

## Optical properties and formation of oxygen-perturbed $F_2^+$ color center in NaCl

Efstratios Georgiou, Joseph F. Pinto, and Clifford R. Pollock

*Materials Science Center, and School of Electrical Engineering, Cornell University, Ithaca, New York 14853*

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The optical properties of a recently discovered laser-active color center in oxygen-doped NaCl are reported. The color center is produced through a two-step photoaggregation process in additively colored crystals. Optical spectroscopy indicates that the point defect is a perturbed  $F_2^+$  center. The center has very broad absorption and emission bands peaking at 1.09 and 1.55  $\mu\text{m}$ , respectively, with a dipole moment oriented along the  $\langle 110 \rangle$  directions of the crystal. The center population can be fully aligned along any  $\langle 110 \rangle$  direction by using two-photon pumping. Ground- and excited-state absorption spectra compare well with the dielectrically embedded  $H_2^+$  model for the eight transitions observed. uv spectroscopy has identified the substitutional  $O^{2-}$  ion as being the necessary impurity for the center formation. The proposed model for the color center is an  $O^{2-}$ -perturbed  $F_2^+$  defect. The perturbing  $O^{2-}$  ion serves both as a stable electron trap as well as a spatial trap for the  $F_2^+$  center.

### INTRODUCTION

The nearly ideal laser properties of the  $F_2^+$  color center in the alkali halides have led to attempts at improving its operational stability. The  $F_2^+$  center has a strong dipole moment, a sufficient Stokes shift to allow low self-absorption, yet high efficiency, and broad emission bands in the 1–2- $\mu\text{m}$  region, making it a potentially useful laser medium. Unfortunately, the  $F_2^+$ -center laser suffers from degradation of output power during operation.<sup>1</sup> This decay mechanism is not fully understood, but is thought to involve either electron capture, which converts the center to an  $F_2$  defect, or center migration through multiple reorientations that eventually associate the  $F_2^+$  with other defects. Various divalent metal<sup>2,3</sup> and molecular<sup>4</sup> substitutional impurities have been tried in pure  $F_2^+$ -center systems to create efficient electron traps, which serve to stabilize the ionized  $F_2^+$  population. Unfortunately, even with the electron securely bound in the trap, the  $F_2^+$  center is observed to be operationally unstable because of the induced reorientation caused by the intense optical pumping. An excellent review of the history and specific properties of earlier color-center lasers is given by Mollenauer.<sup>5</sup>

An effective method for spatially stabilizing the  $F_2^+$  center in the lattice is to trap it beside an adjacent cation impurity.<sup>6,7</sup> One such stabilized center is the  $(F_2^+)_A$  center,<sup>8–10</sup> shown to be a stable laser medium. In the  $(F_2^+)_A$  systems demonstrated to date, the density of active centers produced has been about an order of magnitude lower than desired for efficient laser operation. This is apparently due to lack of strong electron traps in the crystal.

In this paper, we will describe the optical properties of a new type of perturbed  $F_2^+$  center that appears to be as stable as the  $(F_2^+)_A$  center, but which has demonstrated far superior cw laser powers and tuning range. The center is tentatively identified as an  $F_2^+$  defect located beside a double-negative chalcogen impurity, namely an  $O^{2-}$  sub-

stitutional ion, as shown schematically in Fig. 1. This oxygen-perturbed  $F_2^+$  defect, which we label as the  $F_2^+ : O^{2-}$  center, is formed in additively colored NaCl crystals, doped with low concentrations of oxygen ions, generally in the range of about 5–50 ppm.

To our knowledge, the first report of an  $F_2^+ : O^{2-}$  color center appeared in 1978 by Lobanov *et al.*<sup>11</sup> in a study of oxygen-doped LiF. The authors noted the broadening and slight shifting of the  $F_2^+$  luminescence band, which they attributed to the formation of the so-called “ $O^{2-} - F_2^+$ ” center. Pulsed stimulated emission was subsequently reported<sup>12,13</sup> from the same system in LiF under the name  $F_2^+ O^{2-}$ . There has been little additional reported work on the laser-active infrared transitions of the system until 1986, when the first NaCl and KCl  $F_2^+ : O^{2-}$  lasers were reported.<sup>14–16</sup>

Identification of this new laser-active color center in NaCl as an  $F_2^+ : O^{2-}$  defect has been made by analysis of spectral data from the uv to the ir region (0.185–20  $\mu\text{m}$ ). The center's optical properties such as peak absorption wavelength (1.09  $\mu\text{m}$ ), emission wavelength (1.55  $\mu\text{m}$ ),

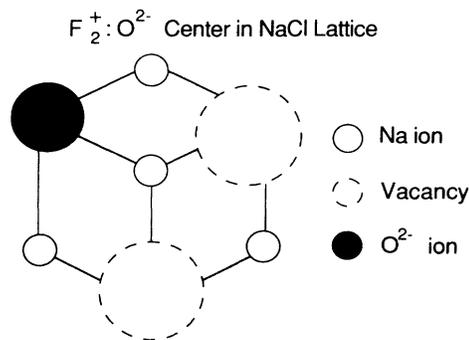


FIG. 1. The proposed configuration of the oxygen-perturbed  $F_2^+$  center.

emission width (0.136 eV), Stokes shift (0.34 eV), and dipole moment direction ( $\langle 110 \rangle$ ) are all consistent with an  $F_2^+$ -type center in NaCl. Furthermore, reorientation properties, radiative lifetime (150 nsec), and excited-state energy levels of this center are also characteristic of an  $F_2^+$ -type center. Although we have not been able to devise a measurement that irrefutably links the  $O^{2-}$  ion with the  $F_2^+$  defect, all measurements and observations that will be discussed in this paper strongly support the  $F_2^+ : O^{2-}$  model.

### EXPERIMENTAL METHODS

Optical absorption measurements were made over a broad spectral range. uv spectra from 0.185–0.5  $\mu\text{m}$  were taken at room temperature (300 K) with a Cary 219 spectrophotometer. Fourier-transform infrared (FTIR) spectra from 2.5 to 20  $\mu\text{m}$  were taken with an IBM IR90 Spectrometer System at 1.7 K. All other data were taken at 77 K with a custom dual beam spectrometer shown in Fig. 2. The crystal was mounted so that the probe light was incident along a  $\langle 100 \rangle$  axis. Light from either a 300-W tungsten-halogen incandescent lamp, or a 75-W xenon arc lamp, depending on the wavelength region of the experiment, was divided into two beams and directed through, and below, the crystal, respectively. The transmitted light was imaged with mirror optics onto the monochromator slit (Jarell-Ash Monospec 27). Appropriate solid-state detectors (Si, Ge, PbS) were used at the monochromator output, and were connected with electronics which normalized the transmission signal with the reference beam.

For pumping the centers to excited states, laser radiation was injected as close to the [001] direction of the crystal as possible ( $\sim 10^\circ$  angle relative to the optical axis). When necessary,  $F$ -band light (400–500 nm) could be injected along  $\langle 100 \rangle$  directions. This light was provided by a 100-W mercury arc lamp filtered through a combination of Corning 5-56 and 1-75 filters, and focused with an  $f/0.85$  Pyrex glass lens. In the following discussion, the term " $F$  light" will refer to this description, unless stated otherwise. All spectral data will be referred to 77 K, unless otherwise specified.

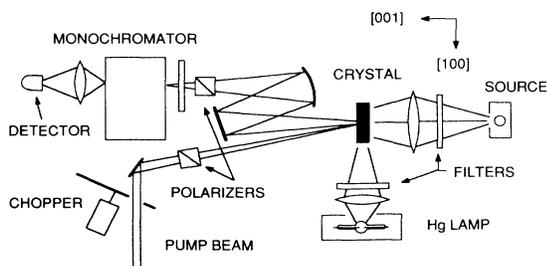


FIG. 2. Schematic drawing of the basic spectrometer arrangement. The crystal is mounted on a cryostat cold finger (not shown).

### EXPERIMENTAL PROCEDURE FOR THE $F_2^+ : O^{2-}$ CENTER FORMATION

Single crystals of pure and oxygen-doped NaCl were grown using the Kyropoulos technique at the Crystal Growing Facility at Cornell University. These crystals were grown in platinum crucibles under an argon atmosphere. For comparison purposes, crystals were also obtained from the Crystal Growth Laboratory of the University of Utah. The nominally pure NaCl stock material used for crystal growth was initially purged of preexisting oxygen-containing anions by bubbling chlorine gas through the melt for 1–2 h prior to growth. Appropriate amounts of NaOH on the order of  $(100\text{--}500) \times 10^{-6}$  mol % were added to the melt, to achieve  $\text{OH}^-$  concentrations in the range of 5–50 ppm incorporated in the crystal. In general, such  $\text{OH}^-$  doping levels were found to lead to optimum  $F_2^+ : O^{2-}$  population densities. Since low concentrations of hydroxyl ions were introduced to the crystals, the chlorine pretreatment of the nominally pure NaCl starting material was extremely important. In many instances, we found that non-negligible amounts of  $\text{OH}^-$  impurities in the untreated stock were sufficient to produce a reasonable  $F_2^+ : O^{2-}$  absorption band without additional doping.

The actual concentration of the  $\text{OH}^-$  impurity in the crystal was determined by measurement of the peak absorption coefficients of the  $\text{OH}^-$  electronic uv band in NaCl at 185 nm and the vibrational ir line at  $3654\text{ cm}^{-1}$ . Conversion factors of  $1.3\text{ ppm OH}^-/\text{cm}^{-1}$  for the 185-nm band and  $130\text{ ppm OH}^-/\text{cm}^{-1}$  for the  $3654\text{-cm}^{-1}$  peak were applied.<sup>17</sup>

For spectroscopic studies, crystals cleaved to 3-mm thicknesses were additively colored in a Na-vapor heat pipe<sup>18</sup> at various Na pressures at  $700^\circ\text{C}$  for 30 min, rapidly quenched to room temperature in an air stream following coloration, and then polished. Figure 3(a) shows the absorption spectrum of an NaCl:OH<sup>-</sup> crystal that was colored at 20-Torr vapor pressure and subsequently handled under weak incandescent light, filtered through a

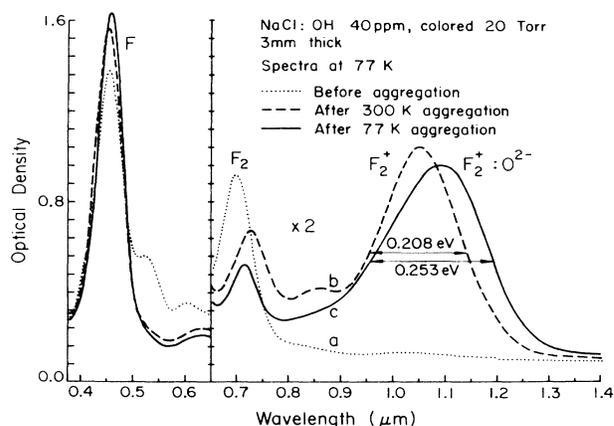


FIG. 3. Visible-near-ir absorption of additively colored NaCl:OH<sup>-</sup>. (a) After coloration, before any photoaggregation. (b) After 30-min aggregation with  $F$  light at 300 K, and cooling to 77 K in the dark. (c) After 5-min subsequent aggregation with  $F$  light at 77 K.

OG590 red filter. This spectrum shows absorption bands only in the visible region, due to  $F$ ,  $F_2$ , and  $F_3$  color centers. The corresponding uv spectrum of this crystal [Fig. 9] shows the formation of oxygen- and hydrogen-related defects.

Exposure of the crystal to  $F$ -band light for 30 min at room temperature leads to the appearance of an infrared absorption band centered at  $1.05 \mu\text{m}$  [Fig. 3(b)]. At the same time, the  $F$ -band (452 nm) absorption increases, the  $F_3$  bands (530 and 600 nm) decrease, and the  $F_2$  band changes in strength, position, and width. We believe that the  $1.05\text{-}\mu\text{m}$  band corresponds to the formation of  $F_2^+$  centers in the crystal. When pumped by a  $1.06\text{-}\mu\text{m}$  Nd:YAG laser (where YAG represents yttrium aluminum garnet), the crystal displays polarized  $\langle 110 \rangle$  fluorescence peaking at  $1.47 \mu\text{m}$ , which is consistent with emission data of the  $F_2^+$  center in NaCl.<sup>19</sup>

To form the  $F_2^+:\text{O}^{2-}$  center, a second photoaggregation process must be performed. The crystal is cooled to 77 K, and then reexposed to  $F$ -band light for 3–5 min. This exposure causes a slight broadening and a swift shift of the absorption band to  $1.09 \mu\text{m}$  [Fig. 3(c)]. The fluorescent emission band is also shifted to a slightly longer wavelength, peaking at  $1.55 \mu\text{m}$  (Fig. 4) when pumped by a  $1.06\text{-}\mu\text{m}$  Nd:YAG laser. These absorption and emission bands centered at  $1.09 \mu\text{m}$  and  $1.55 \mu\text{m}$ , respectively, represent the presence of the  $F_2^+:\text{O}^{2-}$  center.

The  $1.05\text{-}\mu\text{m} \rightarrow 1.09\text{-}\mu\text{m}$  shifting is accompanied by analogous shifting of the  $F$  band to the red ( $452 \text{ nm} \rightarrow 458 \text{ nm}$ ) and the  $F_2$  band to the blue ( $727 \text{ nm} \rightarrow 718 \text{ nm}$ ), possibly due to association of these centers with oxygen ions as well. The effects of Na-vapor coloration pressure on the formation of the  $F_2^+:\text{O}^{2-}$  band are shown in Fig. 5. The optimum coloration pressure 20–25 Torr produces a moderate optical density at  $1.09 \mu\text{m}$  after the aggregation steps, while simultaneously maintaining a low background absorption in the  $1.6\text{-}\mu\text{m}$  region of spectral emission. The rapid increase of this background absorption at higher coloration pressures indicates colloidal aggregate growth

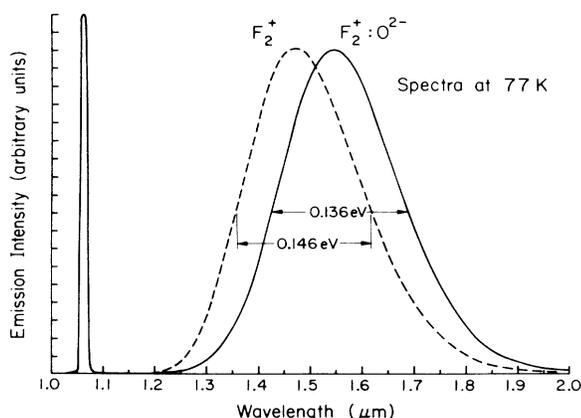


FIG. 4. Emission of  $F_2^+$  and  $F_2^+:\text{O}^{2-}$  centers at 77 K measured with a PbS detector and normalized to equal peak intensity. The centers were excited with  $1.06\text{-}\mu\text{m}$  Nd:YAG laser light.

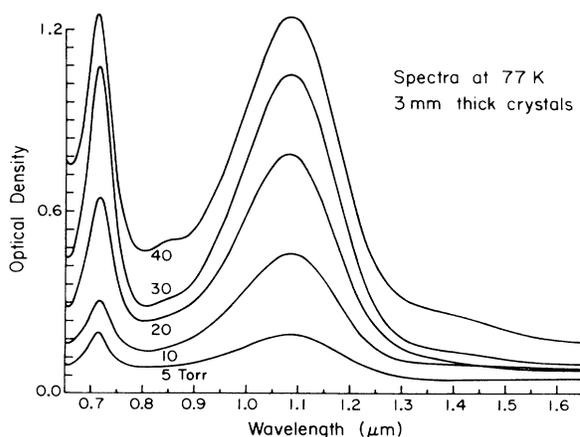


FIG. 5. Absorption of colored NaCl:OH crystals at 77 K (following the photoaggregation steps) for various coloration pressures. All the samples had the same thickness and the same  $\text{OH}^-$  concentration before coloration.

(slower quenching rates had also the same effect).

The effect of the 300-K photoaggregation time on the  $F_2^+:\text{O}^{2-}$  band formation is shown in Fig. 6. Using moderate intensity of  $F$  light (approximately  $0.5 \text{ W/cm}^2$ ), the optimum aggregation time is around 1 h. After the center population has reached saturation, further exposure to  $F$  light at 300 K leads to gradual bleaching.

Colored crystals can be stored for indefinite time periods at room temperature in the dark without observable degradation. The longest storage period which we tested was 6 months; after this time period, the crystals were equally effective in forming the desired near-ir band. However, crystals stored in room light at room temperature degrade within a few days, the deterioration accompanied by a visible change of their color to dark blue. Spectra of these blue crystals showed the presence of large colloidal bands and reduced transmission over extended spectral regions.

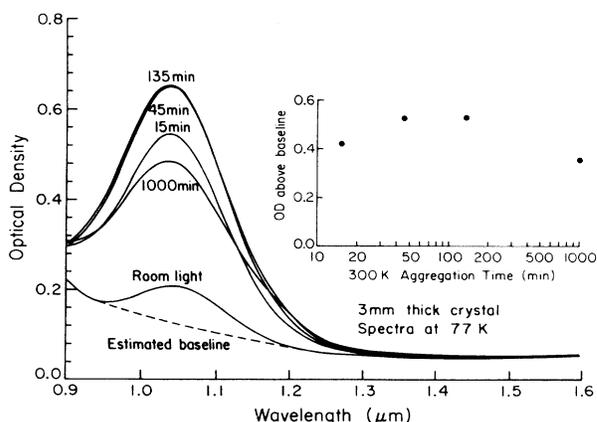


FIG. 6. Optical density (OD) of the  $1.05\text{-}\mu\text{m}$  absorption band for various photoaggregation times.

IDENTIFICATION OF THE  $F_2^+$ -TYPE DEFECT

To characterize the electronic nature and perturbation effects of the  $F_2^+:\text{O}^{2-}$  defect, the energy levels of the center were probed by excited-state techniques and compared to the theoretical spectrum of a  $\text{H}_2^+$  molecular ion embedded in a dielectric medium.<sup>20</sup> Remarkable qualitative agreement is observed between energy levels, polarization behavior, and oscillator strength values of the  $F_2^+:\text{O}^{2-}$  electronic transitions, and the corresponding molecular hydrogen-ion transitions. Comparison of these excited-state energy transitions with corresponding transitions of the  $F_2^+$  center confirm the perturbed nature of the  $F_2^+:\text{O}^{2-}$  defect.

The experimental setup for the excited-state measurements was shown in Fig. 2. Using a technique developed by Mollenauer,<sup>21</sup> the excited-state spectrum of the  $F_2^+:\text{O}^{2-}$  system was measured by modulating the ground-state ( $1s\sigma_g$ ) and the first excited-state ( $2p\sigma_u$ ) populations of the defect and monitoring absorption transitions from each of these two levels. The tagging of the ground-state and first excited-state populations was accomplished with a 4-W chopped cw Nd:YAG laser operating at  $1.06\ \mu\text{m}$ , polarized along the  $\langle 110 \rangle$  axis, pumping the fundamental transition ( $1s\sigma_g \rightarrow 2p\sigma_u$ ) of the aligned centers. A 2.5-mm thick, lightly colored (5-Torr Na vapor pressure) crystal of  $\text{NaCl}:\text{OH}^-$  was used in order to avoid excessive optical absorptions in the  $F$ - and  $F_2$ -band regions of the crystal, which would degrade the signal-to-noise ratio of the excited-state signals. A mechanical chopping wheel operating at rate of  $\sim 15\ \text{kHz}$  was used to modulate the pump laser. The high chopping speed was necessary to avoid spurious effects from other color-center defects having long-lived excited states which overlapped either the  $1.06\text{-}\mu\text{m}$  pump wavelength or the emission fluorescence of the  $F_2^+:\text{O}^{2-}$  center. The  $[110]$  polarized pump beam from the Nd:YAG laser was weakly focused onto a  $5 \times 1\ \text{mm}^2$  spot of the crystal using a cylinder lens ( $f = 30\ \text{cm}$ ). The cylinder lens increased the collection efficiency of the excited-state signal by pumping the entire area that imaged onto the monochromator slits. High pump intensities were avoided to reduce photoinduced reorientation of the centers.  $[110]$  polarized  $F$  light was simultaneously focused onto the probed spot of the crystal, maintaining a continuous alignment of  $F_2^+:\text{O}^{2-}$  centers along the  $1.06\text{-}\mu\text{m}$  pump polarization during the experiment. The alignment of the defects improved the signal-to-noise ratio of the recovered signal, and allowed for the unambiguous measurement of the polarization properties and oscillator strengths of several excited-state transitions. As will be explained in a following section, the alignment of the  $F_2^+:\text{O}^{2-}$  center population was always less than 100% when using  $F$  light; however, the degree of alignment was sufficient to determine polarization effects. Appropriate band pass filters (7-54, KG-3, LS1000) were used in front of the monochromator entrance slit to reject stray reflections from the Nd:YAG laser beam.

The energy-level transitions of the  $F_2^+:\text{O}^{2-}$  defect are indicated in Fig. 7. The chopped pump beam, together with the fast relaxation of the excited state of the  $F_2^+:\text{O}^{2-}$  center ( $\tau_{\text{radiative}} \cong 150\ \text{nsec}$ ) created time-

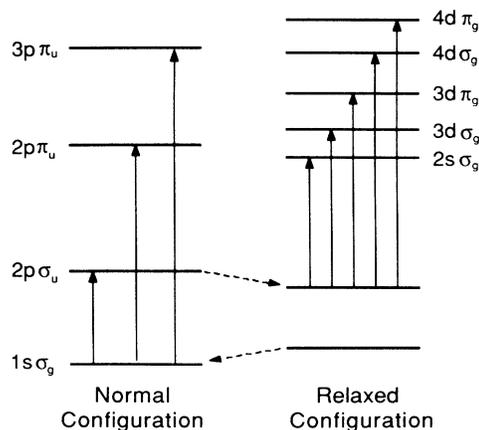


FIG. 7. Energy level diagram of the  $F_2^+:\text{O}^{2-}$  center.

dependent populations in the  $2p\sigma_u$  state and the  $1s\sigma_g$  state, in-phase and out-of-phase with the pump laser, respectively. Excited state absorption signals originating from the  $2p\sigma_u$  state appeared therefore out-of-phase with the pump, while absorption signals originating from the  $1s\sigma_g$  ground state appeared in-phase with the pump. The modulation signals of the absorption spectrum were monitored using a lock-in amplifier at the chopping frequency of the pump laser. The ac lock-in signal was normalized to the transmission of the crystal at each wavelength. Using this scheme, the actual band shapes and oscillator strengths of the excited-state transitions were preserved, free of distortion due to interfering absorption bands of other color-center defects in the visible spectrum.<sup>21</sup>

The excited-state spectrum obtained for the  $F_2^+:\text{O}^{2-}$  system in NaCl is shown in Fig. 8. Eight principal transitions are observed, five of which originate from the first excited state. Positive and negative signals in the graph correspond to transitions from the ground state ( $1s\sigma_g$ ),

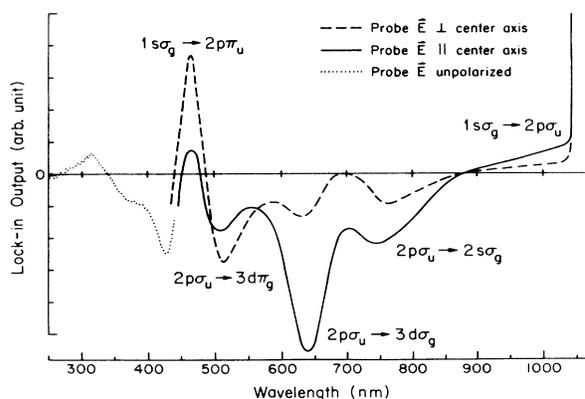


FIG. 8. Excited-state signal of  $F_2^+:\text{O}^{2-}$  centers at 77 K pumped with  $[110]$  polarized  $1.06\text{-}\mu\text{m}$  Nd:YAG laser. Center alignment was maintained along  $[110]$  using polarized  $F$ -light illumination. Solid line: probe light polarized along  $[110]$ ; dashed line: probe light polarized along  $[1\bar{1}0]$ ; dotted line: probe light unpolarized.

and from the first excited state ( $2p\sigma_u$ ), respectively. The solid and dashed lines correspond to spectra recorded with the analyzing polarizer parallel and perpendicular, respectively, to the pump beam polarization. Transition energy values and relative oscillator strengths are tabulated in Table I, along with data for the  $F_2^+$  center in pure NaCl.<sup>21</sup> Also tabulated in this table are the transition energies and oscillator strengths calculated from the dielectric-embedded  $H_2^+$  model.<sup>22,23</sup> The theoretical energy levels of the  $F_2^+$ -type center are related to the corresponding states of the molecular hydrogen ion by

$$E_{F_2^+}(R_{12}, K_0) = (K_0)^{-1} E_{H_2^+}(r_{12}),$$

where  $R_{12}$  is the vacancy pair separation of the  $F_2^+$  defect,  $K_0$  is the high-frequency dielectric constant of the host lattice, and  $r_{12}$  is the internuclear distance of the  $H_2^+$  molecular ion, given by  $r_{12} = R_{12}/K_0$ . The choice of parameters  $r_{12}$  and  $K_0$  was determined by fitting the experimentally observed transition energies of the first two ground-to-excited-state transitions of the  $F_2^+$  center with the theoretical values of the dielectric-embedded  $H_2^+$  ion. Using this technique, the values of  $r_{12} = 1.53$  Å and  $K_0 = 2.32$  were calculated. Comparing these parameters with corresponding tabulated data, we find that the obtained value of  $K_0 = 2.32$  is in close agreement with the experimental value of 2.34. However, the calculated value of vacancy pair separation,  $R_{12} = 3.56$  Å, is 10% lower than the anion-anion separation of 3.97 Å in NaCl, possibly due to distortion effects arising from the removal of chlorine ions from the lattice.

For transitions originating from the upper  $2p\sigma_u$  state, a second value of  $r_{12}$  was required, adjusted to the observed Stokes shift between absorption and emission. This new value of  $r_{12}$  ( $r_{12 \text{ relaxed}} = 1.8$  Å) accounts for the relaxation of the lattice following the excitation of the fundamental transition ( $1s\sigma_g - 2p\sigma_u$ ).

The assignment of the  $F_2^+:\text{O}^{2-}$  transitions was made according to comparisons of relative oscillator strength values and polarization characteristics of excited-state transition bands with the  $H_2^+$ -ion energy spectrum. From the energy positions and relative oscillator strengths listed in Table I, we find that all but one of the calculated energy peaks are within 10% of the experimental data, suggesting an impressive agreement between the  $F_2^+:\text{O}^{2-}$

center and the dielectric  $H_2^+$  model. A discrepancy is observed for the  $2p\sigma_u - 2s\sigma_g$  transition, however, with the measured energy being about 20% lower than the predicted value. Similar disagreement has been noted for the same transition of the  $F_2^+$  system in pure NaCl.<sup>21</sup> One possible explanation for the anomalous behavior of the  $2p\sigma_u - 2s\sigma_g$  transition originates from the strong dependence of the  $s$  orbital on the vacancy radius of the host lattice. It has been suggested that a modification in the potential of the  $F_2^+$  center during lattice relaxation causes a strong perturbation of the  $2s\sigma_g$  energy level, resulting in the discrepancy between observed and predicted energy values.<sup>24</sup>

Continuing with the comparison between the  $F_2^+:\text{O}^{2-}$  center and the  $H_2^+$  model, we now consider the relative oscillator strengths obtained from the excited-state data and the theoretical model. For this discussion, an effective oscillator strength  $f_0$  was calculated from the  $H_2^+$  model according to the equation<sup>20</sup>

$$f_0 = 8\pi^2 m_e E_{fi} g |\langle f | r | i \rangle|^2 / (3h^2),$$

where  $E_{fi}$  is the energy difference between the initial ( $|i\rangle$ ) and final ( $|f\rangle$ ) states of the transition,  $m_e$  is the mass of the electron, and  $g$  is the orbital degeneracy factor. The measured experimental oscillator strengths, which are proportional to the area under the appropriate absorption band transition, were calculated by setting the fundamental transition band area proportional to the theoretical oscillator strength, and normalizing all other band transitions with the fundamental. According to the data tabulated in Table I, the resulting experimental values are in good agreement with the calculated values of the model.

Polarization data from the excited-state experiments was used to characterize  $\sigma$ -like and  $\pi$ -like transitions in the  $F_2^+:\text{O}^{2-}$  spectrum.  $\sigma$  and  $\pi$  state transitions were identified by strong absorptions of the probe light polarized parallel or perpendicular to the aligned  $F_2^+:\text{O}^{2-}$  defects, respectively. Although 100% alignment of the defects was unattainable, the distinction between  $\sigma$ - or  $\pi$ -like transitions for all but three higher-energy states was very clear. For those transition energies about 2.7 eV, the polarization character of the corresponding excited state was unclear because the probe light in this wavelength region ( $\lambda < 400$  nm) was capable of causing reorientation of

TABLE I. Calculated and observed transition energies and oscillator strengths of the  $F_2^+:\text{O}^{2-}$  center in NaCl. Transition energies for the  $F_2^+$  center are listed for comparison. Asterisks indicate that data is unavailable.

| Transition                          | Calculated         |             | Observed           |             | $F_2^+$ center     |
|-------------------------------------|--------------------|-------------|--------------------|-------------|--------------------|
|                                     | $\Delta E$<br>(eV) | $f_0$       | $\Delta E$<br>(eV) | $f_0$       | $\Delta E$<br>(eV) |
| $1s\sigma_g \rightarrow 2p\sigma_u$ | 1.14               | 0.29        | 1.14               | 0.29        | 1.20               |
| $1s\sigma_g \rightarrow 2p\pi_u$    | 2.70               | 0.24        | 2.70               | 0.13        | 2.92               |
| $1s\sigma_g \rightarrow 3p\pi_u$    | *                  | $\sim 0.03$ | 3.91               | $\sim 0.03$ | *                  |
| $2p\sigma_u \rightarrow 2s\sigma_g$ | 2.0                | 0.09        | 1.63               | 0.14        | 2.01               |
| $2p\sigma_u \rightarrow 3d\sigma_g$ | 2.19               | 0.32        | 1.95               | 0.39        | 1.76               |
| $2p\sigma_u \rightarrow 3d\pi_g$    | 2.41               | 0.15        | 2.40               | 0.15        | 2.48               |
| $2p\sigma_u \rightarrow 4d\sigma_g$ | *                  | $\sim 0.05$ | 2.88               | $\sim 0.09$ | *                  |
| $2p\sigma_u \rightarrow 4d\pi_g$    | *                  | $\sim 0.04$ | 3.29               | $\sim 0.04$ | *                  |

the aligned centers. Consequently, molecular orbital assignments of these excited state levels of the  $F_2^+ : O^{2-}$  spectrum were made according to oscillator strength values and model predictions of energy transitions.

Comparison of the excited-state energy transitions of the  $F_2^+ : O^{2-}$  defect with the corresponding measured transitions of the  $F_2^+$  center in pure NaCl (Table I) shows similarity in polarization behavior, oscillator strength, and energy levels for all transitions. However, it is important to note that all observed energy levels of the  $F_2^+ : O^{2-}$  center are shifted to lower values than the  $F_2^+$  center, confirming that the laser active defect is in fact a perturbed  $F_2^+$  center.

### OXYGEN IMPURITIES

To confirm that the formation of the 1.09- $\mu\text{m}$  absorption band depended on oxygen impurities in the crystal, control boules were grown from chlorine-pretreated undoped NaCl which contained less than 1 ppm  $\text{OH}^-$ . Following additive coloration, samples from these purified NaCl crystals did not develop the 1.09- $\mu\text{m}$  band that indicated the presence of the laser-active center. One of these boules was subsequently regrown with the addition of 100 ppm NaOH in the melt. After additive coloration and photoaggregation of a regrown crystal, a strong 1.09- $\mu\text{m}$  absorption band developed, indicating that the essential impurity was indeed an oxygen bearing ion.

As further precaution, most crystals were tested for cation metal impurities with atomic absorption, nuclear activation, and plasma resonance techniques. The results indicated trace amounts of various atomic impurities (generally less than 1 ppm), however, no correlation was found between such impurities and the ability of a crystal to form the 1.09- $\mu\text{m}$  absorption band. In fact, it was observed that the formation of the 1.09- $\mu\text{m}$  band in the NaCl crystals was basically insensitive to the presence of other impurities. A case in point was the presence of large amounts of  $\text{K}^+$  ions in some of the original crystals we tested.<sup>25</sup> Finally, FTIR spectroscopy detected, apart from the  $\text{OH}^-$  ions, small concentrations of other molecular anion impurities in some of the crystals ( $\text{BO}_2^-$ ,  $\text{NCO}^-$ ,  $\text{CN}^-$ , plus many unreported lines). At such concentration levels, none of these impurities were significant to the formation of the 1.09- $\mu\text{m}$  band.

The optimum range of  $\text{OH}^-$  concentration was found to be 5–50 ppm in the crystal. This level of concentration consistently led to the largest 1.09- $\mu\text{m}$  absorption. Higher doping levels proved unsuccessful, probably because of the low  $F$ -center density achieved in the crystal after additive coloration at 20-Torr Na-vapor pressure. The attempt to incorporate more  $F$  centers in these highly doped crystals by increasing the coloration pressure led to colloidal  $F$ -aggregate formation, in agreement with previous observations in  $\text{OH}^-$ -doped alkali halides.<sup>26</sup> Doping the NaCl material with  $\text{Na}_2\text{O}$  instead of NaOH produced equivalent results as far as the 1.09- $\mu\text{m}$  band is concerned. It must be mentioned, however, that, despite our precautions, a significant amount of the  $\text{Na}_2\text{O}$  dopant converted to NaOH during preparation for crystal growth, as subsequent uv and ir spectra revealed. Improvements on this method of introducing oxygen in the crystal are still under

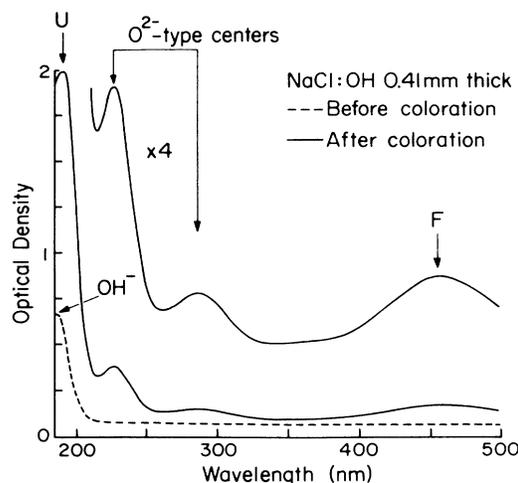


FIG. 9. uv absorption (185–500 nm) of thin NaCl:OH crystal before and after coloration.

investigation.

Spectral comparison of the same crystals before and after additive coloration indicates a consistent reduction of the  $\text{OH}^-$  concentration in the crystal, detectable from the decreased  $3654\text{-cm}^{-1}$  ir line. The uv spectrum shows (apart from the development of the typical  $F$  band) appearance of characteristic oxygen-related absorptions peaking at 226 and 286 nm. Simultaneous formation of  $U$  centers (substitutional  $\text{H}^-$ ) is observed, detectable from uv absorption bands peaking at 190 nm (Fig. 9). Crystals free of oxygen or  $\text{OH}^-$  did not develop any of the above uv bands. These observations indicate that the  $\text{OH}^-$  ion dissociates in the lattice upon additive coloration to form  $U$  centers and substitutional oxygen-ion defects.<sup>26,27</sup>

Previous research on oxygen centers in NaCl has led to the assignment of the 226- and 288-nm bands to  $\text{O}^{2-}$ -related defects.<sup>26,28–31</sup> The 226-nm band is attributed to the  $\text{O}^{2-}$ -anion vacancy center, while the 286-nm band is linked to an  $\text{O}^{2-}$ -type center, whose structure has not been unambiguously determined. Whether or not  $\text{O}^{2-}$  appear also as free ions in the lattice is still unclear in the literature.

The presence of these uv absorption bands was necessary for the formation of the characteristic 1.09- $\mu\text{m}$  absorption band of the perturbed  $F_2^+$  center, linking the perturbed  $F_2^+$  center with the presence of oxygen. In view of the fact that there is an abundance of  $\text{O}^{2-}$  ions formed in the crystal during coloration, and also considering that an anion impurity which acts as an electron trap for the singly ionized  $F_2^+$  center must be doubly charged, we conclude that the most plausible candidate for the  $F_2^+$  perturbation is the  $\text{O}^{2-}$  ion.

### OPTICAL PROPERTIES

The  $F_2^+ \rightarrow F_2^+ : \text{O}^{2-}$  band conversion under the influence of  $F$  light is completed within a time period on the order of 2 min. The transformation appears to be irreversible at 77 K; the crystals must be warmed up for the opposite conversion to occur. At temperatures  $T > 250$  K, the binding energy of the impurity appears to be too small

to keep the  $F_2^+$  center attached to the  $O^{2-}$  trap, and the characteristic absorption band shifts back to  $1.05 \mu\text{m}$ , corresponding to the fundamental absorption of the  $F_2^+$  center.

To determine the temperature at which the decomposition  $F_2^+ : O^{2-} \rightarrow F_2^+ + O^{2-}$  takes place, and therefore estimate the binding energy, the fluorescence peak wavelength was measured in the temperature range from 77 to 340 K. A low-intensity  $1.06\text{-}\mu\text{m}$  laser beam was used to pump the  $F_2^+ : O^{2-}$  band, and emission spectra were taken at various temperatures under otherwise similar conditions. As the crystal temperature rose, the emission band became broader, its peak intensity decreased, and a continuous shift toward shorter wavelengths was observed (Fig. 10). This shift was caused by the changing relative populations of the  $F_2^+ : O^{2-}$  center, and the  $F_2^+$  center. For comparison, the emission peak of the  $F_2^+$  center as a function of temperature is also plotted in Fig. 10. The data indicate that at temperatures higher than  $\sim 260$  K the dissociation of the  $F_2^+ : O^{2-}$  population is essentially complete.

From Fig. 10 a simple approximation for the binding energy of the  $F_2^+ : O^{2-}$  center can be made. We assume that the  $F_2^+$  center can exist either as a free defect within the crystal, or as a bound defect adjacent to an  $O^{2-}$  ion, with binding energy  $U$ . Using simple Boltzmann statistics, the probabilities that the defect is either trapped,  $P_{\text{trap}}$ , or is free in the lattice,  $P_{\text{free}}$ , are given by

$$P_{\text{trap}} = 1/[1 + g \exp(-U/kT)],$$

$$P_{\text{free}} = g \exp(-U/kT)/[1 + g \exp(-U/kT)],$$

where  $g$  is the ratio of degeneracies between the two configurations. If  $g$  is set equal to the concentration ratio of  $[Cl^-]/[O^{2-}]$ , which is on the order of  $10^5$ , we find a binding energy,  $U = 0.22$  eV. This model for the binding energy predicts an inverse relation between the transition temperature  $T_c$ , defined as the temperature at which 50%

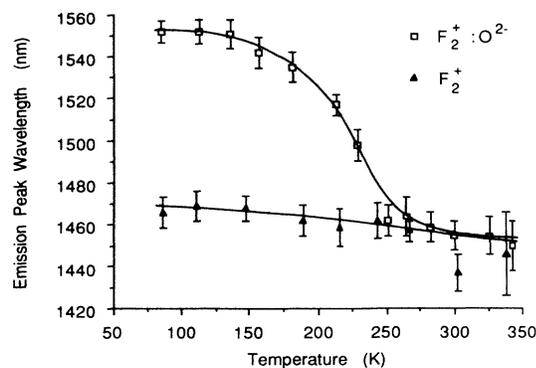


FIG. 10. Measured peak emission wavelength of  $F_2^+ : O^{2-}$  and  $F_2^+$  centers as a function of crystal temperature when pumped by  $1.06\text{-}\mu\text{m}$  Nd:YAG laser. Nearly total dissociation of the  $F_2^+ : O^{2-}$  center occurs above 260 K.

dissociation has occurred, and the logarithm of the oxygen concentration of the crystal. This was confirmed by measuring  $T_c$  for two samples, with  $OH^-$  concentrations  $1.1 \times 10^{-5}$  and  $4.0 \times 10^{-5}$ , respectively. The measured  $T_c$  were found  $227 \pm 10$  K and  $257 \pm 10$  K, respectively, which agree well with the above model, despite its crude approximations.

The  $F_2^+ : O^{2-}$  center is stable at 77 K and is not destroyed under intense optical excitation. Any observable decrease of its absorption after hard pumping at  $1.06 \mu\text{m}$  is due to reorientation of the centers, as will be discussed in the following section. The radiative lifetime of the  $F_2^+ : O^{2-}$  fluorescence has been measured to be 150 nsec, using pulsed (20 nsec) Nd:YAG pumping.<sup>14</sup> This lifetime appears to be temperature independent, for temperatures ranging from 85 to 330 K, suggesting the absence of phonon-assisted nonradiative decay processes from the first excited state.

#### REORIENTATION OF THE $F_2^+ : O^{2-}$ CENTER

Many  $F_2^+$ -type color-center lasers require an auxiliary light (apart from the pump light) for efficient operation. Without this auxiliary light, power fading is observed, due to debilitating effects induced by intense optical pumping. Although not fully understood, the purpose of the auxiliary light is thought to maintain a sufficient equilibrium population of  $F_2^+$ -type defects during lasing by realignment of the centers into preferred orientations in the lattice and/or by regeneration of the center population via ionization. For the  $F_2^+ : O^{2-}$  center in NaCl, we have determined that the auxiliary light required for lasing is solely for reorientation purposes. The reorientation of an  $F_2^+$ -like defect consists of flipping the center's axis (connecting the two vacancies) between two of the six possible  $\langle 110 \rangle$  directions. This reorientation may occur through thermal or optical excitation.

An accepted model of the optically induced process consists of reorientation during a radiationless transition from  $2p\pi_u$  (second excited state) to  $2p\sigma_u$  (first excited state).<sup>32</sup> Excitation to the  $2p\pi_u$  energy level (or higher, in which case a nonradiative transition to  $2p\pi_u$  first occurs)<sup>33</sup> can be accomplished either directly from the ground state using  $F$ -light photons, or by two-photon pumping.<sup>21,34</sup> We have experimentally confirmed reorientation of the  $F_2^+ : O^{2-}$  center through these two mechanisms. Furthermore, we have also observed the reorientation of the  $F_2^+ : O^{2-}$  center by intense optical pumping at its fundamental absorption wavelength. The exact mechanism of this latter reorientation process, which leads to deleterious decay of laser power in the absence of an auxiliary light source, is still under investigation.

Alignment of the  $F_2^+ : O^{2-}$  centers using the  $1s\sigma_g \rightarrow 2p\pi_u$  (455 nm) transition, was achieved with polarized mercury arc light (which has a strong line at 436 nm) filtered through 5-56 and 1-75 filters. Illumination of the crystal with this  $F$  light incident along  $[001]$  and polarized along  $[110]$  caused dichroism of the  $F_2^+ : O^{2-}$  band [Figs. 11(b) and 11(c)], resulting in an increase of the absorption for  $1.09\text{-}\mu\text{m}$   $[110]$  polarized probe light, and a corresponding bleaching of the absorption for probe light with the orthogonal  $[\bar{1}10]$  polarization. The ratio of the

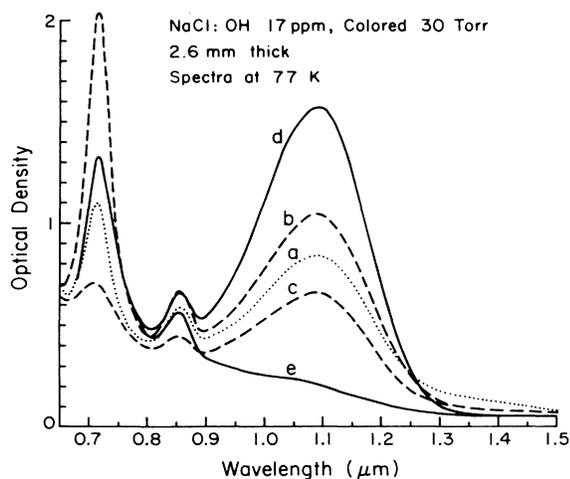


FIG. 11. Polarized absorption at 77 K before and after aligning the  $F_2^+ : O^{2-}$  population. (a) Randomly oriented centers. (b) Centers aligned using  $[110]$  polarized  $F$  light for 30 min, probed with  $[110]$  polarized light. (c) Centers aligned as in (b), probed with  $[\bar{1}10]$  polarized light. (d) Centers aligned using collinear  $1.06\text{-}\mu\text{m}$  and  $0.6328\text{-}\mu\text{m}$   $[\bar{1}10]$  polarized light for 90 min, probed with  $[110]$  polarized light. (e) Centers aligned as in (d), probed with  $[\bar{1}10]$  polarized light.

absorption coefficients at  $1.09\text{ }\mu\text{m}$ ,  $\alpha_p/\alpha_t$ , for probe light polarizations parallel and transverse to the aligning  $F$ -light polarization, respectively, had a typical maximum value  $\alpha_p/\alpha_t = 1.7$ . This contrast ratio was low in comparison to other alignment techniques, since competing effects such as ionization of  $F$  and  $F_2$  centers led to continuous creation of new randomly oriented  $F_2^+$  populations.<sup>35</sup> With additional filtering of the polarized  $F$  light through a 430-nm long pass filter to reduce these photoionization processes, the contrast ratio increased to  $\alpha_p/\alpha_t = 3.3$ .

The alignment-induced dichroism of the sample allows the determination of the dipole moment direction of the  $F_2^+ : O^{2-}$  centers, using probe light incident along  $[001]$ . After aligning the centers with  $F$  light propagating along  $[001]$  and polarized along  $[110]$ , the sample exhibits  $\langle 110 \rangle$ -type ir dichroism (maximum absorption for  $[110]$   $1.09\text{-}\mu\text{m}$  probe polarization, minimum for  $[\bar{1}10]$ ). After aligning with  $F$  light incident along  $[010]$  and polarized  $[011]$ , the sample exhibits  $\langle 100 \rangle$ -type ir dichroism (maximum absorption for  $[100]$   $1.09\text{-}\mu\text{m}$  probe polarization, minimum for  $[010]$ ). This is absolutely consistent with  $\langle 110 \rangle$  direction of the center  $\sigma$ -dipole moment.

For reorientation of the  $F_2^+ : O^{2-}$  centers through the two-photon pumping mechanism, the excited-state data indicated that after pumping the centers to the first excited level with Nd:YAG  $1.06\text{-}\mu\text{m}$   $\langle 110 \rangle$  polarized light, use of  $\sim 650\text{-nm}$  light polarized parallel to the pump beam, or  $\sim 515\text{-nm}$  light polarized perpendicular to the pump beam, would be the most efficient way to achieve the reorientation, based on the measured oscillator strengths and polarizations of the excited states. For this purpose, there is excellent coincidence between two of the excited-state transition wavelengths and those of the He-Ne  $632.8\text{-nm}$  and Ar<sup>+</sup>-ion  $514.5\text{-nm}$  lasers.

An example of the dichroism induced by polarized two-photon pumping is presented in Fig. 11, curves  $d$  and  $e$ . Alignment along  $[110]$  was achieved by using collinear  $1.06\text{-}\mu\text{m}$  and  $632.8\text{-nm}$  laser beams propagating along  $[001]$ , both  $[\bar{1}10]$  polarized. Similar results were obtained by using  $[\bar{1}10]$  polarized  $1.06\text{ }\mu\text{m}$ , and  $[110]$  polarized  $515\text{-nm}$  laser beams. This technique causes reorientation of only the  $F_2^+ : O^{2-}$  centers, without affecting any other color centers in the lattice. As can be seen in Fig. 11, using polarized  $F$  light causes dichroism in the  $F_2$  band as well as in the  $F_2^+ : O^{2-}$  band. This is in agreement with the accepted model of  $F_2$  center reorientation mechanism through an  $F_2^+$  stage,<sup>36,37</sup> and probably also explains the observed inefficiency of the  $F$  light to fully align the  $F_2^+ : O^{2-}$  population.

It was finally shown that pumping the basic  $1.09\text{-}\mu\text{m}$  transition with  $1.06\text{-}\mu\text{m}$  laser beam propagating along  $[001]$  and polarized along  $\langle 110 \rangle$  direction, causes persistent depletion of the absorption parallel to that polarization, and corresponding increase of the absorption along the perpendicular polarization. Eventually the dipole moments are driven into the orientation perpendicular to the pump light polarization. For this experiment we used a 5-W  $[\bar{1}10]$  polarized  $1.06\text{-}\mu\text{m}$  YAG beam to pump a 1-mm-diameter spot on the NaCl crystal. The achieved dichroism of the sample after 70 min of pumping is shown in Fig. 12, although most of the reorientation occurs in a much shorter time. The effect is fully reversible, indicating that the  $F_2^+ : O^{2-}$  centers are not destroyed through intense pumping, as is the case with  $F_2^+$  centers.

Reorientation induced by photons of the fundamental absorption wavelength alone was shown to have significantly smaller quantum efficiency than reorientation induced by pumping to higher excited states. The comparison was made by measuring the decaying polarized emission signal at  $1.55\text{ }\mu\text{m}$  (parallel to the  $1.06\text{-}\mu\text{m}$  pump polarization). The centers were initially aligned along the

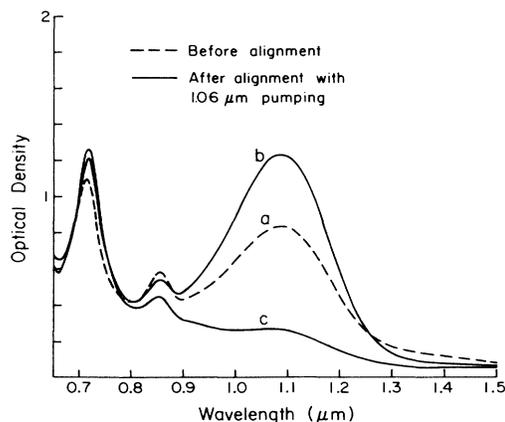


FIG. 12. Polarized absorption at 77 K before and after aligning the  $F_2^+ : O^{2-}$  population with polarized  $1.06\text{-}\mu\text{m}$  excitation. (a) Randomly oriented centers. (b) Centers aligned with  $[\bar{1}10]$  polarized  $1.06\text{-}\mu\text{m}$  laser beam for 70 min, probed with  $[110]$  polarized light. (c) Centers aligned as in (b), probed with  $[\bar{1}10]$  polarized light.

[110] direction, using 1.06- $\mu\text{m}$  beam polarized along  $[\bar{1}10]$  and 515-nm beam polarized along [110]. This two-photon combination forced the centers eventually into the [110] direction, where they were no longer excited. Once the desired degree of alignment had been achieved (approximately equal for all the experiments), the 1.06- $\mu\text{m}$  pump polarization was adjusted parallel to [110], acting on the  $F_2^+:\text{O}^{2-}$  population either alone or combined with a 633-nm He-Ne or 515-nm  $\text{Ar}^+$  collinear laser beam. The decay of the 1.55- $\mu\text{m}$  emission polarized parallel to the [110] is plotted versus time in Fig. 13. It should be noted that the power of the He-Ne or  $\text{Ar}^+$  beams was on the order of 0.1% of the 1.06- $\mu\text{m}$  pump power (1 W, same for all four curves). It is evident that the presence of auxiliary photons to pump the centers into higher excited states can dramatically increase the reorientation rates. This is exactly the function of the auxiliary light used in the  $F_2^+:\text{O}^{2-}$  laser.<sup>14,16</sup>

From Fig. 13 it is seen that the reorientation rate is enhanced even with 515-nm light polarized parallel to the 1.06  $\mu\text{m}$ . This can be explained if we consider that the reorientation from [110] to  $[\bar{1}10]$  happens through at least one intermediate orientation. Any polarization of the auxiliary light will enhance the reorientation rates of these intermediate orientations, and the net effect will be again an enhancement of the total rate.

In the absence of any optical excitation, no thermally induced reorientation of the  $F_2^+:\text{O}^{2-}$  aligned population was noticeable at 77 K, for observation periods up to 30 min. This sets a lower limit of 0.26 eV for the reorientation barrier, calculated with the formula

$$1/\tau = \nu \exp(-U/kT),$$

assuming a typical vibrational attempt frequency  $\nu = 10^{13}$  Hz.

It is worth mentioning that the same mechanism that causes reorientation of the  $F_2^+:\text{O}^{2-}$  centers can also

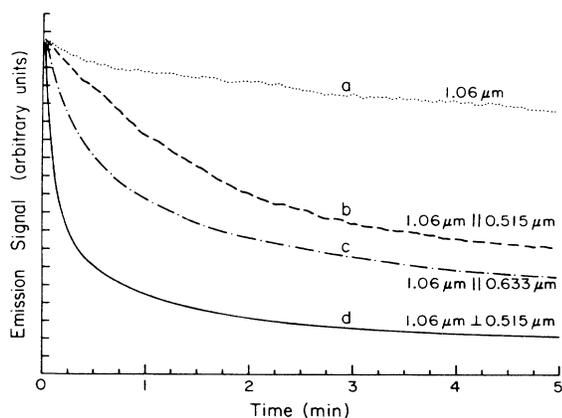


FIG. 13. Time decay of  $F_2^+:\text{O}^{2-}$  1.55- $\mu\text{m}$  polarized emission signal due to reorientational bleaching. The  $F_2^+:\text{O}^{2-}$  population was initially aligned along [110], and was then excited with [110] polarized 1.06- $\mu\text{m}$  light, in combination with other sources, as indicated. Excited-state transitions caused by two-photon pumping led to dramatic enhancement of the reorientation rate.

cause the shifting of the 1.05- $\mu\text{m}$   $F_2^+$  absorption band to the 1.09- $\mu\text{m}$   $F_2^+:\text{O}^{2-}$  band at 77 K. This suggests that the conversion is accomplished through successive optically induced reorientations. The fact that  $F$  light is effective in both cases (reorientation and shifting) has been shown above. It remained to be proven whether two-photon pumping can accomplish the band shifting, too. To this purpose the unshifted 1.05- $\mu\text{m}$  absorption band was pumped with a combination of collinear unpolarized 1.06- $\mu\text{m}$  (9-W) and 0.6328- $\mu\text{m}$  (2.5-mW) laser beams tightly focused on the crystal. The fluorescence spectrum indicated that the emission peak shifted from 1.47 to 1.55  $\mu\text{m}$  within a 10-min time interval. We therefore interpret the 77 K photoaggregation process to occur in the following manner: When the crystal is cooled from 300 to 77 K in the dark, the  $F_2^+$  centers are "frozen" in the lattice. Optical excitation then causes slow migration of the  $F_2^+$  centers through successive random reorientations, until they are trapped at an  $\text{O}^{2-}$  ion forming the  $F_2^+:\text{O}^{2-}$  center. This process is similar to that of the  $(F_2)_A$  center formation.<sup>38</sup>

## DISCUSSION

The overwhelming presence of  $\text{O}^{2-}$  anions in the crystal suggests that the stabilizing impurity for the perturbed  $F_2^+$  center is indeed  $\text{O}^{2-}$ . Other substitutional oxygen defects in the lattice such as  $\text{OH}^-$ ,  $\text{O}_2^-$ , and  $\text{O}^-$  ions could also be considered as possible candidates for the cause of the  $F_2^+$  perturbation, but they are very unlikely. An  $F_2^+$  center associated with a neighboring  $\text{OH}^-$  ion does not seem as likely a possibility for the 1.09- $\mu\text{m}$  band since FTIR and uv data show the dissociation of  $\text{OH}^-$  following coloration. Similarly, the possibility of the  $\text{O}_2^-$  ion as the perturbing impurity is precluded since its strong uv absorption is not observed in crystals which form the shifted 1.09- $\mu\text{m}$  absorption band.

For consideration of the  $\text{O}^-$  ion as a possible candidate for the perturbation of the  $F_2^+$  defect, absorption spectra were taken on  $\text{NaCl}:\text{OH}^-$  crystals irradiated at room temperature with  $\gamma$  rays ( $^{60}\text{Co}$  source;  $10^7$  rad). This irradiation resulted in the dissociation of  $\text{OH}^-$  ions, presumably to  $\text{O}^-$  and a variety of substitutional and interstitial hydrogen defects.<sup>39</sup> No divalent oxygen centers were detected following the coloration. With the absence of  $\text{O}^{2-}$  ions in the lattice, as determined by the absence of the characteristic uv absorption bands, the formation of the perturbed  $F_2^+$  band did not occur when the crystal was cooled to 77 K and exposed to  $F$  light, in spite of the presence of a small  $F_2^+$  population. However, a 20-min photoaggregation of the same crystal at room temperature with  $F$  light resulted in formation of uv absorption bands corresponding to  $\text{O}^{2-}$  ions. Upon cooling this photoaggregated crystal to 77 K and reexposing it to  $F$  light, the perturbed  $F_2^+$  band was observed. These results offer indirect evidence that the stabilizing impurity must indeed be the  $\text{O}^{2-}$  defect. More research is necessary to establish the kinematic reactions that lead to the formation of the observed bands in this case, as well as in the additively colored crystals.

To conclude, the presence of  $\text{O}^{2-}$  ions in the lattice ap-

pears to be essential to the formation of the perturbed  $F_2^+$  band at  $1.09 \mu\text{m}$ , suggesting that the  $F_2^+:\text{O}^{2-}$  model is the best candidate for the center. The doubly negative oxygen ion serves to both spatially stabilize the  $F_2^+$  center and to act as an electron trap. The Coulombic attraction between the positively charged  $F_2^+$  center and the negatively charged impurity would further explain the observed stability of the system. Excited-state spectroscopy of the center conclusively demonstrates the  $F_2^+$ -like character of the center. The reorientation properties of this center have been determined, and explain why cw

lasers based on this system benefit from crystal exposure to auxiliary light of the appropriate wavelength. Future work will be needed to confirm this identification, and to establish the details of  $F_2^+:\text{O}^{2-}$  center formation in NaCl and other crystal lattices.

#### ACKNOWLEDGMENT

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