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Spectroscopy of reversible-bleaching centers in hydrogenated $SrF_2:Pr^{3+}$ and $CaF_2:Pr^{3+}$ crystals

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We report the results of laser-selective-excitation studies on several centers in hydrogenated $SrF_2:Pr^{3+}$ and $CaF_2:Pr^{3+}$ crystals that exhibit a bleaching mechanism associated with light-induced ion motion. These bleaching effects arise as the constituent hydrogenic ions of the centers migrate to new positions in the lattice, which changes the crystal field at the Pr^{3+}-ion site and detunes that center from the laser. For some centers the ion motion is found to be reversible with a switch in the laser polarization, while for other cases distinct photoproduct centers are formed with different excitation wavelengths. The models and bleaching mechanisms proposed for several of the centers are successful in explaining the observed effects.

I. INTRODUCTION

Recently an unusual phenomenon of reversible polarized bleaching was reported for some hydrogenic centers in calcium and strontium fluorides containing rare-earth ions.[1-3] It was found that bleaching of an inhomogeneously broadened absorption line could be reversed by a change in the laser polarization which would allow an apparently indefinite series of bleaching and recovery cycles to be recorded. The bleaching mechanism of light ion motion is new to inorganic materials and offers new insights into the dynamics of light-induced ion migration. It also produces persistent spectral holes which have been proposed as a basis for frequency-domain information storage.[4]

The bleaching is observed on pumping R^{3+} (R denotes rare earth) electronic transitions, where the intensity of fluorescence typically decreases by a factor of 5 in times ranging from a few seconds to several minutes depending on the particular center. This bleaching is persistent at low temperatures, showing only a slight recovery ($<5\%$) after 2 h in the dark at 14 K. Spectral holes burnt into an absorption line show little degradation after 8 h at a temperature of 1.6 K. Thermal cycling above 100 K restores the lost intensity.

The centers that were observed undergoing this effect are rhombic-symmetry modifications of the hydrogenic C_{4v} center with the addition of extra hydrogenic ions.[1] All three H^-, D^-, and T^- isotopic variations of the centers exhibit the effect; the center with a light isotope gives a more rapid decay of fluorescence than the corresponding center with a heavier isotope. The bleaching effects arise as constituent hydrogenic ions of the center migrate to new positions placing the R^{3+} ion in a new environment and out of resonance with the laser. This mechanism is analogous to photochemical hole burning which is common for many organic systems and molecules in glasses.[5]

In the fluorite crystals studied here, the hydrogenic ions are observed to migrate either to inequivalent positions to form a discrete photoproduct center with a different excitation wavelength, or to equivalent positions where the photoproduct is the same center reoriented by 90°. It is in this latter case that reversible polarized bleaching is observed. The ion motion is also reversible in the former case, as excitation of the photoproduct leads to restoration of the original center. Similar reversible switching between photoproducts occurs by proton transfer in metal-free pthalcyanine[6] and porphin.[7]

We report here on studies of four bleaching centers in both hydrogenated $SrF_2:Pr^{3+}$ and $CaF_2:Pr^{3+}$ crystals. Results from all three H^-, D^-, and T^- isotopic varieties of these centers were used to unravel the complicated vibronic spectra obtained. Center configurations and bleaching mechanisms are proposed to explain the experimental results.

II. EXPERIMENT

The bleaching centers under study were characterized in the optical region using laser selective excitation techniques. A tunable dye laser of bandwidth 1 cm^{-1}, pumped by an argon-ion laser, was used to selectively excite the Pr^{3+} ion of a particular center with the laser usually tuned to match the transition between the lowest-crystal-field components of the $^3H_4$ and $^1D_2$ multiplets. Rhodamine 590 dye was appropriate for exciting transitions in this region of the optical spectrum. The fluorescence was collected at 90° to the incident beam and analyzed by a Spex 1403 double monochromator using photon counting techniques. The laser excitation spectra were recorded by scanning the birefringent tuning element of the dye laser, while the fluorescence was monitored using a 0.25-m Baush and Lomb monochromator. All experiments were done with the samples mounted on the cold finger of a closed-cycle helium refrigerator. The sample temperature could be varied from 12 to 300 K, with most of the spectra recorded at 12 K.

The crystals used in this study were either purchased from Optovac Inc. or grown from the melt in this laboratory with Pr^{3+} concentrations in the range 0.02–0.1 mol %. For some experiments $\langle 100 \rangle$ oriented crystals were required and these were cut from aligned boules using $\{111\}$ cleavage planes for reference. Hydrogen, deuterium, or tritium was diffused into the samples using the techniques of Hall and Schumacher.[8] The samples were heated to 850 °C in the appropriate gas while in contact with molten aluminum. Treatment times up to 65 h were used and the samples were cooled to room temperature over a period of 3–4 h.

The alternative procedure of cooling samples to room temperature by quenching them in liquid nitrogen enhances the hydrogenic C_{4v} center at the expense of other centers. In such quenched crystals, the rhombic-symmetry centers of interest here are not seen initially but become observable after storing the crystals for several months at room temperature. During this time the mobile ions migrate to new positions in order to give the equilibrium center distribution that is appropriate to the storage temperature. The rhombic center concentration also increases with the length of hydrogenation treatment.

With the annealing conditions used here, significant quantities of these rhombic centers exist in freshly hydrogenated samples. Absorption coefficients measured for these centers were as high as 2×10^{-3} mm^{-1} compared to 6×10^{-3} mm^{-1} for the H^- C_{4v} Pr^{3+} center and 12×10^{-3} mm^{-1} for the F^- C_{4v} Pr^{3+} center, which is the dominant absorbing center in these crystals.

Most experiments in this study used the D^--ion versions of the bleaching centers because these gave the strongest fluorescence. The quantum efficiency of fluorescence for hydrogenic-ion centers is substantially lower than that for the fluoride-ion centers. The rare-earth ion excitation is efficiently channeled into nonradiative decay processes by the high-frequency local-mode vibrations of the light hydrogenic ions, leading to quenching of the fluorescence.[3] For SrF_2:Pr^{3+} the F^- C_{4v} center has a $^1D_2$ fluorescence lifetime of 2.03±0.05 msec, while the additional nonradiative relaxation pathways which were provided by the interstitial D^- ion in the D^- C_{4v} center reduced this lifetime to 405±10 μsec. The higher-frequency local-mode vibrations of the lighter H^- ion permit lower-order multiphonon processes, giving an even shorter lifetime of 2.7±0.1 μsec for the H^- C_{4v} center. For the bleaching centers studied here, there are additional hydrogenic ions present, and a further reduction in the fluorescence lifetime is observed as more nonradiative relaxation pathways are available. In theory, the T^--ion centers should have the greatest efficiency for fluorescence, however, the technical difficulties involved in doping T^- ions into these crystals reduce the concentration of the T^- centers which are obtainable. Thus, deuterated crystals generally provide the strongest fluorescence.

III. RESULTS

Fluorite crystals such as SrF_2 and CaF_2 are ideal hosts for optically active rare-earth ions because they are transparent in the optical region and exhibit a high degree of mechanical stability over a wide temperature range. Substitution of divalent alkaline-earth metal ions by trivalent rare-earth ions requires charge compensation. Each position for the charge-compensating ion produces a spectroscopically different center which is characterized by a unique set of energy levels. A variety of different absorbing centers can be present in these crystals giving complex spectra which require the techniques of laser selective excitation to unravel.[9]

For the Pr^{3+}-doped fluorite crystals studied here, the dominant absorbing center has a charge-compensating F^- ion residing in a neighboring $\langle 100 \rangle$ interstitial position giving a point-group symmetry of C_{4v} at the Pr^{3+} site. Upon hydrogenation of these crystals, new absorbing centers appear as H^- ions replace F^- ions in the lattice. The H^- C_{4v} center, where the interstitial F^- ion is replaced by an H^- ion, has been identified as the principal hydrogenic center in hydrogenated SrF_2:Pr^{3+} and CaF_2Pr^{3+} crystals.[10]

The presence of an H^- ion in the composition of a center can be inferred from the observation of Pr^{3+}-H^- vibronic transitions in the optical spectrum. The vibrations of the light H^- ions are localized about the H^- ion site and can couple to the Pr^{3+} electronic transitions through the electron-phonon interaction.[11] A vibronic transition appears as a spectral line separated from a zero-phonon transition of the Pr^{3+} ion by an interval matching the local-mode frequency. The position of the H^- ion can be inferred from the number and strength of the vibronic lines observed. As the H^- C_{4v} center has axial symmetry the transverse local-mode vibration of the H^- ion is doubly degenerate and only two fundamental vibronic intervals are observed.

In addition to the interstitial H^--ion vibronics, the centers that give bleaching effects exhibit a set of stronger local-mode vibronics originating from H^- ions substituting for lattice F^- ions. Their vibronic intervals have a mean frequency that is close to the frequency of an isolated H^- ion in the regular T_d symmetry lattice anion site.[12] The greater intensity of the vibronic lines in this set indicates a smaller Pr^{3+}-H^- separation, and it is concluded that the bleaching centers are derived from the H^- C_{4v} center by substituting H^- ions for lattice F^- ions in the first coordination shell about the Pr^{3+} ion. The doubly degenerate (Γ_5) crystal-field ground state of the Pr^{3+} ion in a C_{4v} center is split as the hydrogenic ion in the nearest-neighbor shell lowers the point-group symmetry of the Pr^{3+}-ion site to rhombic (C_S). Some idea of the departure from a C_{4v} site symmetry can be obtained from the magnitude of this splitting.

For some rhombic-symmetry centers the absorption lost by bleaching the center with one laser polarization could be substantially restored by merely rotating the polarization of the laser by 90°. This effect has been termed reversible polarized bleaching,[1] and is most pronounced for ⟨100⟩ oriented samples. Qualitatively, reversible polarized bleaching can be understood in these cubic crystals if the optical excitation of the Pr^{3+} ion in the C_S center induces a reorientation of the center to either of the two orthogonal alignments. As there are three equivalent ⟨100⟩ directions, but only two possible laser polarizations, a preferential excitation of some center orientation occurs. Selective excitation with one laser polarization can then alter the distribution of the centers between the three originally equivalent orientations, thus reducing the number of centers which can absorb that laser light. Subsequent excitation with the orthogonal laser polarization returns some of the centers to their original alignment, giving rise to the reversible process.

For the centers where a photoproduct with a different set of energy levels is formed, there is no reorientation to an equivalent center, and the fluorescence from each of the two laser polarizations bleaches independently. A similar bleaching of center orientations was shown recently using photochemical hole burning of CN^- molecules in cubic alkali halide crystals.[13]

Figure 1 shows the laser excitation spectra in the $^1D_2$ region for both $\mathrm{SrF_2{:}Pr^{3+}{:}D^-}$ and $\mathrm{CaF_2{:}Pr^{3+}{:}D^-}$ crystals. Using the usual nomenclature for the crystal-field levels of the rare-earth ions, the $Z_1,Z_2 \rightarrow D_1$ excitation lines for the various C_S centers studied are indicated. The spectroscopic properties of each of the four main C_S centers will be described in turn.

A. The $C_S(1)$ center

The dominant rhombic-symmetry center in hydrogenated $\mathrm{SrF_2{:}Pr^{3+}}$ and $\mathrm{CaF_2{:}Pr^{3+}}$ crystals has been labeled $C_s(1)$; the experimental results suggest that these centers have the same configuration in each crystal.

The $^1D_2 \rightarrow {}^3H_4$ fluorescence spectra were recorded for all three isotopic varieties (H^-, D^-, and T^-) of the $C_S(1)$ center in both crystals. The spectra of the $\mathrm{SrF_2{:}Pr^{3+}}$ crystals are shown in Fig. 2 as being representative of the rhombic centers. The lines in these spectra consist of transitions to $^3H_4$ crystal-field levels and to local-mode vibronic levels. The vibronic lines are easily identified by their shift with changes in the hydrogenic ion consistent with the expected $m^{-1/2}$ mass dependence of the local-mode frequency. Table I summarizes the spectral data for the $C_S(1)$ centers.

The $C_S(1)$ centers undergo reversible polarized bleaching for all three isotopes in both crystals with a recovery level between successive cycles of better than 90%. Figure 3(a) shows the curves obtained from the $C_S(1)$ center in $\mathrm{SrF_2{:}Pr^{3+}{:}D^-}$. At an incident-laser-power density of approximately 1.1 kW/cm^2, the D^- ion centers have a characteristic decay time of 30 sec but this time decreases to 3 sec for the H^--ion centers due to the much greater mobility of these ions. Correspondingly, the T^--ion centers decay at a much slower rate than the D^--ion centers, having an observed decay time of 360 sec.

After bleaching the D^- $C_S(1)$ centers, the laser excitation spectrum was recorded over a wide frequency range in a search for any photoproduct. No new centers were observed for either crystal. This suggests that the only photoproducts created are equivalent centers in orthogonal directions formed by the reversible polarized bleaching mechanism. This conclusion is consistent with the

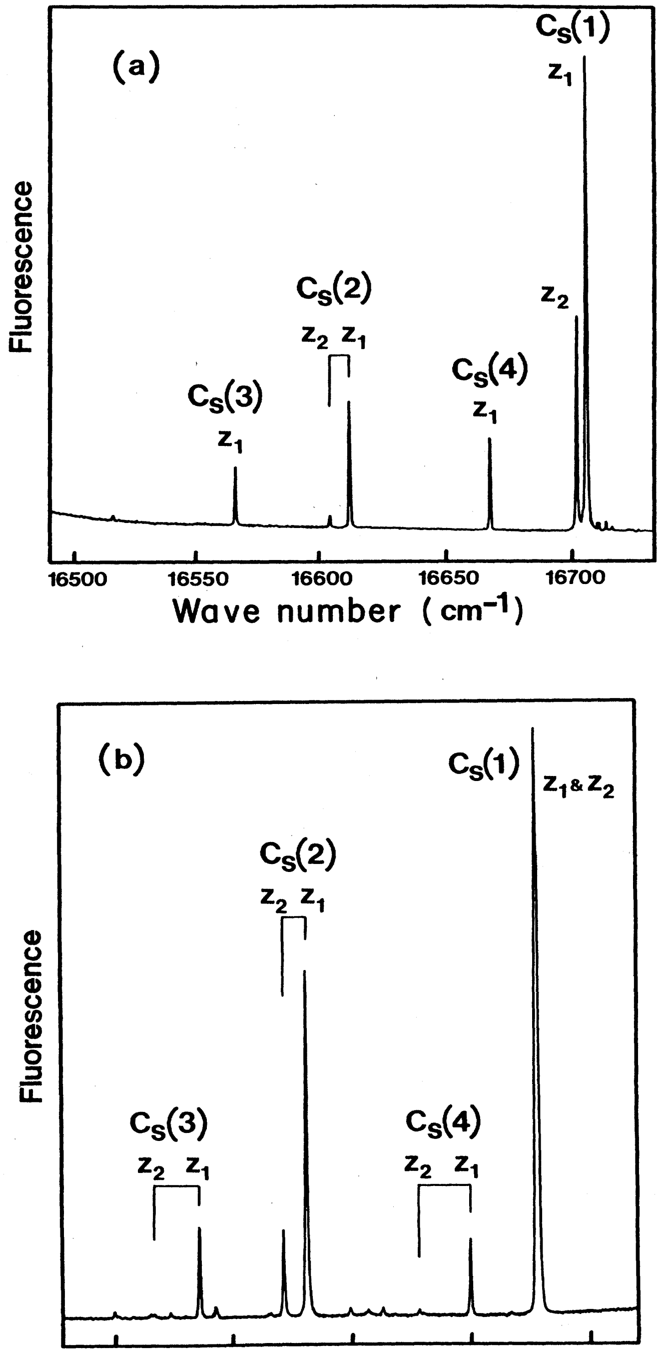

FIG. 1. Laser excitation spectra of the $^1D_2$ region of the Pr^{3+} ion for (a) a $\mathrm{SrF_2{:}0.05\%Pr^{3+}{:}D^-}$ crystal at 14 K and (b) a $\mathrm{CaF_2{:}0.05\%Pr^{3+}{:}D^-}$ crystal at 30 K. The excitation lines of the various C_S centers studied are indicated.

bleaching curves of Fig. 3(a) where the high level of recovery shows most centers switching backwards and forwards in step with the laser polarization.

Since each hydrogenic ion has three vibrational degrees of freedom, the number of vibronic lines observed gives an indication of the number of ions in the center. For the $C_S(1)$ center in SrF_2:Pr^{3+}:D^- three interstitial and three substitutional vibronic lines are observed, indicating one hydrogenic ion of each type. The local-mode vibronics at 673, 685, and 691 cm^{-1} are close to the frequencies observed for the D^- C_{4v} center, viz., 660 and 685 cm^{-1}, and are thus identified as originating from an interstitial D^- ion. Similarly, the substitutional D^--ion vibronics at 529, 569, and 829 cm^{-1} can be identified by their greater strength (as discussed earlier) and their mean frequency being close to 642 cm^{-1}, the frequency of a D^- ion occupying a regular lattice site.[12] A similar pattern of vibronics was observed in CaF_2:Pr^{3+}:D^-.

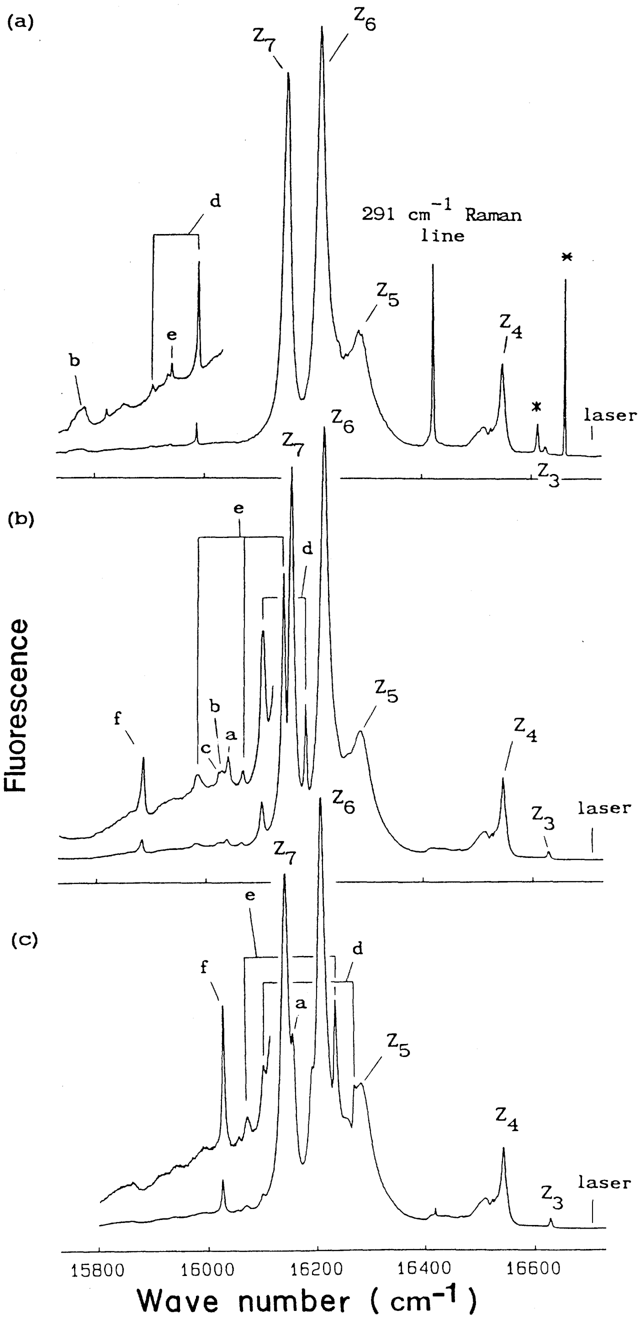

FIG. 2. 14-K ${}^1D_2 \rightarrow {}^3H_4$ fluorescence spectra for the (a) H^-, (b) D^-, and (c) T^- $C_S(1)$ centers in SrF_2:Pr^{3+} crystals. The Z_i labels identify zero-phonon electronic transitions, while $a, \ldots, f$ label vibronic transitions corresponding to the vibronic intervals listed in Table I. The spectral lines labeled * indicate transitions of an unidentified F^- center showing through the weak H^- center fluorescence.

B. The $C_S(2)$ centers

The second most prevalent rhombic center in these crystals has been designated $C_S(2)$ and again it is concluded that these centers have the same configuration in SrF_2 and CaF_2 crystals. The spectral data for $C_S(2)$ centers are included in Table I. These centers also exhibit reversible polarized bleaching, however, the recovery of fluorescence is observed to be decreasing between successive cycles. Figure 3(b), which shows the bleaching curves for the $C_S(2)$ center in SrF_2:$Pr^{3+}D^-$, should be contrasted to the curves in Fig. 3(a) for the $C_S(1)$ center in the same crystal. This reduction in the recovery level is associated with an additional bleaching mechanism where a photoproduct at a different excitation wavelength is created. The formation of this photoproduct, labeled $C_S(2)^*$, can be observed in an excitation spectrum. In Fig. 4 the unbleached intensity of $C_S(2)$ shown in Fig. 4(a) is reduced to that in Fig. 4(b) by the growth of $C_S(2)^*$. Subsequent excitation of $C_S(2)^*$ restores almost all the lost intensity in $C_S(2)$ at the expense of $C_S(2)^*$.

The vibronic spectra of the $C_S(2)$ centers show an additional substitutional ion vibronic interval which suggests the presence of two substitutional hydrogenic ions; this is in contrast to the $C_S(1)$ case where there is evidence for only one. The new vibration has the lowest frequency of the four substitutional hydrogenic ion local-mode vibronics and is readily identified for all three H^-, D^-, and T^- isotopes in SrF_2:Pr^{3+} crystals.

C. The $C_S(4)$ centers

The $C_S(4)$ centers are discussed next as their spectral properties are closer to those of $C_S(1)$ and $C_S(2)$ than those of $C_S(3)$, which is the fourth and last center to be considered. The $C_S(4)$ centers in CaF_2:Pr^{3+} were not studied to the same extent as those in SrF_2:Pr^{3+}, but from their position in the sequence of centers (Fig. 1) and from the results of hole-burning studies currently in progress,[14] there is a very good correlation between the centers in the two crystals. The known spectral data are summarized in Table I.

The $C_S(4)$ bleaching does not exhibit any reversible bleaching effects with polarization, and each laser polarization bleaches independently. Figure 3(c) shows the curves obtained for the $C_S(4)$ center in SrF_2:$Pr^{3+}D^-$. According to a comparison with the $C_S(2)$ centers, such a decay is indicative of discrete photoproduct formation.

This conclusion is supported by a laser excitation spectrum where a line of a new center, $C_S(4)^*$, is created when the $Z_1 \rightarrow D_1$ transition of the $C_S(4)$ center is bleached. Excitation of the photoproduct restores the intensity of the original center and no other centers are created by either the bleaching or recovery processes.

D. The $C_S(3)$ centers

The spectroscopy of the $C_S(3)$ centers suggests that they contain more hydrogenic ions than the three centers discussed previously. Multiple local-mode vibronic lines corresponding to both substitutional and interstitial ions are observed in the fluorescence spectra. Unfortunately the weak emission from these centers makes it difficult to record the fluorescence from the H$^-$ and T$^-$ centers required for an unequivocal assignment of the lines. Correspondingly, the correlation for this center between the two crystals is weaker than for the other centers. The D$^-$-ion centers were studied in more detail and the results that were obtained are summarized in Table I.

Like the other rhombic-symmetry centers, the $C_S(3)$ centers show bleaching of their fluorescence, which, in this case, is not reversible with laser polarization [Fig. 3(d)]. The characteristic decay time is the fastest of all the centers measured; it is only a few seconds for the D$^-$ centers. This suggests that additional reorientation pathways are available, further supporting the model that more hydrogenic ions are involved in this center. The nonreversible nature of the decay suggests photoproduct formation, which is confirmed by the observation of $C_S(3)^*$ in the excitation spectrum. As was found for the other rhombic-symmetry centers, excitation of the photoproduct restored the lost intensity in the original center with no other additional lines appearing.

An interesting feature of the $C_S(3)$ center in SrF$_2$:Pr^{3+}:D$^-$ is the almost exact coincidence of the $^3H_4 \rightarrow {}^3P_0$ absorption transition at 487.99 nm with the 488.0-nm line of the argon-line laser (Table I). The iso-

TABLE I. 14 K spectral data for hydrogenic C_S centers present in SrF$_2$Pr^{3+} and CaF$_2$Pr^{3+}. Units are vacuum wave numbers in cm^{-1}. NA's are not applicable to those centers.

Center		$C_s(1)$						$C_s(2)$					
Crystal		SrF$_2$			CaF$_2$			SrF$_2$			CaF$_2$		
Light ion		H$^-$	D$^-$	T$^-$	H$^-$	D$^-$	T$^-$	H$^-$	D$^-$	T$^-$	H$^-$	D$^-$	T$^-$
$Z_1 \rightarrow D_1$ wave number (± 0.1 cm^{-1})		16 707.4	16 706.5	16 706.2	16 628.0	16 627.2	16 628.1	16 611.5	16 612.2	16 612.5	16 529.3	16 530.3	16 529.7
^{3}H$_4$ energy levels (± 1 cm^{-1})	Z_2	3	3.3±0.1	3	<2	0.53±0.01	<2	8	8.3±0.1	8		9.5±0.1	
	Z_3	85	83	80	64	62	62	37	51	49±5		39	
	Z_4	163	165	165	212	212	213						
	Z_5	427	427	472				491±5	475±5	477±5			
	Z_6	499	495	501	542	536	547	559	571	550	625	645	641
	Z_7	561	555	567	636	644	642	576	581	582	645	645±5[c]	651
Interstitial ion local mode vibrational interval (± 1 cm^{-1})	a		637	553	1027	743	621		658			741	619
	b	934[a]	685	b	1174	844	701	951[a]	682	b			
	c		691	b					687	567			
Substitutional ion local mode vibrational interval (± 1 cm^{-1})	d	723	529	439	765	568		665	480	410		525	
	e	774	569	474	814	596	486	745	533	452		581	
	f		829	682	834	618	504	773	554	468		615	526
	g					901	742		812	666		877	723
$Z_1 \rightarrow {}^3P_0$ wave number (± 1 cm^{-1})		20 768	20 760					20 646	20 642				
Photoproduct $Z_1 \rightarrow D_1$ wave number (± 1 cm^{-1})		NA	NA	NA	NA	NA	NA		16 664.3			16 577.8	
Photoproduct $Z_1 \rightarrow Z_2$ wave number (± 1 cm^{-1})		NA	NA	NA	NA	NA	NA		16.6				

[a] Broad line with structure.

[b] Vibronic lines obscured by overlapping electronic transitions.

[c] Line at 645 cm^{-1} has a shoulder.

tope effect shifts this transition to 487.90 nm in hydrogenated crystals and out of resonance with the laser. This coincidence was used to excite the D$^-$ $C_S(3)$ centers to record the fluorescence spectra, however, due to the efficient nonradiative processes in these centers most fluorescence originated from the $^1D_2$ level. In principle, high-resolution laser studies could be carried out on the $C_S(3)$ centers by Zeeman sweeping the transition through a single-mode argon laser line.

IV. BLEACHING MECHANISMS AND CENTER MODELS

Before any discussion of the mechanisms and ion pathways involved in the bleaching can take place, it is important to determine the exact positions of the constituent ions for each center. The experimental results discussed in the preceding section suggest that the simplest configuration has a charge-compensating hydrogenic ion in a regular ⟨100⟩ interstitial position, and a second hydrogenic ion substituting for a lattice F$^-$ ion in the nearest-neighbor shell of the Pr^{3+} ion. The two possible models satisfying these criteria are shown in Fig. 5.

A possible interstitial mechanism[15] for reversible polarized bleaching is shown in Fig. 6(a) using the center configuration of Fig. 5(a). The substitutional hydrogenic ion moves to a vacant neighboring interstitial position and is replaced by the original charge-compensating ion to complete the reorientation. For each of the two possible vacant interstitial positions to which the substitutional ion can move, the photoproduct is the equivalent center reoriented by 90° as required for reversible polarized bleaching. An alternative mechanism[15] leading to the same reorientation would have the charge-compensating hydrogenic ion tunneling directly along a ⟨110⟩ direction.

Both of these mechanisms have been discussed as possible processes for the reorientation of the R^{3+}-F$^-$ dipole of the C_{4v} center, observed at elevated temperatures in ionic thermocurrent and dielectric loss experiments.[16] Allowing for some relaxation in the lattice, Catlow[15] calculated that both mechanisms had a similar activation energy. The EPR results for CaF$_2$:Gd^{3+} crystals[17]

TABLE I. (*Continued*).

	$C_s(4)$			$C_s(3)$	
	CaF$_2$		SrF$_2$	CaF$_2$	
H$^-$	D$^-$	T$^-$	D$^-$	D$^-$	D$^-$
16 666.0	16 667.1	16 667.7	16 598.8	16 566.6	16 586.3
				. . .4.8(H$^-$)	
				. . .6.9(T$^-$)	
	21.3±0.1		20.2±0.1	16.3±0.1	18.5±0.1
	68	66		40±2	35±2
				558±2	627±2
515	508	513		590±2	685±2
578	582	585			741±2
	659	539		454	493
	681			523	565
	699			558	636
				580	815
				612	838
				675	868
	479	411		743	
	558	456		790	
	789	648		818	
20 674	20 665			20 487	
	16 676.6			16 568.7	16 478.3
	11.7			13.6	

showed that the activation energy of the H^- C_{4v} center is similar to that of the F^- C_{4v} center in that system. As the extra mobility of the H^- ion did not appear to make a significant contribution to the activation energy, it was concluded that the interstitial mechanism was dominant for both centers. Since bleaching is not observed for either the H^- or F^- C_{4v} centers in the low-temperature experiments here, the activation energy for dipole reorientation in the C_S centers appears to be substantially less, but any differences in electron-phonon coupling need to be taken into account.

A simple mechanism that describes reversible polarized bleaching using the configuration depicted in Fig. 5(b) is more difficult to construct. The interstitial hydrogenic ion is surrounded by a coordination cube containing eight F^- ions. Apart from small perturbations from the distant substitutional hydrogenic ion, it has the same environment as the interstitial ion in the H^- C_{4v} center which does not bleach. For this reason it is unlikely that reorientation of the center through $\langle 110 \rangle$ migration of the interstitial H^- ion would occur. An interstitial-type mechanism would require complicated F^- ion motion to produce an equivalent reoriented center, and it is likely that other photoproducts would also be created.

Using the above considerations, we assign the $C_S(1)$ center to the configuration depicted in Fig. 5(a). This model satisfactorily explains the properties observed for $C_S(1)$, viz., the center exhibits reversible polarized bleaching, but does not exhibit photoproduct formation.

Because of the difficulties in explaining reversible po-

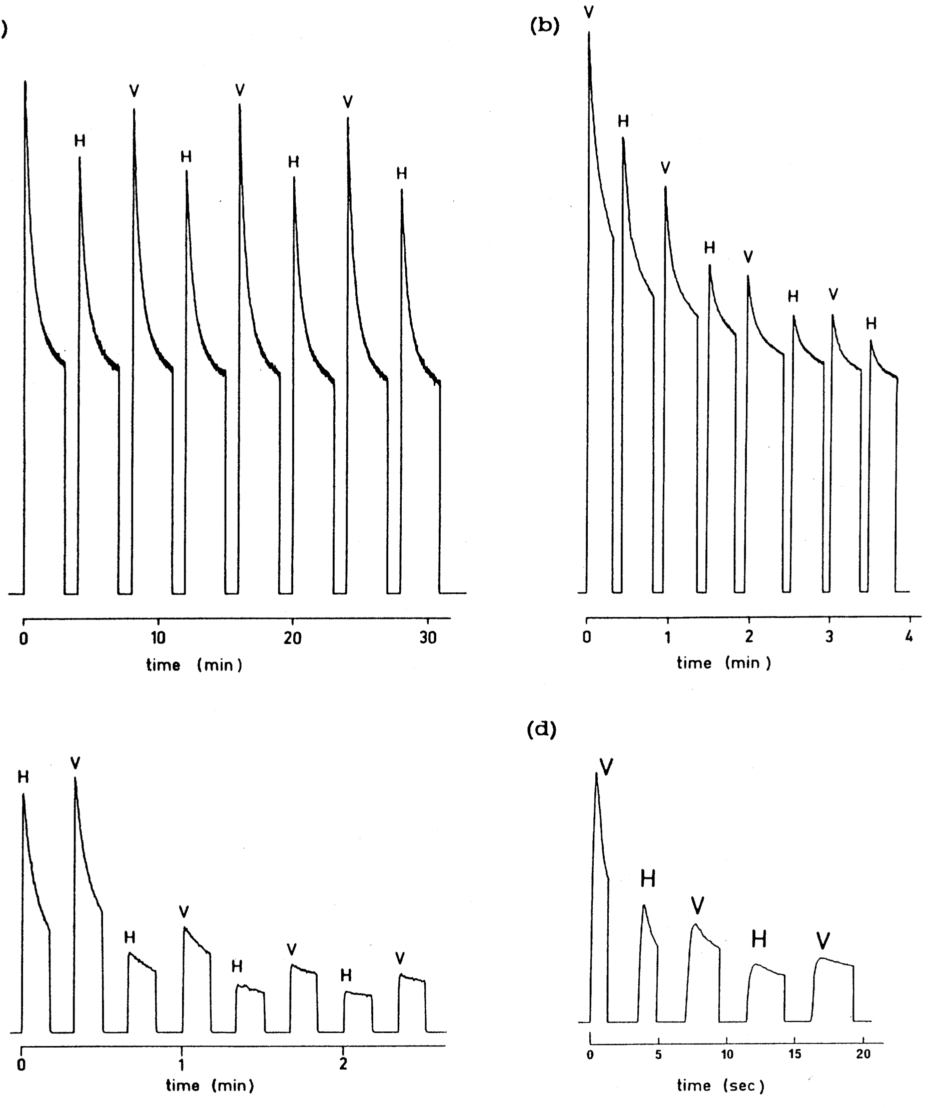

FIG. 3. 14-K fluorescence intensity as a function of time for a sequence of laser excitations in the two possible polarization directions $V[001]$ and $H[010]$ for the various C_S D^- centers in a $\langle 100 \rangle$ oriented $SrF_2{:}Pr^{3+}{:}D^-$ crystal. (a) For $C_S(1)$ centers showing the recovery of fluorescence on switching laser polarization that is characteristic of reversible polarized bleaching, (b) for $C_S(2)$ centers where the reduction in the level of recovery is associated with the formation of photoproduct centers, for $C_S(4)$ centers where there is no reversible bleaching and photoproducts are formed, and (d) for $C_S(3)$ centers also showing nonreversible bleaching.

larized bleaching, the model depicted in Fig. 5(b) can also be discounted for the $C_S(2)$ center. Rather, the model shown in Fig. 6(b) is proposed where two substitutional hydrogenic ions are present in the nearest-neighbor shell as required by the number of substitutional ion vibronics observed. Since these two positions are equivalent, there may be some orientational degeneracy in the vibronic lines. The interstitial hydrogenic ion still has approximately C_{4v} symmetry because all the surrounding ions are electrically equivalent, however, a greater departure from the exact C_{4v} symmetry would be expected in comparison with the $C_S(1)$ center. This is confirmed by the greater separation of the two lowest-frequency interstitial vibronics, which are associated with the transverse vibrations.

The bleaching results for the $C_S(2)$ center can be understood using this model as follows. Reversible polar-

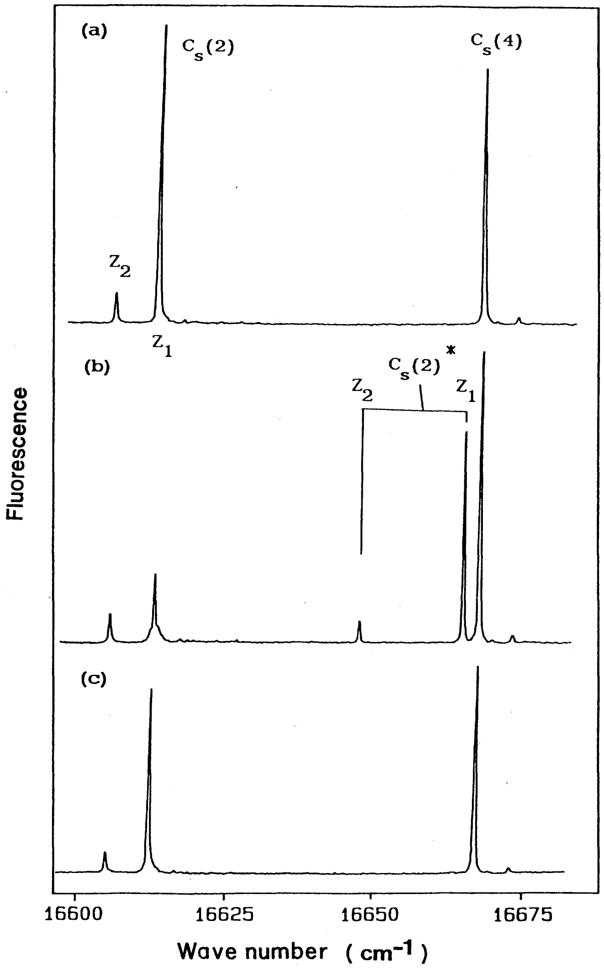

FIG. 4. 14-K laser excitation spectra of the $C_S(2)$ center in SrF_2:Pr^{3+}:D^-. (a) Before bleaching. (b) After bleaching for several minutes with a laser power density of 1.1 kW/cm^2, showing a photoproduct $C_S(2)^*$ at 16 664.3 cm^{-1}. (c) After subsequent bleaching of $C_S(2)^*$, showing restoration of almost all the lost intensity of the $C_S(2)$ center.

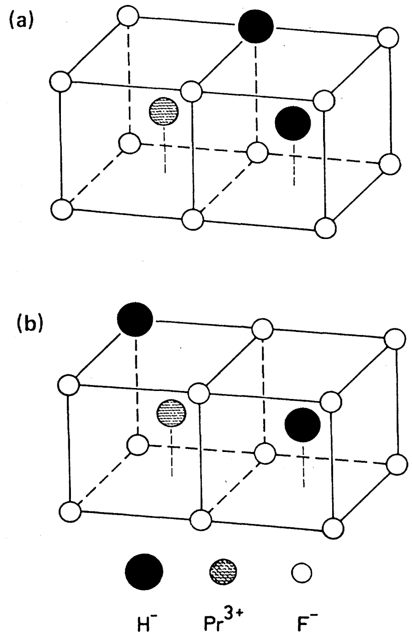

FIG. 5. The two possible site configurations for double hydrogenic-ion centers having nearest-neighbor substitutional and interstitial hydrogenic ions.

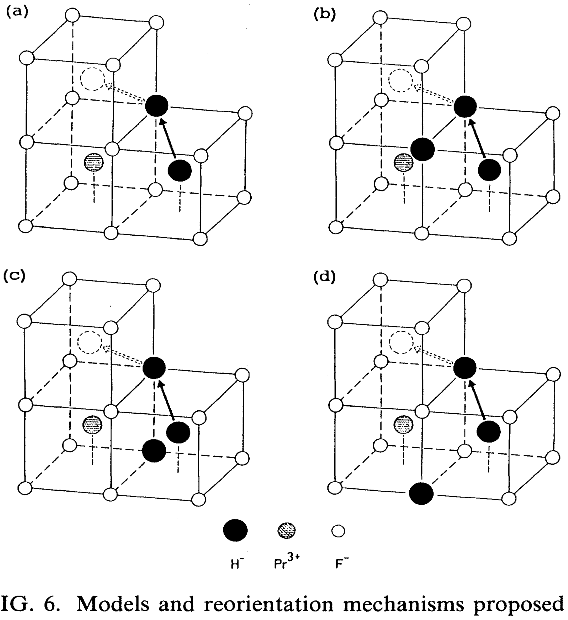

FIG. 6. Models and reorientation mechanisms proposed for the $C_S(1)$, $C_S(2)$, and $C_S(4)$ centers. (a) An interstitial mechanism for a $C_S(1)$ center giving an orthogonally aligned equivalent center. (b) An interstitial mechanism in a $C_S(2)$ center giving orthogonal reorientation of the center. (c) A similar mechanism producing a distinctly different photoproduct from the $C_S(2)$ center. (d) A model for the $C_S(4)$ center showing an interstitial mechanism producing a distinct photoproduct center.

ized bleaching takes place by either the direct jump or interstitial mechanism and is illustrated in Fig. 6(b). In agreement with the experimental results, this model predicts a faster bleaching rate for $C_S(2)$ than for $C_S(1)$ centers because the two substitutional ions provide additional channels for the ion migration. For each $C_S(2)$ center there is only one equivalent center oriented at 90° as reorientation in the other orthogonal direction leads to a different arrangement of ions. This reorientation, shown in Fig. 6(c), is associated with photoproduct formation where the change in crystal field shifts the Pr^{3+} absorption frequency out of resonance with the laser. Only one discrete photoproduct will be formed, and using the same migration mechanisms there are only two possible return paths for the photoproduct, namely, back to the original center or its orthogonal equivalent. This agrees with the experimental results which showed that only one photoproduct is formed and that excitation of this new center leads to restoration of the original center.

The $C_S(4)$ centers do not undergo reversible polarized bleaching but only exhibit discrete photoproduct formation. The proposed model and bleaching mechanism is depicted in Fig. 6(d). As for the model proposed for the $C_S(2)$ center, there are two substitutional hydrogenic ions in the first coordination shell. For each center there are four possible reorientation directions, each giving an equivalent photoproduct differing from the original center. Moreover, the model predicts that excitation of the photoproduct will produce either an equivalent reoriented photoproduct center or a center of the original configuration. Thus, this model satisfies the observed bleaching characteristics, i.e., it is not polarization reversible; there is only one photoproduct center created and there is some return to the original center on excitation of the photoproduct.

The remaining center to be discussed, $C_S(3)$, is distinctly differently from the other three because there is evidence of additional hydrogenic ions. Since there are many positions in the basic center configuration where further hydrogenic ions could be added to explain the observed features, no definite model can be proposed on the basis of the present experimental data.

An underlying feature of the models proposed for these centers is that the constituent hydrogenic ions are grouped as close together as possible. Such clustering may create more stable center configurations than the arrangements in the photoproducts where the hydrogenic ions are more dispersed, thus explaining why the photoproducts are not observed in any crystal before optical excitation.

V. CONCLUSIONS

Results of a detailed study of a number of bleaching centers in hydrogenated $SrF_2:Pr^{3+}$ and $CaF_2:Pr^{3+}$ crystals have been presented. Four centers have been characterized and shown to be present in both crystals. All the centers examined exhibit bleaching of their fluorescence when excited with a cw laser under constant pumping conditions. The experimental data suggest that there are at least two hydrogenic ions in close proximity to the Pr^{3+} ion and that the bleaching of the fluorescence is a result of movement of these light ions. Since the single hydrogenic ion C_{4v} center does not exhibit such effects, the presence of a second hydrogenic ion appears to be necessary to the process.

For two centers studied [$C_S(1)$ and $C_S(2)$], the bleaching was found to be reversible with a change in the laser polarization. In the $C_S(1)$ case a seemingly indefinite sequence of bleaching and recovery cycles could be observed. The mechanism proposed has the hydrogenic-ion motion, creating equivalent centers oriented at 90° to the original center alignment. The geometrical arrangement of the centers relative to the laser beam and the transition selection rules result in the laser driving the center population between these three orthogonal orientations in step with the laser polarization.

For three of the centers studied [$C_S(2)$, $C_S(3)$, and $C_S(4)$], the ion movement created a photoproduct center at a different absorption wavelength. In this case the bleaching of fluorescence cannot be recovered with a switch of laser polarization, but excitation of the photoproduct restored the lost intensity without the formation of other centers, yielding reversible center-photoproduct movement.

Configurations proposed for three of the centers studied are surprisingly successful in explaining the observed effects. The phenomena of reversible polarized bleaching and photoproduct formation can be accounted for by using reorientation processes which are well known for explaining dipole reorientation in dielectric loss and ionic thermocurrent experiments.

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[1] N. J. Cockroft, T. P. J. Han, R. J. Reeves, G. D. Jones, and R. W. G. Syme, Opt. Lett. **12**, 36 (1987).

[2] R. M. Macfarlane, R. J. Reeves, and G. D. Jones, Opt. Lett. **12**, 660 (1987).

[3] R. J. Reeves, G. D. Jones, N. J. Cockroft, T. P. J. Han, and R. W. G. Syme, J. Lumin. **38**, 198 (1987).

[4] G. Castro, D. Haarer, R. M. Macfarlane, and H. P. Trommsdorff, U. S. Patent No. 4 101 976 (1978); W. E. Moerner, J. Mol. Electron. **1**, 55 (1985).

[5] J. Friedrich and D. Haarer, Angew. Chem. Int. Ed. Engl. **23**, 113 (1984), and references therein.

[6] A. A. Gorokhovskii, R. K. Kaarli, and L. A. Rebane, Pis'ma

Zh. Eksp. Teor. Fiz. **20**, 474 (1974) [JETP Lett. **20**, 216 (1974)].

[7] S. Volker, R. M. Macfarlane, A. Z. Genack, H. P. Trommsdorf, and J. H. van der Waals, J. Chem. Phys. **67**, 1759 (1977).

[8] J. L. Hall and R. T. Schumacher, Phys. Rev. **127**, 1892 (1962).

[9] D. R. Tallant and J. C. Wright, J. Chem. Phys. **63**, 2074 (1975).

[10] R. W. G. Syme, R. J. Reeves, and G. D. Jones, J. Lumin. **31**, 248 (1984).

[11] I. T. Jacobs, G. D. Jones, K. Zdansky, and R. A. Satten, Phys. Rev. B **3**, 2888 (1971).

[12] R. J. Elliott, W. Hayes, G. D. Jones, H. F. Macdonald, and C. T. Sennett, Proc. R. Soc. London, Sect. A **289**, 1 (1965).

[13] R. C. Spitzer, W. P. Ambrose, and A. J. Sievers, Opt. Lett. **11**, 428 (1986).

[14] R. J. Reeves and R. M. Macfarlane (unpublished).

[15] C. R. A. Catlow, J. Phys. C **9**, 1845 (1976).

[16] W. Bollmans, P. Gorlich, W. Hauk, and H. Mothers, Phys. Status Solidi A **2**, 157 (1970); Z. C. Nauta-Leefers and H. W. den Hartog, Phys. Rev. B **19**, 4162 (1979), and references therein.

[17] A. Edgar and H. K. Welsh, J. Phys. C **8**, L336 (1975).