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Nonradiative relaxation and ionization of the F center in NaBr studied with picosecond optical pulses

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With a picosecond pump-probe laser technique the recovery of the ground-state population after optical excitation of the F center in NaBr is studied. Two decay components are observed, the fastest one dominating at low temperatures. Its time constant is interpreted as the lifetime of the relaxed excited state and is established to be 6±1 ns at 10 K. This value is perfectly consistent with the experimental emission efficiency and the expected radiative lifetime, provided that the nonradiative transition to the ground state is assumed to occur *after* the relaxed excited state is reached. Within the same assumptions a nonradiative lifetime of 27 ns at zero temperature is predicted for the F center in NaI. A theoretical expression for vibronic tunneling to the ground state from a thermalized excited state is applied to the F center in alkali halides and is shown to agree equally well with the experimental emission efficiencies as the Dexter-Klick-Russell criterion. The same expression also accounts for the strong temperature dependence of the nonradiative relaxation process observed in NaBr below 100 K. At higher temperatures an accurate analysis of the radiationless transition rate is encumbered by the influence of ionization on the lifetime of the excited state. The relative contribution of the second, much slower decay component increases rapidly above 70 K and is related to retrapping of electrons released by ionization of F and F' centers.

I. INTRODUCTION

After optical excitation in its main absorption band, the F centers in the potassium and the rubidium halides relax radiatively with a quantum efficiency very close to one.[1,2] The lifetime of the first excited state is typically of the order of ~1 μs at low temperatures and it was determined from the time evolution of the luminescence or photoconductivity after exciting pulses of nanosecond duration,[1–3] and by single photon counting techniques.[4] Perturbing the F center, the luminescence is often quenched as a result of much faster nonradiative processes. At high-power resonant optical excitation, energy transfer between excited F centers has been established in KI.[5,6] Also, the intramolecular vibrational mode of CN^- and OH^- impurities were observed to accept the electronic energy of the F center efficiently.[7–9] In the case of F-center aggregation in KCl, picosecond F-center decay is explained by $F \rightarrow F_2$ radiationless energy transfer.[10]

In contrast, the absence of luminescence in the earlier investigations of the F center in the lithium halides, NaI, and NaBr was believed to be an intrinsic feature of the *pure* and *dilute* F-center system in these host crystals. Bartram and Stoneham demonstrated it to be in agreement with the Dexter-Klick-Russell (DKR) criterion.[11] According to the DKR rule,[12] nonradiative deexcitation during lattice relaxation of the optically excited F state should occur, whenever the energy reached in the vertical optical transition lies above the crossing point of the potential energy curves of the ground and the excited states (Fig. 1). The nonradiative electronic relaxation near the crossover point has been theoretically investigated, yielding indeed quantum efficiencies of the order of a few percent for the cases, in which no luminescence had been observed.[13–16] Afterward, luminescence has been observed for both LiCl (Refs. 17 and 18) and NaBr (Ref. 19) and decay times comparable to those of the other F centers were established. A more recent investigation of the F center in NaBr casts doubt on the interpretation of the latter measurements, since two different emission signals at 1200 and 2000 nm with very small quantum efficiencies were reported, the latter corresponding to the normal optical cycle relaxation.[20] A 330-ps nonradiative decay time for the F center was estimated from the temperature dependence of the $F \rightarrow F'$ conversion efficiency. Moreover, it is argued in the latter work that the system reaches the relaxed exited state (RES), *before* horizontal vibronic tunneling to the ground state occurs.

At higher F-center concentrations, the situation is more complex: The excited F-center electron may tunnel to another F center to form an F' center. The back-tunneling from the F' center to the unrelaxed F-center ground state has also been observed for a number of host crystals, but it is absent for NaI and NaBr.[20] At higher temperatures, the F-center electron is believed to be thermally excited from the optically excited state to the conduction band. Afterward, it is trapped again in an empty anion vacancy or either by an F center, to form an F' center. Recently, Georgiev showed that the temperature dependence of the $F \rightarrow F'$ conversion at low F-center concentrations could also be accounted for by a

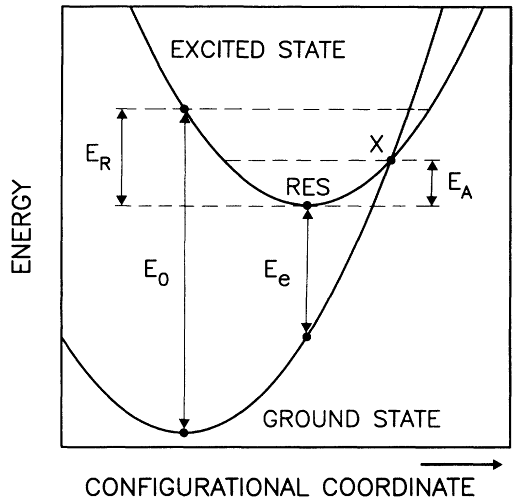

FIG. 1. Configurational coordinate diagram for the ground and the excited state, appropriate to F centers possessing intrinsic luminescence quenching. The figure shows the absorption energy (E_0), the configurational relaxation energy after optical excitation (E_R), the activation energy (E_A) from the relaxed excited state (RES) to the crossover point (X), and the emission energy (E_e).

vibronic tunneling process of the excited F-center electron to a polaron state, bound to another F center.[21,22] Since this process is exothermic, it explains the nonvanishing $F \rightarrow F'$ conversion at low temperatures in NaI and NaBr.[20]

A more detailed description of the processes and the models involved, is found in Refs. 22 and 23. We have investigated the relaxation behavior of excited F centers in NaBr with ps optical pulses over a wide temperature region. A pump pulse at $t_D = 0$ excites the F center. A delayed probe pulse senses the time evolution of the transparency induced by the pump, and as such, it detects the recovery of the ground-state population. This experimental approach[24] has three important features: (i) The picosecond time resolution is higher than the one of earlier photoconductivity or luminescence measurements, which was typically a few tens of nanoseconds (ns); (ii) by measuring transient absorption properties one circumvents the experimental difficulty of measuring the time evolution of a luminescence signal at 2 μm, which possesses at the same time a low quantum efficiency and a fast time response; (iii) by interrogating the time evolution of the excitation induced by the pump beam, there is no discrimination between the normal optical cycle F-center decay and other processes. In particular, $F \rightleftharpoons F'$ conversion also affects the absorption of the probe beam: The F'-center absorption overlaps the F band, and the creation of an F' center necessarily implies the destruction of an F center.

After giving the details concerning the experimental setup and the samples used in Sec. II, the relaxation measurements will be presented and their characteristics will be analyzed in Sec. III. It will be argued in Sec. IV that extrinsic effects on the F-center relaxation can be neglected. Section V A concentrates on the low-temperature relaxation, where the fastest decay component dominates. It will be discussed whether the nanosecond decay time arises from a nonradiative electronic transition during or after configurational relaxation to the relaxed excited state. The effects of temperature on the nonradiative transition rate, ionization, and recapture of conduction electrons are discussed in Sec. V B. In Sec. V C the theoretical expression for horizontal vibronic tunneling from a thermalized excited state, due to Englman and Jortner,[25] is applied to the F center in alkali halides and to the F center in NaBr, in particular.

II. EXPERIMENTAL DETAILS

The NaBr crystals were always handled under dry N_2 atmosphere. Freshly cleaved samples ($\sim 10 \times 5 \times 1.5$ mm^3) were quenched to room temperature from 600 K. The F-center concentration was monitored with a spectrophotometer (CARY05). F centers were produced by x-ray irradiation at room temperature for $\frac{1}{2}$ h (50 kV, 50 mA) in samples containing traces of OH^-. The relatively high F-center concentration obtained ($\sim 10^{17}$cm^{-3}) is possibly a consequence of the impurity content.[26] Pure NaBr (grown at the Crystal Growth Laboratory of the University of Utah and at the University of Rome, La Sapienza) was colored by x-ray irradiation and additive coloration. In the pure crystals the concentration is limited to $\sim 10^{16}$cm^{-3}.[20] In these samples the resonant Raman spectra at several depths under the surface showed a rather homogeneous F-center concentration for both F-center production methods.

The pump-probe setup for picosecond time-resolved measurements has been described in detail in Ref. 24. Two slightly different excitation configurations have been used. (i) The pump and probe beam originate from two synchronously pumped Rhodamine 6-G (R6G) dye lasers, tuned at slightly different wavelengths ($\Delta\lambda \sim 5$ nm). After interaction in the sample, pump and probe are separated spectrally. (ii) The output beam of a single R6G dye laser or of a frequency-doubled pulse-compressed mode-locked YAG laser is split into a pump and a probe beam with mutually orthogonal polarizations. Their angle of incidence on the sample is slightly different. Before detection, the probe beam is isolated both by an analyzer and a pinhole. Depending on cases (i) and (ii) the time resolution is 20 and 7 ps, respectively. The spectral range of the dye lasers coincides with the tail of the F-center band (λ_{max}=523 nm, FWHM of 65 nm at 10 K) and falls well within the F'-center band, which possesses nearly the same maximum position but which is much broader.[20] The 532-nm excitation of the frequency-doubled YAG laser is close to the maximum of both the F and the F' band. The average excitation power used is typically 10 mW. The double modulation and phase-sensitive detection allows one to measure relative intensity changes of the probe beam, induced by the pump, down to 10^{-7}.[24]

III. CHARACTERISTICS OF THE RELAXATION MEASUREMENTS

In Fig. 2 typical relaxation measurements are depicted. At 10 K a decay with a characteristic time of (6±1) ns is observed. This process is strongly thermally activated above 70 K yielding a picosecond decay time, which shortens beyond resolution above 160 K. We will indicate this process as channel 1 (CH1). At temperatures above 100 K the time-delay scans markedly exhibit a second component (CH2), which appears as a nearly constant background for CH1 in the 100-K spectrum (Fig. 2). The characteristic time of this second contribution at 100 K is too long to be determined with the optical delay stage, which permits a maximum retardation of the interrogating pulse of 1.6 ns. However, for temperatures above 160 K, the decay time of CH2 lies in the ps region. In this temperature region both decay signals can be easily distinguished, since CH1 is reduced to a fast transient, i.e., the sharp peak at zero delay (Fig. 2). The contribution of CH2, relative to the total induced transparency at zero time delay, is shown in Fig. 3 as a function of temperature. Apparently, the increase of the amplitude of CH2 with respect to that of CH1 with increasing temperature is correlated with the increasing *F*-center ionization after optical excitation. The F-center ionization efficiency is equal to half the optical *F*-to-*F*′-conversion efficiency measured in Ref. 20.

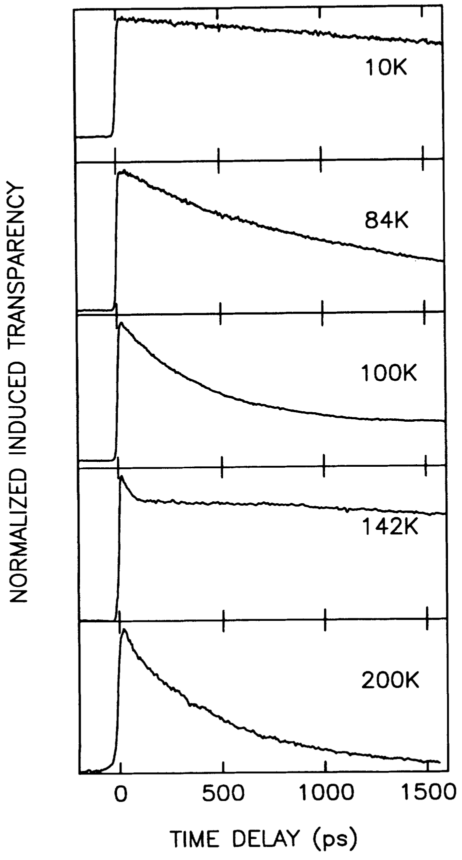

FIG. 2. Decay of the induced transparency of the *F* center in NaBr at different temperatures. The wavelength of the excitation pulses is 580 nm.

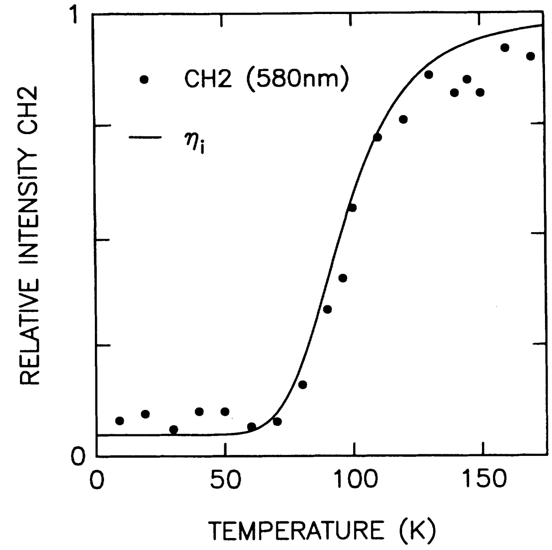

FIG. 3. Intensity of decay channel 2 (CH2) relative to the total induced transparency at zero time delay, compared with the thermal ionization efficiency ν_i after optical excitation of the *F* center in NaBr. For the ν_i curve the results of Ref. 20 are used.

Below 120 K and for sufficiently large delay times above 150 K, the time-delay scans mainly reflect one decay channel, and fitting to a single exponential function is appropriate. For the case of isolated CH1 decay curves, the background is associated with the nonvarying (on ps time scale) amplitude of CH2. In the temperature region between 100 and 160 K, the spectra were fitted to a double exponential decay or to one exponential decay on a linearly decreasing background. The consistency of the

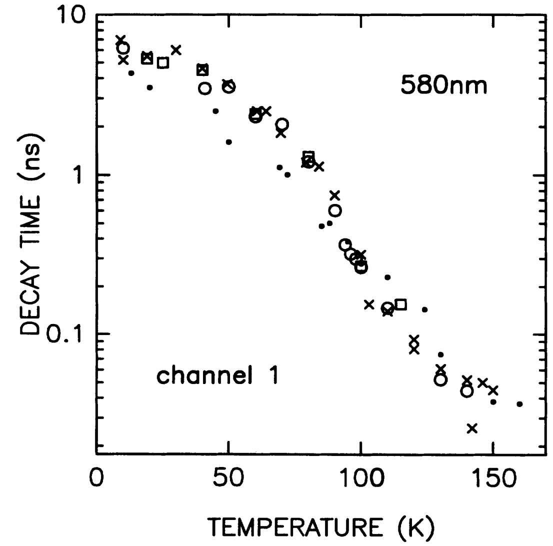

FIG. 4. Decay time of the fastest relaxation channel (CH1) of the *F* center in NaBr as a function of temperature and for different samples. (i) NaBr, trace OH$^-$ (●). Pure NaBr: (ii) x-ray irradiated (×), (iii) additively colored (○), (iv) additively colored, well aged, and exposed to light at high temperatures (□).

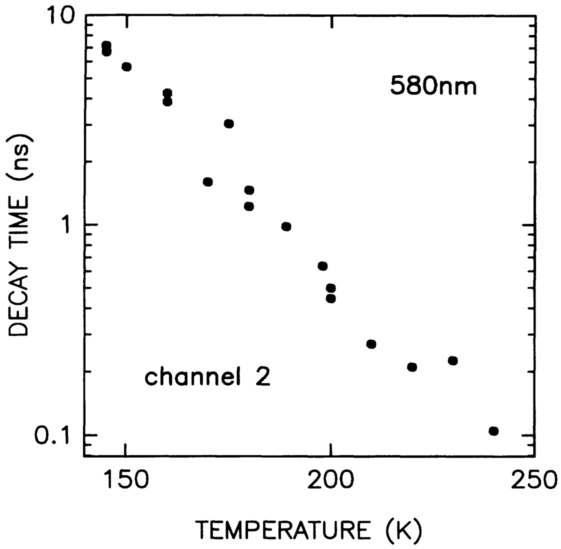

FIG. 5. Decay time of the slowest channel (CH2) of the F center in NaBr as a function of temperature, from measurements on x-ray irradiated, and additively colored pure NaBr.

results obtained from different fit functions was extensively checked, together with the reproducibility of the decay times of CH1 and CH2 for several experiments. The accuracy of the relaxation times is established to be about 15%. The decay times as a function of temperature for CH1 and CH2 are presented in Figs. 4 and 5, respectively.

The majority of the data is obtained under 570- to 590-nm excitation, which lies in the low energy tail of the F-center band. Measurements were also performed under 532-nm excitation, close to the F-band maximum, as well as under 630-nm excitation, which is out of the F band but still within the F' band. Comparison of all these data shows that the relaxation times obtained are essentially independent of the excitation wavelength. The fact that the decay times do not depend on whether F or F' centers are excited, is not surprising, since their transient absorption properties are expected to be closely interrelated through the $F \rightleftharpoons F'$ conversion (see also Sec. I). It was verified that the same decay curves are observed for mutually parallel and perpendicular polarizations of the pump and probe beams, as should be the case for an isotropic center.

IV. EFFECT OF EXTRINSIC RELAXATION PROCESSES

It has been demonstrated that impurities may have drastic effects on the F-center decay. In particular, this is true for OH^- defects in KCl at concentrations above 1000 ppm.[7,27] To exclude the possible influence of unwanted impurities on the relaxation data, we compared the decay measurements on crystals from different origins and colored by different F-center production methods (Fig. 4). The decay times obtained show no essential differences. Also, the maximum and the width of the F-center absorption band, which may be an indication for the impurity content, agrees with the one of Ref. 20.

For the crystal, nominally doped with 0.1 wt% of OH^-, a decrease of the decay time from 6 ± 1 ns to 4 ± 1 ns has been observed at 10 K (Fig. 4). This is only a very small effect on the lifetime of the excited F center, compared to the reduction of some orders of magnitude observed in KCl.[7,27] The nonobservability in Raman scattering of the OH^- stretching vibration at 3600 cm^{-1} yields, by comparison with the signal intensity in alkali halide crystals with well-known amounts of OH^- and OD^-, an upper bound of 25 ppm for the effective OH^- concentration in this NaBr sample. However, the somewhat faster decay can also be due to an F-center concentration effect (cf. Sec. II), or even more likely, due to bleaching effects, which could not be completely avoided in this sample.

As was observed in KCl, RbCl, and KBr,[10] $F \rightarrow F_2$ energy transfer is another process, which may be responsible for an F-center relaxation much faster than 1 μs. To our knowledge the F_2 band in NaBr has not been reported yet. From the Mollwo-Ivey law one would expect it to occur near 760 nm.[28] In our samples no trace of the F_2 absorption band was found. Moreover, the F-center emission in NaBr is shifted much farther to the IR, reducing its spectral overlap with the absorption of the F-aggregate centers. As a consequence, the energy transfer to F aggregates is expected to be less efficient in NaBr.

The possible influence of the extrinsic processes was further investigated by an optical bleach of colored samples in the F band at 250 K. Such excitation may have two effects: (i) the formation of F-aggregate centers and (ii) the association of F centers to impurities, thus enhancing their effect on the F-center properties. After the optical bleach both the position and the shape of the F band remained unchanged and no F-aggregate formation was observed. For pure NaBr crystals the F-center decay was checked not to be influenced by the optical excitation at high temperatures.

In the case of pure samples without F-center aggregation, a decrease in the F-center lifetime is reported in Refs. 5 and 6 and related to interaction between excited F-center pairs. In this work energy transfer was observed only for concentrations of *excited* F-centers higher than $2 \times 10^{16} cm^{-3}$. With an F-center concentration of $10^{16} cm^{-3}$ and with the low pulse power used, exciting only of the order of 0.1% of the F centers, we also avoid this kind of relaxation process.

V. DISCUSSION

A. Lifetime of the relaxed excited state

During the relaxation measurements, a stationary equilibrium between the F and F' concentrations exists, depending on the temperature and the excitation wavelength. At low temperatures and low initial F-center concentrations the F' concentration is negligible, because of the small $F \rightarrow F'$ optical conversion efficiency and the very efficient backconversion. In this situation we can restrict ourselves to the relaxation processes within the F-center system itself: the vibrational cooling in the excited state, the electronic transition to the ground state and the vibrational cooling in the ground state. All of them contribute to the decay curves of our measurements. Moreover, the ground-state recovery measurements do not discriminate between processes occurring at the crossover point and at the RES, neither between radiative and nonradiative processes.

The ionization of the F center after optical excitation possesses in NaBr a rapidly increasing efficiency above 70 K (cf. Fig. 3).[20] The fact that two decay channels are observed experimentally and that the relative contribution of CH2 to the initial induced transparency follows the same temperature dependence as the ionization efficiency (Fig. 3), confirms that CH1 results from the fraction $1-\eta_i$ of the excited F-center electrons, which directly relaxes to the ground state. From the previous arguments it also follows that CH2 is associated with the other fraction η_i of the electrons, which is released from the excited F centers and eventually relaxes after being trapped again at an F center or an empty vacancy. Therefore, the 1200-nm emission, which was also related to the recapture of electrons,[20] possibly contributes to the relaxation time of CH2. Considering the amplitude of CH2 in more detail, one should include the recapture of conduction electrons arising from optically ionized F' centers. This does not change the foregoing conclusions, since also the F' concentration is proportional to the F-center ionization efficiency. Analysis of the recapture rate from the time constant of CH2 is quite involved, since it depends on the F-center doping and the relative equilibrium concentrations of F and F' centers. The latter depends in its turn on the excitation wavelength, the temperature dependence of the F- and F'-center absorption, the ionization efficiency, and the trapping rate itself. Therefore, CH2 will not be discussed further in this paper.

The observed nanosecond F-center relaxation in NaBr (CH1) at low temperatures agrees with the DKR criterion in the sense that it provides direct evidence for a relaxation process which is much faster than the typical radiative lifetime of the F center of the order of 1 μs. It does not necessarily imply that the nonradiative electronic transition occurs at the crossover point.[20] In the crossover model the configurational relaxation should be associated with the 6-ns decay at 10 K, since it is the rate determining process in this case. On the one hand, this process is "generally assumed" to occur on a picosecond time scale. Experimentally, lifetimes of optical phonons of the order of 1 – 10 ps are established.[29,30] For color centers, measurements of the configurational relaxation in the excited state after optical excitation yield decay times on the same picosecond time scale.[31–33] On the other hand, resonant Raman measurements reveal that the F-band transition in NaBr and NaI mainly couples with a single gap mode, whose width has not yet been resolved.[34] As a consequence, the configurational relaxation of the F center in these host crystals may be exceptionally slow.

The radiative lifetime τ_r of the F center in NaBr can be estimated from the relation established in other host lattices between τ_r and the high-frequency dielectric constant ϵ_∞:

$$\tau_r = \epsilon_\infty^{5.5} \times 14.4\,\text{ns} = 2.7\mu\text{s}. \tag{1}$$

This relation was derived from the hydrogen-atom model of the F center and it has been verified to agree with the experimental lifetime data within 20%.[35] If in contrast to the DKR model the decay time of the low temperature measurements is interpreted as the lifetime τ of the RES, the radiative lifetime τ_r can also be obtained from

$$\tau_r = \eta_e^{-1}\tau = 3\ \mu\text{s}, \tag{2}$$

with the emission efficiency[20] η_e equal to 0.002 and $\tau = 6$ ns. In the model of Bartram and Stoneham[13] the emission efficiency is determined by the ratio of the vibrational cooling rate in the excited state and that in the ground, whereas in the extended-crossing model the small η_e is a result of the competition between the vibrational cooling in the excited state and the crossover process.[15,16,36] Therefore, one does not expect Eq. (2) to hold in the crossover model. As a consequence, the correspondence between (1) and (2) shows that our measurements are consistent with vibrational cooling to the RES, from which horizontal vibronic tunneling to the ground state occurs. This agrees with the conclusions of Ref. 20. Since in the latter work the 2000-nm emission in NaBr has been associated with the normal optical cycle of the F center,[20] this emission should exhibit the same time evolution as CH1. The relatively slow configurational relaxation, which possibly applies for NaBr, would show up as a retardation of the decay of the induced transparency. We did not observe any evidence for this. Of course, at the lowest temperatures the range of the time delay covered by the delay stage is not large enough to analyze details of the decay curves with a time constant considerably longer than 1 ns.

Further confirmation of the foregoing conclusions is indicated through a study of the vibrational relaxation of the F center in NaBr, e.g., by means of high-resolution linewidth measurements of the gap mode in the Raman spectrum or by time-resolved measurements of excited state absorption. It is evident that the present study should be extended to NaI. Applying formula (1), one finds a radiative lifetime of 5.3 μs for the F center in NaI and inserting this value in expression (2) one predicts a RES lifetime of about 27 ns.

In the literature a number of other values are reported for the relaxation time of the F center in NaBr. Bosi *et al.* established from single-photon counting measurements near 1200 nm a slow decay component of the order of 1 μs and a faster one of 22.9 ns, which they attributed tentatively to the lifetime of the relaxed excited state of the F center and to the F_2 center, respectively. Since the emission from the relaxed excited state has been established to occur at 2000 nm,[20] neither of them can be associated with the normal optical cycle of the F center. At 77 K a recovery of the ground state within the 10-ps time resolution of the experiment has been claimed,[37] although no measurements are presented. Possibly, such an observation can be explained as an interference spike, which often occurs in induced transparency measurements when the pump beam is not properly eliminated before detection of the probe beam. Also, with the excitation power used in those experiments 80% of the F centers are pumped to the excited state, in contrast to 0.1% in our case. From measurements of the $F \rightarrow F'$ conversion efficiency, a 330-ps lifetime of the relaxed excited state has been estimated.[20] This value was derived from data between 80 and 130 K, with the assumption of a temperature-independent nonradiative decay time. The latter assumption, however, is not justified in the case of horizontal vibronic tunneling (Secs. V B and V C).

B. *F*-center ionization and temperature dependence of the relaxation

Analyzing the temperature dependence of the RES lifetime (CH1), the ionization rate τ_i^{-1} should be included in the total transition rate τ^{-1}:

$$\tau^{-1} = \tau_i^{-1} + \tau_{\mathrm{nr}}^{-1} . \tag{3}$$

The radiative contribution is neglected in (3), because of its very small efficiency in NaBr. Since ionization is ineffective below 70 K,[20] and since the total lifetime already varies by a factor of 3 in this temperature range (see Figs. 3 and 4, respectively), τ_{nr}^{-1} cannot be assumed constant in expression (3), as was done in Ref. 20 in the analysis of the ionization efficiency. Combining ionization efficiency and lifetime data, the ionization rate and the nonradiative relaxation rate can be obtained separately by means of

$$\tau_i^{-1} = \eta_i \tau^{-1} \tag{4}$$

and

$$\tau_{\mathrm{nr}}^{-1} = (1 - \eta_i)\tau^{-1} , \tag{5}$$

respectively. These expressions are independent of any assumption concerning the particular nature of the processes and apply as long as both processes take place from the thermalized excited state. The ionization data of Ref. 20 and the lifetime data of this work (CH1) were inserted in formulas (4) and (5). If at a particular temperature η_i and τ_{nr} were not available simultaneously, a linear interpolation between the nearest data points was used. The result is shown in Fig. 6. Usually, an Arrhenius-type ionization rate is assumed, representing thermal activation of the F-center electron from the RES to the conduction band:

$$\tau_i^{-1} = \nu_i \exp\left(-\frac{\Delta E_i}{k_B T}\right) . \tag{6}$$

The best fit of the obtained ionization rate to expression (6) yields an attempt frequency $\nu_i = 4.2 \times 10^{13}\ \mathrm{s}^{-1}$ and an energy gap $\Delta E = 86$ meV. This is considerably larger than the one expected from the linear relation reported between the energy gap ΔE and ϵ_s^{-2}, with ϵ_s the static dielectric constant of the host crystal.[20,38] However, if other experimental data for the dielectric constant[39] are used than in Ref. 38 and if more host crystals are considered, this relation yields only a rough tendency.

The Arrhenius behavior (6) predicts a zero ionization efficiency at zero temperature, in contrast to the experimental observations (cf. Fig. 3).[20] In order to explain the measured ionization efficiency, Georgiev *et al.*[21,22,40] propose that after optical excitation the F-center electron tunnels vibronically from the thermalized excited state to a polaron state, bound to another F center. Once in the bound polaron state (BPS), the electron relaxes into this other F center to form an F' center on a time scale much faster than the RES-BPS transition. Energy calculations from vibronic model potentials for the excited F center and the bound polaron result in a smaller energy for the bound polaron state than for the RES of the F center. As such, the RES-BPS transition is exothermal and can occur even at zero temperature. This model has been shown to account for the dependence of the $F \rightarrow F'$ conversion on the initial F-center concentration,[40] which has been treated in an empirical way before. Even at low F-center concentrations this mechanism is able to explain the observed temperature dependence of the $F \rightarrow F'$ conversion in NaI, without the necessity to include a contribution arising from thermal excitation of the F-center electron to the conduction band.[21,22] It is clear that in the latter case the ionization rate of Fig. 6 must be interpreted as the vibronic transition rate from the RES of the F center to the BPS, instead of thermal excitation to the conduction band. Taking into account the small emission efficiency $\eta_e = 0.005$ and the small ionization efficiency $\eta_i = 0.1$ of the F center in NaI at low temperatures,[20] one concludes that the nonradiative relaxation to the F-center ground state is much faster than the radiative one and than the transition to the BPS. In Sec. V A the nonradiative relaxation rate of the F center in NaI was estimated to be 27 ns at zero temperature,

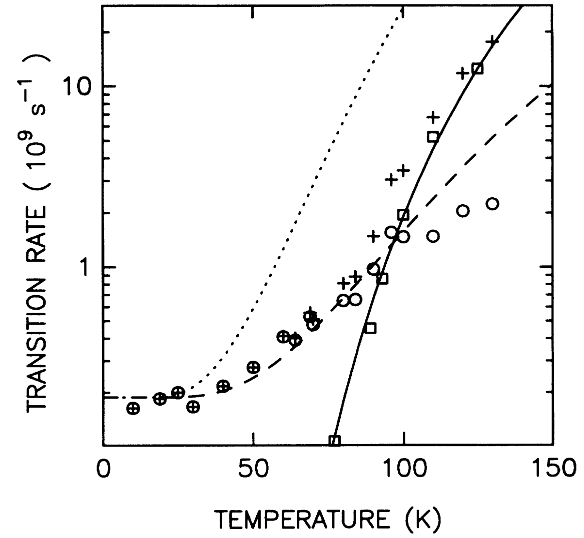

FIG. 6. The ionization rate (□) and the nonradiative transition rate (○) of the RES of the F center in NaBr, derived from expressions (4) and (5), respectively. The ionization efficiency data of Ref. 20 and the total transition rate (+) from this work are used. The solid line is the best fit of the ionization rate to an Arrhenius behavior. The other two curves show the horizontal vibronic tunneling rate (7) with $E_A = 110$ meV and $E_R = 875$ meV: For the dashed curve also the best-fit values $C = 167\ \mathrm{cm}^{-1}$ and $\hbar\langle\omega\rangle = 19.2$ meV are used, whereas for the dotted line $C = 1298\ \mathrm{cm}^{-1}$ and $\hbar\langle\omega\rangle = 14$ meV, the effective phonon frequency for absorption, are used.

whereas the τ_r was expected to be 5.3 μs. This is in contrast to the picture presented by Georgiev *et al.*,[21,22,40] in which the relaxation to the F-center ground state is assumed to be determined by the ***radiative lifetime*** $\tau_r = 20$ ns. This discrepancy does not affect the relevancy of their calculations on NaI, since they depend only on the *value* of the total relaxation rate to the F-center ground state. An aspect which is neglected in their work on NaI and which may be expected, as observed for NaBr in this paper, is the temperature dependence of the relaxation rate. As such, the experimental data presented in this paper provide an appropriate input for similar calculations on the RES-BPS transition in NaBr.

C. Horizontal vibronic tunneling

In Sec. V A it was argued that after optical excitation the F center in NaBr reaches the RES. The relaxation to the ground state is dominantly nonradiative, which is possibly attributed to horizontal vibronic tunneling. For the F center in alkali halides vibronic tunneling rates have been estimated in a very simplified model from the overlap of the $n = 0$ vibrational wave function of the excited state and the vibrational wave function of the ground state with the same energy.[41] It yields at zero temperature a lifetime of the RES of 33 and 10 ps for NaBr and NaI, respectively. More general theoretical treatments of nonradiative electronic processes exist, starting from a vibrationally thermalized excited state.[25,42,43] They are able to explain a variety of phenomena, at least qualitatively. If configurational relaxation is reduced to one effective coordinate with a *large* equilibrium displacement in the excited state, and if linear electron-phonon coupling is assumed, a thermally activated nonradiative transition rate $\tau_{\rm nr}^{-1}$ is obtained:[25,42,43]

$$\tau_{\rm nr}^{-1} = \frac{C^2\sqrt{2\pi}}{\hbar\sqrt{E_R k_B T^*}} \exp\left(-\frac{E_A}{k_B T^*}\right). \tag{7}$$

The effective temperature T^* is defined as

$$k_B T^* = \frac{1}{2}\hbar\langle\omega\rangle \coth\left(\frac{\hbar\langle\omega\rangle}{2k_B T}\right), \tag{8}$$

with $\langle\omega\rangle$ the frequency of the effective configurational coordinate. In contrast to the well-known Arrhenius law, Eq. (7) results in a nonzero transition rate at zero temperature:

$$\tau_{\rm nr}^{-1} = \nu_{\rm nr} \exp\left(-\frac{2E_A}{\hbar\langle\omega\rangle}\right), \quad \nu_{\rm nr} = \frac{C^2\sqrt{4\pi}}{\hbar\sqrt{E_R \hbar\langle\omega\rangle}}. \tag{9}$$

The parameter C is proportional to the electronic matrix elements of the nonadiabatic part of the Hamiltonian. The activation energy E_A, which is the energy difference between the crossover energy and the energy of the RES (cf. Fig. 1), is related to the absorption energy E_0 as

$$E_A = \frac{E_0}{4}\Lambda^{-1}(1-2\Lambda)^2 \quad , \tag{10}$$

whereas the configurational relaxation energy E_R is given by

$$E_R = \Lambda E_0. \tag{11}$$

In the simple two-level system it makes no difference whether the parameter Λ is derived from

$$\Lambda = \frac{E_0 - E_e}{2E_0} \tag{12}$$

or from the broadening of the absorption band with temperature.[11] The situation for the F center is more complex. The F-band absorption occurs from the $1s$-like state to the $2p$-like state. The latter is lower in energy than but nearly degenerate with the $2s$ state.[44] In the vibrationally relaxed configuration, however, the $2s$-like state turns out to be slightly lower in energy.[45] Since horizontal vibronic tunneling starts from the relaxed excited state, the relevant effective phonon frequency in (7) is the one for the $2s \rightarrow 1s$ transition, which can be derived from emission data. For the same reason Λ will be calculated using expression (12).

In principle, the expression for the vibronic tunneling rate (7) can be fit to the nonradiative relaxation rate data of Fig. 6 to obtain values for the parameters E_A, E_R, $\hbar\langle\omega\rangle$, and C. The reliability of the values for $\tau_{\rm nr}^{-1}$ above 100 K, however, is doubtful. It is clear from expression (5) that for high ionization efficiencies, i.e., above 100 K, the data for $\tau_{\rm nr}^{-1}$ are very sensitive to errors on the ionization data. In particular, they are sensitive to the absolute calibration of the ionization efficiency, which was not performed explicitly in Ref. 20 for NaBr. Another reason why the nonradiative lifetime derived by expression (5) may be inaccurate, is that ν_i represents the ionization rate from the RES, whereas thermal ionization does not necessarily require the F center to pass through the RES. The excess vibrational energy acquired after optical excitation may activate the transition of the electron to the conduction band before the RES is reached.[12,42,46] A theoretical treatment of this process is not yet performed for the F center, but it is an alternative way to explain the nonzero ionization efficiency at zero temperature. Even if only a small fraction of the observed ionization efficiency is due to such a process, relatively large systematic errors may be expected for $\tau_{\rm nr}$ at higher temperatures using expression (5).

Because of the previous arguments, the analysis of $\tau_{\rm nr}^{-1}$ by means of (7) is limited to the data below 100 K: In this temperature range the nonradiative relaxation rate is larger than or comparable in magnitude to the ionization rate. Also, the number of fit parameters can be reduced. With expression (12) and the results of Ref. 20 one finds $\Lambda = 0.369$, and from (10)

$$E_A = 110\,\text{meV}, \tag{13}$$

and from (11)

$$E_R = 875\,\text{meV}. \tag{14}$$

The effective phonon frequency for emission is not available for NaBr and is kept as a free parameter, as well as the parameter C. The best fit (cf. Fig. 6) results in

$$\hbar\langle\omega\rangle = 19.2\,\text{meV} \tag{15}$$

and

$$C = 167\,\text{cm}^{-1}. \tag{16}$$

The value (16) for C is of the order of magnitude found for this parameter for a number of transitions in large molecules[25] and results in a pre-exponential factor at zero temperature (9) of $\nu_{\text{nr}} = 1.8 \times 10^{13}\ \text{s}^{-1}$. Extrapolated to zero temperature, the fit to expression (7) gives $\tau_{\text{nr}} = 5.3$ ns, which agrees within experimental error with the time constant of the decay curve at 10 K. Comparison of (15) with $\hbar\langle\omega\rangle = 14$ meV for the F-center absorption band in NaBr (Ref. 20) confirms that the relevant effective phonon frequency is the one for emission. Indeed, on an average the effective phonon frequency for emission is found to be 36% higher than the one for absorption in other host lattices.[44]

Assuming that the parameter C does not critically depend on the host lattice, (16) is used to estimate in other host lattices the nonradiative lifetime at zero temperature from expression (9). The results are listed in Table I. Λ was derived using expression (12). For the lithium halides no F-center emission has been observed yet. In these cases, the emission energy E_e used in (12) is estimated by means of the semiempirical rule from the hydrogen-atom model of the F center:[3]

$$E_e = \epsilon_\infty^{-2} \times 5.25\,\text{eV}. \tag{17}$$

When $\hbar\langle\omega\rangle$ was not available from emission data, the value for absorption was multiplied with 1.36, as was argued above. The relevancy of a correct choice for $\hbar\langle\omega\rangle$ is clear from the exponential dependence of τ_{nr}^{-1} (9) on the effective phonon frequency. It is also illustrated in Fig. 6: τ_{nr}^{-1} from expression (7) is displayed for NaBr, using the effective phonon frequency for absorption $\hbar\langle\omega\rangle = 14$ meV and constraining the RES lifetime at zero temperature to $\tau_{\text{nr}} = 5.3$ ns. Apparently, at 100 K it already exceeds the experimental values for the total transition rate by almost an order of magnitude. Considering the approximations used to derive Eq. (7) and considering its critical dependence on the activation energy E_A and the effective phonon energy $\hbar\langle\omega\rangle$, the estimated values for τ_{nr} have a limited quantitative significance and merely represent an order of magnitude. Qualitatively, Table I yields exactly the same conclusions as the DKR criterion: (i) For NaBr, NaI, and the lithium halides the nonradiative lifetime is shorter than the radiative lifetime (~1 μs). In particular, the estimated nonradiative lifetime for NaI is reasonably close to the 27 ns estimated in Sec. V A; (ii) the other host lattices exhibit a nonradiative decay which is orders of magnitude slower than the radiative relaxation. Only in the case of NaCl, for which an emission efficiency of 0.33 has been observed experimentally[2,16] and which is a borderline case for the DKR criterion,[11] the radiative and nonradiative decay rates lie relatively close together.

TABLE I. Estimate of the nonradiative lifetime τ_{nr} of the relaxed excited state of the F center by means of expression (9) for horizontal vibronic tunneling and taking C=167 cm^{-1}. The values used for the parameter Λ defined by Bartram and Stoneham (Ref. 11), the effective phonon frequency $\langle\omega\rangle$, the configurational relaxation energy E_R, and the activation energy E_A are also given. The values for τ_{nr} represent only an order of magnitude and should be compared with a radiative lifetime of the order of 1 μs.

Host	τ_{nr} (s)	Λ[a]	$\langle\omega\rangle$ (meV)[a]	E_R (eV)	E_A (eV)
LiBr	1.0×10^{-11}	0.406[b]	24.5[c]	1.122	0.061
LiCl	1.6×10^{-10}	0.397[b]	23.0[c]	1.310	0.088
LiF	2.2×10^{-9}	0.366[b]	51.7[c]	1.868	0.250
NaBr	6.0×10^{-9}	0.369	19.0[c]	0.875	0.110
NaI	7.2×10^{-9}	0.364	17.7[c]	0.758	0.105
NaCl	1.8×10^{-4}	0.324	24.4	0.898	0.265
NaF	1.2	0.276	44.9[c]	1.028	0.677
KBr	1.2×10^{7}	0.278	15.5	0.574	0.366
KI	4.6×10^{7}	0.279	13.5	0.523	0.328
RbBr	2.2×10^{14}	0.265	12.4	0.492	0.397
KCl	6.8×10^{17}	0.237	18.8	0.548	0.675
RbF	6.8×10^{18}	0.226	21.8[c]	0.549	0.807
RbI	1.5×10^{20}	0.262	9.5	0.448	0.369
RbCl	3.7×10^{25}	0.234	13.8	0.480	0.620
KF	9.2×10^{30}	0.208	22.9	0.592	1.167

[a] From data of Ref. 44; from data of Ref. 20 for NaI and NaBr.

[b] Using expression (17) for the emission energy.

[c] 1.36 times the effective phonon frequency for absorption.

VI. CONCLUSIONS

In this paper the results of ground-state recovery measurements after picosecond optical excitation of the F

center in NaBr were presented. Two contributions could be distinguished. Based on the temperature dependence of their relative amplitudes, the slowest one is related to the recapture of electrons released by ionization of *F* and *F'* centers, whereas the fastest one is associated with the relaxation within the *F* center itself. In contrast to the crossover model, in which the electronic transition in NaBr is proposed to occur during vibrational cooling,[11,12] we conclude that our observations are consistent with sufficiently fast configurational relaxation, such that the relaxed excited state is reached.

The time constant of the fastest decay channel is associated with the total lifetime of the relaxed excited state and involves ionization and nonradiative relaxation. The transition rates of the latter two processes were determined from the total lifetime and the ionization efficiency data of Ref. 20. Within the temperature range where the nonradiative relaxation rate can be determined accurately, its temperature dependence is well accounted for by a theoretical expression for horizontal vibronic tunneling[25] with realistic input parameters for the *F* center in NaBr. The vibronic tunneling rate at zero temperature was estimated in the same way for the *F* center in other alkali halides and yields the same conclusions as the DKR criterion concerning the observability or nonobservability of the *F*-center luminescence.[11] The correspondence at this point between the two different models is not surprising: Lowering the crossover point implies an increased overlap between the vibrational wave functions of the ground and the excited state with the same energy, which is a crucial factor in the horizontal vibronic tunneling rate.[25]

The interpretation of the ionization rate remains incomplete. In particular, from our data it is not possible to decide to what extent the *F*-center ionization through a bound polaron state, proposed by Georgiev *et al.*,[21,22] plays a role. Measurement of the concentration dependence of the *F*-center relaxation can possibly contribute to solve this problem. The same measurements are probably also useful for the determination of the recapture rate from the time constant of the slowest decay channel, which was left undiscussed in this work.

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