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Optical free-induction decay of the F_3^+ center in NaF

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We have measured the optical dephasing time T_2 of the $^1A_1 \leftrightarrow {}^1E$ zero-phonon transition of the F_3^+ color center in NaF by optical free-induction decay. In this way we eliminate the effect of the 54-GHz inhomogeneous broadening, and find a homogeneous linewidth of 20 ± 5 MHz ($T_2 = 16 \pm 4$ nsec). We have also measured a spontaneous emission lifetime of $T_1 = 10 \pm 2$ nsec. In the range 1.5–4 K, our results are consistent with the relation $T_2 = 2T_1$, indicating that optical dephasing is limited by population-decay processes. This relation was even more clearly demonstrated by performing the same experiment on the D lines of sodium vapor at 3×10^{-5} Torr, where the effects of collisions are negligible. We find that the dephasing is again limited by radiative decay, and that $T_2(32 \pm 3 \text{ nsec}) = 2T_1(16.3 \pm 0.4 \text{ nsec})$.

I. INTRODUCTION

Color centers in alkali halides have been studied spectroscopically for many years,[1] and have recently attracted renewed interest because of their promise as materials for tunable cw lasers.[2] In spite of this, there appear to have been few studies of their homogeneous linewidths.[3] In this paper we apply high-resolution laser techniques to the problem.

A number of color centers, especially aggregate centers, exhibit relatively sharp zero-phonon lines,[3] in addition to the strong broad multiphonon sidebands which give rise to the "color" of the materials. Relaxation of these sidebands is dominated by the fast relaxation of the vibrational states. Therefore, in order to observe the homogeneous dephasing of the purely electronic state of the centers, it is necessary to investigate the zero-phonon lines. Spectroscopy of color centers has, in the past, been limited by the inhomogeneous (strain) broadening of these lines, whereas at the lowest temperatures it should be possible to observe a linewidth limited only by the population decay rate. Such a result is demonstrated here.

We have recently shown[4] that the optical free-induction decay[5] (FID) can be used to eliminate the effects of inhomogeneous broadening in solids at low temperatures. In our FID experiments, a coherent polarization is induced in the sample by resonant excitation with a narrow-band laser. The sample then exhibits the FID effect when the laser frequency is abruptly switched outside the homogeneous linewidth.[6] The resulting FID beat signal under these conditions is given by[7]

$$V_s \propto [1 - \Gamma/(\Gamma^2 + \hat{\Gamma}^2)^{1/2}] \times \exp\{-[\Gamma + (\Gamma^2 + \hat{\Gamma}^2)^{1/2}]t\} \cos\Delta\omega t \ . \tag{1}$$

Here, $\Delta\omega$ is the laser frequency shift and the FID damping rate

$$\Gamma_{\text{FID}} = \Gamma + (\Gamma^2 + \hat{\Gamma}^2)^{1/2} \tag{2}$$

is a function of the dipole dephasing time

$$\Gamma \equiv 1/T_2 \tag{3}$$

and a power broadening term

$$\hat{\Gamma}^2 = (\chi^2\Gamma/2\Gamma_1\Gamma_2)(\Gamma_1 + \Gamma_2 - \gamma) \ . \tag{4}$$

For this two-level quantum problem, the upper level (labeled 2) depopulates at a rate Γ_2 and the lower level (labeled 1) at a rate Γ_1. The radiative spontaneous emission decay rate for the transition $2 \rightarrow 1$ is γ and $\chi = (\vec{\mu} \cdot \vec{E})/\hbar$ is the Rabi frequency, $\vec{\mu}$ being the transition dipole moment and $\vec{E}$ the electric-field vector of the laser. Note that when the upper state depopulates solely from radiative spontaneous emission, i.e., $\Gamma_2 = \gamma$, then $\hat{\Gamma}^2 = \chi^2\Gamma/2\Gamma_2$ independent of the value of Γ_1. At low laser powers ($\hat{\Gamma}^2 \ll \Gamma^2$), the polarization decays in a time $\frac{1}{2}T_2$, and this gives the homogeneous linewidth $(\pi T_2)^{-1}$. In our earlier measurements on solids[4] we investigated the dephasing of the $^1D_2 \leftrightarrow {}^3H_4$ transition of LaF$_3$: Pr^{3+}, where $T_2 \approx 1$ μsec. Here we have extended the technique to much higher speeds in order to apply it to the color center system and to atomic sodium, where radiative decay times are rather fast ($\sim$10 nsec).

II. LINEWIDTH CONTRIBUTIONS

Before presenting the measurements, we will discuss contributions to the homogeneous linewidth in terms of a two-level quantum model and compare some limiting examples of the optical case with the well known magnetic resonance and infrared cases. In general, the total dephasing rate is made up of lifetime and phase interrupting effects. In the latter,

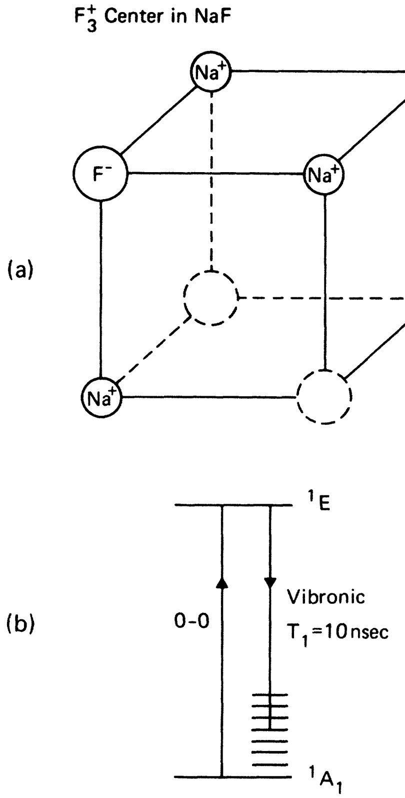

FIG. 1. (a) Model for the F_3^+ center in NaF. Two electrons are localized around three adjacent F^- vacancies in the (111) plane. (b) Energy-level diagram for the $^1A_1 \leftrightarrow {}^1E$ transition at 5456 Å. Most of the intensity of the transition is in the multiphonon vibronic band which peaks about 1000 cm^{-1} from the zero-phonon line.

the level populations are unchanged, but a random jump is introduced in the relative phase of the amplitudes of the coherently prepared states in the wave function. The total dipole dephasing rate is given by[8]

$$\Gamma = \tfrac{1}{2}(\Gamma_1 + \Gamma_2) + \Gamma_\phi \ , \qquad (5)$$

where Γ_ϕ is the rate of phase interruptions. The rates Γ_1 and Γ_2 can often be simply related to the relaxation time T_1 as we see below. The factor of $\frac{1}{2}$ in Eq. (5) arises since dephasing (Γ_ϕ) reflects the randomization in the relative phase of two amplitudes, whereas Γ_1 and Γ_2 are the decay rates of populations which are given by the square of the amplitudes. Hence the populations decay at twice the rate of the corresponding amplitudes. There are some interesting limiting cases of Eq. (5).

A. Magnetic resonance

The normal case is $kT >> E$ (the energy-level difference), so that the thermally induced upward and downward transition rates are equal ($\Gamma_1 = \Gamma_2$). Since T_1 is defined as the rate at which the population difference relaxes to equilibrium (in this case $n_1 - n_2 \cong 0$) it can easily be shown that $T_1 = \frac{1}{2}\Gamma_2^{-1}$. Further, when the mechanism for population relaxation and pure dephasing is the same (e.g., fluctuating dipole-dipole interactions),[9] there is a definite relation between T_1 and T_2. For dipole-dipole interactions it has been shown[9] that the dephasing and population decay contributions to T_2 are equal. This gives $T_2 = T_1$ which is an unusually simple relationship in the presence of nonvanishing Γ_ϕ.

B. Infrared transitions in a gas

Here the initial and final states are relaxed by collisions into nearby rotational levels. In the usual case these rates are equal,[10] and there are no purely dephasing terms,[11] i.e., $\Gamma_1 = \Gamma_2$, $\Gamma_\phi = 0$, $T_1 = \Gamma_2^{-1}$, and $T_2 = T_1$.

C. Optical transitions

For this case $kT << E$, so that the upper level is not thermally populated. In a low-pressure atomic gas with a dominant relaxation path (e.g., Na) we again have a true two-level system as in Sec. II A. The lower state is normally the ground state so $\Gamma_1 = 0$. The excited state population decay is limited by spontaneous emission. At low pressure $\Gamma_\phi = 0$ so that $\Gamma = \frac{1}{2}\Gamma_2$. Now T_1 measures the rate at which the population difference relaxes to the condition $n_2 = 0$, $n_1 = N$, where N is the total population. This rate is given by

$$\dot{n}_2 - \dot{n}_1 = -\Gamma_2[(n_2 - n_1) - N] \qquad (6)$$

and $T_1 = \Gamma_2^{-1}$. We now have $T_2 = 2T_1$, in contrast to the cases in Secs. II A and II B. Note that for a two level system it is only when $\Gamma_1 = 0$ (this case) or $\Gamma_1 = \Gamma_2$ in Secs. II A and II B, that T_1 is defined.

In solids, phase interruptions are usually caused by phonon scattering, fluctuating hyperfine fields, or ion-ion interactions. At low temperatures, phonon scattering and absorption can be frozen out. In the special case where the other contributions to Γ_ϕ can be neglected, then again $T_2 = 2T_1$. Note, however, that a common situation in solids is for the dominant radiative pathway to terminate on excited phonon levels of the ground state [see Fig. 1(b), for example]. When, as is almost always the case, these phonon levels relax to the ground state in a time that is short compared to the decay from level 2, it is possible to replace the complicated level structure by the two levels 1 and 2.

The simple relations between T_1 and T_2 discussed above do not, of course, hold in general. At high temperatures or molecular concentrations $\Gamma_\phi \neq 0$ and T_1 and T_2 are unrelated.

III. F_3^+ CENTER IN NaF

The F_3^+ center in NaF which we study here is an aggregate center composed of two electrons localized around three adjacent F^--ion vacancies lying in a (111) plane [see Fig. 1(a)].[12] Our samples were prepared by Professor F. Lüty, by x-ray irradiation of NaF for about 12 h at room temperature. In addition to the F_3^+ center, there are expected to be other active centers. In particular, there is some background absorption from M centers.[13] The inhomogeneous width of the 5456-Å zero-phonon line in our samples, measured at 2 K, is 54 GHz (1.8 cm^{-1}), and the concentration of centers was such that we had 52% absorption at the peak of the line, in a sample 4 mm thick.

Previous absorption and emission studies under applied stress[13,14] led to the assignment of the ground state as an orbital singlet and the excited state as an orbital doublet, and they were consistent with a trigonal symmetry for the center. The orbital degeneracies were confirmed by Stark-effect measurements[15] and the center was shown to have C_{3v} symmetry. A simple theoretical model[14] predicts that the ground state is a spin singlet and hence that the observed strong optical absorption arises from a singlet-singlet transition (i.e., ${}^1A_1 \rightarrow {}^1E$). Davis and Fitchen[16] confirmed the singlet-spin nature of the states by magnetic circular dichroism measurements, and further found that the orbital moment of the ${}^1E$ level is quenched, probably due to the dynamic Jahn-Teller effect. We came to the same conclusion from our Zeeman measurements on the zero-phonon line in fields up to 70 kG, which gave $|g({}^1E)| < 0.1$.

IV. RELAXATION MEASUREMENTS

A. Spontaneous emission

The population decay (T_1) of the ${}^1E$ excited state was studied by observing the fluorescence decay in the phonon sideband around 5800 Å after pulsed excitation of the sample using a nitrogen-pumped dye laser with a pulse width of 5 nsec. The quantum efficiency of the transition is very high, so a high speed (HP5082-4227) p-i-n photodiode could be used to detect the fluorescence. After 30 dB of amplification, the signal was displayed on an oscilloscope. The total electronic bandwidth of the apparatus is estimated to be 350 MHz. A Corning 3-66 filter was used to eliminate laser light scattered from the exciting pulse. The data were taken from photographs of the oscilloscope trace.

The zero-phonon line of the ${}^1A_1 \leftrightarrow {}^1E$ transition rides on top of the phonon sideband of the M center[13] which is also present in the sample. In order to obtain T_1 for the zero-phonon transition, we subtracted the fluorescence signal in the case of near-resonant excitation (5461 Å), from the signal obtained in the case of resonant excitation (5456 Å). This involved approximately a 30% correction to T_1. The results at a temperature of 1.8 K are shown in Fig. 2, and give an exponential decay with $T_1 = 10 \pm 2$ nsec, which is close to the value of $T_1 = 8$ nsec obtained by Modl *et al.*[17] for the F_3^+ center in LiF at 4874 Å. The time origin was taken to be 6 nsec after the onset of fluorescence by which time the exciting pulse had terminated. As we have seen, T_1 is still defined in terms of a two level system even though the dominant decay path is to vibronic levels of the ground state.

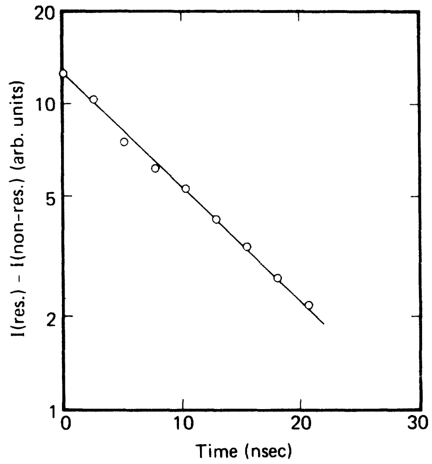

FIG. 2. Decay of the fluorescence intensity (I) of the ${}^1A_1 \rightarrow {}^1E$ transition measured at the peak of vibronic band around 5800 Å. The ordinate measures the difference in intensity under resonant I (res.) and nonresonant I (non. res.) excitation. The sample temperature was 1.8 K.

B. Dephasing time (T_2)

The value of T_2 at 1.8 K was obtained from the FID observed by the method of laser-frequency switching which has been described elsewhere.[6,18] Here we will briefly outline the experiment and emphasize differences from previous experiments which are introduced because of the short time-scale of the present measurement.

The sample is coherently prepared by irradiation at a frequency ω_0 with a Spectra-Physics single-frequency dye laser. This is in resonance with a set of F_3^+ centers within the inhomogeneous line, and it induces a polarization with a width determined by Γ and the frequency width of the laser. The laser width was less than 1 MHz, i.e., negligible here, and the power used of up to 10 mW unfocused was far below

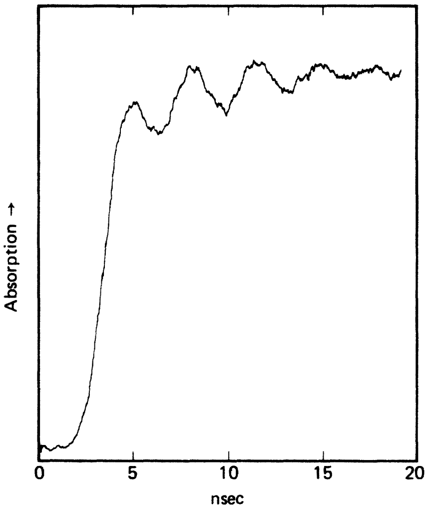

FIG. 3. Optical FID measured in the zero-phonon line at 5456 Å using a 500-V switching pulse.

that which would produce saturation [$\Gamma^2 >> \hat{\Gamma}^2$ see Eq. (2)]. The laser frequency is then switched to ω_1 by applying a voltage across an electro-optical modulator in the cavity, and the sample freely radiates at ω_0. The light beams from the sample and the laser interfere, producing beats at $\omega_0-\omega_1$ which are detected by the p-i-n photodiode. The *AD*P* modulator was supplied by Lasermetrics[19] and had a switching coefficient in our laser of 0.6 MHz/V. To observe the FID signal it is necessary to switch the frequency in a time less than T_2 and by an amount greater than the homogeneous linewidth so that the laser does not continue to interact with the original group of centers. It is further advisable to shift the laser frequency by several linewidths, since then several beats will be observed in a time T_2. We used a high-voltage Huggins pulser, which is a charged cable discharged by a mercury relay at a 60-Hz rate. This low repetition rate gave us a relatively poor signal to noise ratio (e.g., compared to Ref. 4). Signal averaging was performed with a Tektronix sampling oscilloscope, using a 100-sec scan with an integrating time constant of 1.5 sec. A rise time of 3.5 nsec was observed across the phase modulator and terminating 50-Ω resistor. The signal observed with 500 V switched across the modulator, is shown in Fig. 3, the beat frequency corresponding to the 300-MHz laser-frequency switch. The phase of the beat $\theta(t)$ is equal to the additional phase imposed on the laser light by the voltage across the modulator. The beat signal decays because of (i) dephasing processes affecting the individually excited isochromats and (ii) the homogeneous linewidth ($\sim T_2^{-1}$) excited in the steady-state preparation process. Hence the observed rate is twice the intrinsic rate, i.e., $2/T_2$. As seen from Eq. (1) with $\hat{\Gamma}=0$, the signal measured is

$$V_s = \text{const} \cos\theta(t) \exp(-2t/T_2) \ , \qquad (7)$$

the envelope of the beats giving $\frac{1}{2}T_2$. The dephasing time ($T_2 = 16 \pm 4$ nsec) was obtained from the data by computer fit to Eq. (7), including a shift in baseline (see Fig. 3) after the frequency switch.

V. DISCUSSION

We begin by discussing the effect of the fast frequency switch on the observed signal. The voltage rise time in this experiment is only slightly longer than the round-trip time of light in the cavity $t_c = 2.5$ nsec. Consequently, light in different parts of the cavity at a given time will not have experienced an equivalent phase-frequency modulation by the voltage across the modulator. A general discussion of the phase-frequency modulation of the laser for arbitrary applied voltage is given by Genack and Brewer.[18] We merely note that the laser-frequency shift here is in contrast to previous experiments[4] where the rise time (~10 nsec) of the voltage was considerably longer than t_c and the rate of phase advance was fairly uniform. The fast frequency switch introduces sidebands on the laser whose amplitudes increase with increasing voltage.[18] The jump in absorption in Fig. 3 then appears as a consequence of the increase in spectral width of the laser which reduces the degree of saturation.

We now turn to the experimental data, viz., $T_2 = 16 \pm 4$ nsec (i.e., a homogeneous linewidth of 20 ± 5 MHz) and $T_1 = 10 \pm 2$ nsec. These suggest that the dephasing time Γ_ϕ^{-1} is greater than 50 nsec, and are consistent with the relation $T_2 = 2T_1$ obtained in Sec. II C with $\Gamma_\phi = 0$. At the lowest temperatures, population-decay limited dephasing occurs because the optical transition is allowed, so the $\Gamma_2 >> \Gamma_\phi$. Several measurements are relevant to the smallness of Γ_ϕ in the F_3^+ center. From the measured decay time, the oscillator strength of the ${}^1A_1 \leftrightarrow {}^1E$ band is $f \simeq 0.1$, and since the integrated absorption in our sample is $\simeq 10^3$ cm^{-2}, we estimate the concentration of centers to be $\simeq 10^{16}$ cm^{-3}. At this low concentration energy transfer is improbable, especially since the zero-phonon line has only about 10^{-3} of the total oscillator strength. The g value of the ${}^1E$ level of ($g = 0.04$) (Ref. 16) is small, so the hyperfine field of the F$^-$ ions which is less than 10 G, would produce less than 0.6 MHz of broadening. In any case only a small fraction of this contributes to the homogeneous width, since nuclear T_2 processes due to mutual spin flips (=20 μsec),[20] are slower than the optical dephasing. Finally since we found T_2 to be independent of temperature from 2 to 4 K we conclude that phonon scattering does not contribute to dephasing in this temperature range. At higher temperatures this will certainly no longer be true, and phonon scattering will provide the dominant contribution.

We have seen that under our experimental conditions, Γ_ϕ is very small for the color center, and this provides a nice example of the limiting case of Sec. II C, viz., $T_2 = 2T_1$. It is expected that a low-pressure gas, in which collisions are negligible—the classical system where $\Gamma_\phi \approx 0$ would provide an even clearer illustration of this. We have therefore studied the optical FID of the D lines of atomic sodium. The experimental apparatus is the same as used for the FID in the F_3^+ center, but the signal-to-noise ratio was sufficiently high so that the data were not averaged, and Fig. 4 shows a typical single oscilloscope trace. At a pressure of 3×10^{-5} Torr, we find for the $3p\ {}^2P_{3/2} \leftrightarrow 3s\ {}^2S_{1/2}$ transition at 5889.95 Å, $T_2 = 32 \pm 3$ nsec, which is twice the radiative decay time T_1 of 16.3 ± 0.4 nsec.[21]

The case $T_2 \approx 2T_1$ has also been observed recently in photochemical hole-burning experiments.[22] It contrasts with our earlier measurement of FID in LaF_3:Pr^{3+},[4] where the forbidden ${}^1D_2 \leftrightarrow {}^3H_4$ transition gave a long T_1 (500 μsec), and $\Gamma_\phi >> \Gamma_2$.

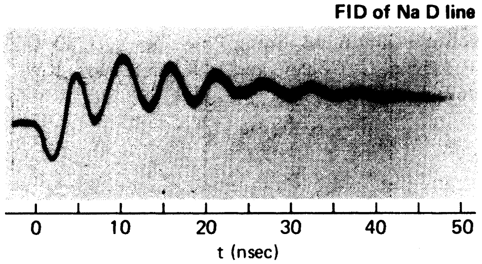

FIG. 4. FID of the D line (${}^2P_{1/2} \rightarrow {}^2S_{1/2}$ at 5889.95 Å) of atomic sodium at 3×10^{-5} Torr.

VI. CONCLUSION

We have measured both the population decay time (T_1) and the dephasing time (T_2) for the zero-phonon transition of the F_3^+ center in NaF at 5456 Å. Below 4 K the dephasing is limited by population-decay processes. Our data are consistent with the relationship $T_2 = 2T_1$, and correspond to a homogeneous linewidth of 16–20 MHz which is much narrower than the inhomogeneous width of 54 GHz. This suggests the possibility of very high resolution spectroscopy of color centers, to study for example, the effect of applied perturbations. The regime of population decay limited dephasing was further explored by optical FID measurements on the D lines of sodium vapor.

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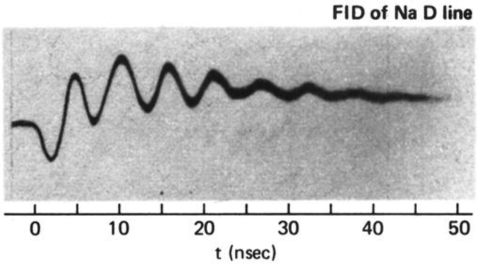

FIG. 4. FID of the *D* line ($^2P_{1/2} \rightarrow {}^2S_{1/2}$ at 5889.95 Å) of atomic sodium at 3×10^{-5} Torr.