Polarization-spectroscopy measurement of the homogeneous linewidth of an inhomogeneously broadened color-center band

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A polarized laser beam can bleach narrow, long-lived, anisotropic holes in the 607-nm zero-phonon line of the NaF N_1 center. The width of these holes is twice the homogeneous linewidth, and three orders of magnitude less than the inhomogeneous width of the line. We report a polarization-spectroscopy technique which detects the dichroism and birefringence of the hole with better sensitivity than absorption spectroscopy. A simple rate-equation model is developed to account for hole burning, but the recovery of the initial isotropic absorption profile appears to be a complex, slow, and intractable process.

INTRODUCTION

For many years it has been known that certain color-center absorption bands in x-ray-irradiated alkali halide crystals can be made dichroic by bleaching with polarized light.[1] The dipole moments for such centers are oriented along definite crystallographic axes, and light polarized along one such axis thus can excite only one orientational class of centers.[2] If the excited centers return slowly to their initial state, a long-lived anisotropy is produced. Previously studied absorption bands have generally proved to be homogeneously broadened with the linewidth of the light-induced dichrosim and birefringence comparable to that of the absorption band.

Recently the zero-phonon line associated with the F_3^+ center in NaF was shown to be inhomogeneously broadened by bleaching a narrow hole in the zero-phonon line with a narrow band laser and subsequently probing the absorption with reduced laser intensity.[3] The reduction in the absorption due to the bleaching of one frequency class was detected by monitoring fluorescence emitted into the phonon sideband. The hole width measured at 1.7 K was 38 MHz, more than three orders of magnitude less than the width of the zero-phonon line. Experience with polarization techniques in other high-resolution experiments suggests that the use of such techniques should yield improved sensitivity in color-center spectroscopy.[4-7] The high symmetry of the F_3^+ center, however, sharply limits the expected degree of anisotropy.

We have employed polarization-spectroscopy techniques to detect birefringent and dichroic holes burned into the 607-nm zero-phonon line in x-ray-irradiated NaF. This 607-nm feature has been associated by Baumann[8] with an N_1 center[9] having a transition moment along the [110] axes and overall monoclinic symmetry. There are thus six different possible orientations for the transition moment; if the population of color centers is uniformly distributed among them, no birefringence or dichroism is detectable.

Linearly polarized radiation can, however, introduce anisotropies. It is clear that light polarized along [110] bleaches mainly one class of center, but light polarized along [100] also introduces anisotropies by leaving [011]- and [$0\bar{1}1$]-oriented centers unbleached while affecting the other four orientations equally. In either case the dichroism that results causes light polarized in the same plane as the bleaching beam to be attenuated less than light in the orthogonal polarization. The Kramers-Kronig relations imply a birefringence associated with this dichroism, and symmetry forbids either effect appearing when circularly polarized light is employed to bleach the sample.

The polarization-spectroscopy experiment is shown schematically in Fig. 1. The sample—a

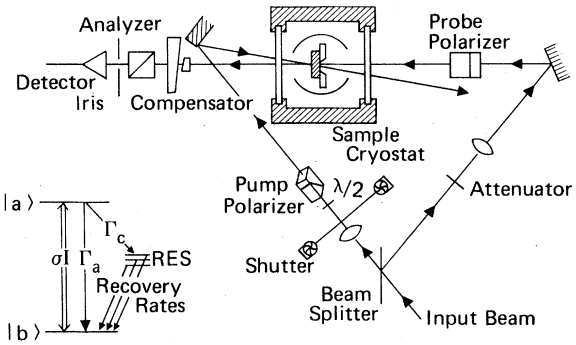

FIG. 1. Apparatus for reading and writing anisotropic holes in a zero-phonon absorption line. The pump beam is polarized in the plane of the page, while the analyzer transmits light polarized perpendicular to that plane. The pump beam is polarized at 45° to the probe. The inset shows the energy-level diagram used to model the hole-writing process. The rates at which the population reservoirs empty into the ground state are much slower than all of the other rates.

2-mm-thick crystal of NaF that had been irradiated at room temperature with Mo x rays for several hours—was mounted on the cold finger of a Helitran cryostat. A 1-mm-diam region of the sample could be bleached by the linearly polarized 40-mW "hole-writing" beam and probed by a much weaker (40-μW) probe beam polarized at 45° to the writing beam. Both beams propagated along the [001] axis. The hole-writing beam was switched on and off by means of a mechanical shutter. After the sample, the probe beam passed through a Babinet Soleil compensator plate which could be set to counteract any residual birefringence in the sample and optics or to supply the phase-shifted local oscillator wave necessary to detect small changes in birefringence.[6] A Glan-Thompson prism acted as polarization analyzer, rejecting the transmitted probe light. The intensity at the detector when the compensator and analyzer are adjusted for minimum transmission was normally less than 10^{-4} of the incident probe intensity. Anisotropies induced in the sample by the writing beam increased the amplitude transmitted through the analyzer and thus increased the detected intensity.

At the peak of a 607-nm zero-phonon line, the absorption of our sample was only 10%, and the maximum change in the absorption due to a "hole" burned in for ~30 ms was only a few percent of that. Detecting the small dichroism and birefringence expected under such conditions required "biasing" the polarization analyzer or compensator to provide a local oscillator wave which interferes constructively or destructively with the polarization-signal amplitude.[4-6] The resulting change in the detected intensity is proportional to the geometric mean of the local oscillator and polarization-signal intensities and can be orders of magnitude larger than the polarization-signal intensity itself [see Eqs. (12) and (13)]. When the polarization analyzer is rotated by a degree or so from the angle of minimum transmission, the transmitted portion of the probe interferes with the amplitude produced by the sample dichroism. If the hole written in the absorption band has a Lorentzian line shape, the change in intensity at the detector has a positive or negative Lorentzian line shape depending upon whether the analyzer polarization has rotated towards or away from the pump polarization. Similarly the positive or negative dispersion line shape associated with hole birefringence can be obtained by adjusting the Babinet Soleil compensator to make the beam at the analyzer slightly elliptically polarized in the absence of a hole. The additional birefringence induced by the writing beam increases or decreases the ellipticity of that wave, creating a detectable change in intensity. In the actual experiment, the probe laser frequency was scanned over a range of ~2 GHz centered at the hole and the detector current was plotted as a function of laser frequency on an x-y plotter. Scans typically required 10 sec, during which time the hole did not noticeably recover. All four line shapes could be easily obtained and are shown in Fig. 2. In Fig. 3 is a comparison of the polarization signals obtained for two very deep holes with those found in transmission. The remarkable increase in sensitivity is apparent.

Anisotropic holes were readily burned with pump light polarized along the [110] crystal axes and readily detected with a probe polarized along [010]. When the writing beam was polarized along [010] with the probe and analyzer nearly orthogonal to one another and polarized along [110] axes, the detected polarization signals were approximately equal to those obtained for the same exposure in the former case. This observation is consistent with transition dipole moments oriented along the [110] axes. No polarization signal was detectable when the pump was circularly polarized.

THEORY

The dynamics of the creation of an anisotropic hole can be understood from a simple rate-equation model. Assume that the dipole moments for transition between the ground state $|b\rangle$ and first singlet state $|a\rangle$ of the N_1 centers have magnitude μ and are directed along the six [110] axes which are specified by the unit vectors $\hat{e}_i$. Each individual center has a resonant frequency Ω and a homogen-

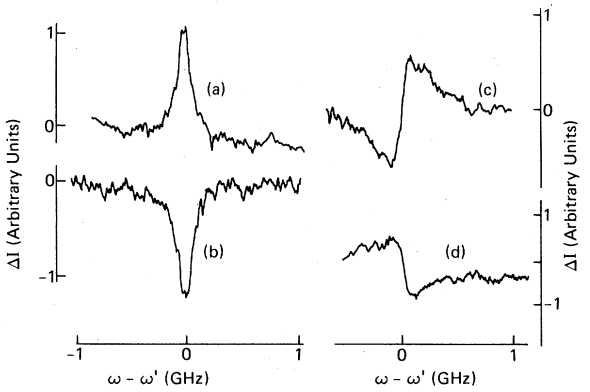

FIG. 2. Line shapes obtained with various phases of local oscillator. All traces correspond to a single hole burned with [110] polarization at an exposure of 0.25 W/cm^2 for 66 ms. The dispersion line shapes in (c) and (d) were obtained by adjusting the Babinet Soleil compensator, while the positive and negative Lorentzians in (a) and (b) resulted from rotating the analyzer slightly.

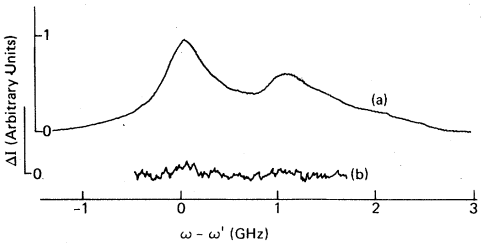

FIG. 3. Two deep exposure-broadened holes detected in polarization and transmission spectroscopy. In the polarization-spectroscopy trace (a) the zero level has been suppressed but the increase in detected intensity at peak is roughly 100%. In trace (b)—obtained in transmission without polarization selection—the zero level has been greatly suppressed, and the holes result in only a 2% increase in the intensity at the detector.

eous linewidth Γ_2. From the excited state, population can flow into various long-lived reservoir states with total rate Γ_c, and the intial (ground) state is repopulated from the reservoirs at a very slow rate.

Since the transition is inhomogeneously broadened with a distribution of resonant frequencies having a width $\Delta\Omega \gg \Gamma_2$, a correct model must deal separately with the various classes of center, each class characterized by a unique dipole orientation $\hat{e}_i$ and resonant frequency Ω. The function $\mathfrak{N}_i(\Omega - \Omega_0, \Delta\Omega)$ describes the distribution of resonant frequencies around the average frequency Ω_0 for centers with orientation $\hat{e}_i$ and is essentially the population of a given class. Initially that population is $\mathfrak{N}_i^0(\Omega - \Omega_0, \Delta\Omega)$ and the inhomogeneous linewidth $\Delta\Omega$ can be obtained from the absorption spectrum at low temperature. When radiation excites centers of a given class, the populations of the ground state and excited state are altered. In each unit of volume, N_a centers of this class are then in the excited state while N_b remain in the ground state, but these populations obey $N_a + N_b = \mathfrak{N}_i(\Omega - \Omega_0, \Delta\Omega)$.

The dispersion of the refractive index and the absorption due to a single ground-state center with orientation $\hat{e}_i$ and resonant frequency Ω is described by the polarizability tensor

$$\vec{\alpha}_i(\omega, \Omega) = \frac{\mu^2(\hat{e}_i\hat{e}_i)}{2\hbar(\Omega - \omega + i\Gamma_2)}, \tag{1}$$

where $(\hat{e}_i\hat{e}_i)$ is the outer product of the unit vectors describing the dipole orientation. A crystal with centers in all orientations and with all resonant frequencies will have a susceptibility of

$$\vec{\chi}(\omega) = \sum_i \int_{-\infty}^{\infty} \mathfrak{N}_i(\Omega - \Omega_0, \Delta\Omega)\vec{\alpha}_i(\omega, \Omega)\, d\Omega \tag{2}$$

when all the centers are in the ground state. If all of the $\mathfrak{N}_i$ are equal, and all centers are in the ground state, the crystal will be optically isotropic.[1,2]

The rate equations for the populations of the ground and excited states of a single polarization and frequency class of centers excited by a writing beam at frequency ω are

$$\dot{N}_a + (\Gamma_a + \Gamma_c)N_a = \sigma_j(N_b - N_a)I, \tag{3}$$

$$\dot{N}_b - \Gamma_r N_a + \{\text{recovery terms}\} = -\sigma_j(N_b - N_a)I, \tag{3'}$$

where

$$\sigma_j I = \hbar^{-1}\vec{E}(\omega) \cdot \vec{\alpha}_j''(\omega, \Omega) \cdot \vec{E}(\omega) \tag{4}$$

is the excitation rate, $\vec{\alpha}_j''(\omega, \Omega)$ is the imaginary part of the center polarizability and Γ_a is the rate of direct decay from $|a\rangle \rightarrow |b\rangle$, and Γ_c represents the rate of crossing into population reservoirs (which could be intensity dependent). The subscript j refers to a particular pumping geometry. Under the conditions of our experiment, the rate constants obey the inequality

$$\Gamma_2 > \Gamma_a > \Gamma_c \gg \sigma_j I \gg \{\text{recovery rates}\}. \tag{5}$$

The hole-writing process begins with all of the color centers in the ground state and all of the $\mathfrak{N}_i$ equal. The writing beam has uniform intensity and exposes the crystal for a time t of several msec, altering the distribution functions of resonant frequencies. The differential equation for the distribution function can be derived easily from Eq. (3')

$$\dot{\mathfrak{N}}_j(\Omega - \Omega_0, \Delta\Omega) = \dot{N}_a + \dot{N}_b = -N_a\Gamma_c. \tag{6}$$

Equations (3') and (6) and the initial conditions imply that at the end of the writing pulse, the distribution function has been changed by the amount

$$\Delta\mathfrak{N}_j = -\Gamma_c \int_0^t N_a\, dt$$

$$= -\mathfrak{N}_j\left[1 - \exp\left(-\frac{\sigma_j I \Gamma_c t}{\Gamma_a + \Gamma_c}\right) - \frac{\sigma_j I \Gamma_c}{(\Gamma_a + \Gamma_c)^2}\right], \tag{7}$$

where the relation $\Gamma_a t \gg 1$ has been used to simplify the expression, and recovery from the reservoirs has been neglected. The first two terms correspond to the filling of the reservoirs and the third to two-level saturation of the transition excited by the laser. Since this two-level contribution recovers with the excited-state lifetime $(\Gamma_a + \Gamma_c)^{-1}$, it is not observed in our experiments and will be ignored. The frequency dependence of the burning rate is contained in the parameter σ_j. The width and depth of the hole resulting from this frequency dependence depend upon the exposure time t. If $\sigma_j I t \ll 1$, the depth is proportional to the ex-

posure time and power broadening of the hole is avoided. In this case the change in the distribution function becomes

$$\Delta\mathfrak{N}_j = \frac{\mathfrak{N}_j \sigma_j I \Gamma_c t}{\Gamma_a + \Gamma_c} . \tag{8}$$

After the writing pulse is turned off, the unbleached centers return to the ground state. The change in the distribution functions results in a change in the susceptibility of the crystal

$$\Delta\vec{\chi}(\omega) = \sum_j \int \Delta\mathfrak{N}_j(\Omega)\vec{\alpha}_j \cdot (\omega, \Omega) d\Omega , \tag{9}$$

which is clearly anisotropic. When $\Delta\Omega \gg \Gamma_2$, the integral in (9) can be performed analytically

$$\Delta\vec{\chi}(\omega') = \sum_j \frac{\pi\mu^4 [\hat{e}_j \cdot \vec{E}(\omega)]^2 (\hat{e}_j \hat{e}_j) \mathfrak{N}_j(\omega - \Omega_0, \Delta\Omega)}{4\hbar^3(\omega' - \omega - 2i\Gamma_2)} \times \frac{\Gamma_c t}{\Gamma_a + \Gamma_c} . \tag{10}$$

The imaginary part of this tensor describes the change in absorption due to the hole; the line shape is clearly Lorentzian with a width equal to twice the homogeneous linewidth. The real part of $\Delta\vec{\chi}(\omega')$ reflects the dispersion and dichroism.

These effects decay as the distribution functions recover and the population reservoirs empty. The recovery processes are very slow—requiring second to hours—and their rates can be neglected during the hole-writing phase. Afterwards, their effects can be treated phenomenologically by allowing $\Delta\vec{\chi}(\omega')$ to vary with time.[3]

Equation (7) implies that long exposures at high intensity can bleach the absorption completely. Experimentally this is not the case, and we attribute the absorption remaining after long exposure to centers for which the crossing rate Γ_c is low or the reservoir lifetime short.

The optically induced effects are small enough that a linear theory correctly describes the alteration of the probe-beam amplitude. If $\vec{E}(\omega')$ is the probe amplitude and polarization that would have been transmitted through a sample with an unperturbed distribution function, the effect of the holes can be written as

$$\vec{E}_s = \frac{8\pi^2 i}{n_s} \frac{l}{\lambda} \Delta\vec{\chi} \cdot \vec{E}(\omega') , \tag{11}$$

where l is the sample length and λ is the vacuum wavelength.[6] In ordinary polarization spectroscopy, $\vec{E}_\perp$, the component of $\vec{E}_s$ orthogonal to $\vec{E}(\omega')$

$$\vec{E}_\perp = \vec{E}_s - [\vec{E}_s \cdot \vec{E}(\omega')]\vec{E}(\omega')/|\vec{E}(\omega')|^2 \tag{12}$$

is selected by a polarization analyzer and detected. The resulting electrical signal is proportional to $|\vec{E}_\perp|^2$.[4,6]

More information and greater sensitivity can be achieved by purposely injecting a local oscillator amplitude $\vec{E}_{1o}$ into the detector along with $\vec{E}_\perp$.[5,6] The local oscillator can be generated conveniently by tilting the polarization analyzer by a degree or so or by adjusting the Babinet Soleil compensator plate. The detected intensity is then

$$I = \frac{c}{8\pi}|\vec{E}_\perp + \vec{E}_{1o}|^2 = I_{1o} + \frac{c}{8\pi}|\vec{E}_\perp|^2 + \frac{c}{4\pi}\mathrm{Re}\vec{E}_{1o}^* \cdot \vec{E}_\perp . \tag{13}$$

If the local oscillator intensity is constant, the third term in Eq. (13) provides the dominant intensity variations when $|\vec{E}_{1o}| \gg |\vec{E}_\perp|$. Depending upon the relative phase of the local oscillator, this intensity variation can map out either the real or imaginary part of $\Delta\vec{\chi}$. This phase sensitivity and the other advantages of the polarization selective optical heterodyne detection technique have been discussed extensively in the context of coherent Raman spectroscopy.[5,6]

RESULTS AND DISCUSSION

For most of our experiments, the pump wave was polarized along the [110] axis, parallel to the dipole moment unit vector $\hat{e}_j = (\hat{x} + \hat{y})/\sqrt{2}$. The resulting change in the crystal susceptibility had a line shape and symmetry given by

$$\Delta\vec{\chi}(\omega') = \frac{H}{(\omega' - \omega) - 2i\Gamma_2} \begin{pmatrix} 3 & 2 & 0 \\ 2 & 3 & 0 \\ 0 & 0 & 2 \end{pmatrix} , \tag{14}$$

$$H = \frac{\pi\mu^4 |\vec{E}(\omega)|^2 \mathfrak{N}_j \Gamma_c t}{16\hbar^3(\Gamma_a + \Gamma_c)} f(t') , \tag{15}$$

where the coefficient H depends upon intensity, exposure time t, and observation time t'. The initial probe polarization was along the x axis [100] and the analyzer transmitted y-polarized light. Thus the perpendicular signal component was

$$\vec{E}_\perp = \frac{8\pi^2 i}{n} \frac{l}{\lambda} \hat{y} \cdot \Delta\vec{\chi}(\omega') \cdot \hat{x} E(\omega') \hat{y} = \frac{8\pi^2 H E(\omega') l}{n\lambda} \frac{1}{2\Gamma_2 - i(\omega' - \omega)} \hat{y} . \tag{16}$$

Rotating the polarizer by angle $\theta \ll \pi/2$ to allow a bit of x-polarized probe to enter the detector as a local oscillator resulted in an intensity change of

$$\Delta I = \frac{nc}{4\pi}\mathrm{Re}(\vec{E}_{1o}^* \cdot \vec{E}_\perp) = \frac{4\pi^2 H l}{n\lambda} I_{\omega'} \sin\theta \frac{2\Gamma_2}{4\Gamma_2^2 + (\omega' - \omega)^2} \tag{17}$$

as the probe frequency was scanned over the hole frequency. Since the local oscillator is in phase with the probe, this line shape reflects the dichroism due to the hole. The width of the resonance

will be $4\Gamma_2$ (full width at half maximum) (FWHM) so long as the probe intensity is not sufficient to cause further bleaching or power broadening. Adjusting the Babinet Soleil compensator to make the beam slightly elliptically polarized at the analyzer even in the absence of holes is equivalent to injecting a local oscillator in quadrature with $E(\omega')$. The resulting electrical signal is proportional to the hole dichroism

$$\Delta I = \frac{8\pi^2 Hl}{n\lambda} I_{\omega'} \sin\theta \frac{\omega' - \omega}{4\Gamma_2^2 + (\omega' - \omega)^2} , \tag{18}$$

where $|\theta|$ is the ratio of minor or major axes of the elliptical polarization at the analyzer.

The recovery of the holes burned in the N_1 zero-phonon line is a complex process that cannot be characterized by a single recovery rate. As in the case of the F_3^+ center,[3] excitation spectroscopy measurements reveal a fast recovery rate that probably involves the return of population from a low-lying triplet state with a 3.1-sec lifetime. A slower recovery requiring 44 min for the hole depth to decay to $1/e$ of its initial value can also be observed by excitation techniques, but in other systems this lifetime is known to depend upon the total energy deposited in the sample by the probe beam. In polarization spectroscopy, quite weak probe intensities are employed, and under the best conditions, the anisotropy associated with a hole was observed to decay by less than 40% in one hour of observation. The estimated $1/e$ time was 2.5 ± 0.5 h. Moreover, an additional recovery process with an anisotropy decay time of one minute was also observed. The fraction of the initial anisotropy that recovers at this faster rate depends upon the writing-beam intensity. For a writing-beam intensity below 0.1 W/cm^2, the entire hole vanishes in a few minutes. At higher intensities the fast decay ceases after a few minutes leaving 80% of the initial hole depth to recover more slowly. Since power broadening of the hole widths became important for high intensities or long exposures, the narrowest long-lived holes were obtained by exposing the sample to an intensity of several tenths of a W/cm^2 for 30 msec.

At temperatures below 4.2 K, the holes were written and probed using a Coherent 599 laser with a 2-MHz bandwidth and an immersion cryostat. The hole width was 45 ± 6 MHz (FWHM) at these temperatures and independent of temperature. Above 5.1 K, a Spectra 380A tunable laser with a measured linewidth of 40 MHz (limited by low-frequency jitter) was employed. Consequently, the holes burned at low temperatures with this laser are broadened by jitter, as are the polarization-spectroscopy traces. In an attempt to account for the effects of laser jitter, the widths of the holes observed at low temperature were subtracted from the widths at higher temperature.

Figure 4 shows the temperature dependence of the hole widths (FWHM) obtained in this manner. The data fit a function of the form

$$\Delta\nu = \nu_0 + \nu' e^{-\Delta E/kT} , \tag{19}$$

where $\nu_0 = 45 \pm 6$ MHz, $\Delta E/k = 63 \pm 8$ K, and $\nu' = (4.7 \pm 0.8) \times 10^4$ MHz. The activation energy in Eq. (19) corresponds to broadening by a local phonon mode with an energy of $\Delta E = 44 \pm 5$ cm^{-1}.[10] These values of ν' and ΔE imply that above roughly 60 K, the zero-phonon line at 607 nm becomes homogeneously broadened. While the 44-cm^{-1} activation energy does not correspond to a particular phonon mode of the NaF lattice or to a definite feature of the phonon sideband of the N_1 center, it does correspond to a peak in the phonon sideband of a center with a zero-phonon line at 575.4 nm.[8] Such peaks can be attributed to local modes of the ions very near the vacancy aggregate centers, and

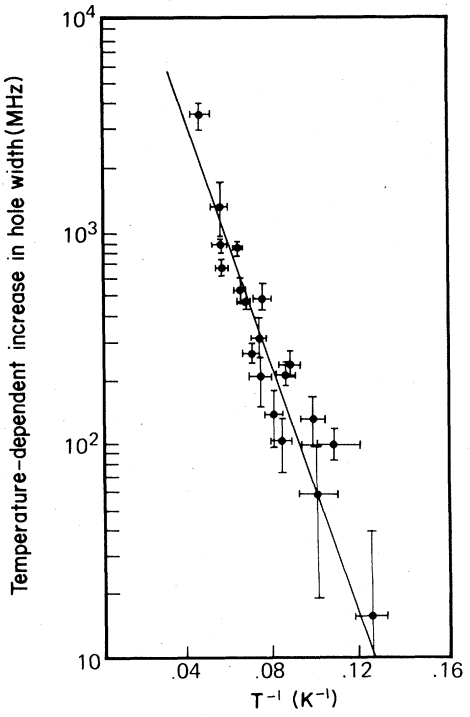

FIG. 4. Increased linewidth of holes as the temperature is raised. Plotted is the increase in hole width (FWHM) above the low-temperature value of 45 ± 6 MHz. The 40-MHz linewidth of the laser used in these measurements has been subtracted off, but some of the indicated uncertainty results from this deconvolution procedure. Other uncertainties result from difficulties in measuring the crystal temperature exactly. The solid line corresponds to the function $\Delta\nu = (4.7 \times 10^4)\, e^{-63/T}$ MHz. The inhomogeneous linewidth is roughly 50 000 MHz.

it is reasonable to expect a commensurate activation energy for hole broadening.

CONCLUSION

In conclusion, we have shown that anisotropic holes can be bleached in the inhomogeneously broadened zero-phonon line of an aggregate color center. The hole width is comparable to that observed by excitation spectroscopy in the F_3^+ center and broadens with increased temperature above roughly 5 K. A portion of the hole depth recovers quickly, but a considerable fraction of the recovery requires an hour or more. This complex time dependence of the hole depth implies that several distinct phenomena contribute to stabilizing the bleached absorption and to creating the anisotropies. The writing beam pumps population from the color-center ground state into an excited state. From that level, some centers decay into long-lived triplet states, some change configuration by moving nearby ions, and some probably ionize. To recover the initial isotropic absorption, all of these processes must be reversed and very different time scales are required for the various processes. Our polarization-spectroscopy technique yields improved sensitivity in comparison to absorption spectroscopy. Since the sample remains optically isotropic except near the frequencies at which the color centers have been bleached, anisotropic holes can be written and unequivocally detected even in the wings of the absorption line.

ACKNOWLEDGMENT

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