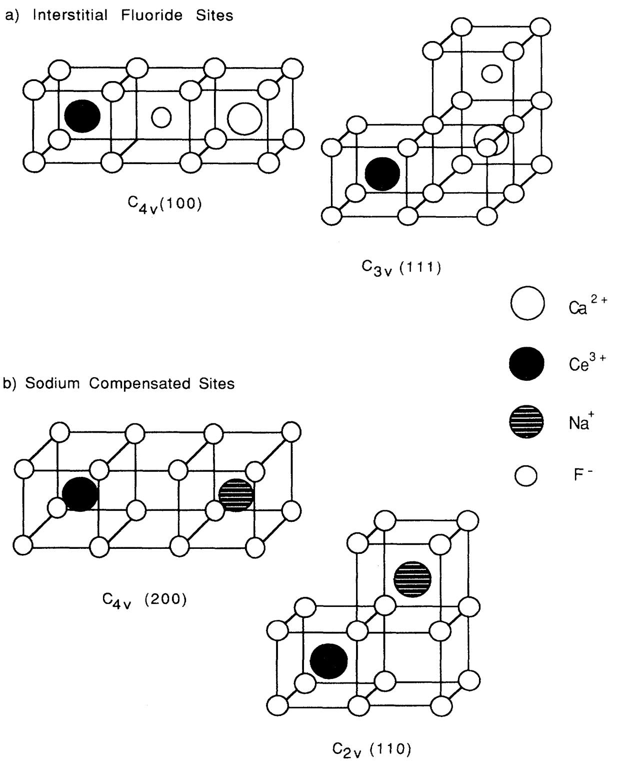

FIG. 1. Model pictures of some Ce^{3+} charge-compensation pairs. (a) Examples of the F^- interstitial sites. (b) Two of the possible Na substitutional sites.

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to be an experimental artifact. However, the report is correct in all other respects. The spectra show a number of lines in the region of 309–310 nm. These lines are assigned as zero-phonon lines of the various Ce^{3+}:Na^+ pairs.

EXPERIMENTAL

The doped crystals were prepared by the gradient freeze method from CaF_2 with CeF_3 (0.003–0.01 %) added. For the doubly doped crystals, larger amounts of NaF (0.10%) were also added. The percentages are by weight with respect to CaF_2. Carbon crucibles were covered to reduce the escape of volatilized NaF. In spite of this precaution, it is impossible to avoid some loss of Na^+; therefore, the final concentration of Na^+ in the samples is not known, but is certainly less than the initial amount added to the melt.

Crystals from several sources were used and several of the samples were used in previous studies.[8,12] Complete details of the growing conditions and previous annealing treatments are not known; however, all of the samples studied gave identical results under identical experimental conditions.

The crystals were cleaved to a thickness of approximately 1 mm along ⟨111⟩ planes and polished to optical quality. The samples were sandwiched between copper foil with holes to allow the passage of a laser beam or the beam of the absorption spectrometer and attached to the cold finger of a vacuum dewar equipped with quartz windows. Indium metal and Cry-con thermal conducting grease were used to insure good thermal contact. Liquid nitrogen was used to cool the sample. The exact temperature of the sample is not known; however, it is less than 100 K and probably between 80 and 90 K based on the resolution of the absorption spectra. Absorption spectra were recorded with a Cary 14 spectrophotometer. All of the absorption spectra shown here were recorded at liquid-nitrogen temperature (LNT). The instrumental resolution was on the order of 35 cm^{-1}.

A XeCl excimer laser provided 308-nm radiation. The output of the laser was directed with mirrors through a quartz lens and focused to a spot size of approximately 1 cm in diameter at the sample. The laser intensity through the sample was monitored with a Scientech power meter. The power flux was approximately 4–6 MW/cm^2. The total photons incident on the sample in a 1-h irradiation was on the order of 10^{20}.

For the low-temperature irradiation, the sample was mounted in the dewar and cooled, and the initial spectrum was recorded. Then, the sample was irradiated for up to one hour with 308-nm light. The absorption spectrum was recorded again after the irradiation. Then the sample was allowed to warm to room temperature in the dark, recooled, and the absorption spectrum was once again recorded.

For room-temperature irradiation, the sample was simply held in the unfocused beam of the excimer laser running at 10 Hz with pulse energy of approximately 100 mJ/pulse. The sample was then transferred to the dewar, cooled to 80 K, and the spectrum was recorded.

RESULTS

Figure 2(a) shows the UV absorption spectrum of a crystal doped with 0.01% Ce^{3+} before irradiation. Initially, the sample was transparent throughout the visible and infrared regions of the spectrum. The only measurable absorption occurred in the UV. The spectrum shows very clearly the zero-phonon line of the Ce^{3+} with an interstitial fluoride charge compensator in the (100) nearest-neighbor position at 313.2 nm (31 928 cm^{-1}).

Room-temperature irradiation of the singly doped crystal produces divalent cerium. Within seconds after exposure to the laser beam, the crystal develops a reddish brown color and the absorption spectrum of the colored crystal in the visible region is characteristic of divalent Ce^{2+} in CaF_2 (vide infra). The divalent cerium formed in this process is stable at room temperature; however, it is not stable at temperatures above 100 °C and the crystal is easily converted back to the initial state with only moderate heating.

In contrast, crystals irradiated and held at low temperature show markedly different behavior. Figure 2(b) shows the absorption spectrum of a crystal irradiated for one hour at LNT. The spectrum exhibits a strong zero-phonon line at 311.8 nm (32 072 cm^{-1}) due to Ce^{3+} with an interstitial fluoride in the (111) position with only a weak band at 313.2 nm. This is the only change in the spectrum. No new absorption bands appear in the visible and infrared regions of the spectrum.

The trigonal site is not stable at room temperature. After the sample was warmed to room temperature and

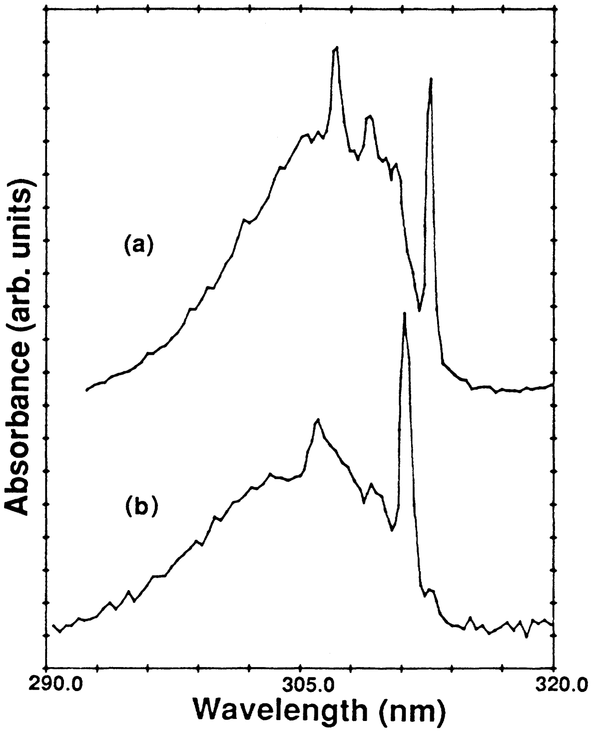

FIG. 2. Absorption spectra of CaF_2:0.01% Ce^{3+}. (a) Before irradiation. (b) After irradiation with 308 nm at 80 K. Spectra were recorded at 80 K.

then cooled to LNT again, the absorption spectrum was identical to the spectrum obtained before irradiation.

From these results, it is seen that, while irradiation at room temperature produces Ce^{2+}, irradiation at low temperature causes ionic motion and forces the charge compensator into the (111) position. Upon warming the fluoride moves back to the thermodynamically favored (100) position. No net photoionization was observed in the singly doped crystals irradiated at LNT.

The initial absorption spectrum of the doubly doped crystal showed a broad band centered at 309.5 nm. This band is comprised of the zero-phonon lines of the many possible Ce^{3+}:Na^{+} pairs.[12] No lines appeared at 311.8 or 313.2 nm, indicating the absence of interstitial fluoride compensators. No other absorption bands were seen in the visible or infrared regions.

In contrast to the singly doped crystals, doubly doped crystals irradiated and held at LNT show net photoionization. Figure 3(a) shows the absorption spectrum of a doubly doped crystal after irradiation. The spectrum in the visible region is the same as that reported for Ce^{2+} in CaF_2 by Alig *et al.* with the exception of an additional shoulder at 450 nm.[13] Alig *et al.* produced Ce^{2+} by γ irradiation. The bands shown in Fig. 3(a) are not assigned to specific transitions in Ce^{2+}. Crystal-field calculations failed to adequately reproduce these bands[13] and no clear assignments can be made. They are apparently due to color centers associated with the impurity ions. However, we also see weaker but more characteristic peaks in the near IR at 1412, 1134, and 830 nm. The bands in the IR can be assigned to the transitions in Ce^{2+}. The bands shown in Fig. 3(a) always accompany these more characteristic peaks and so we take them as evidence for Ce^{2+}.

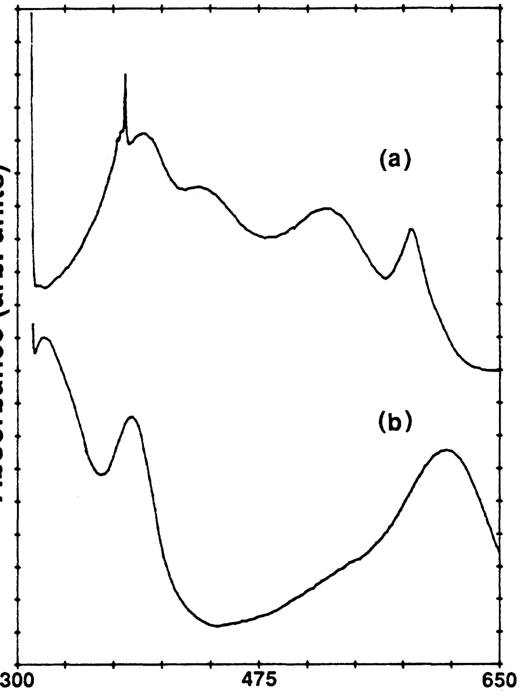

FIG. 3. Absorption spectra of CaF_2:0.003% Ce^{3+}, 0.1% Na^{+}. (a) After irradiation with 308 nm at 80 K. Sample was held at 80 K. (b) Absorption spectrum of irradiated crystal after cycling to room temperature. Spectrum was recorded at 80 K.

The Ce^{2+} produced by the low-temperature irradiation is not stable at room temperature. Upon warming to room temperature, the crystal develops a blue color. The absorption spectrum of the crystal after cycling to room temperature is shown in Fig. 3(b). The bands in this spectrum occur at the same wavelengths as bands in the spectrum of CaF_2:Na^{+} colored by energetic electrons[14] or x- or γ rays.[15,16] That is, the spectrum is characteristic of color centers associated with sodium, not cerium.

Room-temperature irradiation of the doubly doped crystal produces the same spectrum shown in Fig. 3(b). However, the blue color is not produced immediately. The crystal first develops the reddish brown color characteristic of divalent cerium. Then, within a few seconds, the blue color develops. Irradiation of the blue crystal gives a red emission. The red emission has not been characterized; however, it is almost certainly associated with the absorption band at 615 nm. This absorption and its associated emission have been studied by several others.[15,17] The band has been assigned to a F_{2A} center[15] (two F centers adjacent to a Na^{+}) or a F_{2A}^{+}. Other bands in the spectrum shown in Fig. 3(b) are assigned to different complexes of F centers, e.g., F_{3A}^{+}.

Continuous irradiation is not necessary to produce the blue coloration. Several samples were irradiated for a few seconds until the reddish brown color appeared and then placed in the dark. These samples developed the blue color within a few hours and gave the same spectrum.

DISCUSSION

The results presented in the preceding section show that similar spectra may be obtained regardless of the method of irradiation. In the singly doped crystal, reduction of trivalent cerium to the divalent state may be effected with x or γ irradiation or by irradiation at room temperature with 308 nm. The production of Ce^{2+} in CaF_2 by 308-nm irradiation was studied by Pogatshnik and Hamilton.[1] They showed quite clearly that a stepwise two-photon process was involved. In their investigation of the temperature dependence of the process, they observed coloration of samples containing 0.05% Ce^{3+}. However, the temperature at which their study was conducted is not known and was probably somewhat higher than LNT. In our study, irradiation with 308 nm at temperatures near 80 K did not produce Ce^{2+}, but rather, caused motion of the charge compensator. This change indicates that the compensator must be intimately involved in the mechanism of photoreduction.

In the doubly doped crystal, divalent cerium is observed only when the sample is held at low temperature. Clearly, the production of Ce^{2+} is only the first step in the coloration of these crystals. The final result is characteristic of color centers associated with sodium.

Again, the method of excitation is irrelevant. Spectra similar to Fig. 3(b) are obtained from CaF_2:Na^+ colored with electrons[14] or x- or γ rays.[15,16]

The similarity in the results under such varying conditions implies that the different methods of excitation produce a common factor. It has been shown that the production of color centers with ionizing irradiation in alkali halides and alkaline-earth fluorides involves the formation of self-trapped excitons.[18]

In pure CaF_2 the self-trapped exciton is comprised of the closest possible pair of an *F* center and an *H* center. The *H* center is a F_2^- molecular ion on a fluoride lattice site with a ⟨111⟩ orientation. Williams *et al.*[19] and Tanimura, Katoh, and Itoh[20] have studied the transient optical absorption of the self-trapped exciton produced by an electron pulse. Two absorption bands have been identified: one due to excitation of the *F* center at 435 nm and a broad band centered at 308 nm due to the transition from the σ_g orbital to the σ_u antibonding orbital of the F_2^- molecular ion. Excitation into the band at 308 nm causes dissociation of the *H* center and ejection of one of the fluorine atoms from the lattice point resulting in the formation of separated, stable *F*-*H* pairs.[19]

In the case of CaF_2:Ce^{3+}, formation of an *H* center adjacent to the rare-earth impurity can account for the experimental results by the following argument. (See Fig. 4.) We begin with the low-temperature results. Consider a Ce^{3+} ion with its fluoride compensator in the tetragonal (100) site. Excitation with 308 nm creates something like a self-trapped exciton by removing an electron from a fluoride ion. The Ce^{3+} acts as an electron acceptor. The fluorine atom then forms an *H* center with a neighboring fluoride. This *H* center may incorporate the interstitial fluoride and a fluoride on a lattice site or two fluorides from adjacent lattice sites. In the case of two lattice fluorides, a vacancy is created which can be filled by the interstitial fluoride. In either case, the *H* center has a ⟨111⟩ orientation. Excitation of the *H* center by a second phonon causes dissociation. One fluorine atom or ion moves into an interstitial site and one remains on the lattice site. The electron is then recaptured. If the interstitial position occupied is the (100) site, no net change has occurred. However, there is an equal probability that the interstitial site occupied will be the (111) position. If this occurs, the net result is a movement of the charge compensator from a tetragonal to a trigonal position.

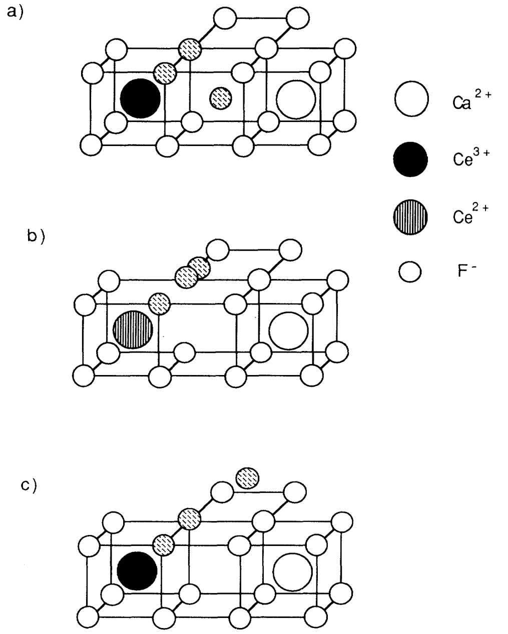

FIG. 4. Schematic diagram of the mechanism of fluoride compensator motion. Small cross hatched circles are the fluoride ions on the lattice sites and the interstitial compensator.

In the mechanism outlined above, the electron is recaptured by the fluorine atom returning the cerium ion to the trivalent state. This insusceptibility to reduction is a consequence of the local charge compensation. In a study on the charge conversion of x-irradiated rare-earth ions in calcium fluoride, Merz and Pershan[21] put forth the following idea (Fig. 5). Consider a trivalent rare earth with its interstitial compensator. The electron which provides the charge compensation may reside ei-

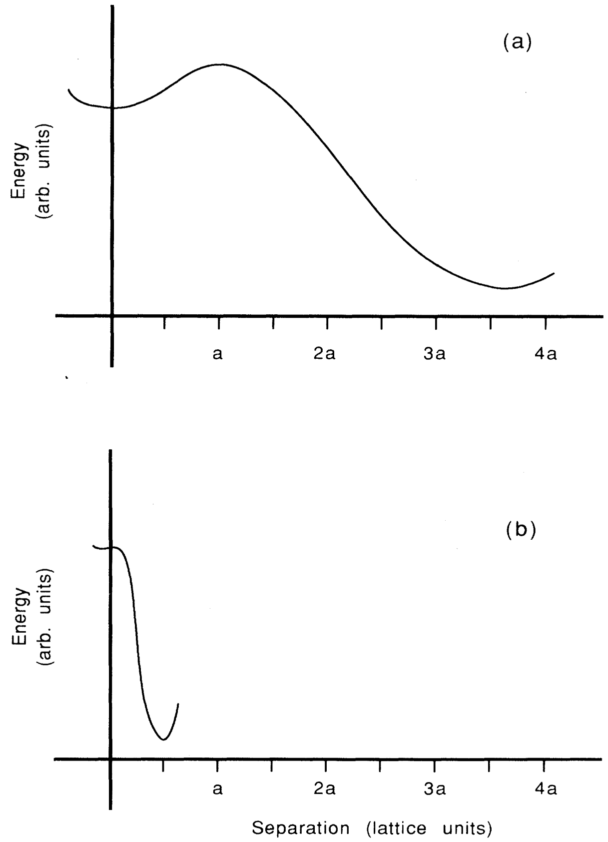

FIG. 5. Potential energy between a trivalent rare earth and an interstitial fluoride. Interstitial fluoride separation from the rare earth is plotted along the horizontal axis in units of the lattice constant. (a) Nonlocal compensation. A metastable energy minimum is located at the rare-earth ion. (b) Local compensation. Taken from Ref. 21.

ther on the compensator or on the rare earth, leaving an interstitial fluorine atom. For rare-earth ions with local compensators the lowest energy position for the extra electron is on the interstitial compensator. In this case, the rare earth cannot be reduced. On the other hand, for rare-earth ions with remote compensators, a metastable energy minimum for the compensating electron is located at the rare-earth ion. The potential-energy barrier between the rare-earth ion and the remote compensator is high enough to prevent recombination at room temperature.

For crystals irradiated at room temperature, the same mechanism applies. However, there is the additional possibility of motion of the *H* center away from the impurity ion. Diffusion of the *H* center in CaF_2 has been shown to occur at about 100 K.[18] If diffusion occurs, according to the idea of Merz and Pershan, the electron is trapped at a cerium ion in a cubic site. Thus, without sufficient thermal energy to diffuse away from the impurity center, the *H* center recombines with the electron, restoring the Ce^{3+}. At higher temperatures, diffusion occurs and the electron remains trapped at the impurity ion. Because of the diffusion, the divalent rare-earth ion is left in a site of cubic symmetry. This differs from the usual model of photoionization and electron trapping in fluorite crystals. In a typical photoionization mechanism involving rare-earth ions, the electron is trapped by a rare-earth ion in a cubic site. In the proposed model, the cubic site is created by the diffusion of the *H* center. Electrostatic considerations suggest that diffusion of only a few crystal lattice units is sufficient to leave the rare-earth ion in an effectively cubic site.

It is important to note that small changes in temperature can produce significant changes in the observed photoproducts. Motion of the *H* center is an activated process. The activation energy for diffusion of the *H* center in CaF_2 is not known; however, we may assume that it is similar to the activation energy for motion of the V_k center which is approximately 0.2 eV.[22] With this value for E_A, it is seen that a change in temperature as small as 20 K can produce a change of two orders of magnitude in the rate of diffusion.

The proposed mechanism accounts for the two-photon nature of the coloration process and explains the observed temperature dependence. The ideas presented above can also explain the results of studies on the doubly doped crystals.

The initial absorption spectrum of the doubly doped crystals shows a strong absorption at 310 nm due to the Ce^{3+} with a sodium compensator. The sodium ions occupy divalent calcium sites. No absorption due to other compensators is seen. Based on this observation, the concentration of the Na^+ ions in the crystal must be at least as much as the concentration of Ce^{3+} and, considering the relative amount of NaF added to the melt, could be much higher. The high (relative to Ce^{3+}) concentration of Na^+ means that additional F^- vacancies are present in the crystal.

The absorption spectrum of a doubly doped crystal irradiated at LNT and maintained at low temperature shows the presence of Ce^{2+}. The spectrum is the same as those reported by other workers for CaF_2:Ce^{3+} which was colored by γ irradiation.

The Ce^{2+} is not stable in the presence of excess sodium. Whether the crystal is irradiated at low temperature and allowed to warm or irradiated at room temperature, the final result is the same. The absorption spectrum shows the same bands as crystals containing just sodium colored with electrons or γ rays. The development of the blue color in the dark shows that diffusion processes are important. The absorption spectrum has been assigned as due to aggregates of *F* centers. Formation of these centers is only possible if F^- vacancies are already present or are produced by the excitation.

Several sites have been identified for the sodium compensator. In the discussion that follows, we will consider only one. Other sites may be treated by simple extensions of the same arguments.

Consider a Ce^{3+} with a sodium compensator in the (110) position (Fig. 6). Electron paramagnetic resonance studies have shown this to be the most common site in crystals with low dopant concentrations.[10] Excitation with 308-nm light leads to the formation of self-trapped excitons as before. However, while the position of minimum potential energy for the extra electron is on the compensator for singly doped crystals, this need not be true for the doubly doped crystals. For the singly doped crystals, electric neutrality is accomplished by the addi-

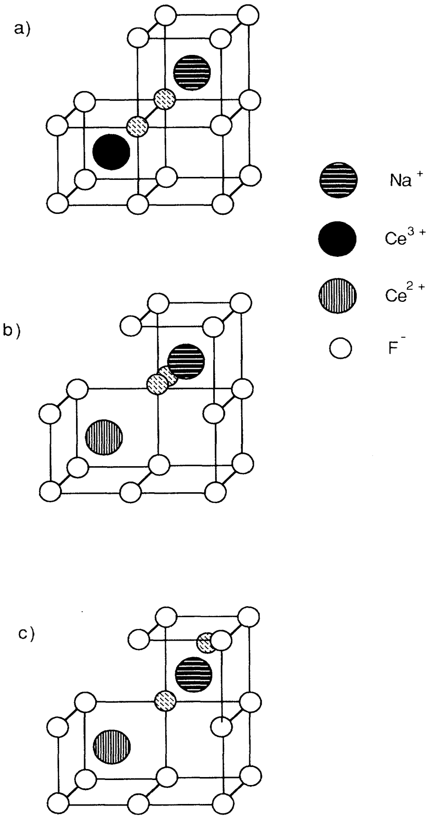

FIG. 6. Schematic representation of the mechanism of photoreduction in doubly doped crystals.

tion of an extra negative charge. In the doubly doped crystal, neutrality is achieved by substitution of a single positive charge for the divalent calcium. This single charge has its own compensation mechanism. The transfer of an electron from a fluoride ion to the Ce^{3+} and formation of an *H* center at or near the Na^+ also satisfies the requirement for neutrality at each of the impurity centers separately. Subsequent excitation of the *H* center would result in the formation of a distant *H* center and a vacancy around the Na^+ ion giving a structure which is stable at 80 K. Therefore, the spectrum of divalent cerium is observed. Upon warming, the electron can be captured at the vacancy, returning the cerium ion to the trivalent state and producing an *F* center. Diffusion and aggregation of the *F* centers produces the other centers. This diffusion is enhanced by the presence of additional vacancies associated with the excess Na^+.

CONCLUSION

We have shown that a mechanism involving production and excitation of self-trapped holes can account for the photochemical processes in $CaF_2{:}Ce^{3+}$ and $CaF_2{:}Ce^{3+}$, Na^+. Schematically, the initial step of the mechanism can be represented as a transition from the valence band to the Ce^{3+}. The band gap of CaF_2 is 10–12 eV. The $4f$-$5d$ transition of Ce^{3+} is approximately 4 eV. The exact positions of the energy levels within the band gap are not known; however, it is known that the $5d$ orbitals are well below the conduction band. If the energy levels of the Ce^{3+} lie in the middle of the band gap, the lowest levels would be at roughly 4 eV or 308 nm above the valence band.

Admittedly, the mechanism proposed is somewhat speculative and alternative models[1] must be considered. However, the experimental observations are clear. Irradiation of the singly doped crystals at temperatures near 80 K produced ionic motion resulting in interstitial fluorides in trigonal positions without producing Ce^{2+}. This result is not accommodated by a model which involves ionization of the Ce^{3+} to form Ce^{4+} and Ce^{2+}.

For the doubly doped crystals, the spectrum of the crystal held at low temperature after irradiation is virtually the same as the spectra of $CaF_2{:}Ce^{2+}$ reported by others. The final spectrum shows the same absorption bands as crystals doped with sodium alone. Also, the method of excitation is irrelevant. The earlier works used x or γ irradiation to produce the same spectra. This coincidence is possible only if the different methods of excitation produce a common factor. That common factor must be the F_2^- molecular ion. Therefore, the proposed mechanism is consistent with the experimental facts and precedents for each of the steps may be found in the literature.

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