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Picosecond radiationless relaxation of the F center in NaBr induced by hydrogen impurities

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With a pump-probe laser-induced transparency technique the ground-state recovery of the F center in hydrogenated NaBr is measured. For a random distribution of F and substitutional hydrogen (H_s^-) centers a nonexponential F-center relaxation is observed, faster than the one in undoped crystals. The aggregation of F and H_s^- centers by subsequent optical bleachings is monitored by means of resonant Raman scattering. The corresponding relaxation measurements reveal three decay components, which we associate with the formation of $F_H(H_s^-)$ and $F_{H2}(H_s^-)$ centers and to the remaining F centers. The relaxation time of the $F_H(H_s^-)$ center is established to be $\sim$290 ps, which is 20 times faster than the one of the pure F center. An estimate of the decay rate assuming dipole-dipole coupling between the F-center electron and the H_s^- vibration shows that this interaction may play an important role in reducing the lifetime of the excited F center. The frequency shift of the hydrogen vibration of the $F_H(H_s^-)$ center with respect to the one of the H_s^- centers can not be explained by dipole-dipole coupling only. This is possibly related to a displacement of the H_s^- equilibrium position of the $F_H(H_s^-)$ center, away from the lattice site.

I. INTRODUCTION

After optical excitation of the F center in alkali halides, its relaxation to the electronic ground state can be either radiative or nonradiative. In NaBr, NaI, and the lithium halides the luminescence is quenched by a fast radiationless process intrinsic to the pure F center. The poor or zero emission efficiency in these cases is empirically well predicted by the Dexter-Klick-Russel (DKR) criterion.[1] The nature of the nonradiative relaxation process, responsible for the luminescence quenching, has been the subject of many experimental and theoretical studies.[2–4]

The electronic decay of the F center may be influenced by the presence of impurities, causing extrinsic quenching of the luminescence due to energy transfer to the impurity. Transfer of the F-center energy to electronic energy of the F_2 center has been reported for KCl.[5] F-center luminescence quenching has also been observed in OH^- and CN^- doped alkali halides.[6–8] In the latter cases, the electronic energy of the F center is transferred to the internal vibration of the molecular ion. This process has been studied by transient absorption, emission efficiency measurements, and anti-Stokes resonant Raman scattering. In the case of OH^- it has been observed both for randomly distributed F centers and impurities, and for the $F_H(OH^-)$ aggregate center.[9,10] In the CN^- case, energy transfer has only been reported for the $F_H(CN^-)$ center and is most clearly demonstrated by observation of vibrational luminescence of the CN^- stretching mode after electronic excitation of the F center.[11] Theoretical calculations of the electronic transition rate from the relaxed excited state (RES) in thermal equilibrium have been fitted to the experimental data and a different nature of the energy transfer for the two impurities has been proposed. Whereas the energy transfer to CN^- was attributed to the accepting character of the molecular vibration,[6] the OH^- stretching mode would act as a promoting mode due to its dipole-dipole coupling to the F-center transition.[9]

In contrast, the presence of substitutional alkali or hydrogen (H_s^-) impurities has only a small influence on the emission lifetime of the F center in KCl.[12] In hydrogenated NaBr an emission band at 1.65 μm was tentatively assigned to the $F_H(H_s^-)$ center.[3] The creation and symmetry of the $F_H(H_s^-)$ center in the alkali chlorides has been studied with polarized Raman scattering of the H_s^- vibrations,[13] demonstrating the $\langle 110\rangle$ position of the H_s^- ion with respect to the F center. The presence of the F center splits the threefold-degenerate hydrogen vibration of the unperturbed H_s^- center. The magnitude of their frequency shift with respect to the vibrational frequency of the isolated impurity can be explained within 20% by dipole-dipole interaction between the F-center electron and the H_s^- displacement.

This paper studies the influence of H_s^- impurities on the radiationless electronic relaxation of the F center in NaBr by means of a picosecond pump-probe laser technique for induced transparency.[14] After the experimental details in Sec. II, optical absorption and Raman measurements are used to monitor the defect content and aggregation after each hydrogenation and light-bleaching procedure (Sec. III). The structure and vibrational properties of the observed defect centers are further characterized in Sec. IV. Section V presents the time-resolved measurements. The possibility of energy transfer from the F center to the H_s^- impurity is discussed in Sec. VI on the basis of theoretical expressions for the relaxation rate and the shape of the decay curve. Final remarks and conclusions are found in Sec. VII.

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II. EXPERIMENTAL DETAILS

Crystals of ultrapure NaBr were grown by the Crystal Growth Laboratory of the University of Utah, and Harshaw Chemical Co. Because of their hygroscopicity, the crystals were always stored and handled under dry N_2 atmosphere. Substitutional hydrogen (H_s^-) doping was performed with the technique of simultaneous additive coloration and hydrogenation. An apparatus was built very similar to that of Kondo *et al.*,[15] using steel with a low carbon content and nickel for the crystal container. Pieces of NaBr of maximum 2 mm thickness were hydrogenated for 3–4 days at 600 or 625 °C and at a H_2 pressure of 6 bars. Afterwards, the samples were slowly cooled to 200 °C to remove the *F* centers from the crystal and subsequently quenched to room temperature (RT). A long baffle, filling almost the entire lower-temperature part of the heat pipe, was used to prevent sodium hydride formation. The latter would make long treatments inefficient, due to a drop in Na vapor pressure.[15] We did not use treatments longer than 4 days because damage to the crystal increases with hydrogenation time. After hydrogenation the samples were cleaved to a thickness of ≈1 mm. *F* centers were created by x-ray irradiation of the hydrogenated samples at room temperature with a Siemens tungsten x-ray tube, operating at 50 kV and 30 mA. Aggregation of *F* centers and H_s^- impurities was obtained by exposing the samples to 514.5-nm light from an Ar^+ laser at 250 K. A 150-mW laser beam was expanded by a lens to cover the entire sample.

The effect of each treatment on the NaBr crystals was monitored by means of optical absorption (CARY 05) and Raman scattering (SPEX double monochromator). The Raman measurements were performed under 514.5-nm Ar^+-laser excitation and under 580-nm excitation from a Rhodamine 6G dye laser. Both wavelengths are resonant with the *F*-, F^--, and $F_H(H_s^-)$-absorption bands (Fig. 1). The pump-probe setup for picosecond time-resolved measurements has been described in detail in Ref. 14. The pump and probe pulses originated from one Rhodamine 6G dye laser, synchronously pumped by a mode-locked Ar^+ laser. The pump beam is blocked by an analyzer after interaction in the sample by using orthogonal polarizations for the pump and probe beams.[14] The optical delay stage covers approximately 2 ns and the time resolution is 7 ps.

III. CHARACTERIZATION OF THE SAMPLES

A. H_s^- concentration and distribution

In the process of simultaneous additive coloration and hydrogenation the pressures of the hydrogen and the alkali vapor determine the equilibrium hydrogen content of the crystal surfaces. The penetration depth of the hydrogen into the crystal depends on the crystal temperature and is proportional to the square root of the hydrogenation time.[16] In our setup the sample and the alkali metal were at almost equal temperatures. The hydrogen distribution over the crystal was checked by observing the spatial dependence of the Raman intensity of the overtone of the H_s^- localized vibration relative to the second-order phonon band. A 5 × 5 × 20-mm^3-sized sample, which turned out to be much larger than the penetration depth, was hydrogenated for 5 days at 600 °C under 7 atm H_2 pressure. The exposed regions at the long ends of the sample were cleaved off, and the crystal was used for Raman measurements. The excitation beam was positioned parallel to the long axis of the crystal. This way, the Raman measurements do not average for different concentrations. A hydrogen concentration linearly decreasing with depth was observed (cf. Ref. 16). It fell to zero at 1.2 mm below the surface. Therefore the thickness of the hydrogenated crystals should be limited to about this value to guarantee a homogeneous concentration. For practical reasons we had to use crystals of about 2 mm thickness. As such, a considerable inhomogeneity of the hydrogen concentration can be expected.

The hydrogen concentration was also estimated from the UV absorption of the H_s^- center (5.97 eV at RT). Using a common absorption spectrometer, this yields only an average over the whole depth of the crystal. At the H_s^- concentrations used in our experiments, the optical density of this absorption peak is far too high for measurement. Also, the absorption band overlaps with the UV absorption of the host crystal. Thus only the long-wavelength tail of the band is known. We estimated the hydrogen concentration by comparing this tail with the absorption of a sample with a relatively low hydrogen content. The concentration in this last sample was calculated using the formula of Smakula.[17] In this way average hydrogen concentrations in the range 10^{17}–10^{19} cm^{-3} were estimated. Although this procedure does not provide accurate quantitative information on the H_s^- concentration, it enabled us to classify the crystals according to their relative H_s^- content.

B. *F*-center production

The x-ray irradiation of hydrogenated NaBr results in an efficient formation of *F* centers. Thereby, interstitial hydrogen impurities (H_i^-) are formed, which combine[18] at sufficiently high temperatures to interstitial H_2. It was observed that when crystals were x-ray irradiated at 100 K the *F* centers are optically unstable even at low temperature, probably due to recombination of the *F* center and the interstitial hydrogen. Irradiating the samples above 200 K, the initial *F*-center concentration decreased immediately with 20%, when they were exposed to visible light at 10 K. Afterwards the concentration remained stable. A typical x-ray-irradiation time of 15 s at 30 mA and 50 kV resulted in average *F* concentrations of $\approx 5 \times 10^{16}$ cm^{-3}, as was established by means of optical absorption. Concentration effects on the *F*-center relaxation have been clearly observed[19] in the same samples at average concentrations above about 2×10^{17} cm^{-3}. By limiting the *F*-center concentration, we avoided this effect.

The above mentioned 5 × 5 × 20-mm^3-sized crystal was used to check the spatial distribution of *F* centers in hydrogenated samples. A slice was cleaved from it, perpendicularly to the long axis of the sample, and x-ray irradiated along the direction of the original long axis. The *F*-center absorption strength was measured at different positions with a focused Rhodamine-6G dye laser beam at 580 nm. It was found that the *F*-center concentration is proportional to the hydrogen concentration, except in the region of the sample deeper than the hydrogen penetration depth. Here, a small amount of *F* centers ($\approx 10^{14}$ cm^{-3}) is created by the hydrogenation procedure itself, in spite of the slow cooling at the end.

C. Optical aggregation of F and H_s^- centers

Optical excitation of the *F*-center absorption band near 250 K is known to result in the aggregation of the *F* center to other defect centers in the crystal. Considering the purity of the starting material and the high concentration of H_s^- with respect to the concentration of *F* centers, interstitial H_2, and H_i^-, an *F* light bleaching most likely creates an *F* center associated with one H_s^-, called an $F_H(H_s^-)$ center. $F \rightarrow F_H(H_s^-)$ conversion is expected to shift and broaden the absorption band only slightly.[3] In contrast, resonant Raman scattering is more sensitive: Because of resonant enhancement and the breaking of inversion symmetry, the fundamental H_s^- vibration is only Raman active in the vicinity of an *F* center. As such, one expects to observe after light bleaching localized modes near 498 cm^{-1}, the ir mode of the unperturbed H_s^- center in NaBr.[20]

A sample was hydrogenated at 600 °C and x-ray irradiated for 15 s, resulting in average H_s^- and *F*-center concentrations of 1×10^{19} cm^{-3} and 3.5×10^{16} cm^{-3}, respectively. We performed on this sample subsequent light bleachings and monitored the aggregation at each stage by means of optical absorption and resonant Raman scattering. These measurements are presented in Figs. 1 and 2.

Before bleaching, the observed absorption is the same as that of the unperturbed *F* center. The *F*-absorption band has its maximum at 2.37 eV; its width is 0.30 eV. No broadening of the *F* band due to the presence of H_s^- impurities was seen. Also, the resonant Raman spectrum exhibits the typical features of the *F* center in NaBr:[21] Beside the broad phonon bands, it consists of a pair of intense narrow resonances at 137 cm^{-1} and 149 cm^{-1}. No signal of a H_s^- mode was found after x-ray irradiation. The first-order modes are symmetry forbidden, and the second-order modes are too weak in comparison to the *F*-center background. Before conversion, only the 137-cm^{-1} and 149-cm^{-1} modes of the *F* center itself are visible.

After bleaching, the absorption band broadens and shifts approximately 0.04 eV to lower energies (Fig. 1) and the integrated absorption strength decreases. Since F_A and F_H centers are known to have essentially the same oscillator strength as the *F* center, part of the *F* centers must have been destroyed by migration to the crystal surfaces or, more probably, by recombination with interstitial hydrogen.[18] Optical aggregation could result in the formation of F_2 centers, but no F_2 band is observed. Figure 2 shows the Raman spectrum of the narrow resonances and their evolution under stepwise bleaching. The shift of the *F*-center resonance due to aggregation with an impurity is commonly observed for F_A centers.[22] It can be used to monitor how far the conversion of *F* centers to aggregate centers has proceeded. In the first phase of bleaching, a mode arises at 132 cm^{-1}, and the signal at 149 cm^{-1} broadens to higher frequencies. At the same time the localized hydrogen vi-

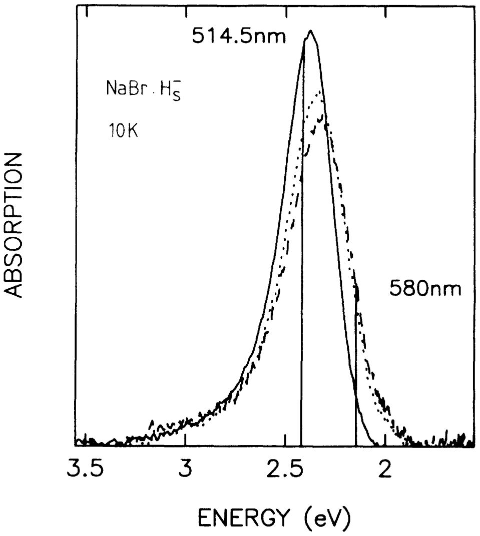

FIG. 1. Absorption spectra of hydrogenated NaBr (10^{19} cm^{-3} of hydrogen) at 10 K showing the *F* band before optical aggregation (solid curve), the superposition of the *F*, F_H, and F_{H2} absorption after a 20-min light bleaching at 250 K (dashed curve), and the F_H contribution after optical aggregation and subtraction of the *F*-center contribution (dotted curve). The spectra are normalized to the integrated absorption.

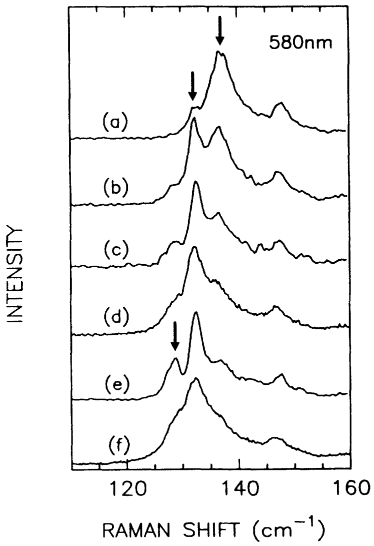

FIG. 2. Raman spectra of the narrow resonances after stepwise bleaching, recorded with 580-nm excitation at 10 K. The average hydrogen concentration is 1×10^{19} cm^{-3}. The 0-min spectrum is recorded on a different sample. Bleaching times are (a) 0 min, (b) 2 min, (c) 5 min, (d) 10 min, (e) 20 min, (f) 40 min.

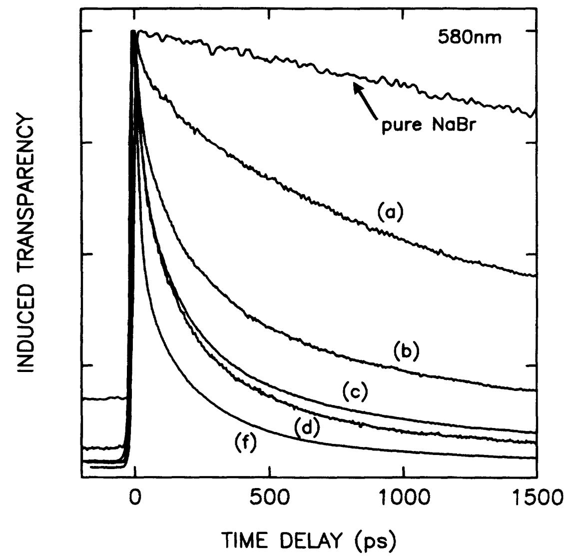

FIG. 3. Time-resolved induced transparency measurements under 580-nm excitation at 10 K, recorded after stepwise bleaching. The decay curves should be compared with the Raman spectra of Fig. 2, where also the corresponding bleaching times are indicated. The spectrum labeled (a) is, in this case, recorded on the same sample as the other spectra.

brations are most clearly observed in the 450–550 cm^{-1} range (Fig. 5). We associate the 132-cm^{-1} resonance, as well as the hydrogen modes at 469 cm^{-1}, 491 cm^{-1} and 528 cm^{-1} to the $F_H(\mathrm{H}_s^-)$-center (see Sec. IV A). Longer light bleachings result in further qualitative changes of the Raman spectrum, indicating that a second type of center is formed. When the intensity of the 132-cm^{-1} resonance under 580-nm excitation reaches that of the 137-cm^{-1} resonance, a new one at 129 cm^{-1} and a further broadening in the 155-cm^{-1} range arise. This is accompanied by a broadening of the local hydrogen modes. We identified this center as a combination of an *F* center with two hydrogen ions, the $F_{H2}(\mathrm{H}_s^-)$ center (Sec. IV B). The optical conversion of the 137-cm^{-1} resonance of the *F* centers to the 132-cm^{-1} resonance is more efficient in crystals with a higher hydrogen concentration. This effect is even more pronounced for the 129-cm^{-1} resonance and is illustrated in Fig. 4. A 1.5-mm-thick sample, hydrogenated at 600 °C and 7 atm for 3 days, with an average hydrogen concentration of 2.4×10^{19} cm^{-3}, turned out to have a 4 times lower hydrogen concentration in the center of the crystal than at the surfaces. After a 20-min light bleach, only the *F*-center resonance is observed in the middle of the crystal. The closer to the surface, the stronger the resonances of the aggregate centers are observed. In the crystals in which the highest hydrogen concentration was obtained, the two kinds of aggregates are simultaneously formed after the shortest bleaching times used. Also, after prolonged bleaching the Raman peak extends from 129 cm^{-1} to 160 cm^{-1}, instead of distinct resonances.

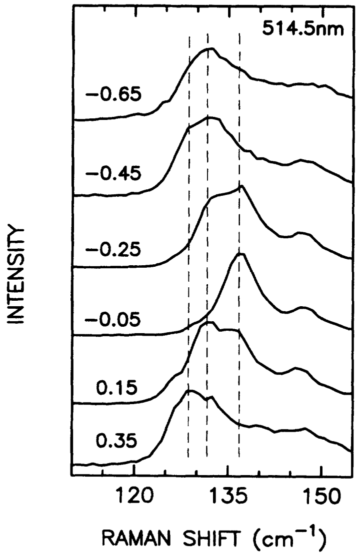

FIG. 4. Raman spectra of the narrow resonances with a resolution of 3 cm^{-1} after a 20-min bleaching. The spectra are recorded at different depths in a 1.36-mm-thick sample with an average hydrogen concentration of 2×10^{19} cm^{-3}. The depth is indicated in mm, relative to the center of the sample. The hydrogen concentration is 4 times lower in the center of the crystal than at the surfaces. The dashed lines mark the positions of the 129-cm^{-1}, the 132-cm^{-1}, and the 138-cm^{-1} mode, which are associated with the $F_{H2}(\mathrm{H}_s^-)$, the $F_H(\mathrm{H}_s^-)$, and the *F* centers, respectively.

IV. CHARACTERIZATION OF THE DEFECTS

A. Structure and vibrational properties of the $F_H(\mathrm{H}_s^-)$ center

The observation of localized modes near 500 cm^{-1} is a clear indication for a hydrogen-related defect. When the three hydrogen modes at 469 cm^{-1}, 491 cm^{-1}, and 528 cm^{-1} are optimally observed, also the 132-cm^{-1} resonance is most prominent. Since it is the first center created as a function of both bleaching time and hydrogen concentration, we identify the aggregate center with the 132-cm^{-1} resonance as the $F_H(\mathrm{H}_s^-)$ center. Under the most favorable conditions, i.e., after a 2- to 10-min light bleach (Fig. 2), polarized Raman measurements were recorded under 514.5-nm excitation for polarizations of incident and scattered light along the ⟨100⟩ crystal axes only (Fig. 5). The 469-cm^{-1} mode is visible for both polarizations of the scattered light. The 528-cm^{-1} and the 491-cm^{-1} modes are only observed, if the polarizations of the incident and the detected light are parallel and perpendicular to each other, respectively. The weaker features, which are most obvious for the ⟨100⟩ ⟨100⟩ scattering geometry, are due to higher-order Raman scattering of the resonant modes and the phonon spectrum.

A model for the position and symmetry of the local modes was presented in Ref. 13 for the $F_H(\mathrm{H}_s^-)$ center in the alkali chlorides. The observation of a triplet of hydrogen modes in NaBr is consistent with the C_{2v} symmetry established in that work, which means that the H_s^- impurity is positioned at a ⟨110⟩ site with respect to the *F* center. By comparison of the polarization properties

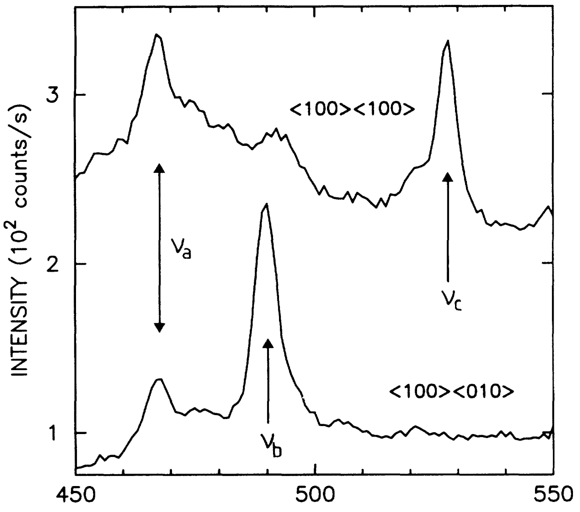

FIG. 5. Polarized Raman spectra of the hydrogen modes of the $F_H(H_s^-)$ center, in NaBr under 514-nm excitation.

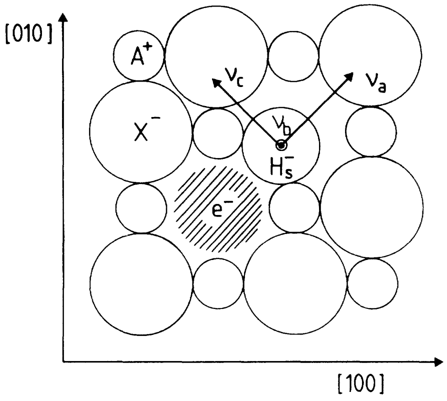

FIG. 6. Hard-sphere model of the $F_H(H_s^-)$-center structure in the {001} symmetry plane. The dimensions apply to the case of NaBr. The small size of the H_s^- ion allows it to relax towards the F center. The arrows show the motion associated with the H_s^- vibrations at $\nu_a = 469\ cm^{-1}$, $\nu_b = 491\ cm^{-1}$, and $\nu_c = 528\ cm^{-1}$. The frequency of the unperturbed H_s^- is $498\ cm^{-1}$.

with those reported earlier for the localized vibrations of the $F_H(H_s^-)$ center, the $469\text{-}cm^{-1}$ mode is identified with the H_s^- vibration parallel to the $\langle 110\rangle$ defect axis (ν_a). The $491\text{-}cm^{-1}$ (ν_b) and $528\text{-}cm^{-1}$ (ν_c) vibrations are both perpendicular to the defect axis. They are parallel to a $\langle 001\rangle$ and a $\langle 1\bar{1}0\rangle$ crystal axis, respectively (Fig. 6).

Assuming that the shift from the unperturbed vibrational frequency is mainly caused by dipole-dipole interaction between the F-center electron and the H_s^- displacement, the frequency of the H_s^- modes of the F_H center is given by[13]

$$\frac{\omega_0-\omega_a}{\omega_0} = -\left(\frac{\bar{e}e}{2\pi\epsilon_0}\right)^2 \frac{1}{m_H\omega_0^2 r^6}\left(\frac{e^2}{m_e}\frac{f}{\omega_F^2}-\alpha_-\right) \times\left(\frac{\epsilon+2}{3\epsilon}\right)^2 , \tag{4.1}$$

$$\frac{\omega_0-\omega_b}{\omega_0} = \frac{\omega_0-\omega_c}{\omega_0} = \frac{1}{2}\frac{\omega_0-\omega_a}{\omega_0} , \tag{4.2}$$

with $\omega_0 = 498\ cm^{-1}$ the vibrational frequency of the isolated hydrogen ion, $\bar{e}$ the effective charge of the ion, m_H the H_s^- mass, r the F-center–H_s^- distance, f and ω_F the oscillator strength and the position of the F band, α_- the polarizability of the halogen ion, and ϵ the high-frequency dielectric constant of NaBr. Because of the axial symmetry of the interaction, the vibrations perpendicular to the defect axis remain degenerate. They are, however, split by the lower symmetry of the crystal lattice, and the shifts of the neighboring ions and the H_s^- itself. Applying Eq. (4.1) to the F_H center in NaBr gives, for the frequencies of the hydrogen modes,

$$\nu_a = 479\ cm^{-1},$$
$$\nu_b = \nu_c = 489\ cm^{-1} .$$

The predicted magnitude of the shift of ν_a and the average shift of ν_b and ν_c deviates much more from the experimental value for NaBr than for the alkali chlorides.[13] More important is the shift of ν_c to a higher frequency, whereas Eq. (4.1) predicts a softening of the hydrogen modes of the F_H center with respect to that of the unperturbed H_s^- center. This shows that the dipole-dipole coupling is not the dominating interaction determining the frequency shift of the localized modes in NaBr.

The frequency increase of the localized vibration may be caused by a displacement of the impurity ion from the substitutional lattice position, as argued in Refs. 22 and 23. An extreme example is the shift of the Li^+ oscillation from $16.3\ cm^{-1}$ for KBr:Li^+ to $227\ cm^{-1}$ for KBr:$F_A(Li^+)$, due to the Li^+ displacement away from the lattice site parallel to the defect axis in the latter case. Figure 6 illustrates an analogous hard-sphere model for the F_H center. The H_s^- ion is allowed to relax, due to the fact that an anion is missing at the F-center site, until it touches the neighboring ions. The displacement is directed most likely towards the F center. The direction is opposite to the case of the F_A center, because of the opposite charge of the impurity ion. The inward relaxation of the nearest neighbors of the F center is neglected. Taking 1.46 Å for the radius of the H_s^- ion,[24] one concludes that the F-H_s^- separation is reduced by the H_s^- displacement to 89% , 88% , 86%, and 81% of its original value for RbCl, KCl, NaCl, and NaBr, respectively. At the same time, the deviation of Eq. (4.1) from the experimental data increases going from RbCl to NaBr.[13] This suggests indeed that the displacement of H_s^- contributes strongly to the observed frequency shifts in NaBr. In Ref. 24 a parameter is calculated for several aggregate centers in the alkali halides, which is a measure for the stabilization energy of the so-called "saddle-point configuration." For the F_H center this means that the H_s^- is positioned on a $\langle 110\rangle$ direction between the two anion vacancies, between which the F-center electron is tunneling. It turns out that the reduction of the energy barrier at the saddle-point configuration is the strongest in the order NaBr, NaCl, KCl, and RbCl. This is in agreement with the conclusion that the H_s^- ion in NaBr has the strongest displacement towards the saddle-point configuration, i.e., towards the F center.

The absorption features of the F_H center cannot be derived directly from the absorption spectrum. The narrow resonances of the Raman spectrum (Fig. 2) show that there is always a contribution of F and/or F_{H2} centers present. Assuming that at a particular excitation wavelength the absorption strength of F and F_H centers and the resonant Raman intensity of their resonances are directly proportional to each other, the relative contributions of F and a F_H centers to the absorption spectrum are known and the F-center contribution can be subtracted. The F_H resonance is relatively more prominent under 580-nm excitation than under 514-nm excitation, since it is then more resonant with the F_H band. Still we did use the 514-nm spectra to calculate the F_H absorption band, since the absorption at 580 nm is weak. As long as there is no important F_{H2} contribution this procedure leads to the same absorption features for the F_H center, when it is applied to the corresponding Raman and absorption spectra after different light bleaching times. The $F_H(H_s^-)$ band has its maximum at 2.32 eV and a width of 0.38 eV (Fig. 1).

B. The $F_{H2}(H_s^-)$ center

Considering the defect content of the samples, the 129-cm^{-1} resonant mode observed in the Raman spectrum should be related to an aggregate center consisting of F center(s) and hydrogen impurities. F-H_i^- aggregation evidently results in the recombination to an H_s^- center at the conversion temperatures used.[18] Also, in the case of F-center aggregation with interstitial hydrogen molecules, one expects localized vibrations in a frequency range considerably higher than 500 cm^{-1}. In contrast, we observed only a perturbation of the hydrogen vibrations of the F_H center. Previously, several modes at slightly different frequencies were observed in KCl, joining the three hydrogen vibrations of the F_H center after long bleachings and at high hydrogen concentrations. They were ascribed to aggregation of an F center with a substitutional hydrogen pair (F_{H2} center) or even larger hydrogen clusters.[12,13] In our case only a washing out of the H_s^- modes is observed, possibly because the weak Raman intensity of the hydrogen modes in NaBr renders measurements with a higher resolution impossible. Another possibility is the formation of an H_s^- center associated with two F centers (F_{2H} center). Both F_{H2} and F_{2H} centers have been studied in OH^--doped cesium halides.[25] It was concluded there that F_{2H} centers are only created when F center concentrations are higher than or comparable to the OH^- concentrations and that they are more alike to F_2 centers than to F_H centers. A relatively low F-center concentration was used and under no circumstances was an absorption band found near 760 nm in our samples. Instead, a redshift of the F-center absorption spectrum is observed, when the 129-cm^{-1} mode is most strongly observed in the Raman spectrum. This slight redshift of the absorption band is also reflected by the fact that the relative Raman intensity of the 129-cm^{-1} mode with respect to the F_H-center narrow resonance is larger under 580-nm than under 514-nm excitation. Considering also that the appearance of the 129-cm^{-1} mode depends more strongly on the hydrogen concentration than the creation of the F_H center does, the 129-cm^{-1} resonance most probably arises from the F_{H2} center, an F center associated with a H_s^- pair.

The F_{H2} formation can occur in two different ways.[25] (i) The F center is trapped by a H_s^- pair statistically present in the lattice. Although the concentration of the pair centers is much smaller than that of the isolated hydrogen impurities, the F_{H2} and F_H centers may be created in comparable concentrations, if the light bleaching occurs selectively for F and F_H centers by a proper choice of the excitation wavelength or polarization. Since the absorption band of the F_H and the F_{H2} center is unsplit and only slightly shifted from the F-center band, the observed efficient F_{H2}-center formation may suggest that it is optically more stable than the F_H center. (ii) After optical excitation of the F_H center, the H_s^- ion can exchange its position with the F center. Afterward the F_H center can be optically dissociated. When the F center is retrapped at another H_s^- impurity or at the same one in another orientation, the same site-exchange process can occur again. In this way the H_s^- center is mobile and pair centers which were initially not present in the crystal, can be formed. The site-exchange process is only effective if the energy barrier for the H_s^- ion is low enough at the saddle-point configuration. It was already mentioned in the previous subsection that the potential energy at the saddle point is strongly reduced in NaBr with respect to the case of other host lattices. It was even suggested that it could be the most stable configuration for the electronic excited state in this host lattice.[24] Therefore, it would be interesting to compare the formation efficiency of F_{H2} centers with other host lattices.

V. EFFECT OF HYDROGEN IMPURITIES ON F-CENTER RELAXATION

Figure 3 compares the time-resolved induced transparency measurements on hydrogenated NaBr under 580-nm excitation at 10 K after F light bleachings of different duration at 250 K. Three decay components are observed: a slow nonexponential one mainly observed before light bleaching, and two components with amplitudes that increase with increasing bleaching time. One of the latter two possesses a decay time of a few hundreds of picoseconds. The other one has a time constant close to the time resolution of the experiment and is, at lower hydrogen concentrations, only clearly observed after long light bleachings. Comparing their relative amplitudes with those of the three narrow resonances observed in the Raman spectra recorded under the same excitation wavelength (Fig. 2), the decay components can be identified with the ground-state recovery of the F center perturbed by a random distribution of H_s^- impurities, and of the $F_H(H_s^-)$ and $F_{H2}(H_s^-)$ centers, respectively. Even before light bleaching the relaxation appears to be faster than the 6-ns F-center relaxation observed in undoped NaBr. Considering also that there is no evidence for other impurities than those mentioned above (cf. Sec. IV), one concludes that the presence of H_s^- impurities causes a considerable decrease of the relaxation time of the F center.

For a quantitative analysis of the decay curves a sample containing only one kind of color centers is desirable. In Sec. III we pointed out that at low hydrogen concentrations and short bleaching times the conversion to $F_H(H_s^-)$ is insufficient, whereas after long light bleachings and at high hydrogen concentrations $F_{H2}(H_s^-)$ centers cannot be avoided. The best compromise for selecting the $F_H(H_s^-)$ center turns out to be an average hydrogen concentration of about $\approx 1\times 10^{19}$ cm^{-3} and a light bleaching of 2–10 min (cf. Fig. 2). The unavoidable presence of three different contributions to the relaxation measurements is a very limiting constraint for retrieving decay constants from a fitting procedure, especially for measurements at higher temperatures. A large number of variable parameters must be introduced. Moreover, the nonexponential decay curve of the F center perturbed by a random distribution of H_s^- impurities is not known accurately analytically (cf. Sec. VI A). One can make use of the experimental decay measurement before light bleaching to take into account the latter contribution. Using the same sample, its contribution in a measurement after conversion can be scaled by means of the amplitude at a 1.6-ns delay, since the contributions of the $F_H(H_s^-)$ and $F_{H2}(H_s^-)$ centers decay much faster. After subtracting the F-center contribution, the two components from the aggregate centers remain (Fig. 7). These components are found to be exponential with a decay time for the F_H center of (290 ± 30) ps and for the F_{H2} center of (29 ± 5) ps.

The temperature dependence of the relaxation before and after F_H formation was studied below 150 K. Higher temperatures were not used to avoid possible bleaching effects. At temperatures up to ~ 100 K, the observed decay of both the F and the F_H centers is clearly faster than the lifetime of the RES of the F center in pure NaBr, and increases with temperature. The effect seems to become small above 110 K for the F center and 130 K for the F_H center. This observation might indicate that above these temperatures the lifetime of the RES is limited by the ionization rate, as is the case for the unperturbed F center.[3,4] However, these measurements are difficult to interpret, because it becomes increasingly difficult to separate the F_H center, F_{H2} center, and F center decays from each other and from the interference spike at zero delay. Besides the relaxation component associated with the lifetime of the RES, a second one has been established for the F center in pure crystals at higher temperatures, which has been related to the retrapping of conduction electrons.[4] At 120 K a similar slow component is observed in hydrogenated crystals, with a contribution to the total signal which is nearly 10 times smaller than the one in pure samples at the same temperature. The difficulty for a clear explanation for this apparent decrease of the ionization efficiency is that the effect is the same before and after F-F_H conversion and that the lifetime of the RES seems to be limited by the ionization rate at these temperatures.

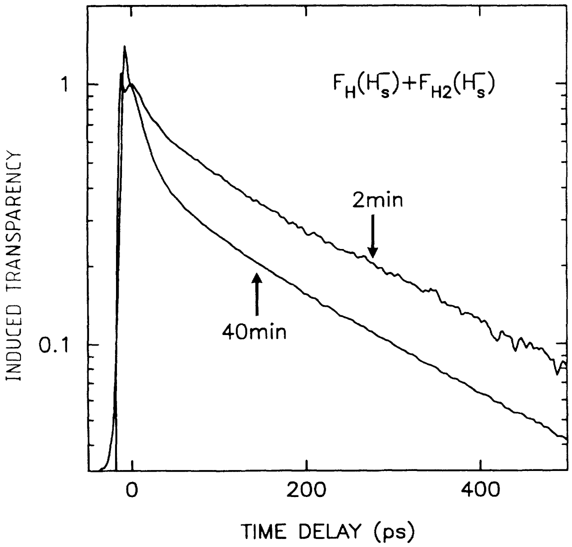

FIG. 7. Logarithmic plot of the F_H and the F_{H2} center decays after two different bleaching times. The F-center contribution has been subtracted (cf. text). The fast contribution of the F_{H2} center (29 ps) has clearly enhanced after long bleaching times with respect to that of the F_H center (290 ps).

VI. NATURE OF THE IMPURITY-INDUCED RELAXATION

As was established for F_A(I)-type centers, which occupy the "normal" substitutional configuration in the RES, *ionic* impurities seem to have no essential effect on the F-center relaxation.[26] Also for the $F_H(H_s^-)$ center in KCl only a marginally smaller (radiative) lifetime has been reported than for the unperturbed F center.[12] The lifetime of the RES of the F center in NaBr, however, is limited by the nonradiative relaxation rate which is extremely sensitive to the optical parameters. The observed small changes in the emission energy of the F_A(I)-type centers, e.g., are sufficient to explain a reduction of 30 meV in the activation energy for the F_H center in NaBr with respect to the unperturbed F center [cf. Eqs. (9)–(12) of Ref. 4]. A reduction of this magnitude is able to account for the RES lifetime of the F_H center. Since already before F-H_s^- aggregation a considerable effect on the relaxation curve is observed, one should also be able to explain a reduced activation energy when the F center is further away from the H_s^- impurity than the ⟨110⟩ lattice position.

The perturbation of the F center by an alkali impurity resulting in the saddle-point configuration in the RES [F_A(II)-type center] is known to change totally the properties of the RES.[26] Consequently, a much larger effect on the nonradiative relaxation rate would be expected than the observed one, if the F_H center possesses the latter configuration in the RES. This suggests that the $F_H(H_s^-)$ center in NaBr does not occupy the saddle-point configuration in the RES, as was tentatively proposed in Ref. 24.

Beside these static impurity-induced effects on the nonradiative decay, the impurity vibration can play an active role in the reduction of the RES lifetime, as in the case of *molecular* impurities.[6–11] The observed electronic-vibrational energy transfer was related to the large frequency of the intramolecular stretching vibration. In the following sections the possibility of energy transfer from the F center to the H_s^- vibration will be investigated. Electronic-electronic energy transfer may be excluded, because our samples contain only F centers, H_s^- centers, and their aggregates, and because no electronic absorption band of these centers lies close to the F-center emission band.

Two essentially different features of the electron-phonon coupling may be responsible for the enhanced nonradiative relaxation of the F-center electron to the ground state: (i) A mode for which the electron-phonon coupling possesses matrix elements between different electronic states stimulates the electronic transition and is called a promoting mode. This is assumed to be the case for the stretching vibration of the OH^- impurity.[9] In the harmonic approximation only one promoting-mode quantum is absorbed or emitted. (ii) A mode for which the electron-phonon coupling possesses matrix elements between the same electronic state absorbs the excess energy after the transition to the ground electronic state and is called an accepting mode. According to the available energy, a multiphonon transition occurs. This was proposed for the CN^- stretching vibration.[6] The accepting character of a mode is reflected in its Huang-Rhys factor and a contribution to the broadening of the absorption spectrum. Before aggregation of the F and H_s^- centers no effect on the F-center absorption is observed, while the relaxation measurements are already considerably affected by the presence of the hydrogen impurities. Therefore, the accepting character of the H_s^- vibration is probably rather small and not the main origin of the faster nonradiative transition rate.

A. Shape of the decay curve

The vibration of the hydrogen ion induces an oscillating electric field, which couples to that of the excited F-center electron. Often the dipole-dipole interaction term is the most important one. In principle, the term of the multipole expansion responsible for the nonradiative transfer can be retrieved from the shape of the decay curve for a random distribution of F and H_s^- centers: The typical dependence of the interaction strength on the acceptor-donor separation is contained in the nonexponential shape through the statistical average over all possible configurations of F and H_s^- centers with respect to each other. In the case of randomly distributed energy donors (F centers) and acceptors (H_s^-) and a molar impurity concentration much smaller than 1, the time evolution of the F-center relaxation can be expressed by[27]

$$\bar{\rho}(t) = A \exp\left(-\frac{t}{\tau_0} - \frac{C_A}{N} \sum_{i=1}^{\infty} N_i \left\{ 1 - \exp\left[-\left(\frac{r_1}{r_i}\right)^m \frac{t}{\tau_1} \right] \right\} \right) . \tag{6.1}$$

In Eq. (6.1) only the dominant interaction term is considered, with $m = 6$ for the dipole-dipole interaction, $m = 8$ for the dipole-quadrupole interaction, $m = 10$ for the quadrupole-quadrupole interaction, etc. N_i is the number of possible sites for acceptors at distance r_i from the F center, and C_A and N the concentration of the acceptors and anion sites, respectively. τ_1 is the relaxation time for the smallest possible acceptor-donor separation r_1, i.e., for the F_H center. The linear term in the exponent takes into account the intrinsic nonradiative relaxation of the F center.

It should be realized that expression (6.1) is not limited to an (electric) promoting interaction between the impurity vibration and the F-center electron. It can be applied more generally, whenever the impurity-induced relaxation rate depends as $\tau^{-1} \sim r^{-m}$ on the F-center–impurity separation. As formula (6.1) is too complicated for practical purposes, it is generally approximated by replacing the sum by a volume integral from 0 to ∞. The discrete character of the lattice is then replaced by an homogeneous acceptor density. This reduces Eq. (6.1) to

$$\bar{\rho}(t) = A \exp\left(-\frac{t}{\tau_0}\right) \times \exp\left[-\frac{4\pi}{3} C_A r_1^3 \, \Gamma\left(1 - \frac{3}{m}\right) \left(\frac{t}{\tau_2}\right)^{\frac{3}{m}} \right] . \tag{6.2}$$

The experimental data were fitted to expression (6.2) without success, even if $\tau_0 = 6$ ns was used as a known parameter. The fact that a fitting procedure on numerically generated curves from Eq. (6.1) does not converge either shows that the problem is technical rather than physical. Fitting values could only be obtained when the intrinsic F-center relaxation was neglected ($\tau_0 = \infty$), which results in values for m between 4.6 and 6 depending somewhat on the hydrogen concentration. Values for m smaller than the one expected for dipole-dipole interaction indicate that the exponential factor in Eq. (6.2), arising from the intrinsic F-center relaxation, has an important contribution to the shape of the decay curve. This is also clear if one realizes from the relaxation of the F_H center that at most two configurations of an F-center and one H_s^- impurity give rise to a relaxation time shorter than 6 ns. These configurations have a small probability below 1 mol % impurity concentration. Apart from that, the fitted curve was sharper at short delay times than the experimental decay curve. The latter deviation is due to the fact that no lower limit for the donor-acceptor distance is assumed in (6.2), whereas the configuration with the closest separation possesses a relaxation time of 290 ps, which is well above the time resolution of the experiment. This was verified by numerically generating decay curves, using the summation (6.1) for m= 6, 8, and 10 and fixing τ_0 and τ_1 to 6 ns and to 290 ps, respectively. The shape of the decay curve looked quite similar in the three cases. Fitting the simulated decay curves in the same way as the experimental ones ($\tau_0 = \infty$), comparable values of m were obtained for dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions. Similar results were obtained when an exponential dependence of the relaxation rate on the F-center–impurity separation was assumed. This implies that no conclusions can be drawn about the nature of the F-H_s^- interaction on the basis of the shape of the relaxation curves, due to the non-negligible interference of the intrinsic F-center decay. Another result obtained from the numerical simulations is that the *average* hydrogen concentration estimated in Sec. III is too low to explain the observed ground-state recovery. A concentration of 10^{19} cm^{-3} yields a minor deviation from the intrinsic F-center relaxation, and it should be as high as 5×10^{20} cm^{-3} to obtain a decay as fast as the observed one. As pointed out in Sec. III an accurate quantitative determination of the hydrogen concentration was not possible. It was also demonstrated in that section that the hydrogen distribution is not completely homogeneous because of the limited penetration depth of the hydrogen impurities. Since the F-center production is proportional to the hydrogen concentration, the relaxation measurements probe preferentially the regions of the crystal with the highest hydrogen concentration. These effects might account for a factor of 10 between the average H_s^- doping, determined by absorption, and the local concentration relevant for the time-resolved measurements. Coagulation of impurities would affect the observations in the same way. An experimental indication that the local hydrogen concentration is indeed of the order of 1 mol % is that in some samples the Raman intensity of the F_H resonance is already about 10% of the F-center resonance before optical aggregation (cf. Ref. 12).

B. Estimate of the energy-transfer rate

It has been demonstrated that the dipole-dipole coupling between the F-center electron and the H_s^- vibration is the dominant one in the alkali chlorides in determining the shift of the hydrogen vibrations due to the presence of the F center.[13] This suggests to evaluate the effect of the dipole-dipole coupling between the F center and the vibration of the H_s^- impurity on the nonradiative relaxation. In Sec. IV A it was shown that for NaBr strong deviations from the dipole-dipole model were observed. These were, however, related to repulsive forces with the nearest neighbors of the hydrogen ion and not to the interaction with the F-center electron.

To estimate the nonradiative relaxation rate of the F_H center, a transition between the states $|\phi_e\rangle|n_a^{(e)}\rangle|0_p\rangle$ and $|\phi_g\rangle|n_a^{(g)}\rangle|1_p\rangle$ is considered, in which $|\phi_g\rangle$ and $|\phi_e\rangle$ are the ground and excited electronic states of the F center, respectively. The electronic relaxation excites one H_s^- vibrational quantum $|0_p\rangle \to |1_p\rangle$, which is assumed to promote the transition due to dipole-dipole interaction with the F-center electron. A thermal average over the accepting-mode levels $|n_a^{(g)}\rangle$ in the electronic excited state is performed, whereas the occupation number of the accepting mode in the ground state is determined by energy conservation. In the limit of strong electron-phonon coupling the nonradiative transition rate can be written as[28]

$$\tau_{\mathrm{NR}}^{-1} = \sum_{p=a,b,c} \frac{C_p^2}{\hbar}\sqrt{\frac{2\pi}{E_R kT^*}}\exp\left(-\frac{E_A}{kT^*}\right) , \tag{6.3}$$

in which the contribution of all three hydrogen modes with frequency $\nu_{a,b,c}$ is taken into account. The effective temperature T^* is defined by

$$kT^* = \frac{\hbar\omega_a}{2}\coth\left(\frac{\hbar\omega_a}{2kT}\right) , \tag{6.4}$$

with E_R the vibrational relaxation energy after optical excitation (Fig. 8), E_A the activation energy, and ω_a the accepting mode frequency.

The additional promoting interaction constant C for the F_H center, due to the dipole-dipole interaction, is given by

$$C_p^2 = \left(\frac{\eta_p \bar{e}\mu_e}{4\pi\epsilon_0 r^3}\right)^2 \left(\frac{\hbar}{2m_H\omega_p}\right) , \tag{6.5}$$

with m_H the hydrogen mass and r the distance between F center and the H_s^- impurity. The promoting-mode frequency ω_p is in this case the frequency of the H_s^- vibration. The effective charge $\bar{e}$ of the H_s^- ion is taken to be 0.8 times the electron charge.[29] The dipole moment for the electronic transition of the F center is calculated from the radiative lifetime as in Ref. 13. The geometrical factor η_p depends on the orientation of the two dipoles with respect to each other. For a random orientation the average value is[27] $\eta_p = (2/3)^{1/2}$. In our case the directions of the dipole moment, induced by the hydrogen vibrations, have a fixed orientation with respect to the

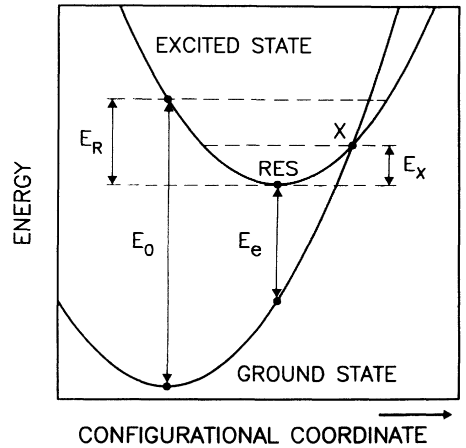

FIG. 8. Configurational coordinate diagram for the ground and the excited states appropriate to F centers possessing intrinsic luminescence quenching. The figure shows the absorption energy (E_0), the configurational relaxation energy after optical excitation (E_R), the crossover energy (E_X) from the relaxed excited state (RES) to the crossover point (X), and the emission energy (E_e).

defect axis of the $F_H(\mathrm{H}_s^-)$ center. For the vibration parallel to the defect axis one finds $\eta_a = (4/3)^{1/2}$ and for the orthogonal vibrations $\eta_{b,c} = (1/3)^{1/2}$. Expression (6.5) should still be multiplied with the local-field correction factor. Since one of the dipole moments is obtained from the radiative lifetime, whereas the other one is calculated, the appropriate correction factor is[27]

$$n^{-5}\left(\frac{n^2+2}{3}\right)^2 , \tag{6.6}$$

with n the refractive index. Assuming that the separation between the F center and the H_s^- impurity is equal to $2^{1/2}a$, with a the cation-anion distance, the promoting interaction constant (6.5) is equal to

$$C_a = 88 \text{ cm}^{-1}, \quad C_b = 43 \text{ cm}^{-1}, \quad C_c = 41 \text{ cm}^{-1} \quad . \tag{6.7}$$

In Sec. IV A it was suggested that the F-H_s^- distance is reduced to about 82%, which increases the previous values to

$$C_a = 152 \text{ cm}^{-1}, \quad C_b = 74 \text{ cm}^{-1}, \quad C_c = 72 \text{ cm}^{-1} \quad . \tag{6.8}$$

Clearly the calculated promoting interaction constants (6.7) and (6.8) are of the same order of magnitude as the $C = 167 \text{ cm}^{-1}$ for the unperturbed F center, obtained by fitting the relaxation measurements.[4] This already indicates that the dipole-dipole coupling between the F and H_s^- center is competitive with the *nonradiative* relaxation of the pure F center in NaBr.

The activation energy E_A in Eq. (6.3) is defined as

$$E_A = \frac{(E_e - \hbar\omega_p)^2}{4E_R} \quad . \tag{6.9}$$

When ω_p is put equal to zero, the activation energy E_A equals the crossover energy E_X, as was done in Ref. 4 in the case of the pure F center. This is only adequate if the promoting-mode energy is negligible compared to the emission energy E_e. A high promoting-mode frequency effectively reduces the activation energy. As a result, the exponential factor in Eq. (6.3) is enhanced by a factor of ~ 10 in the case of the F_H center compared to the case of the pure F center in NaBr. The contributions to the nonradiative transition rate due to the three hydrogen modes and also the (smaller) intrinsic contribution of the F center are added. Depending on whether or not the proposed displacement of the H_s^- is taken into account, this yields a RES lifetime of 500 or 1500 ps for the F_H center in NaBr. The agreement with the experimental value of 290 ps is quite good, if one realizes that the result is sensitive to relatively small shifts of the H_s^- position and to the local-field correction. It depends also critically on the emission parameters and the configurational relaxation energy, which were taken to be the same as for the unperturbed F center.[4] Corrections of this kind can have an important effect, as was already mentioned in Sec. VI. A possible further mixing of the $2p$- and $2s$-like states of the F center increases the oscillator strength and, as such, increases the dipole-dipole promoting interaction. Changes of the configurational coordinate diagram influence all terms in the nonradiative transition rate in the same way, in particular also the one involving the dipole-dipole promoting interaction. This means that efficient energy transfer may occur, even if static impurity-induced effects on the relaxation rate are larger. This is true as long as the promoting interaction associated with the impurity vibration (together with the activation-energy reduction due to the promoting-mode frequency) dominates the other promoting interactions of the F center.

For the F_H center in KCl both the interaction strength and the increase of the exponential factor are comparable to the case of NaBr. The nonradiative relaxation of the F center in KCl, however, is many orders of magnitude slower than the radiative decay, as is evident from the full quantum efficiency for emission[30,31] and from a theoretical estimate.[4] Therefore, an increase of the nonradiative transition rate of one or two orders of magnitude does not affect the RES lifetime of the F center in KCl. This explains why experimentally only a minor effect is observed when the F center is perturbed by a H_s^- impurity. The situation is completely different for the OH^- impurity in KCl. Although the promoting interaction constant is about 10 times smaller due to the higher vibrational frequency and the larger distance r [cf. Eq. (6.5)], the same high promoting-mode frequency increases the exponential factor in Eq. (6.3) with a factor of 10^{15}, compared to the case of the pure F center. Total quenching of the F-center luminescence can therefore be understood.

VII. CONCLUSIONS

We identified the optical absorption and resonant Raman scattering properties of the F, $F_H(\mathrm{H}_s^-)$, and $F_{H2}(\mathrm{H}_s^-)$ centers in hydrogenated NaBr. The absorption bands of the aggregate centers exhibit the usual slight broadening and redshift with respect to the F band. The most efficient way to probe the aggregation of the F center with hydrogen impurities turned out to be the resonant Raman scattering of the narrow resonances, which possesses a clearly resolvable shift for the F_H and F_{H2} centers with respect to the one of the F center. The polarized Raman intensities of the three hydrogen modes of the F_H center are consistent with the model established before for this center in the alkali chlorides. In contrast to the latter case, the frequency of the hydrogen vibration with respect to the one of the unperturbed H_s^- cannot be explained by dipole-dipole interaction between the F center and the hydrogen vibration. Therefore, enhanced repulsive forces with its neighbors were suggested, due to a displacement of the H_s^- equilibrium position from the substitutional lattice site towards the F center. The displacement may be related to a lower-energy barrier at the saddle-point configuration of the H_s^- ion, which in turn might explain the observed efficient F_{H2} formation in NaBr.

The presence of H_s^- impurities in the crystal reduces the RES lifetime of the F center, even before aggregation. The information on the nature of the interaction responsible for this effect, is in principle contained in the shape of the relaxation curve before F-center–H_s^- conversion. This information is obscured mainly due to the minimum transition rate (corresponding to the unperturbed F center), which is not negligible with respect to the one of the closest F-center–hydrogen separation. As a result, decay curves associated with a different separation dependence of the defect-induced relaxation rate give rise to a very similar shape. The time scale of the relaxation is determined by the interaction strength and the impurity concentration. The latter, however, is not known accurately enough because of the inhomogeneity of the impurity doping, so that this feature of the decay curves cannot provide decisive arguments either. The use of more homogeneously doped samples, grown from an alkali hydride doped melt, can possibly solve this problem.

The faster nonradiative relaxation for the F_H center may be the result of small differences of the optical properties with respect to the unperturbed F center. An estimate of the promoting interaction due to dipole-dipole coupling between the F-center electron and the H_s^- vibration shows that this interaction, together with the activation-energy reduction due to the promoting-mode frequency, may dominate the promoting interaction of the unperturbed F center. This opens the possibility of electronic-vibrational energy transfer. Although the effect is considerably smaller because of the much smaller vibrational frequency, this process is the same as the one proposed for OH^--doped alkali halides. Measurements on deuterated NaBr are indicated to confirm or reject the possibility of energy transfer due to dipole-dipole interaction.

Equation (6.3) predicts the relaxation rate for the F_{H2} center to be about twice as fast as for the F_H center, whereas experimentally it is 10 times faster. This might be related to (relatively small) differences between the features of the RES of the two centers and shows that the dipole-dipole interaction is not the only effect playing a role in the impurity-induced nonradiative relaxation. Since the relaxation time of the F_{H2} center lies in the region of the vibrational cooling, the observed relaxation time is not necessarily limited by the electronic transition.

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[1] R.H. Bartram and A.M. Stoneham, Solid State Commun. **17**, 1593 (1975).
[2] R.H. Bartram, J. Phys. Chem. Solids **51**, 641 (1990).
[3] G. Baldacchini, D.S. Pan, and F. Lüty, Phys. Rev. B **24**, 2174 (1981).
[4] F. De Matteis, M. Leblans, W. Joosen, and D. Schoemaker, Phys. Rev. B. **45**, 10 377 (1992).
[5] J. De Kinder, W. Joosen, and D. Schoemaker, Phys. Rev. B. **42**, 9674 (1990).
[6] G. Halama, S.H. Lin, K.T. Tsen, F. Luty, and J.B. Page, Phys. Rev. B **41**, 3136 (1990).
[7] L. Gomes and F. Luty, Phys. Rev. B **30**, 7194 (1984).
[8] Y. Yang and F. Luty, Phys. Rev. Lett. **51**, 419 (1983).
[9] G. Halama, K. Tsen, S. Lin, F. Lüty, and J. Page, Phys. Rev. B **39**, 13 457 (1989).
[10] D. Jang, T.C. Corcoran, M.A. El-Sayed, L. Gomes, and F. Luty, in *Ultrafast Phenomena V*, edited by G. R. Fleming (Springer-Verlag, Berlin, 1986), p. 280.
[11] Y. Yang, W. von der Osten, and F. Lüty, Phys. Rev. B **32**, 2724 (1985).
[12] Y. Kondo and F. Lüty, Solid State Commun. **40**, 325 (1981).
[13] D.S. Pan and F. Lüty, Phys. Rev. B **18**, 1868 (1978).
[14] C. Sierens, W. Joosen, and D. Schoemaker, Phys. Rev. B **37**, 3075 (1988).
[15] Y. Kondo, J.R. Duffey, and F. Lüty, Phys. Rev. B. **23**, 28 (1981).
[16] R. Hilsch, Ann. Phys. (Leipzig) **29**, 407 (1937).
[17] W.B. Fowler, in *Physics of Color Centers*, edited by W.B. Fowler (Academic, New York, 1968), Chap. 2.
[18] D. Bäuerle, in *Solid-State Physics*, Springer Tracts in Modern Physics Vol. 68, edited by G. Höhler (Springer-Verlag, Berlin, 1973), p. 114.
[19] F. De Matteis, E. Gustin, M. Leblans, and D. Schoemaker (unpublished).
[20] D. Bäuerle, in *Solid-State Physics*, Springer Tracts in Modern Physics Vol. 68, edited by G. Höhler (Springer-Verlag, Berlin, 1973), p. 92.
[21] C. Buchenauer, D. Fitchen, and J. Page, Jr., in *Light Scattering Spectra of Solids*, edited by G.B. Wright (Springer-Verlag, Berlin, 1969), p. 521.
[22] M. Leblans, W. Joosen, and D. Schoemaker, Phys. Rev. B **42**, 7220 (1990).
[23] M. Leblans, Ph.D. thesis, University of Antwerp, 1990.
[24] A.Y.S. Kung, J. Lagowski, and J.M. Vail, Phys. Status Solidi B **100**, 621 (1980).
[25] M. Krantz, F. Luty, V. Dierolf, and H. Paus, Phys. Rev. B **43**, 9888 (1991).
[26] F. Lüty, in *Physics of Color Centers*, edited by W.B. Fowler (Academic, New York, 1968), Chap. 3.
[27] *Electronic Excitation Energy Transfer in Condensed Matter*, edited by V.M. Agranovich and M.D. Galanin (North-Holland, Amsterdam, 1982).
[28] R. Englman and J. Jortner, Mol. Phys. **18**, 145 (1970).
[29] B. Fritz, in *Localized Excitations in Solids*, edited by R.F. Wallis (Plenum, New York, 1968).
[30] R.K. Swank and F.C. Brown, Phys. Rev. **130**, 34 (1963).
[31] S. Honda and M. Tomura, J. Phys. Soc. Jpn. **33**, 1003 (1972).