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Evidence for the crossover process after optical excitation of the F center in NaI

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Ground-state recovery measurements on the F center in NaI were performed with time resolutions of both 7 ps and 200 fs. The measurements confirm the expectation of an electronic relaxation with a decay time of the order of tens of nanoseconds, which can be associated with a nonradiative transition from the relaxed excited state (RES) at low temperatures. Different from the case of NaBr, the decay channel related to the recapture of conduction electrons cannot clearly be distinguished. This is possibly related to the fact that the available time delay is considerably shorter than the ground-state recovery in the temperature range in which the dominant contribution changes from the component related to the RES lifetime to the retrapping component. Measurements of the ground-state recovery with a 200-fs time resolution show that a very fast relaxation component is present for the F center in NaI. It possesses a time constant of 9 ps at low temperature and its relative contribution with respect to the total induced transparency signal is roughly 33%. The temperature dependence of its time constant follows closely the vibrational lifetime derived from linewidth measurements of the resonant Raman spectrum. This feature is expected for the contribution to the induced transparency arising from an electronic transition during vibrational relaxation, the so-called "crossover process."

I. INTRODUCTION

The F center in alkali halides (an electron trapped at an anion vacancy) is a model system for a bound electron with strong electron-phonon coupling.[1] The energy scheme for the first two electronic states of the F center is presented in Fig. 1 within the commonly used configurational coordinate diagram.

It has been shown that the F center in NaI exhibits a strongly reduced emission efficiency.[2] This feature distinguishes it, together with NaBr and the lithium halides, from the other alkali halides for which a quantum efficiency for the F-center luminescence close to 1 has been established. Clearly, a fast nonradiative process occurs competing with the normal radiative decay, which is known to occur on a microsecond time scale for the other alkali halides. The crossover model[3–5] explained the quenching of the luminescence by an electronic nonradiative transition at the crossing point X of the two potential energy curves during the relaxation of the lattice energy E_R which follows the optical excitation E_0. Doubts on the latter interpretation were cast by $F \to F'$ conversion measurements.[2]

Ground-state recovery measurements with a 7-ps time resolution have been performed for the F center in NaBr.[6] They have shown the presence of two contributions. Based on the temperature dependence of their relative amplitudes, the slowest one has been related to the recapture of electrons released by ionization of F and F' centers. The fastest one, which exhibited a time constant of 6 ns at 10 K, has been associated with the nonradiative relaxation within the F center itself. It has been concluded that the observations were consistent with a sufficiently fast configurational relaxation, such that the relaxed excited state (RES) is reached. The time constant of the fastest decay channel has been associated with the total lifetime of the RES, which involves ionization and nonradiative relaxation. Within the temperature range where the nonradiative relaxation rate could be determined accurately, it has been shown that its temperature dependence is well accounted for by a theoretical expression[7] for nonradiative relaxation from the RES. From this expression the nonradiative transition rate has been estimated for the F center in other alkali halides, and appeared to explain the strong or weak F-center luminescence observed in different host lattices. For the F center in NaI a RES lifetime of the order of 10 ns was predicted at 0 K, which was afterward also observed in preliminary ground-state recovery measurements.[8,9]

In the case of the crossover mechanism the vibrational relaxation is the rate-limiting process and, as such, it would determine the time constant of the ground-state

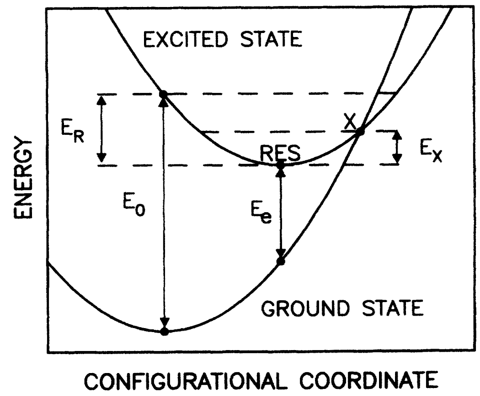

FIG. 1. Configurational coordinate diagram for the ground and excited states of the F center in NaI.

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recovery. To exclude completely that a relaxation process of the *F* center on a time scale of 10 ns is related to the "crossover" mechanism, one should show that the vibrational relaxation occurs much faster. The configurational relaxation in similar systems is known to occur on a picosecond time scale[10–14] or even less.[15] Recently, it has been shown that this is also true in the case of the *F* center in NaI and NaBr.[8,16] This has been established by measuring the linewidth of the main vibrational modes excited after the (vibronic) optical absorption, namely the 114-cm^{-1} and the 137-cm^{-1} modes in the resonant Raman spectrum of the *F* center in NaI and NaBr, respectively. Extrapolated to zero temperature, their linewidth could be related to a vibrational lifetime of 10.5 ps for NaI and 0.6 ps for NaBr. This is indeed some orders of magnitude shorter than the 6-ns relaxation observed in the time-resolved measurements in NaBr.

Although these experiments demonstrate that a large fraction of the excited *F* centers makes the electronic transition from the RES, they cannot exclude a comparable efficiency of the crossover process. The short vibrational lifetime established by the linewidth measurements show that the time resolution used in the measurements of the ground-state recovery was possibly insufficient to resolve the contribution of the crossover process. Therefore, this work studies the ground-state recovery of the *F* center in NaI also with a higher time resolution than before. After giving the details concerning the experimental setup and the preparation of the samples in Sec. II, the relaxation measurements will be presented in Sec. III. The characteristics of the relaxation will be analyzed in Sec. IV and the observed decay components will be associated with the different processes following the optical excitation. Also, it will be argued that extrinsic effects on the *F*-center relaxation due to the presence of H_s^- impurities are sufficiently small, probably because of the relatively small H_s^- concentration used.

II. EXPERIMENTAL DETAILS

The samples of pure NaI were cleaved from a single crystal (Fairlight) and always handled under dry N_2 atmosphere. *F* centers were produced by simultaneous hydrogenation and additive coloration at 540 K for 4 days. The subsequent $2\mathrm{H}_s^- \rightarrow F + \mathrm{H}_2$ conversion was performed by means of a short x-ray irradiation at room temperature (RT) (5–10 s). The samples were hydrogenated at different H_2 pressures ranging from 0.4 bar to 6 bars. No trace of the first overtone of the H_s^- vibration was found in the Raman spectra of the sample which was hydrogenated at 6 bars. This fact indicates that the H_s^- concentration was much lower than in the case of NaBr for which average concentrations of the order of 10^{19} cm^{-3} were obtained.[17]

F-center concentrations of the order of 10^{16} cm^{-3} were created after 5 s of x-ray irradiation at RT. The distribution of *F* centers in a crystal which was hydrogenated at 6 bars of H_2 pressure was checked by means of Raman measurements at several depths under the surface, and appeared homogeneous over the tickness of the samples. This is in agreement with the observation that the *F*-center production is proportional to the H_s^- concentration[17] and that the latter is homogeneous over several millimeters under the surface of the sample.[2]

The ground-state recovery measurements were performed by measuring the transmittance changes induced by a pump pulse on a delayed probe pulse. Part of the measurements was performed using pulses from a Rhodamine-6G dye laser synchronously pumped by a mode-locked Ar$^+$ laser. The time resolution of the experiment is determined by the autocorrelation of the pulses (~7 ps). The typical average power on the sample was 10 mW. A 10-MHz high-frequency intensity modulation was applied to the pump beam, with corresponding lock-in amplifier detection. An enhancement of the resolution was obtained with a frequency-doubled pulse-compressed mode-locked Nd-YAG laser which pumped synchronously a Rhodamine-6G dye laser. The pulses from the dye laser were then compressed by a fiber-prism pulse compressor, achieving a final autocorrelation of about 200 fs. The average power on the sample was of the order of 1 mW at 600 nm. An electro-optical modulator operating at 4 MHz was used in this case. More details about the experimental technique can be found in Refs. 6 and 18.

III. INDUCED-TRANSPARENCY MEASUREMENTS

The ground-state recovery measurements with a time resolution of 7 ps are shown in Fig. 2. The decay of the induced transparency has a characteristic time in the order of tens of nanoseconds below 40 K. A more accurate determination of the decay time below that temperature

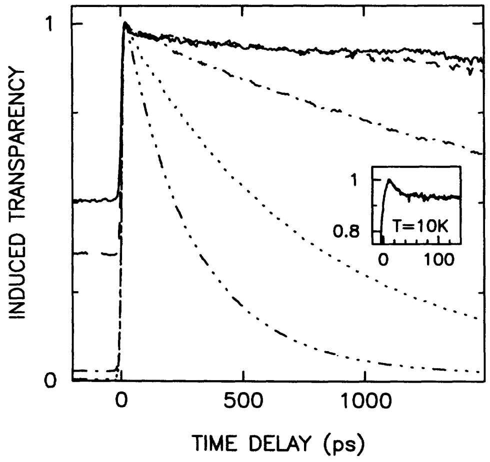

FIG. 2. Decay of the induced transparency of the *F* center in NaI at different temperatures for a sample which was hydrogenated at 0.4 bar: (———) T=10 K, (– – –) T=50 K, (– · –) T=70 K, (· · · · ·) T=90 K, (– · · ·) T=110 K. The wavelength of the excitation pulses was 600 nm and the time resolution 7 ps. The inset shows the decay curve for short delay times at 10 K. A small structure with a width close to the time resolution is visible.

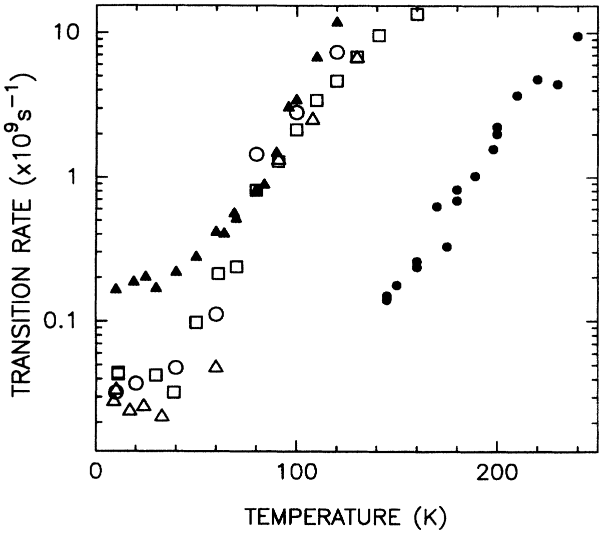

FIG. 3. Comparison of the temperature dependence of the decay times of the main decay component for three different hydrogenation pressures: □ 0.4 bar, ○ 0.7 bar, △ 3 bars. It is compared to the experimental data of Ref. 6 for the F center in NaBr: The solid triangles display the temperature dependence of the RES lifetime, whereas the dots are associated to retrapping of conduction electrons.

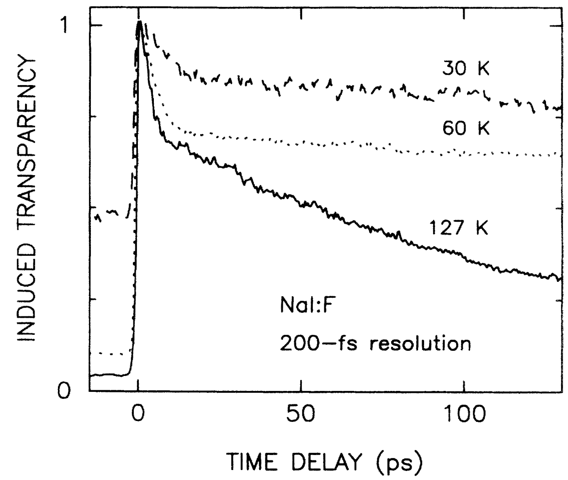

FIG. 4. Decay of the induced transparency of the F center in NaI at three temperatures. The wavelength of the excitation pulses is 600 nm and the time resolution is 200 fs.

is hindered by the limited delay between the pump and the probe pulse achievable with the optical delay stage (about 2 ns). The decay time decreases strongly at temperatures above 50 K, reaching a value of 100 ps at 160 K. The decay time as a function of the temperature is presented in Fig. 3 for three samples hydrogenated at different H_2 pressures, which shows no marked differences.

Closer inspection of the measurements at small time delays yields also a structure with a very small amplitude and with a width close to the 7-ps time resolution (inset in Fig. 2). The observed component could also be an interference spike due to the coherent interaction of the two light beams. Therefore, higher time-resolution measurements are indicated to clarify this point. The ground-state recovery of the F center in NaI with a resolution of 200 fs is presented for the temperature range 20–130 K in Fig. 4. They show the presence of a relaxation component decaying in about 9 ps at 20 K. The time constant of this fast component shortens with increasing temperatures. The accuracy of the values displayed in Fig. 5 is estimated to be ±2 ps. Due to the pulse compression of the dye laser and the lower excitation power, the signal-to-noise ratio is worse than in the measurements with lower resolution. This inevitably affects the accuracy of the analysis of the decay curves and the measurements with 7-ps resolution are superior to characterize the slower relaxation component.

At 20 K, the amplitude of the 9-ps component appears to be 13±3 % of the total induced transparency at zero time delay. The relative contribution of this fast decay channel apparently grows with increasing temperature to a maximum of 33±4 % at 80 K and decreases again above this temperature (Fig. 6). The decay time and the amplitude of the fast contribution can be determined less accurately above 130 K since the time scale of the slower relaxation component progressively approaches that of the fast channel and it turns out less obvious to separate the two contributions. It is even not obvious whether the fastest relaxation component is still present or not. The displayed 15% at 167 K is an upper limit.

At lower temperatures a nonzero signal is observed in Figs. 2 and 4 at negative time delay. A delay just smaller than zero is actually equivalent to a delay equal to the repetition period t_R of the pulse train. The signal can be adjusted in phase with the reference signal from the high-frequency modulation ω at a positive delay $\tilde{t}$, where the fast relaxation component already damped out. Un-

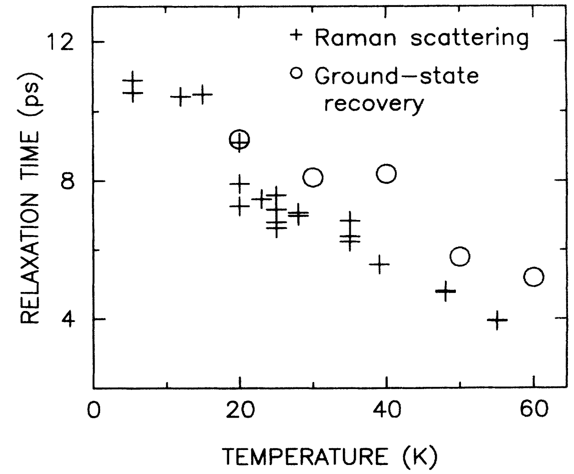

FIG. 5. Decay time of the fast relaxation channel of the F center in NaI as a function of the temperature (○). The values of the inverse linewidth of the gap mode dominating the vibrational resonant Raman spectrum in NaI (Ref. 16) are also reported for comparison (+).

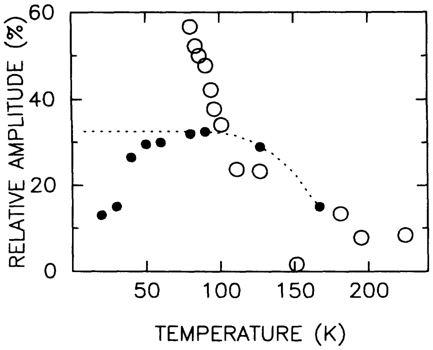

FIG. 6. Intensity of the fast relaxation channel relative to the total induced transparency at zero time delay as a function of the temperature (●), and an estimate of the real values if the relative intensity is corrected for effects of the experimental technique (dotted line). The intensity of the fast channel is compared to $1-\eta_i$ (○), with η_i the ionization efficiency data of Ref. 2.

der the assumption that a single slow decay component is present, the magnitude of the observed signal after a delay t_R is then $\cos[\omega(t_R-\tilde{t})]\exp[-(t_R-\tilde{t})/\tau]$ times the amplitude of the slow decay component at $\tilde{t}$ (cf. Sec. IV D). This way, the signal at negative time delay can be used to estimate the relaxation time of the slow decay component. The cosine arises from the phase shift introduced by the time delay.

IV. DISCUSSION

A. Extrinsic effects

Since the presence of H_s^- ions cannot be totally eliminated, an influence on the decay times by such impurities cannot be excluded *a priori*. It has been shown for NaBr that the lifetime of the relaxed excited state is reduced in samples with an average H_s^- concentration of about 10^{19} cm^{-3}.[17] In particular, after aggregation of the F center with the H_s^- impurity [$F_H(H_s^-)$ center] by an F-light bleach the 6-ns relaxation time of the unperturbed F center is lowered to ~290 ps.[8,17] In NaI, however, the concentration of hydrogen impurities which can be introduced in the crystal by simultaneous hydrogenation and additive coloration is considerably lower. This is related to the intrinsic inefficiency of the additive coloration process in comparison with NaBr and to the lower alkali vapor pressure due to the lower melting point of NaI. The decay times for the NaI crystals, which were treated at different H_2 pressures, are compared in Fig. 3. There is no clear correlation between the hydrogenation pressure and the relaxation time. As such, the influence of hydrogen impurities on the decay time of the slower relaxation component of the F center is only limited.

Association of the fastest relaxation component with an H_s^--F-center aggregate and the slower one with the unperturbed F center is very unlikely for several reasons: (i) The temperature during the optical measurements was limited on purpose to 170 K to prevent aggregation. (ii) For a random distribution of F centers and H_s^- impurities, the fraction of F-centers forming to a $F_H(H_s^-)$ center would be much smaller than the one suggested by the relative amplitudes of the two decay components at the low hydrogen concentrations used. (iii) Aggregate formation is difficult in the case of NaI. Attempts to produce $F_H(H_s^-)$ centers have never succeeded in NaI (cf. also Ref. 19). In contrast to the case of NaBr,[17] no splitting of the F-center gap mode in the resonant Raman spectrum was observed after F-light bleaching at high temperatures, neither was a shift of the F-band absorption. Therefore, the two observed relaxation components can be considered as intrinsic features of the F center.

B. Lifetime of the relaxed excited state and crossover process

As was the case for NaBr,[6] one also deals with two decay components in the ground-state recovery measurements of the F center in NaI. For NaBr the fastest and slowest channel have been attributed to the lifetime of the RES and to retrapping of electrons released by ionization, respectively. This attribution does not apply to the decay components observed for NaI for the following reasons. (i) If the nonradiative relaxation occurs from the RES, one expects a time constant in the order of 10 ns, as was the case for NaBr. The time constant of the fastest component in NaI is ~ $10^3\times$ smaller than the one observed in NaBr. (ii) The contribution arising from retrapping of conduction electrons is expected to be small below 50 K, since the ionization efficiency is small in that temperature range. In contrast to the case of NaBr, the slowest decay component already dominates at the lowest temperatures in NaI. The observation of a very small amplitude for the fast component at the lowest temperatures is somewhat misleading, as will be explained in Sec. IV D. Although its actual amplitude is larger than the observed one, the slowest decay component has still the largest amplitude.

Below 50 K the thermal excitation of electrons from the excited state to the conduction band can be neglected[2] and one can restrict oneself at low temperatures to the relaxation processes to the F-center ground state, namely, the crossover process and the nonradiative transition from the RES. Figure 5 compares the temperature dependence of the fast decay time with the configurational relaxation time. The latter was derived from the inverse linewidth of the gap mode, which dominates the resonant Raman spectrum of the F center in NaI and which is the most important vibrational mode coupling to the F-center electron. The decay time of the fast channel follows closely the behavior of the inverse linewidth of the gap mode. This is exactly what one expects for the time evolution of the contribution from the crossover process to the induced-transparency measurements, since the ground-state recovery is in this case rate limited by the vibrational relaxation. In order to determine the characteristic time of the process, the decay has been assumed to be exponential. The relaxation from the nth vibrational level is expected to be not purely exponential.[20] This probably affects the accuracy with which the relaxation time can be determined. Also, at higher temperatures other line-broadening processes possibly contribute to the linewidth of the gap mode.[16] For that reason the inverse linewidth may be expected to exhibit a more pronounced temperature dependence than the decay time. The nonradiative transition from the RES was estimated to occur on a time scale of 10 ns from a theoretical expression for horizontal vibronic tunneling.[6,7] Also, assuming that the F center reaches the RES with a probability equal to 1, a lifetime τ=27 ns at low temperatures was derived[6] from the experimental emission efficiency[2] η_e and the expected radiative lifetime τ_r=5.3 μs:[21]

$$\tau_r = \eta_e^{-1} \tau = 3\mu s . \tag{4.1}$$

When the efficiency to reach the RES is smaller than 1, the RES lifetime is correspondingly larger. The time constant of the slow decay component is in the order of magnitude estimated from Eq. (4.1) and can therefore be interpreted as the lifetime of the RES, at least at temperatures below 50 K. The uncertainty on the values for Eq. (4.1) is large enough to allow for a contribution from the crossover process with a comparable efficiency.

C. Retrapping of conduction electrons

At temperatures higher than 50 K the optically excited F centers are thermally ionized and the released electrons can be trapped at another F center, forming an F' center.[2] The F' centers are ionized when excited in their absorption band. The conduction electrons thus created at higher temperatures are expected to give rise to a relaxation component in the ground-state recovery measurements. In the case of NaBr a slower decay component, activated at higher temperatures, was indeed observed and related to the retrapping of conduction electrons.[6] The situation in NaI is different, since there is only clear evidence for two components which were related in Sec. IV B to the lifetime of the RES, at least at low temperatures, and to the crossover process. A slowly decaying signal with a relative amplitude less than 10% shows up above 100 K in some series of measurements. In most of the samples, treated under several different H_2 pressures and containing largely differing F-center concentrations, this component is absent. Therefore, it is probably not related to retrapping of conduction electrons by vacancies or F and probably even not associated to F or F' centers at all.

One might argue that the decay component related to retrapping of conduction electrons could be reduced due to much smaller overlap of the F and the F' absorption bands in NaI than in NaBr. This implies that under F-band excitation at 600 nm a negligible amount of F' electrons is ionized to the conduction band. Nevertheless, one expects that at sufficiently high temperatures most of the excited F centers produce a conduction electron. It can therefore not explain the absence of the decay component related to retrapping. A possible explanation for the situation in NaI is the following. In NaBr the relaxation component due to retrapping starts to dominate from about 100 K on, where the lifetime of the RES is considerably slower than 1 ns and can be distinguished from the much slower retrapping rate. Due to the smaller activation energy for ionization in NaI, the retrapping component can already be the dominating one at lower temperatures than in NaBr. Up to 70 K, the observed decay of the induced transparency is still much slower than 1 ns and also slower than in the case of NaBr. Therefore it is possible that below this temperature both the component associated to the lifetime of the RES and the one related to retrapping of conduction electrons are present for the F center in NaI, but that we cannot distinguish them in the limited time-delay range (~2 ns) available with our optical delay stage. This implies that at 10 K the relaxation rate displayed in Fig. 3 must be attributed to the processes which limit the lifetime of the RES, whereas at temperatures well above 70 K, the relaxation rate corresponds to the retrapping of conduction electrons. In this case the analysis of the ionization rate reported in Ref. 9 should be considerated with some more caution, since in that paper the decay times have been interpreted as the lifetime of the RES over the whole temperature range. Comparison of the relaxation rate observed in NaI with those in NaBr for the two different decay channels shows that at higher temperatures the observations in NaI lie close to those associated with the RES lifetime in NaBr and are 100 times faster than retrapping rates in NaBr. Retrapping rates, however, are known to depend strongly on the host crystal.[22]

D. Efficiency of the crossover process

In Sec. IV B we obtained experimental evidence for the occurrence of the crossover process, proposed by Bartram and Stoneham[3] to explain the quenching of the intrinsic F-center luminescence. Different from their original proposal the crossover process turns out to possess only a limited efficiency, since a relaxation channel from the RES is observed in the ground-state recovery measurements with a comparable amplitude. The analysis of the intensity of the fast relaxation channel relative to the total induced transparency at zero delay suggests a smaller effect of the crossover process at lower temperatures (Fig. 6). This observation seems in contrast to the expected tendency, since at lower temperatures the vibrational lifetime is longer and a longer vibrational lifetime increases the efficiency of the crossover process.[16] However, one should take into account correctly effects of the experimental technique on the relative amplitudes of the observed relaxation components. The relaxation component related to the RES lifetime possesses a time constant longer than or comparable to the repetition period of the excitation pulses (12 ns). On the one hand, its amplitude relative to the one of the much faster decay component is therefore increased, due to the accumulation of the excitation from different pulses. On the other hand, the accumulation effect is limited by the high-frequency intensity modulation and phase-sensitive detection. One actually subtracts the probe-beam intensity with the pump beam on and off, respectively. Only part of the total excitation is thus observed for a component decaying slower than the modulation period.

Applying a pump and probe pulse train, with a repetition period t_R and δ-shaped pulses, and modulating the pump beam with a frequency ω, the output signal of a lock-in amplifier $S(t,\varphi)$ for a time delay t between pump and probe beam is proportional to

$$S(t,\varphi) \sim \sum_{i=1}^{n} A_i \frac{\cos(\omega t-\varphi)-\exp(-t_R/\tau_i)\cos(\omega t-\omega t_R-\varphi)}{1+\exp(-2t_R/\tau_i)-2\exp(-t_R/\tau_i)\cos(\omega t_R)}\exp(-t/\tau_i)\ . \tag{4.2}$$

A_i are the amplitudes in a single-shot experiment of the decay components with time constant τ_i. φ is the phase difference between the reference signal of the electro-optical modulator and the modulated signal on the probe-beam intensity and can be adjusted by the lock-in amplifier to obtain a maximum in-phase signal at a particular time delay. Assuming a single exponential decay, its amplitude at zero time delay is proportional to

$$A\left[1+\exp(-2t_R/\tau)-2\exp(-t_R/\tau)\cos(\omega t_R)\right]^{-\frac{1}{2}}\ , \tag{4.3}$$

if the phase is adjusted at $t = 0$. For a relaxation time much shorter than the repetition period of the pulse train, the amplitude is proportional to A. For a time constant much longer than the modulation period, (4.3) converges to $1.3A$ and $3.3A$ in the case of a 10-MHz and a 4-MHz intensity modulation of the pump beam, respectively. The requirement for the phase adjustment is that

$$\tan\varphi = \frac{\sin(\omega t_R)}{\exp(t_R/\tau)-\cos(\omega t_R)}\quad . \tag{4.4}$$

Apparently, a phase shift is introduced depending on the observed relaxation time. This effect is similar to the phase shift between a modulated excitation and the resulting modulated emission, which has been used to measure emission lifetimes.[23] Dealing with two strongly differing time constants in our measurements, it is not possible to adjust the phase such that the amplitudes of both decay components are maximum simultaneously. This favors the component with the strongest amplitude at the time delay, at which the phase adjustment is performed. It decreases the relative amplitude of a smaller fast relaxation component with respect to a slow one, especially if the phase adjustment is not performed at zero time delay. The accumulation of the excitation of subsequent pump pulses (4.3) always increases the relative amplitude of the slower relaxation component with respect to the one of a single-shot experiment. The effect is larger for smaller modulation frequencies and for a larger time constant of the slower component.

An earlier attempt to observe the crossover process[24] concentrated on low temperatures, where its efficiency is expected to be largest. However, at 10 K the time constant of the slow relaxation component is several times the repetition period of the pulse trains. Due to the features of the experimental technique described above, together with increasing noise in the measurements at the lowest temperatures, the presence of the fast relaxation component remained unnoticed in that work.

Analysis of the relaxation times of Figs. 3 and 5 and the measured amplitudes of Fig. 6 (4-MHz modulation) by means of expression (4.2) results in an actual amplitude for the fast relaxation component which is almost constant below 80 K (dotted line in Fig. 6). Obviously, the difference between the observed and the actual amplitude is largest below 50 K. With increasing temperatures the decay time of the slow component shortens below 12 ns (Fig. 2) and the effect of the accumulation of this channel disappears. These considerations remove the contrast between the observed amplitude of the fast relaxation component and the expected temperature dependence of the crossover efficiency. The inaccuracy of the slow decay constant below 50 K does not allow for an accurate determination of the actual amplitudes. Taking 100 ns as a concervative upper limit for the slow decay constant, the maximum efficiency of the crossover process is 50%.

Usually, it is assumed that the ionization of the F center occurs from the RES. The ionization rate and the nonradiative relaxation rate from the RES can then be derived from the experimental RES lifetime, the ionization efficiency η_i, and the efficiency of the crossover process η_{co}.[9] The nonzero efficiency of the crossover process η_{co} imposes the following restriction on the ionization efficiency: $1-\eta_i \geq \eta_{\mathrm{co}}$, since an F center making the crossover transition to the ground state cannot ionize any more. Comparison of the amplitude of the fast channel with the ionization efficiency data[2] η_i (Fig. 6) shows that this inequality is fulfilled, if one considers the absolute error of 5% on the amplitude and the scatter in the data points of the ionization efficiency measurements above 100 K.

The efficiency of the crossover process has been estimated theoretically in Ref. 16 for the F center in NaBr and NaI. For the latter case it turned out to depend critically on the electronic transition rate. For the calculations the vibrational relaxation rate derived from linewidth measurements of the resonant Raman spectrum was used and it was assumed that the vibrational relaxation rate in the ground and excited electronic state was equal. Strictly speaking, the Raman data yield information about the ground state of the F center and the effective phonon frequencies and relaxation rates in the ground and the excited states are different in general. The present results exclude the fact that the vibrational relaxation in the excited state is much slower than in the ground state, which would imply a higher efficiency than estimated in Ref. 16. This would also imply that the rate-limiting process in the ground-state recovery is the vibrational relaxation in the electronic excited state, whereas the results of Fig. 5 show that the time scale of the ground-state recovery corresponds to the vibrational lifetime in the ground state. A shorter lifetime in the excited state is still possible and it is also more likely. An increase of the vibrational frequency in the excited state may be expected from the outward relaxation of the nearest neighbors of the F center.[1,25,26] Even a small increase of the effective frequency would move the gap mode into the optical phonon band, thus increasing its coupling to the phonon modes.[27] The broader width of a resonant mode in the optical phonon band with respect to the one of a gap mode is illustrated, e.g., if one compares the width of the 114-cm^{-1} mode and the 137-cm^{-1} mode in NaI and NaBr, respectively[16] (cf. also Ref. 28).

V. CONCLUSION

Ground-state recovery measurements with a 7-ps and 200-fs time resolution were performed for the F center in NaI. Two components could be distinguished: a large component with a decay constant of the order of tens of nanoseconds at low temperatures which, similar to the case of NaBr, can be associated with the transition from the relaxed excited state (RES); a smaller and much faster one (9.5 ps at 20 K) is shown to be related to the so-called "crossover mechanism" of nonradiative electronic relaxation during the vibrational relaxation following the optical excitation. The contribution of the fast decay component relative to the slower one results to be about 1:2. This means that about two-thirds of the excited F centers reach the RES, from where the competition between nonradiative transition to the ground state, thermal ionization to the conduction band, and radiative decay determine the lifetime of the excited state.[29] The latter appears to be in agreement with the emission efficiency measurements of Ref. 2. Also the observed efficiency of the crossover process is consistent, within the experimental accuracy, with the $F \rightarrow F'$ conversion efficiency data of that work. Within the limited range of the available time delay the relaxation component related to retrapping of conduction electrons remains probably indistinguishable from the one related to the lifetime of the RES, due to the longer lifetime of the F center in NaI and the lower activation energy for ionization than in NaBr.

An extension of the ground-state recovery measurements with subpicosecond time resolution to the case of the F center in NaBr would be interesting. The higher time resolution than the 7 ps in Ref. 6 is indispensible because one expects a still faster vibrational relaxation rate than for the F center in NaI. Due to this reason, one also expects for NaBr a smaller efficiency of the crossover process than in the case of NaI. An attempt has been made for such an experiment on the F center in NaBr. Because of the weak excitation power after pulse compression and the fact that with the available equipment we can only excite in the tail of the F band in NaBr, we could not obtain a reliable signal. The results in this paper are also relevant to the case of nonradiative relaxation of F centers perturbed by molecular impurities.[30] Even in host crystals with intrinsic F-center luminescence the vibrational states of molecular impurities create new crossing points.[31] According to the Dexter-Klick-Russell criterion[3] these may result in radiationless electronic relaxation during vibrational relaxation in the excited state. The excitation spectra for vibrational luminescence of CsBr:$F_H(\text{CN}^-)$, e.g., show that electronic relaxation of the F center during vibrational relaxation is a possible relaxation channel.[31] A similar conclusion results from a calculation of the energy surfaces of the $F_H(\text{CN}^-)$ center.[32] The present study shows that the 60-ps resolution of the transient absorption measurements in Ref. 33 is very probably insufficient to observe such a relaxation channel.

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[1] W.B. Fowler, in *Physics of Color Centers*, edited by W.B. Fowler (Academic, New York, 1968), p. 53.

[2] G. Baldacchini, D.S. Pan, and F. Lüty, Phys. Rev. B **24**, 2174 (1981).

[3] R.H. Bartram and A.M. Stoneham, Solid State Commun. **17**, 1593 (1975).

[4] C.H. Leung and K.S. Song, Solid State Commun. **33**, 907 (1980).

[5] R.H. Bartram, J. Phys. Chem. Solids **51**, 641 (1990).

[6] F. De Matteis, M. Leblans, W. Joosen, and D. Schoemaker, Phys. Rev. B **45**, 10 377 (1992).

[7] R. Englman and J. Jortner, Mol. Phys. **18**, 145 (1970).

[8] M. Leblans, F. De Matteis, E. Gustin, and D. Schoemaker, in *Proceedings of the XII International Conference on Defects in Insulating Materials*, Schloss Nordkirchen, Germany, 1992, edited by O. Kanert and J.M. Spaeth (World Scientific, Singapore, 1993), Vol. 1, p. 446.

[9] F. De Matteis, M. Leblans, and D. Schoemaker, J. Lumin. **60&61**, 563 (1994).

[10] M. Dominoni and N. Terzi, Europhys. Lett. **15**, 515 (1991).

[11] R.R. Alfano and S.L. Shapiro, Phys. Rev. Lett. **26**, 1247 (1971).

[12] A. Laubereau, D. von der Linde, and W. Kaiser, Phys. Rev. Lett. **27**, 802 (1971).

[13] J.M. Wiesenfeld, L.F. Mollenauer, and E.P. Ippen, Phys. Rev. Lett. **47**, 1668 (1981).

[14] W.H. Knox and K.J. Teegarden, J. Lumin. **31&32**, 39 (1984).

[15] Y. Mori and H. Ohkura, J. Phys. Chem. Solids **51**, 663 (1990).

[16] F. De Matteis, M. Leblans, and D. Schoemaker, Phys. Rev. B **49**, 9357 (1994).

[17] E. Gustin, M. Leblans, A. Bouwen, and D. Schoemaker, Phys. Rev. B **49**, 916 (1994).

[18] C. Sierens, W. Joosen, and D. Schoemaker, Phys. Rev. B **37**, 3075 (1988).

[19] D.S. Pan and F. Lüty (unpublished).

[20] J. Jortner, Philos. Mag. B **40**, 317 (1979).

[21] G. Spinolo, Phys. Rev. **137**, A1495 (1965).

[22] G. Dokter and H.J. Hoffmann, Phys. Status Solidi B **76**, 241 (1976).

[23] L.F. Mollenauer, N.D. Vieira, and L.H. Szeto, Phys. Rev. B **27**, 5332 (1983).

[24] M. Leblans, F. De Matteis, W. Slootmans, and D. Schoemaker, Bull. Am. Phys. Soc. **38**, 468 (1993).

[25] R.F. Wood and H.W. Joy, Phys. Rev. **136**, A451 (1964).

[26] M. Leblans, W. Joosen, and D. Schoemaker, Phys. Rev. B **42**, 7220 (1990).

[27] R.H. Bartram (private communication).

[28] A.S. Barker, Jr. and A.J. Sievers, Rev. Mod. Phys. Suppl. 2 **47**, 106 (1975).

[29] R.K. Swank and F.C. Brown, Phys. Rev. Lett. **8**, 11 (1962); Phys. Rev. **130**, 34 (1963).

[30] Y. Yang and F. Lüty, Phys. Rev. Lett. **51**, 149 (1983); F. Rong, Y. Yang, and F. Lüty, Cryst. Lattice Defects Amorph. Mater. **18**, 1 (1989); G. Halama, K.T. Tsen, S.H. Lin, F. Lüty, and J.B. Page, Phys. Rev. B **39**, 13 457 (1989).

[31] F. Luty and V. Dierolf, in *Proceedings of the International Conference on Defects in Insulating Materials,* Schloss Nordkirchen, Germany, 1992, edited by O. Kanert and J.M. Spaeth (World Scientific, Singapore, 1993), Vol. 1, p. 17.

[32] K.S. Song, L.F. Chen, P.Q. Tong, H.W. Yu, and C.H. Leung, in *Proceedings of the International Conference on Defects in Insulating Materials*, Schloss Nordkirchen, Germany, 1992, edited by O. Kanert and J.M. Spaeth (World Scientific, Singapore, 1993), Vol. 1, p. 449.

[33] D. Samiec, A. Katerkamp, H. Stolz, and W. von der Osten, in *Proceedings of the International Conference on Defects in Insulating Materials*, Schloss Nordkirchen, Germany, 1992, edited by O. Kanert and J.M. Spaeth (World Scientific, Singapore, 1993), Vol. 1, p. 548.