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Energy transfer and picosecond relaxation of F centers in RbCl, KCl, and KBr

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Possible decay mechanisms of excited F centers are investigated in both additively colored and x-irradiated RbCl, KCl, and KBr, containing typically more than 3×10^{16} cm^{-3} F centers and sizable amounts of dimer (F_2) and higher F aggregates. Time-resolved ground-state recovery measurements under F-band excitation at low temperature and optical-absorption data show a picosecond deexcitation process, occurring for a substantial number of F centers and possessing shorter decay times for higher relative concentrations of F_2 and N centers. This establishes energy transfer from excited F to F_2 centers, a controversial topic throughout the literature, and towards N centers in KCl to be both competitive relaxation channels. Transient absorption measurements in heavily colored KCl by Gadonas *et al.*, which show increased transparency in the F_2-band region 500 ps after pulsed F excitation, fully support the above conclusion. A similar behavior was also observed in RbCl and KBr. This additional decay channel could adversely affect laser operation in several color-center lasers.

I. INTRODUCTION

Depending on the alkali halide crystal, an isolated F center exhibits two different types[1,2] of relaxation behavior after F-band optical excitation. This behavior is governed by the lattice relaxation energy E_R in the excited state. When E_R is below the critical value of one-fourth of the optical excitation energy,[1,2] luminescence occurs in the near infrared (type I) with radiative lifetimes ranging from 50 ns in CsF up to 570, 600, and 1100 ns for KCl,[3] RbCl,[4,5] and KBr,[3] respectively ($T \leq 77$ K). When E_R is larger than this critical value, as is the case in NaBr, NaI (Ref. 6), and the lithium halides,[1] the luminescence is strongly quenched by faster radiationless processes (type II), yielding ns and ps nonradiative lifetimes[7] for the F-center excited state (denoted F^* throughout this paper).

In this paper we focus on the type-I behavior, in particular for F concentrations larger than 3×10^{16} cm^{-3}, where also aggregates of F centers are present. In the alkali halides studied, i.e., RbCl, KCl, and KBr, ps relaxation is observed for F centers produced by x irradiation and by additive coloration. The possible decay mechanisms for this fast deexcitation are investigated, focusing on the interactions between F^* and other excited F centers (F^*-F^*) (Refs. 8 and 9) or F aggregates (F^*-F_n^*), or between F^* and unexcited F centers (F^*-F) (Refs. 10 and 11) or F aggregates (F^*-F_n).[10] The interactions include tunneling[12,10] of the F^* electron to nearby centers with formation of negatively charged centers, such as the F^- center[11] (traditionally known as the F' center) or the F_2^- center,[10] and energy transfer.[8,9,13] New data will be presented, providing information about the relaxation behavior of the F^* state, that are relevant with respect to the color-center lasers.[14-17] The observed fast deexcitation cannot be neglected since the F concentration, initially present[14,16,17] in these laser media, is above 3×10^{16} cm^{-3}.

There is still a controversy over whether or not energy transfer occurs from F^* to F_2 centers in KCl.[4,18] Direct evidence would be the occurrence of F_2-center luminescence under F-center excitation. However, the overlap of the F_2 absorption bands[19] at 553 and 538 nm (the traditionally called M_F bands) with the F band does not allow one to discriminate between the F_2 normal optical cycle luminescence and deexcitation after energy transfer from excited F centers. Swank and Brown[3] observed a quenching of the F luminescence in the presence of F_2 centers. A correlation between the decreasing quantum efficiency for F-center luminescence and the increasing F_2 concentration was established by Van Doorn.[20] However, no irrefutable evidence for F^*-F_2 energy transfer was provided later on. After excitation of F centers with light, perpendicularly polarized to the transition moments of preferentially oriented F_2 centers, Schneider[4,21] found about one-third of the F_2 centers in the triplet state.[22,23] He explained this formation of F_2 triplets by energy transfer from excited F centers. Subsequently, this growth of F_2 triplets was assigned to tunneling processes[4,10] from the relaxed excited state (RES) and it still remained unclear why energy transfer would exclusively produce that large an amount of triplet states, since no *direct* triplet formation by exciting F_2 centers was observed.[22] Measurements of the quantum efficiency of the F^* luminescence[24] even on preferentially oriented F_2 centers did not provide unambiguous[25,26] evidence. Neither energy transfer to other *F* aggregates nor energy transfer in other alkali halide crystals were investigated.

More recently, pump-probe experiments[27] revealed ps ground-state recovery upon *F* excitation in KCl. This fast deexcitation was explained by a model based on an energy transfer between inhomogeneously distributed F^* centers. The authors did not recognize the striking discrepancy between additively colored and *x*-irradiated samples. The contribution of the fast component to the whole decay is about three times higher in additively colored samples for an equal *F*-center concentration. This is probably due to a more prominent *F*-aggregate formation in additively colored crystals. Apart from this, absorption and emission bands of the F^* center do not overlap in KCl,[28] so no (F^*-F^*) energy transfer is likely to occur.

Gadonas *et al.*[29] measured the transient absorption spectrum between 450 and 950 nm under *F*-band excitation for a time delay of the probe pulse of 0 and 500 ps. The whole spectrum shows enhanced absorption apart from two regions of increased transparency at 539 and 800 nm. Direct excitation of the F_2 center due to the absorption bands underlying the *F* band cannot account for this, since they observed an increase of the reduced absorption after a delay of 500 ps. Their time-resolved spectra directly show evidence for F^*-F_2 energy transfer, though it was not recognized as such.

Section II contains a description of the apparatus and the preparation of the samples. In Sec. III the relaxation spectra and optical-absorption data are presented for different concentrations of various *F*-aggregate centers. The pump-and-probe wavelength, the power, and the polarization of both laser beams were systematically varied. In Sec. IV energy transfer is shown to be the most likely fast relaxation process, starting from new ground-state recovery data in RbCl and KCl and from the information available for KCl on the specific time scales for the various deexcitation processes. Evidence for a "coagulation" of *F* centers and aggregates is also provided.

II. EXPERIMENTAL DETAILS

The experimental setup[30] consists of two Rhodamine 6G dye lasers, synchronously pumped by an Ar^+ laser and generating ps pulses, tunable between 570 and 640 nm. This region is resonant with the *F* band in RbCl and KBr, and with the low-energy side of the *F* band in KCl. Using a double modulation detection technique, a change in intensity of the probe, induced by the pump, of 10^{-7} can be detected. By varying the delay of the probe pulse, the decay of the excitation is recorded. The time resolution is determined by the cross-correlation jitter between the two dye laser pulses and is about 20 ps. The high sensitivity of our setup and the low energy of the pulses (100 pJ) permitted us to restrict the fraction of excited *F* centers by one pulse, e.g., in KCl to 0.2%. This allows one to study the interaction between a single F^* center and unexcited centers, in contrast to previous studies.[8,9,27]

Experiments were carried out on both *x*-irradiated and additively colored samples. The additively colored and pure samples were quenched from 420 and 670 K, respectively. *X* irradiation was performed at room temperature (RT) with a Siemens tube with tungsten target (50 kV,50 mA) for time intervals ranging from 15 min to several hours. Regardless of the quenching procedure, sizable differences in the decay spectra were obtained for different regions in the crystal, reflecting inhomogeneities in the concentration of the electron centers. The relative concentration of *F* and F_n centers was varied by *F* bleaching at RT, using filtered light from a halogen lamp. Large concentrations of aggregate centers could not be produced in KBr. Optical-absorption measurements were performed using a double beam Cary 17 spectrophotometer.

III. PICOSECOND GROUND-STATE RECOVERY

A. The fast decay

In Fig. 1 decay curves are shown for four different concentrations of *F* and *F* aggregates in KCl. The decay consists of two parts: a slow component, approximated by a step function $\Theta(t)$ at $t=0$ ps with amplitude A_{sl}, and a fast component with an amplitude A_f, which was fitted to a single, a double, and several stretched exponential functions. As can be seen from Table I, the best fit with the least number of parameters is obtained for the first stretched exponential. A better χ^2 value is reached for a double exponential decay, however with two param-

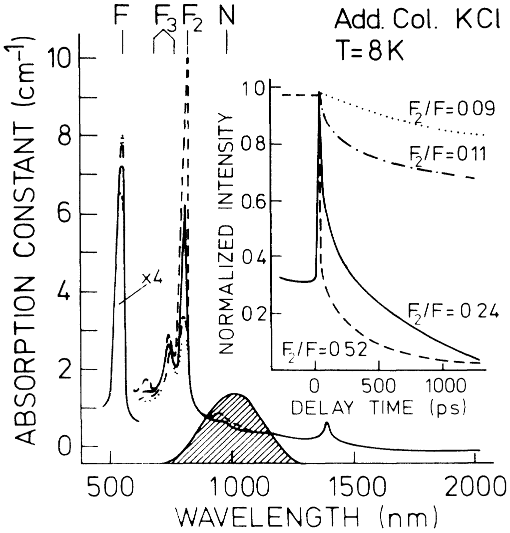

FIG. 1. Ground-state recovery at 8 K after *F* excitation for various concentrations of the aggregate centers, as shown in the accompanying optical-absorption spectra of the thin samples (about 0.5 mm) of additively colored KCl. The concentrations of these aggregates and the best-fit parameters of the decays to a stretched exponential are given in Table II. The absorption peak at 1400 nm is caused by the windows of the cryostate.

TABLE I. χ^2 value of least-squares fits of several exponential functions to a representative decay spectrum of the F center in x-irradiated RbCl at 77 K.

Function	Number of parameters	χ^2
$A_1+A_2\exp(-t/\tau)$	3	5.37
$A_1+A_2\exp(-t/\tau_1)+A_3\exp(-t/\tau_2)$	5	1.51
$A_1+A_2\exp(-\gamma\sqrt{t})$	3	1.72
$A_1+A_2\exp(-\gamma t^{3/8})$	3	3.02
$A_1+A_2\exp(-\gamma t^{3/10})$	3	8.37

eters more. However, no physical significance could be associated with the fitted parameters A_1, A_2, A_3, τ_1, and τ_2 as obtained from the decay spectra after subsequent F bleaches. The decays curves are therefore characterized by the three parameters A_{sl}, A_f, and γ as in

$$S(t)=A_{\mathrm{sl}}\Theta(t)+A_f e^{-\gamma\sqrt{t}}\ . \tag{1}$$

Additional experiments on KCl were performed, using the 120 ps Ar^+ laser pulse as probe beam. Increased time resolution (5 ps) and an even more resonant excitation (532 nm) was achieved using a frequency-doubled Nd:YAG (YAG denotes yttrium aluminum garnet) laser (532 nm,5 ps). The qualitative characteristics of these decays are similar.

The change in intensity of the probe for different excitation wavelengths of the pump in RbCl is shown in Fig. 2. In x-irradiated KCl, the intensity decreased by at least a factor 25 when changing the pump from 580 to 634 nm. No further study was performed in additively colored KCl because of a too-prominent F_3 (650 nm) concentration that reduced the relative contribution of F centers to the decay. We conclude that the observed fast decay is due to F-center ground-state recovery.

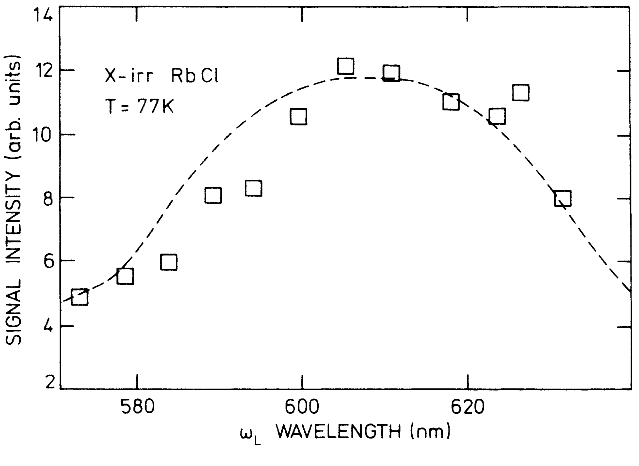

FIG. 2. The signal intensity of the ground-state recovery (□) is given for different wavelengths ω_L of the pump laser (within the R6G tuning range), with ω_P fixed at 618 nm. For comparison, the F-center absorption band in RbCl is presented as the dashed curve.

B. The slow decay

For nearly resonant excitation of the F centers in RbCl and KBr, the slow component is due to the optical μs cycle of the isolated F center. The situation for KCl is more complicated, because not only F centers are excited: The total signal contains contributions from the optical cycles of several excited defects (Sec. III C) and their mutual interactions (see Sec. IV A for a detailed analysis). During the pump-probe measurements, a dynamical equilibrium builds up that depends on the polarization, intensity, and wavelength of both laser beams, and the concentration and the distribution of these defects in the crystals. A detailed analysis of the contribution of all the centers is therefore impossible to perform and we limit ourselves to discuss some qualitative features of the slow component.

The slow decay may be either in phase (positive sign) or in antiphase (negative sign) with the fast one. A positive signal corresponds to a reduced absorption of the probe and is due to the normal optical cycle of the excited centers. Increased absorption (negative step function) can be caused by the formation of new defects or by absorption of defects in their excited state. It can be seen in Fig. 1 that this occurs for high aggregate concentrations in KCl. The signal with opposite phase may be due to formation of triplet F_2 centers, excited state absorption of the F_3 centers,[4] or to F^- centers.[11] The presence of the triplet F_2 centers, absorbing at 505, 600, and 685 nm (Ref. 23), may be prominent,[10,21] but could not be detected by the accompanying optical-absorption measurements, due to their limited lifetime[10] (about 50 s at 77 K). F_3 centers are excited in the high-energy tail of their absorption band at 650 nm, as are F^- centers, who have a continuous absorption band ranging on the long-wavelength side of the F band in these crystals.

C. Correlation with optical-absorption data

Since most information in the literature is available for KCl, we will concentrate first on F aggregates in KCl. Energy transfer may occur to aggregate centers whose absorption bands overlap the broad luminescence band of the F center (peaking at 1020 nm for KCl). The possible acceptors are the F_2 (800 nm), the F_3 (650 nm), the F_3^{so} (1340 nm) center, and the centers absorbing around 975 nm. The lowest optical transition[19] of singlet F_2 centers lies at 800 nm; higher absorptions[19] occur at 546 and 538

TABLE II. Analysis of the ground-state recovery spectra of the F center and the accompanying optical-absorption measurements of several electron centers in additively colored KCl (Fig. 1). When no oscillator strengths were available, the aggregate centers are indicated by optical density—the absorption constant (AC). The F-center concentration is corrected for the underlying absorption bands of the F_2 center (Refs. 19 and 22). The ratio F_2/F is also inserted, since transfer probability should go as the ratio of donor-to-acceptor concentration. Two parameters characterize the decay spectra: γ determines the time scale of the decay and the amount of fast decay is specified by the ratio $A_f/A_{\rm sl}$.

	F center concentration (cm^{-3})	F_2 center concentration (cm^{-3})	F_2/F ratio	F_3 (650 nm) AC (cm^{-1})	N (975 nm) AC (cm^{-1})	$A_f/A_{\rm sl}$ ratio	γ (ps$^{-1/2}$)
1	9.0×10^{16}	8.2×10^{15}	0.09	0.025	~0	0.99	0.016
2	9.0×10^{16}	9.7×10^{15}	0.11	0.06	0.12	1.40	0.041
3	7.2×10^{16}	1.7×10^{16}	0.24	0.17	0.14	3.00	0.044
4	5.2×10^{16}	2.7×10^{16}	0.52	0.34	0.26	1.54	0.062
5[a]	4.9×10^{16}	4.1×10^{15}	0.08			0.96	
6[a]	4.9×10^{16}	4.9×10^{15}	0.10			1.94	

[a] From Ref. 20, with corrected values for the two F_2 bands.

nm. The triangular F_3 $\{111\}$-plane configuration absorbs at 650 and 730 nm. Apart from this configuration, weak absorption bands at 1340, 1670, and 1940 nm correspond to "stretched-out" arrangements[31] (denoted as $F_3^{\rm so}$). No evidence for the presence of $F_3^{\rm so}$ (1340 nm) centers was found by optical-absorption measurements in our samples. The so-called N_1 and N_2 centers are still under investigation (see Refs. 32, 33, and references therein). We cannot distinguish between these centers using F bleaches and therefore we will denote them as N (975 nm).

The optical densities of the F and F aggregates for KCl and RbCl, as taken from the optical-absorption data of Figs. 1 and 3, are presented in the Tables II and III, respectively. These tables also include the parameters γ and $A_f/A_{\rm sl}$, describing the ground-state recovery spectra of Figs. 1 and 3. The data on KBr show similar features, although no such large concentration of aggregate centers could be obtained.

For a low concentration of aggregates in the three alkali halides, no fast decay was observed, as is shown for RbCl (Fig. 3). The amplitude of the fast component and the corresponding decay parameter γ increases for a larger concentration of aggregates. The same behavior was also noticed under 514- and 532-nm excitation in KCl and for the F-center system in KBr. Surprisingly, during the subsequent decrease of the aggregate concentration in RbCl, the $A_f/A_{\rm sl}$ ratio decreases, while γ still increases. For KCl, due to the complex composition of the slow decay component, no information can be retrieved from the $A_f/A_{\rm sl}$ ratio for large aggregate concentrations.

For comparison, the quantum yield measurements by Van Doorn[20] were also included in Table II and compared to $A_f/A_{\rm sl}$. When considering the same F_2/F ratio, this value is much larger than the $A_f/A_{\rm sl}$ ratio, obtained by our pump-probe experiments. This can be explained as follows. First, our value of $A_{\rm sl}$ does not only contain the optical (radiative) cycle of the F center as for the data of Van Doorn, but is a mixture of several contributions. Therefore, the $A_f/A_{\rm sl}$ value should be smaller than the one obtained by measuring the quenching of F-center luminescence.[20] Second, no information about other aggregates to which energy transfer might occur was provided.

D. Polarization properties

Great care was taken to ensure that the same light intensity was sent on the sample for mutually parallel ($\boldsymbol{\varepsilon}_L \parallel \boldsymbol{\varepsilon}_P$) or perpendicular ($\boldsymbol{\varepsilon}_L \perp \boldsymbol{\varepsilon}_P$) polarization of the pump and probe beams. The decay curves were identical for both polarizations in RbCl and KBr. Ground-state recovery spectra for KCl with mutually parallel and orthogonal polarizations are shown in Fig. 4. The total signal intensity for $\boldsymbol{\varepsilon}_L \parallel \boldsymbol{\varepsilon}_P$ is larger than for $\boldsymbol{\varepsilon}_L \perp \boldsymbol{\varepsilon}_P$. A detailed analysis of these two spectra showed the charac-

TABLE III. Analysis of the ground-state recovery and subsequent optical-absorption measurements in x irradiated RbCl (Fig. 3). The amount of F_2, F_3, and N is indicated as the absorption constant, since only for the F centers is the oscillator strength known. Higher state absorptions of the F_2 center are not yet identified in RbCl. The parameters γ and $A_f/A_{\rm sl}$ are as in Table II.

	F center AC (cm^{-1})	F_2 center AC (cm^{-1})	F_3 (738 nm) AC (cm^{-1})	N (1050 nm) AC (cm^{-1})	$A_f/A_{\rm sl}$ ratio	γ (ps$^{-1/2}$)
1	16.1	1.1	~0	0.05	0	
2	13.7	5.8	0.75	0.58	1.07	0.019
3	11.4	2.2	2.6	0.88	7.63	0.029
4	8.9	2.1	2.0	0.77	3.20	0.050

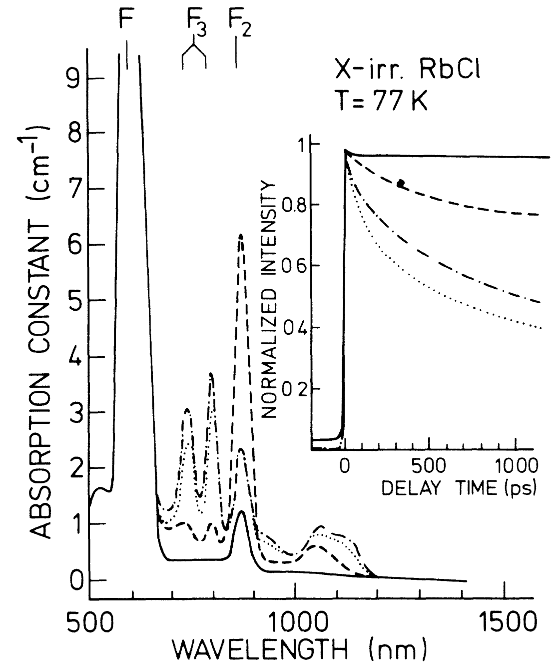

FIG. 3. Normalized decay of excited F centers in x-irradiated RbCl at 77 K after subsequent F bleaches and corresponding optical-absorption measurements. To avoid confusion caused by overlapping curves, only the position of the F band is indicated. Decay parameters and optical-absorption constants are given in Table III, as for Fig. 1.

teristic ps time for both decays to be equal within experimental error. A larger relative contribution of A_f in the spectrum with $\varepsilon_L \| \varepsilon_P$ was noticed.

IV. DISCUSSION

In this section, the observed fast decay mechanism will be clarified. Several decay mechanisms, discussed at length for KCl, which is by far the most documented crystal in literature, can be eliminated, since they occur on a much longer time scale. The novel information on the two other alkali halides is also added in this first part. Other decay mechanisms can also be eliminated, since the moderate pulse energies in combination with the high sensitivity of our setup permit us to study the interaction of isolated F^* centers, in contrast with previous pump-probe measurements.[8,9,27] In a second part, we discuss the experimental data for RbCl. They were recorded with nearly resonant excitation, with substantially different concentrations of aggregates, and with the best signal-to-noise ratio. Direct parallels with the ground-state recovery spectra for KCl and KBr are drawn.

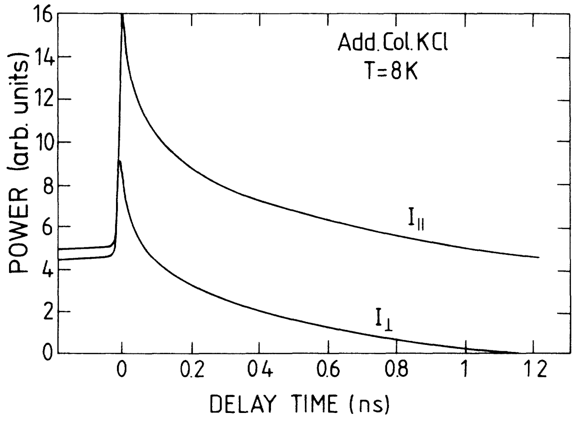

FIG. 4. Ground-state recovery spectra measured with mutually parallel and orthogonal polarizations of pump and probe pulse in a KCl sample. The decay parameter γ is the same for both curves. The different $A_f/A_{\rm sl}$ ratios indicate the polarization dependence of the dynamic equilibrium governed by slow processes (see Sec. III B).

A. F^*-F_n interaction

The isolated F^* centers have a radiative decay time within the ns region. Typical values for the radiative decay at 77 K of these centers for KCl are 570 ns for the F center,[3,34] 28 ns for the F_2 center,[34] and 124 ns for the F_3 (650 nm) center.[34]

For RbCl and also for KCl—as could be partly verified—the intensity of the signal was found to follow the F-center absorption band, when tuning the wavelength of the pump laser. The ps decay therefore corresponds to a fast decay of the F center. The quenching of the F-center luminescence observed by Swank and Brown[3] and Van Doorn[20] indicates that the competing deexcitation process should start from the (relaxed) excited state of the F center. The energy gap (0.15 eV for KCl, 0.135 eV for KBr, and 0.13 eV for RbCl) between the RES and the conduction band is far too high at low temperature for electrons to become thermally ionized.[12]

Unintentionally present OH$^-$ defects in KCl may have a serious effect on the properties of the F center,[35] such as reducing[36] the lifetime of the excited state. Our ps recovery times cannot be caused by OH$^-$ doping, since even for the highest concentration (2300 ppm) of OH$^-$ doping, the relaxation time of the F^* center is higher than 20 ns (Ref. 36) for temperatures lower than 35 K.

Referring to the reactions in (2), the tunneling [process (a)] of an electron from an F^* center, temporarily forming an F^- center, followed by a back tunneling (b) to the ionized vacancy, reforming the F center in the ground state,[6] may also be excluded, since this occurs on a ms to μs time scale. Analogous tunneling processes [(c),(d)] may also occur towards F_2 centers[10] on a comparably long time scale:

$$\begin{aligned} &F+F^* \xrightarrow{(a)} F^- + \alpha \xrightarrow{(b)} F+F\,, \\ &F_2+F^* \xrightarrow{(c)} F_2^- + \alpha \xrightarrow{(d)} F_2+F\,. \end{aligned} \tag{2}$$

Note that in the second reaction [(c),(d)] the resulting F_2 center may be singlet or triplet. Since the tunneling rates are concentration dependent, we only quote some typical values. We have the following transition probabilities (the subscript corresponds to the tunneling process) for KCl at 77 K: $1/\tau_a = 3.3\times10^4$ s^{-1}, $1/\tau_b = 2.5\times10^2$ s^{-1} (Ref. 37) for an F-center concentration 1.4×10^{17} cm^{-1} and $1/\tau_c = 5\times10^3$ s^{-1}, $1/\tau_d = 4.1\times10^1$ s^{-1} (Ref. 10) for an F-center concentration ranging from 10^{16} to 10^{17}.

The F^*-F^* interaction, which has been observed in KI (Refs. 8 and 9) using ns pulses from a Q-switched ruby laser, can be excluded for several reasons. First, we have not observed any fast decay unless a sufficiently large concentration of aggregate centers was present. Second, during the subsequent F bleaches, the total number of F centers was reduced while a faster decay process was observed. Third, the observed process occurs on a μs time scale,[8,9] much slower than our ps decay times. Fourth, the fraction of F centers excited per pulse was about 0.2% in KCl, at variance with the 90% fraction in KI (Refs. 8 and 9). Accumulation due to the μs decay time of the F centers, which is much longer than the repetition rate of the ps pulses, can only account for at most 20% excited F centers. We are therefore in a completely different situation, studying the interaction of an excited F center, predominantly with other unexcited centers. This last argument also eliminates the possible interaction between F^* and F_n^*, in particular F^*-F_2^* in KCl since both F and F_2 centers are excited by the pump pulse.

The characteristic times of these processes are longer than 10 ns and cannot be measured with our apparatus. They all contribute to the step function at $t=0$, which has been observed in the three alkali halides studied. The correlation with optical-absorption measurements (see Figs. 1 and 3 and Tables II and III) shows (i) an increasing ratio of the fast component to the slow component, for an increasing concentration of F aggregates; (ii) a faster decay for a larger concentration of aggregates. This clearly indicates an F^*-F_n interaction to be responsible for the observed ps ground-state recovery.

B. Energy transfer

Energy-transfer processes may occur in a radiative[38] or nonradiative way.[39] The radiative process is not likely to occur. (i) No change in the shape of the luminescence spectrum was observed when aggregate F centers are present (the luminescence should decrease in the region where emission and absorption bands overlap[38]) and (ii) the lifetime of the F^* centers is reduced by more than three orders of magnitude. No such reduction is expected for a radiative energy-transfer process.[39]

The energy-transfer probability scales with the relative concentrations of acceptors and donors systems and goes down with increasing distance between donor and acceptor. The decay curve for a number of donors and acceptors reflects the distribution of these defects and is therefore nonexponential. For a random distribution of acceptors and donors, the time evolution[40] of the excited donors $n(t)$ after δ excitation at $t=0$ is

$$n(t)=n(0)\exp[-t/\tau_0-2q(t/\tau_0)^{3/m}] \ . \tag{3}$$

The factor concerning donor luminescence can be neglected since $\tau_0 \geq 570$ ns. The number m governs the specific energy-transfer process, i.e., $m=6$ for dipole-dipole, $m=8$ for dipole-quadrupole, and $m=10$ for quadrupole-quadrupole coupling. As is illustrated in Table I in the case of RbCl, the best fit is obtained for $m=6$, i.e., dipole-dipole coupling. This is not so obvious for KCl, perhaps due to the many contributing processes. The parameter q equals $\Gamma(1-3/m)(\frac{2}{3})\pi R_0^3 c_D$, with c_D the concentration of the donors, Γ the gamma function, and R_0 the distance at which the transfer probability equals the probability for luminescence of the donors, given by

$$R_0^6 = \frac{3c^4}{4\pi c_A}\int F_D(\omega)\mu_A(\omega)\frac{d\omega}{\omega^4} \ , \tag{4}$$

where $F_D(\omega)$ is the normalized luminescence spectrum of the donor, $\mu_A(\omega)$ is the normalized absorption spectrum of the acceptor, and c_A is the concentration of acceptors. For an increasing concentration of acceptors and the same concentration of donors, the average distance between a donor and an acceptor decreases, resulting in a faster decay. The total probability for energy transfer increases, reducing A_{sl}.

This behavior is clearly observed for the F_2 (800 nm) and the N (975 nm) centers in KCl. In contrast, no direct correlation can be drawn with the F_3 (650 nm)-center concentration, since a growth in absorption constant from less than 0.025 to 0.34 (1400%) corresponds to an increase of the ratio A_f/A_{sl} of but 300% (see Table II). This observation is in accordance with previous work from Gadonas *et al.*,[29] who found a reduced absorption at 532 and 800 nm, under F-band excitation. For convenience, their results are summarized in Fig. 5. We relate the larger induced transparency at 800 nm for increasing delay times to energy transfer from excited F centers. No other regions of reduced absorption were found within the range 450–950 nm, showing that the F_3 (650 nm) centers do not become excited by energy transfer. A larger N (975 nm) concentration yields a faster decay and a larger fast component, as is clear from the two decay curves of Fig. 6. Both decay curves correspond to an equal F- and F_2-center concentration, but a different N (975 nm) concentration. So energy transfer also occurs towards N (975 nm) centers in KCl.

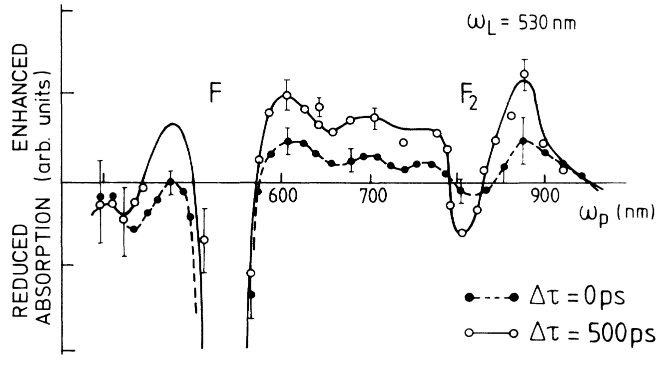

FIG. 5. Transient absorption spectra after F-band excitation ($\omega_L = 530$ nm) in additively colored KCl, for different delay times (after Ref. 29).

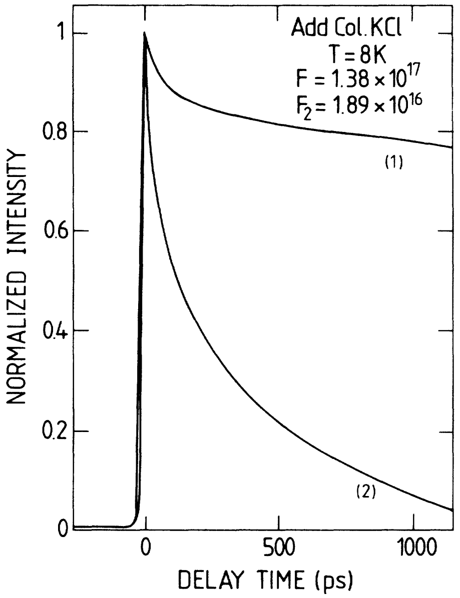

FIG. 6. Decay of the F^* center in x-irradiated KCl at 8 K for almost equal F and F_2 concentrations, while the ratio F_2/F was equal in both cases. A larger optical density of the N (975 nm) centers for curve (2), 1.33, compared to curve (1), 0.61, causes a faster decay of the F^* center.

A similar situation appears in RbCl. The largest A_f/A_{sl} ratio was found for the maximum absorption at 1050 nm. The contribution of the F_2 and the F_3 centers cannot be estimated that easily. For KBr, no sufficiently high concentration of aggregate F centers could be obtained to make a comparison between the various possible acceptors for energy transfer.

C. Polarization properties

The fast decay was similar for mutually parallel and orthogonal polarizations of pump and probe in the three crystals. This is in contrast to the observed strong polarization of the hot luminescence[41,42] (which is however 10^{-5} times weaker[43] than the peak intensity of the ordinary luminescence). The polarization decreases monotonically with increasing Stokes shift. The transition from the $2p$ to the $2s$ state occurs during the relaxation towards the RES or in the RES itself and should occur[44] within 8 ps. Hence no polarization effects should be observed. This indicates that the energy-transfer process occurs after relaxation to the RES. In the case of KCl, the different amplitude of the A_{sl} component for different mutual polarization of both laser beams is caused by a different combination of slow contributions.

D. Coagulation of electron centers

After subsequent F bleaches, a decrease in concentration of aggregates was noticed. Tables II and III show a decrease of the A_f/A_{sl} ratio. In contradiction to Sec. IV B, the decay parameter γ was found to increase. However, this value not only contains the decreasing concentrations of acceptors, but also the critical interaction distance for energy transfer to occur. A further increase of γ can only be caused by a further decreasing distance between excited F center and aggregate centers. We must conclude that by bleaching the F centers at RT, not only F centers are destroyed but also electron centers migrate through the crystal. This inhomogeneous distribution of excess electron centers has been observed for F centers in their initial state prior to aggregate formation[25,45] and fits within the model for aggregate formation.[46] Our foregoing discussion in terms of a random distribution of acceptors is therefore only a rough approximation.

V. CONCLUDING REMARKS

A ps decay of optically excited F centers was observed in three different host crystals: RbCl, KCl, and KBr, for two different types of F-center production, i.e., x irradiation and additively coloring. Our experiments are in accordance with measurements of the quantum yield of the F luminescence as a function of aggregate concentration and with transient absorption measurements. They are explained within the framework of an energy transfer towards an inhomogeneous distribution of aggregate F centers. F_2 and N centers are identified to be the most likely acceptors in KCl for this energy transfer. A similar behavior is assumed in RbCl and KBr. The contribution of the various aggregates to the observed energy transfer may be separated in an elegant way, by pumping in the F band and probing in an aggregate absorption band.

This energy transfer from the excited state of the F center in alkali halides may be relevant for recent laser applications. It sets limits on the use of F-center-associated color centers as a lasing medium since this alternative decay for excited F centers may reduce lasing activity. It points to a still-lacking detailed knowledge of the electronic and vibronic properties of the F^* state, which is also needed to understand the transfer mechanism in F-center-associated color-center lasers, such as the $F_H(CN^-)$ laser.[17] Apart from the lasing centers, a prominent concentration of aggregates may still be present[47] in these crystals.

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