

## Photochemical and Population Hole Burning in the Zero-Phonon Line of a Color Center— $F_3^+$ in NaF

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We report reversible hole burning in the inhomogeneously broadened zero-phonon line of  $F_3^+$  in NaF at 5456 Å. The hole recovery time shows two components: 2.5 sec assigned to triplet-state relaxation and 70 min assigned to electron tunneling from an adjacent center. These holes were used to measure the homogeneous linewidth (17 MHz) and the linear Stark effect. We find the excited  $^1E$  level has a distribution of zero-field splittings inside the inhomogeneous lines, which quenches the first-order Zeeman effect.

Hole burning in homogeneously broadened optical absorption bands due to selective photochemistry has recently been observed for a number of organic molecules in solid matrices.<sup>1</sup> Photochemical bleaching of (homogeneously) broad color-center bands has been known for many years,<sup>2</sup> particularly at high temperatures where thermal excitation to the conduction band is possible. We have shown that irradiation of the inhomogeneously broadened zero-phonon line with a narrow-band (~ MHz) laser at 2 K can lead to selective bleaching (hole burning), thus providing a very-high-resolution spectroscopic probe. Many color centers, notably aggregate centers, exhibit zero-phonon lines in their optical absorption.<sup>3</sup> This has stimulated extensive studies over the past 10–20 years of the effects of external perturbations (e.g., stress,<sup>4,5</sup> electric,<sup>6,7</sup> and magnetic fields<sup>8,9</sup>) on the electronic structure of color centers—studies which have been extreme-

ly important in developing structural models of these centers. One serious limitation has been that zero-phonon lines are inhomogeneously broadened by lattice strains giving widths of 1–20  $\text{cm}^{-1}$ . This has required the use of very high fields and stresses, and in many cases the level of resolution imposed by inhomogeneous broadening was marginal or inadequate.

We have used the high resolution of hole burning to study the homogeneous linewidth and the linear Stark and Zeeman effects of the  $^1A_1 \leftrightarrow ^1E$  transition of the  $F_3^+$  center in NaF at 5456 Å (see Fig. 1). This center is a singly ionized aggregate of three  $F$  centers in a (111) plane.<sup>10</sup> We find evidence that hole burning occurs via two mechanisms. The first (with a lifetime of a few seconds) is optical pumping leading to population buildup in a low-lying triplet state. The second (with a lifetime of ~1 h) is believed to be a (photochemical) electron transfer to an adjacent cen-

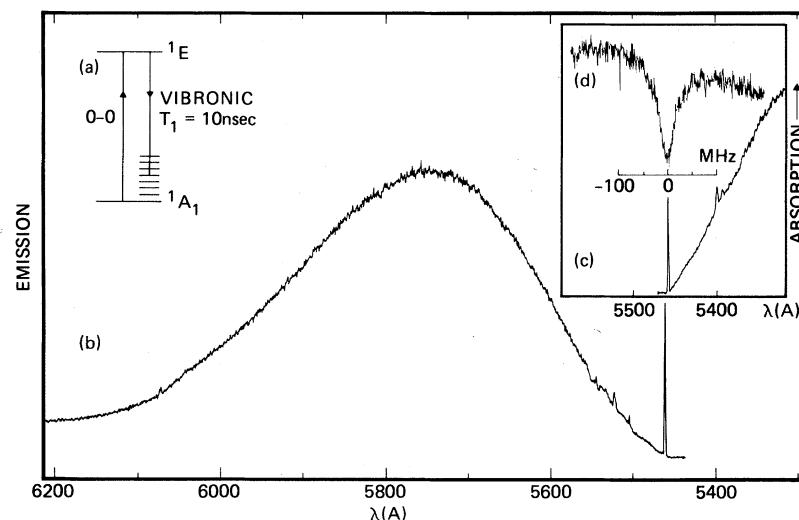


FIG. 1. (a) Schematic energy-level diagram for the  $^1A_1 \leftrightarrow ^1E$  transition of  $F_3^+$  in NaF; (b) the emission spectrum of the zero-phonon line and the vibronic sideband; (c) the excitation spectrum; (d) a hole burnt in the zero-phonon line.

ter. The triplet mechanism should be quite general in systems with low-lying levels of different spin multiplicity from the ground state, and hence have a long lifetime (e.g., triplet states of two-electron centers and organic molecules,  $f^n$  levels of rare-earth ions, etc.). Relaxation kinetics of this kind, implying the possibility of hole burning, have previously been observed.<sup>11</sup> If, as seems likely, these phenomena are widespread in color centers, the increase in spectral resolution by a factor of  $\sim 10^4$  promises to have great impact on color-center spectroscopy. The Stark- and Zeeman-effect measurements are strongly influenced by the presence of a zero-field splitting of the orbitally degenerate  ${}^1E$  level caused by random crystalline strain fields. The hole-burning technique provides a probe of such zero-field splittings, and we find evidence for a distribution of splittings with a width comparable to the inhomogeneous linewidth.

Samples were prepared by x-ray irradiation of single crystals of NaF with unfiltered Mo x rays (tube operated at 50 kV, 20 mA) for several hours at room temperature. Holes were burnt in samples held at 1.5 K by irradiation with  $0.2 \text{ W/cm}^2$  of single-frequency dye-laser light with a (jitter) width of 1–2 MHz. The holes were subsequently probed by scanning the laser, and measuring the excitation spectrum—detecting the  ${}^1E \rightarrow {}^1A_1$  emission in the phonon sideband at  $5800 \text{ \AA}$  [Figs. 1(a) and 1(b)]. The observed hole width  $H$  was 38 MHz (Fig. 1) and since these were shallow holes ( $< 10\%$ )  $H = 2(\Gamma_h + \Gamma_l)$  and  $\Gamma_h = 17 \text{ MHz}$ . The dephasing time  $T_2 \equiv (\pi\Gamma_h)^{-1}$  equals 20 nsec which, within the experimental error of  $\sim 10\%$ , is twice the population decay time of 10 nsec.<sup>12</sup> This confirms an earlier optical free-induction-decay measurement which indicated<sup>12</sup> that dephasing at 1.5 K is limited by population decay. At 4.2 K we find  $H = 80 \text{ MHz}$  or  $\Gamma_h = 38 \text{ MHz}$ , showing the appearance of additional temperature-dependent dephasing.

An interesting result is that the hole recovery time has two components (Fig. 2):  $\tau_T = 2.5 \text{ sec}$  and  $\tau_P = 70 \text{ min}$ . We interpret  $\tau_T$  as the recovery of hole-burning arising from a triplet-state population reservoir. Optical pumping at  $5456 \text{ \AA}$  builds up population in the triplet state as a result of intersystem crossing and this depletes the ground state of those centers resonant with the laser. The lifetime of 2.5 sec is comparable to that of triplet<sup>13</sup> and quartet states<sup>14</sup> in other centers. Direct observation of the triplet state of the  $F_3^+$  center has not yet been made, although

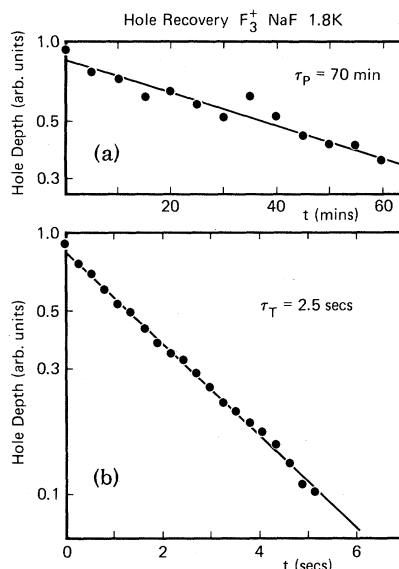


FIG. 2. Hole recovery for the 5456- $\text{A}$  line for  $F_3^+$  in NaF. (a) The (slow) photochemical component; (b) the (fast) triplet population component.

we expect by analogy with the  $H_3^+$  energy levels<sup>15</sup> that the lowest triplet ( ${}^3E$ ) will lie around  $8300 \text{ \AA}$ . We observe phosphorescence in this region but its lifetime is 0.8 sec and it does not show an excitation profile following the  $F_3^+$  zero-phonon line. It is presumed to be due to the  $M$ -band triplet. It appears therefore that the  $F_3^+$  phosphorescence is either  $\geq 10^6$  times weaker than  ${}^1E \rightarrow {}^1A_1$  emission or lies beyond  $8700 \text{ \AA}$  which marked the cutoff of our photomultiplier. The 70-min component is noteworthy because burning occurs at 1.5 K where thermal activation of electrons to the conduction band is not possible. The dark recovery time could be reduced to a few seconds by irradiating with near-uv light from a 75-W Xe arc lamp. The action spectrum of this recovery showed that it was brought about by irradiation in the region of the  $F$  band which peaks at  $335 \text{ nm}$ .<sup>16</sup> The rate of photochemical burning was found to be linear in the laser intensity, showing that two-photon or two-step photoionization was not occurring. At high intensities, the rate of photochemical burning was more than twice that of triplet-state population hole burning, eliminating the triplet as an intermediate in the photochemistry. Finally, the maximum photochemical hole depth that could be produced was about 20%, and this limitation was found not to be due to a light-induced reverse reaction. From these results, the following tentative model of the photochemical component of the burning is

proposed. Irradiation in the zero-phonon line at 5456 Å excites an electron of the  $F_3^+$  center which has a finite probability of tunneling to a physically adjacent center, forming, for example, an  $F$  or  $F'$  center and leaving  $F_3^{++}$ . Irradiation in the  $F$  or  $F'$  band then produces the reverse process. The limit of 20% on the hole depth implies that not all centers can undergo electron transfer, i.e., have a suitable adjacent center. A similar model was proposed<sup>17</sup> to explain the low-temperature bleaching of the broad  $F$  band in KBr.

As was previously shown,<sup>18</sup> Stark splittings of such holes can be measured, since a dc electric field can be applied, and the holes rescanned during their (long) lifetime. The electric field removes the electronic degeneracy of the  ${}^1E$  state with a Stark-splitting coefficient  $A$ , as well as the orientational degeneracy (due to the cubic crystal symmetry) with a pseudo Stark coefficient  $B$ .<sup>6</sup> Rather than cleanly split holes, as we recently observed in  $\text{LaF}_3:\text{Pr}^{3+}$  where only a pseudo Stark effect occurs,<sup>18</sup> we find a distribution of splittings peaking at  $|A - B| = 0.19 \text{ MHz/V cm}^{-1}$  for the laser polarization parallel to the Stark field [ $\vec{E}_L \parallel \vec{E}_S \parallel (100)$ ] and  $|A + B| = 0.43 \text{ MHz/V cm}^{-1}$  for  $E_L \perp E_S$ ; see Fig. 3. The distribution of intensities results from the distribution of magnitudes and orientations of local strain fields with respect to the applied electric field. This provides the first evidence that there exists a distribution of zero-field splittings of the  ${}^1E$  level inside the inhomogeneous line. These splittings

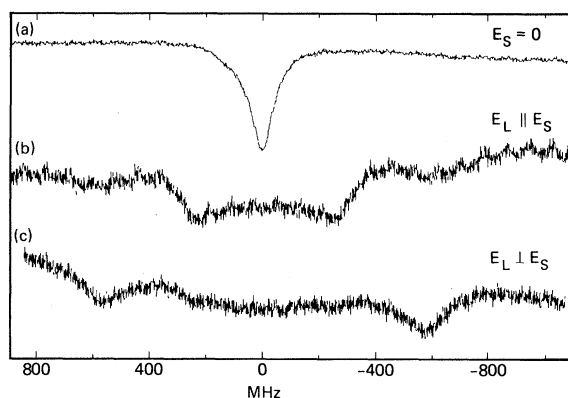


FIG. 3. (100) Stark effect on a photochemical hole in  $F_3^+$  in NaF. (a)  $E_S = 0$ ; (b), (c)  $E_S = 2.7 \text{ kV/cm}$ . The distribution of intensity between the two inner components of the four-line splitting pattern (i.e., those allowed for  $\vec{E}_L \parallel \vec{E}_S$ , see Ref. 6) is interpreted as evidence for a distribution of zero-field splittings of the excited  ${}^1E$  level.

will be on the order of the inhomogeneous linewidth, since the coefficients for stress-induced removal of the electronic degeneracy are comparable to those for removal of orientational degeneracy.<sup>4</sup> Because the strain fields strongly influence only the Stark splitting, it can be distinguished from the pseudo-Stark-effect term by an analysis of the intensity distribution of Figs. 3(b) and 3(c). Such an analysis shows that for (100) fields, the Stark-splitting term ( $A = 0.31 \text{ MHz/V cm}^{-1}$ ) is larger than the pseudo-Stark-effect term ( $B = 0.12 \text{ MHz/V cm}^{-1}$ ).

Finally, we investigated the Zeeman effect by burning a hole and applying magnetic fields up to 50 kG. From magnetic-circular-dichroism measurements, Davis and Fitchen<sup>8</sup> obtained a  $g$  value of  $0.04 \pm 0.02$  for this transition. Thus we expected a linear splitting of up to 2.8 GHz. However, the magnetic field had no observable effect on the hole. This is further evidence that sizable zero-field splittings due to random internal strains quench the linear Zeeman effect. An analysis of the Zeeman effect in the presence of a distribution of zero-field splittings shows that the magnetic interaction between the split components of  ${}^1E$  is certainly less than  $0.05\mu_B$ . This is consistent with the magnetic-circular-dichroism results,<sup>8</sup> which cannot<sup>9</sup> detect the presence of zero-field splittings.

Because of the existence of zero-field splittings, irradiation in a given center reduces the absorption both at the laser frequency and at a frequency shifted by the magnitude of the splitting. Since this magnitude has a random distribution spread over  $\sim 1 \text{ cm}^{-1}$  it is not expected that a discrete second hole would be observed, and indeed it was not.

In conclusion we have observed hole burning in the zero-phonon line of the  $F_3^+$  center in NaF. The two components of the hole recovery time (2.5 sec and 70 min) are interpreted as recovery from population hole burning due to a triplet-state reservoir, and photochemical hole burning involving electron tunneling to an adjacent center. The triplet reservoir should provide a mechanism for hole burning in many other centers, as well as in organic molecules and rare-earth ions. Stark and Zeeman measurements on the long-lived holes show that there is a distribution of zero-field splittings in the excited  ${}^1E$  state comparable to the  $1.7\text{-cm}^{-1}$  inhomogeneous linewidth.

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## Small-Polaronic Diffusion of Light Interstitials in bcc Metals

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The small-polaronic diffusion associated with simple models of light interstitials in bcc metals has been investigated. By transcending the simplifications which are often introduced in studying electronic small-polaron transport, we calculate diffusion coefficients which are reasonably consistent with available data. In particular, an explanation of the "anomalous" isotope dependence observed for hydrogen diffusion in bcc metals emerges from these studies.

The theory of small-polaron hopping motion has been developed to describe the phonon-assisted tunneling of electronic carriers in low-mobility semiconductors and insulators.<sup>1,2</sup> More recently, Holstein's nonadiabatic approach to electronic small-polaron hopping<sup>1</sup> has been adopted in describing the diffusion of light interstitials in metals.<sup>3</sup> However, simplifications which are employed in developing the electronic nonadiabatic theory are thought to be questionable in instances of light-interstitial diffusion in metals.<sup>4</sup> In the present work, a generalization of the semiclassical treatment of small-polaron diffusion which transcends these simplifications is utilized as a basis for investigating simple models of light-interstitial diffusion in bcc metals. These studies not only confirm the necessity of generalizing the formalism but also yield diffusion constants whose magnitudes and temperature dependences

are consistent with the general features of the existing data for the diffusion of hydrogen and its isotopes in bcc metals. In particular, this work provides an explanation of the "anomalous" isotope dependences observed for hydrogen diffusion in these materials.<sup>5,6</sup>

Small-polaron transport is concerned with the motion of a light diffusing atom between adjacent lattice positions in response to the ever-changing potential associated with the vibrations of the relatively heavy atoms of the lattice. At sufficiently high temperatures [typically above a small fraction ( $\leq \frac{1}{3}$ ) of the characteristic phonon temperature<sup>2</sup>], where one may view the vibratory motions of the solid as being classical, this transfer may be described with the occurrence-probability approach.<sup>1</sup> Namely, as the heavy atoms of the material vibrate through a myriad of configurations, they occasionally establish positions for