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Radiative and nonradiative processes of F and F' centers in NaBr and NaI

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The Dexter *et al.* criterion for the occurrence of luminescence in deep centers predicts for F centers in NaBr and NaI a strong quenching of the luminescence due to a crossover process between the excited-state- and ground-state-configuration coordinate curves, implying that most optical absorptions do not lead to the relaxed excited state. We have studied the optical absorption, conversion, and emission properties of pure (dilute and concentrated) F-center systems in zone-refined NaBr and NaI with the following results: An infrared emission of double spectral structure is present in both systems, but has very low quantum efficiency (< 0.01). A detailed study of the electronic kinetics shows that in the optical excitation cycle all electrons reach the relaxed excited state, from which they can be ionized (thermally or by tunneling) to form F' centers with full efficiency. Therefore, while the above criterion predicts the existence of nonradiative processes properly, the mechanism of crossover reactions is not confirmed, and a nonradiative rate process from the relaxed excited state is strongly suggested. The role of the luminescence due to electron recapture by ionized F centers has been examined, and it is proposed that the second observed luminescence is due to a radiative recapture process from a higher state.

I. INTRODUCTION

The F center in alkali halides (an electron bound to an anion vacancy) has served extensively both in theory and experiment as a prototype and test case for our understanding of deep electronic defects in ionic solids. The optical properties and radiationless transitions of this center are dominated by the strong coupling of the electron to lattice modes of various frequencies and symmetries,[1] which can be accurately determined by Raman experiments.[2] This complex situation can be enormously simplified by assuming that the essential electron-phonon coupling can be described by a single mode Q of a fixed frequency value. This leads—within the harmonic approximation—to a representation in which the energy of each electronic state depends quadratically on this "configuration coordinate" Q, as illustrated in Fig. 1. Such a configuration coordinate diagram is extremely useful in illustrating radiative and nonradiative transitions of these centers: Optical absorption transfers the electron from the minimum of the ground- state curve (F_0) in a Frank-Condon transition (vertically, without change of the configuration Q_1) into the nonequilibrium excited state F^*, producing the broad visible F absorption band. Rapid relaxation by phonon emission changes the ionic configuration to the new value Q_2 and brings the system into thermal equilibrium at the relaxed excited state $\widetilde{F}^*$. After a mean lifetime τ (determined by the matrix element connecting the two electronic states in the configuration Q_2), emission occurs as a broad infrared transition between $\widetilde{F}^*$ and $\widetilde{F}_0$, and subsequent relaxation $\widetilde{F}_0 \rightarrow F_0$ closes the optical cycle.

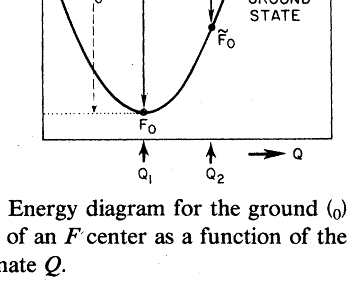

FIG. 1. Energy diagram for the ground ($_0$) and excited (*) state of an F center as a function of the configuration coordinate Q.

Using this simplified configuration coordinate model, Dexter, Klick, and Russell[3] presented a criterion for the occurrence or quenching of the emission process. Arguing that the intersection (X) of the ground- and excited-state curve is responsible for radiationless transitions between both states, they postulate that emission will always occur for $E_X > E_R$. If, however, $E_X < E_R$ holds, the system can cross over between the two states during the relaxation process, so that the relaxed excited state at $\tilde{F}^*$ may not be reached and the luminescence is quenched.

Since the postulation of this criterion by Dexter *et al.* in 1955, F centers have been studied extensively in terms of their absorption[4] and emission[5] properties in most alkali halide hosts. Bartram and Stoneham[6] have reviewed and analyzed this extended experimental material in view of the Dexter criterion, and came to the following conclusions:

(1) For all rubidium and potassium halides as well as for NaF and NaCl, the crossing point X lies *above* F^* in energy, and luminescence *should* occur, as it is observed experimentally.

(2) For NaBr and NaI as well as all lithium halides, the crossing point X lies *below* F^*, thus favoring the nonradiative crossover process. Indeed, in none of these systems had luminescence been observed at that time.

It is amazing that all the hosts under (2), besides LiF, are the most hygroscopic members of the alkali halide family, which due to their handling difficulties have neither been produced in very pure form nor been systematically studied in terms of their F-center properties. On the other hand, it is evident that exactly these systems are the most important and interesting test cases for the study and understanding of radiationless de-excitation processes. For this reason we have undertaken a systematic study of F-center properties in NaBr and NaI crystals, which were prepared for the first time from highly purified (zone-refined) material. We will show that material preparation and proper handling are critical in these hygroscopic materials in order to obtain reproducible properties which can be attributed to pure unperturbed F centers. Besides optical absorption and emission measurements, we investigated the $F \rightarrow F'$-center conversion, a property which critically tests the nature of the optical cycle in F centers. In all systems of type (1), in which the relaxed excited state $\tilde{F}^*$ is reached, an electron transfer from this state is possible, either via thermal ionization into the conduction band[7] or by electron tunneling into a neighboring F center,[8] leading to the formation of the two-electron F' center.[9] The measured $F \rightarrow F'$ electron-transfer behavior and optical emission properties in NaBr and NaI give evidence for the existence of a strong luminescence-quenching process, which however is not in agreement with the picture of a crossover process during the relaxation in the optical cycle. A preliminary report on this work was given at the Gatlinburg meeting.[10]

II. EXPERIMENTAL PROCEDURES

The NaBr and NaI crystals were grown in the Utah Crystal Growth Laboratory by the Kyropoulos technique under pure argon atmosphere, initially using commercial reagent-grade (r.g.) or ultrapure (u.p.) material. In order to obtain F centers with reliable and reproducible properties, a further purification for the material proved to be necessary. Zone refining of the NaBr (u.p.) and NaI (r.g.) material in a quartz container produced a highly visible accumulation of precipitates and impurities. Only the purest material from the up-stream end was used for the crystal growth. The hygroscopic crystals were stored and handled always under protective atmospheric conditions.

Production of "good" F centers is a major problem in both materials. In zone-refined NaI, F centers could not be produced either by additive coloration or by electron or x irradiation, even when these treatments were extended over long periods of time. The only way to introduce F centers was via a hydrogenation process, in which the samples were heated at $\sim 600\,^{\circ}\mathrm{C}$ in Na vapor and 6 atm of H_2 gas.[11] Under this treatment for about 70 – 100 h, U centers (substitutional H^- centers) were produced homogeneously in samples of about 1 cm thickness. By uv or x irradiation, the U centers can be converted into F centers of the desired concentration level. In NaBr, U centers (and subsequently F centers) can be introduced in the same way; the penetration of the hydrogen, however, never exceeded, even for the longest treatments, a range of ~ 2 mm. Different from NaI, F-center production *is* possible by electron or x irradiation in NaBr, however only in a very thin ($\sim 0.2 - 0.4$ mm) layer at the surface. Additive coloration (for 24 h at 700°C in Na vapor) did not succeed for normal ultrapure NaBr, but was successful in zone-refined material where a low-concentration ($\sim 10^{16}\ \mathrm{cm}^{-3}$) homogeneous coloration could be obtained. The absorption spectrum of the latter consists of the F band and a band at 7300 Å, most likely from colloids. By quenching the samples quickly from the highest possible temperature (short of losing the coloration), one can succeed in changing this composite absorption into a pure *F*-band absorption.

The physical properties of these colored systems depend strongly on crystal purity and/or coloration procedure; therefore, extreme caution and care is necessary in attributing observed optical behavior to pure unperturbed *F* centers. Most noticeably, the "*F* absorption" produced by hydrogenation and subsequent irradiation in NaI is clearly different for zone-refined and reagent-grade material, as shown in Fig. 2. While the zone-refined material exhibits a narrow (half-width $H = 0.26$ eV) Gaussian shape, the nonpurified material shows a much broader ($H = 0.32$ eV) band with long extended tails. Optical excitation in this perturbed *F* absorption band leads to an emission at 1.35 μm which is not present in the pure *F*-center systems of the purified material. In all our NaI experiments, we discarded crystals with the broadened absorption and 1.35-μm emission behavior.

In NaBr, *F* centers produced by irradiation of the hydrogenated layer show a slightly broadened absorption curve and an emission at $\sim$ 1.65 μm which increases in intensity towards the surface exposed in the hydrogenation process. This luminescence is not present in *F*-center systems produced by electron or x irradiation. Visible light irradiation at RT broadens the *F* absorption in all these colored systems and leads to a strong increase of the emission at $\sim$ 1.65 μm. In the additively colored (zone-refined) crystal, where we can use *F*-center samples far away from the surface, the absorption band is narrow and the 1.65 μm emission is *not* present. Light irradiation at RT does *not* lead to a broadening of the *F* band nor to a development of the 1.65-μm emission. We conclude that in the front surface part of the hydrogenated layer and in the thin surface layer of the pure electron- or x-irradiated samples, impurities are present which can work as reaction partners for *F* centers, leading to a broadened *F* absorption and extrinsic 1.65-μm emission behavior. In the front layer of the hydrogenated samples these perturbed *F* centers are always present, while in the pure irradiated samples they are only formed by light irradiation at RT. In the volume of the additively colored crystals these impurities are missing, and perturbed *F* centers are neither present nor formed by room-temperature illumination. We therefore discard in our investigations samples with the extrinsic emission behavior, and strictly avoid room-temperature light exposure of the samples.

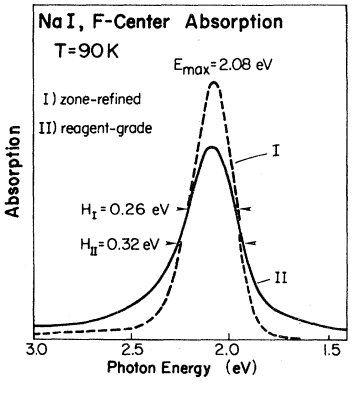

FIG. 2. Comparison of "*F*-center" absorption curves at 90 K, obtained after uv irradiation of hydrogenated NaI crystals of zone-refined (I) and reagent-grade (II) quality.

The optical absorption and conversion measurements were performed with a Cary 14 spectrophotometer. For the luminescence measurements the crystal was illuminated by a focused laser beam, directed through a bottom window of the cryostat vertically into the sample. The emitted light from the beam waist inside the sample was focused with mirrors on the entrance slit of a Spex 1 meter grating monochromator, and detected with a dry-ice-cooled PbS detector. Measurements with an LNT-cooled InSb detector assured that no further emission occurred in the spectral range out to $\sim$ 6 μm. Spectral lines from an HeNe, argon and krypton ion laser were used for optical pumping, keeping the power and power density of the laser light as low as possible to avoid heating effects.

III. EXPERIMENTAL RESULTS

A. Optical absorption and conversion measurements

Figure 3(a) shows optical absorption spectra of "good" *F* centers at various temperatures, displaying the familiar broadening and red-shift effect with increasing temperature. Figure 3(b) displays spectra of the sample crystal after irradiation with monochromatic light in the maximum of the *F* band at $\sim$ 150 K. Evidently, part of the *F* centers have been converted by this irradiation into new centers, characterized by an absorption band at higher energies. Decomposition of these spectra in Fig. 3(b) into a reduced *F* band and the new band, yields for the latter the spectral shape shown in Fig. 3(c) at various temperatures. Figure 4 gives a corresponding set of measurements for NaBr, showing in (a) the pure *F*-band absorption. *F*-band illumination at 130 K produces the spectra in Fig. 4(b), which after decomposition into a reduced *F* band and created

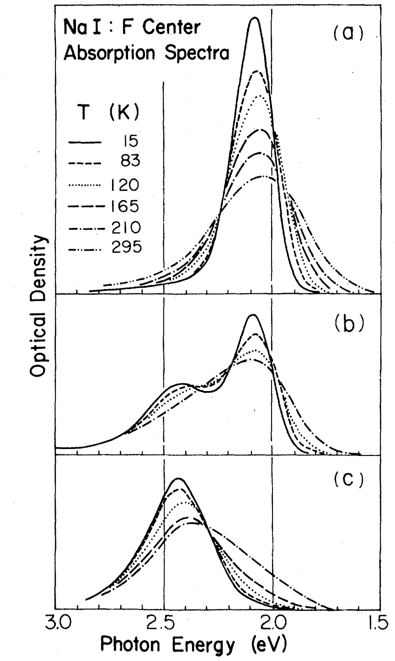

FIG. 3. Absorption spectra of colored NaI crystals at different temperatures: (a) Pure *F*-center spectra, (b) same after *F*-band bleaching at 130 K, and (c) new band obtained from decomposition of spectra in (b) (in absorption scale expanded by factor of 2).

new band, yield the spectral shape of the new band in Fig. 4(c).

The optical conversion by *F*-band illumination observed in Figs. 3(b) and 4(b) can be completely inverted by light irradiation into the new band at a wave length outside the *F* absorption. This reversible conversion process at low temperatures has all the features of the well known $F \leftrightarrow F'$ photochemical reaction,[9,7] as we will prove by further measurements. Figure 5 displays the temperature dependence of the optical conversion rates between the two absorptions, measured in three different NaI *F*-center systems. For low *F* concentrations, the conversion of the *F* into the new center shows the distinct behavior characteristic for a thermally activated process, while the highly concentrated *F* systems yield a high conversion rate over the whole temperature range. The opposite conversion back into *F* centers shows for all concentrations a temperature-independent high efficiency. Figure 6 gives the result of similar measurements as obtained in Fig. 5(b) for NaI for three *F*-center systems in NaBr.

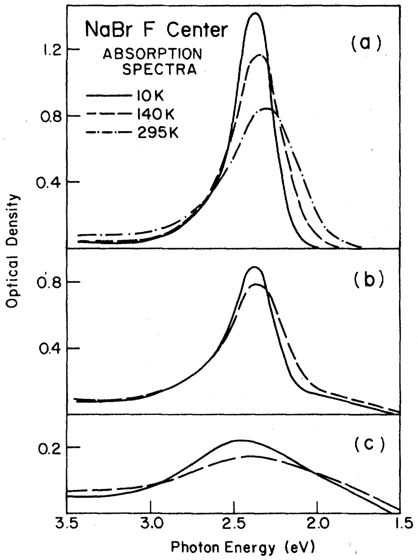

FIG. 4. Same set of measurements as in Fig. 3 for NaBr.

The relative conversion rates, displayed in Figs. 5 and 6, have been calibrated into absolute quantum efficiencies by direct comparison to the $F \rightarrow F'$ conversion rate in KBr, which has been carefully measured in earlier work.[9] Under exactly the same geometry and 5000-Å illumination and for crystals with comparable absorption, the rates of *F*-band bleaching were measured in KBr at 160 K and in NaI at 120 K and were found within experimental error to be the same. The early absolute measurements[9] on KBr had established that *one* absorbed light quantum destroys *two* *F* centers at 160 K, i.e., that the quantum efficiency $\eta(F \rightarrow F') = 2$. Our comparative measurement establishes the same fact for the optical reaction in NaI if we assume the same oscillator strength for the *F*-band absorption in KBr and NaI. By similar comparison with KBr we established that in the temperature-independent back

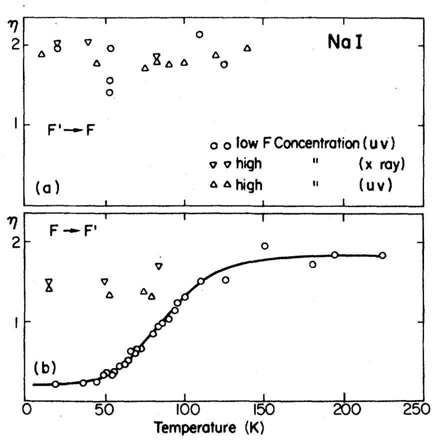

FIG. 5. Summary of optical conversion rates as a function of temperature, measured in crystals of different *F*-center concentration and coloration methods in NaI.

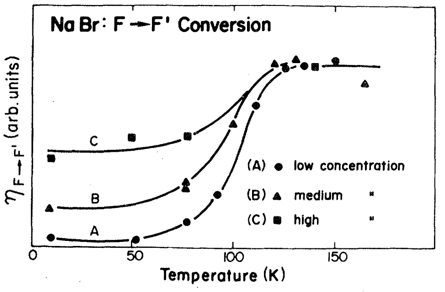

FIG. 6. Temperature dependence of the $F \rightarrow F'$ conversion rate measured in NaBr for three F-center concentrations.

reaction to F centers [Fig. 5(a)] two F centers are formed for each absorbed light quantum. In NaBr the conversion efficiencies (Fig. 6) were found to be of similar magnitude as in NaI, though no quantitative calibration was done. These results, which clearly establish the $F \rightleftharpoons F'$ nature of the observed conversion, will be discussed in detail in Sec. IV.

The temperature dependence of the measured half-width $H(T)$, when plotted in the form $\coth^{-1}[H(T)/H(0)]^2$ versus the inverse temperature, yields for both F and F' absorptions in NaBr and NaI approximate straight-line dependencies as shown in Fig. 7. This indicates that the description of the electron-phonon coupling by an effective single-mode oscillator, as done in the configurational coordinate model (Fig. 1), is not unreasonable. The obtained effective frequencies of the coupled oscillators (see Fig. 7) are in both materials higher for the F' compared to the F-center absorption. However, due to considerable ambiguity in the spectral separation of the F' band from the overlapping F band (Figs. 3 and 4), the obtained effective frequency values for the F' centers should be regarded as more uncertain than those for the F centers.

B. Emission measurements

1. NaI

After eliminating the extrinsic emission features discussed in Sec. II, a reproducible very weak emission was found in colored NaI and was studied systematically. In Fig. 8 we show emission spectra obtained at 10 K under two different spectral excitations in pure F-center systems of three different concentrations in zone-refined NaI. Two emission bands with peaks at 1.65 and 2.20 μm are observed, with the relative intensity of the 1.65- to the 2.20-μm peak increasing with increasing F-center density. The temperature variation of these emission spectra are displayed in Fig. 9 for the low F-center concentration case. In Fig. 10 we plot as a function of temperature the integrated emission of each of the two bands as well as the total emission for both the high and low F-center case. While the total emission is found to decrease gradually and monotonically with temperature, a complementary exchange of intensity is observed between the two emission bands below 70 K. These temperature-dependence features are much more smoothed out in the crystal with high F concentration.

Measurements of the relative emission strength under variation of the exciting laser wavelength yield the results plotted (for normalized laser power)

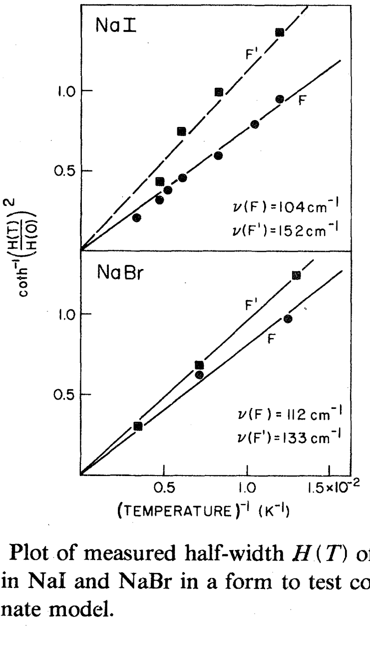

FIG. 7. Plot of measured half-width $H(T)$ of F and F' centers in NaI and NaBr in a form to test configuration coordinate model.

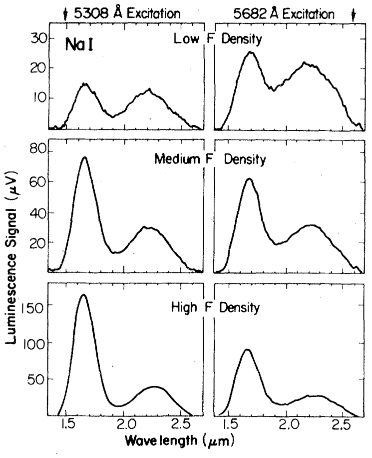

FIG. 8. Emission spectra observed at 10 K in pure F centers of three different concentrations in zone-refined NaI, under laser excitation at 5308 and 5682 Å.

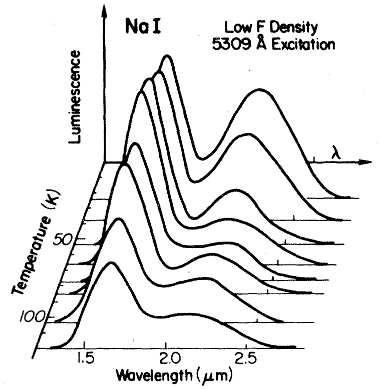

FIG. 9. Temperature dependence of the emission spectra in zone-refined NaI with low F-center concentration.

in Fig. 11. Comparison to the spectral absorption curves of the F and F' bands (from Fig. 3) shows that none of these excitation spectra follow directly the absorption curves, and that the 1.65- and 2.2-μm luminescence are excited in both the F and F' absorption spectral range. While for low-F concentrations both emissions show a similar excitation spectrum corresponding roughly to a composite $F+F'$ absorption curve [as in Fig. 3(b)], in the high-F concentration case the 1.65-μm emission has a markedly stronger response under F'-band excitation.

The interrelation of the two emissions at 1.65 and 2.2 μm were tested in an experiment in which a second laser beam (6328 Å) was superimposed and added to the normal 5309-Å excitation (Fig. 12).

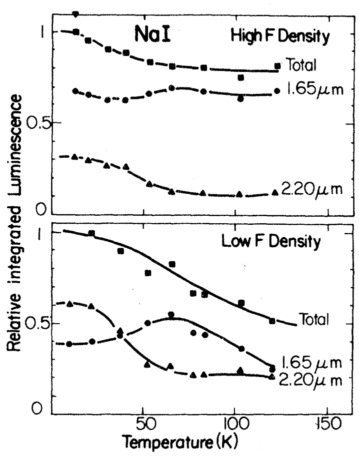

FIG. 10. Temperature dependence of the integrated emission for the individual (1.65- and 2.2-μm) bands and for their sum, obtained under 5309-Å excitation in NaI with high and low F-center concentrations.

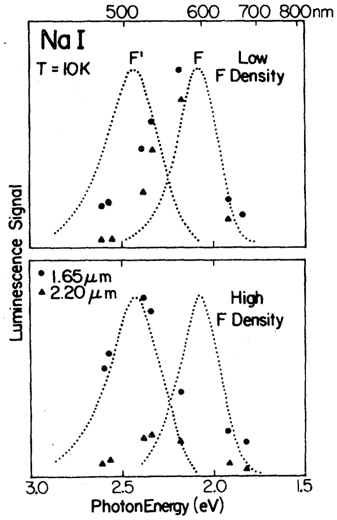

FIG. 11. Measured strength of the 1.65- and 2.2-μm luminescence in NaI as a function of excitation wavelength for low and high F-center concentrations, in comparison to the spectral F and F' absorption curves.

The addition of this extra excitation light produces a small decrease of the 2.2-μm and a small increase of the 1.65-μm emission.

For estimating the quantum efficiency of the observed F luminescence in NaI, we compared the integrated emission (without spectrometer) to that of a KBr crystal with F centers, which is known to have a quantum efficiency of close to one. Though this was not a highly precise experiment, it established clearly that the emission quantum efficiency η in NaI is at least 2 orders of magnitude lower than in KBr, with our best estimate for η lying in the 0.2–0.8 % range.

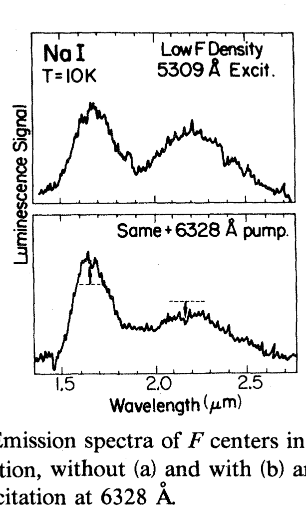

FIG. 12. Emission spectra of F centers in NaI under 5309-Å excitation, without (a) and with (b) an added laser-beam excitation at 6328 Å.

2. NaBr

In NaBr, which was studied much less extensively, a weak emission was found in crystals with "good" *F*-center properties under *F*-band excitation. Its quantum efficiency was estimated—by comparison to the NaI *F*-emission result—to be about a factor of 2 smaller than in NaI. In Fig. 13 we show emission spectra obtained in low-colored NaBr crystals with three different *F*-center production processes. In all three cases the spectrum consists of a prominent broad band (maximum about 2 μm) accompanied by a weaker narrow band at $\sim 1.2\ \mu$m. The excitation spectra of both these bands follow roughly the *F* absorption band [Fig. 4(a)] slightly broadened like a composite $(F+F')$ absorption spectrum [Fig. 4(b)]. With increasing *F* concentration, the strength of the 1.2-μm band relative to the 2-μm band increases strongly. Under temperature variation, the 2.0-μm luminescence decreases rapidly with temperature (more than one order of magnitude when heating to liquid-nitrogen temperature), while the 1.2-μm emission increases by about 10% up to ~ 100 K and decreases only under further heating. All these features, and the spectral appearance of the two peaks, are similar to the more carefully investigated NaI case, hinting towards a similar physical behavior and interrelation of the two emissions.

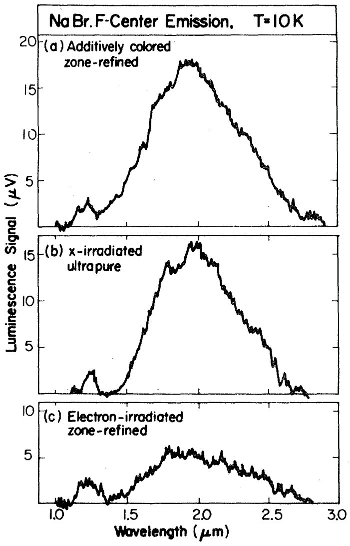

FIG. 13. Emission spectra obtained under 5309-Å excitation at 10 K in NaBr crystals with *F* centers produced by three different techniques.

IV. DISCUSSION

We have shown in this work that pure dilute *F*-center systems in NaBr and NaI show under optical excitation a total emission below 1% quantum efficiency in the measured wavelength range to 6 μm. Therefore these systems are indeed test and model cases for the understanding of nonradiative deexcitation of electronic defects. The Dexter *et al.* criterion for luminescence quenching[3] as applied to *F* centers[6] was recently extended by Stoneham and Bartram,[12] who considered the transition probability at the crossing point *X* during the cooling-down process, calculating the branching ratio into nonradiative processes and into processes leading to the relaxed excited state $\tilde{F}^*$ and subsequent emission. The result obtained for the emission efficiency $\eta = 0.02$ due to this branching reaction at the *X* point is very close to our experimental result.

In spite of this apparent numerical agreement, the physical processes on which the crossover model is based are in disagreement with the electronic kinetics emerging from the analysis of our NaBr and NaI results, as we will show. In presenting this analysis, we first summarize briefly, with the help of an electronic-level diagram [Fig. 14(a)], the electronic processes in normal typical *F*-center systems as derived from various detailed earlier investigations. In this diagram, the processes 1—4 describe the

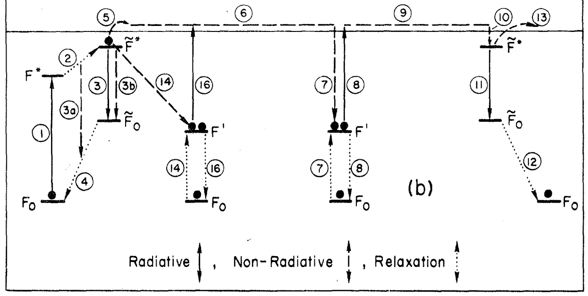

FIG. 14. Electronic energy-level diagram with illustration of the radiative, nonradiative, and relaxation transition for "normal" *F*-center systems (a) and for *F* centers in NaBr and NaI (b), as discussed in detail in the text.

normal optical cycle of an F center, consisting of optical absorption (1), relaxation into the relaxed excited state (2), optical emission (3), and relaxation back into the ground state (4). For dilute pure F centers at low temperatures, the quantum efficiency of the emission is close to 100%, i.e., no competing processes to process (3) are present. This simple situation changes by the presence of two perturbations, *high temperatures* and *high F concentrations*. We consider initially only the first one.

At higher temperatures the optical cycle can be "broken" by a thermal ionization process (5) of the electron from the relaxed excited state into the conduction band.[7] After a (photoconductive) transport in the band (6), the electron can be trapped by another F center, changing the deep one-electron F_0 level into the rather shallow two-electron F' state (process 7). Optical excitation of the F' center leads directly into the conduction band (8), i.e., to electron ionizaton. When ionized F centers (anion vacancies) are present, the migrating electron (9) can be recaptured by them to reform the F center. This capture process consists of a "precapture" of the electron[7] into the relaxed excited state (10), followed by the usual rate processes (3) and (5) which are valid for this state: At low temperatures a full capture of the electron into the F_0 state by emission (11) and relaxation (12), while at high temperatures reionization of the precaptured electron into the conduction band is possible (13).

The rate τ^{-1} for the thermally activated ionization process (5) or (13) is

$$\tau_{\text{ion}}^{-1} = \nu \exp(-\Delta E/kT) \tag{1}$$

($\Delta E =$ depth of the $\tilde{F}^*$ level below conduction band), while the rate for the radiative emission process (3) or (11) is τ_r^{-1}. The branching ratios for the two reactions from the relaxed excited state define the two quantum efficiencies[7]

$$\eta(3) \equiv \eta(\text{fluor}) = [1 + \nu\tau_r \exp(-\Delta E/kT)]^{-1} , \tag{2}$$

$$\eta(5) \equiv \eta(\text{ioniz}) = [1 + (\nu\tau_r)^{-1} \exp(\Delta E/kT)]^{-1} . \tag{3}$$

In a pure F-center system, the ionized electron can only be captured by another F center forming the F' center. As in this process one F center has been destroyed by ionization and one by electron capture, the quantum efficiency for F-center bleaching in the $F \rightarrow F'$ reaction is

$$\eta(F \rightarrow F') = 2\eta(\text{ioniz}) \tag{4}$$

Measurements of the temperature dependence of the fluorescence and $F \rightarrow F'$ conversion in KCl could be perfectly fitted[7] with Eqs. (2) and (3), yielding in this host $\Delta E = 0.16$ eV and $\nu\tau_r = 4.35 \times 10^6$. With the measure lifetime $\tau_r = 0.8 \times 10^{-6}$ sec this yields for the attempt frequency $\nu = 5.5 \times 10^{12}$ sec^{-1}, corresponding to 180 cm^{-1}, a value close to the optical longitudinal frequency (6.4×10^{12} sec^{-1}) for this material.

We observed in dilute F centers in NaI and NaBr a temperature-activated reversible conversion reaction, which in the NaI case was tested to lead at high temperatures to a maximum bleaching efficiency of two F centers per absorbed light quantum, while the back reaction had the same efficiency and was temperature independent. Unquestionably we are dealing with the $F \rightleftarrows F'$ conversion as discussed above. A plot of the observed conversion efficiency $\eta(T)$ from Figs. 5 and 6 in the form $\ln[(1/\eta) - 1]$ versus the inverse temperature (Fig. 15) yields, indeed, for both NaI and NaBr a straight-line dependence, as expected from Eq. (3). The slope of these lines yields for the thermal depth of the relaxed excited state below the conduction band a value $\Delta E = 0.61$ meV for NaBr and $\Delta E = 30$ meV for NaI. Inserting these values in the empirical trend of measured ΔE values in alkali halides, based on an effective-mass continuum model,[13] we obtain a good fit of our data to the observed ΔE trend [Fig. 16(a)]. Therefore we unquestionably measure in the NaI and NaBr $F \rightarrow F'$ conversion a process based on thermal ionization from the relaxed excited state into the conduction band. The fact that this conversion leads to full efficiency at higher temperatures assures experimentally that

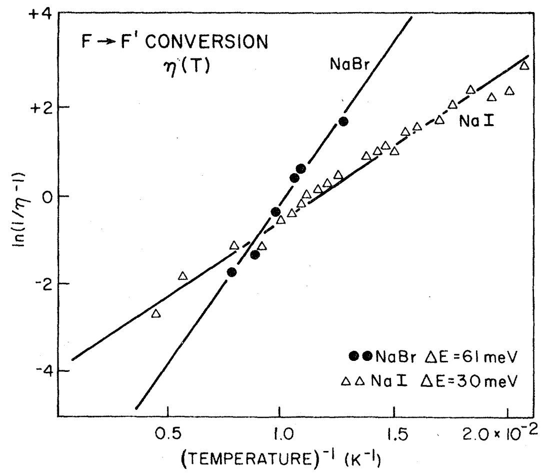

FIG. 15. Plot of measured $\eta(\tau)$ conversion rates (from Figs. 5 and 6) in a form to test Eq. (3).

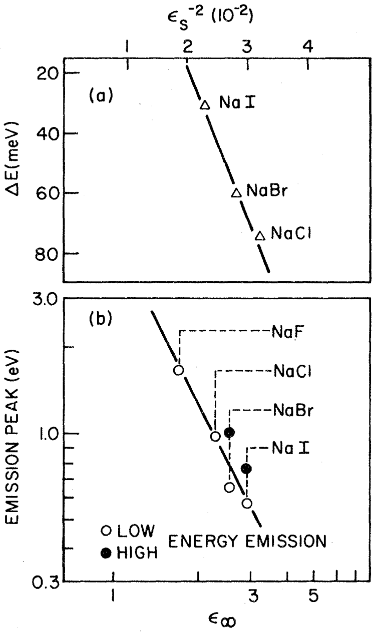

FIG. 16. (a) Plot of the gap energy ΔE as a function of the inverse square of the static dielectric constant ϵ_s (with ϵ values as used in Ref. 13). The straight line is the best fit to ΔE values in various alkali halides as discussed in Ref. 13. (b) Double logarithmic plot of the F-emission energy versus the high-frequency dielectric constant ϵ_∞. The line is the best fit to values in various alkali halides, as discussed in Ref. 5.

after optical F-center excitation (1) and relaxation (2) *all electrons reach the relaxed excited state*.

The intercept of the straight lines in Fig. 15 with $T^{-1}=0$ yields $\nu\tau_r$ (NaI) $=$ 55 and $\nu\tau_r$ (NaBr) $=1800$. If, as in KCl, the attempt frequency ν is given by a value close to the optical longitudinal-phonon frequency, the ν value should be (within less than a factor of 2) close to the $\nu=5.5\times10^{12}$ sec^{-1} value obtained for KCl. This would predict for the lifetime about

$$\tau_0(\mathrm{NaI})=10^{-11}\ \mathrm{sec}$$

and (5)

$$\tau_0(\mathrm{NaBr})=3.3\times10^{-10}\ \mathrm{sec}\ ,$$

values which are several orders of magnitude shorter than lifetimes of normal F emissions.[5]

We have obtained two basic experimental results:

(A) *All* excitations of the optical cycle lead to the relaxed excited state of the F center, similar to that observed in other dilute F-center systems.

(B) The thermal ionization process [Eq. (1)] has to compete with a natural lifetime τ_0 of the excited state which is orders of magnitude smaller than for normal F centers.

Both (A) and (B) are in disagreement with the crossover model for radiationless transitions. If the low ($\eta<0.01$) emission efficiency would be caused by the crossover process, less than 1% of the excited electrons would reach the relaxed excited state, in disagreement with (A). In the crossover model, on the other hand, the few electrons which avoid the crossing at X and which reach the relaxed excited state should have a lifetime determined by the matrix element between the $\tilde{F}^*$ and $\tilde{F}_0$ state which should be comparable to other F centers, in disagreement with (B).

The only way to account for our results is the assumption of a strong nonradiative process which is *not* working *during* relaxation, but is effective *after relaxation into the relaxed excited state.* These two possible processes for radiationless transitions are indicated as (3a) and (3b) in the optical cycle in Fig. 14(b). If we discard the crossover process (3a) but postulate a strong nonradiative process (3b), we can account for our experimental results: All electrons reach via process (2) the relaxed $\tilde{F}^*$ state; at low temperatures a radiative (r) and nonradiative (nr) deexcitation process are possible with a total rate

$$\frac{1}{\tau_0}=\frac{1}{\tau_r}+\frac{1}{\tau_{\mathrm{nr}}}\ . \tag{6}$$

As the quantum efficiency for radiative processes

$$\eta_r=\frac{(\tau_r)^{-1}}{(\tau_r)^{-1}+(\tau_{\mathrm{nr}})^{-1}}\approx\frac{(\tau_r)^{-1}}{(\tau_{\mathrm{nr}})^{-1}} \tag{7}$$

lies between 10^{-3} and 10^{-2} in our systems, i.e., the rate for radiationless processes is 100–1000 times higher than the emission rate, the thermal ionization process [Eq. (1)] has to compete against an effective lifetime τ_0 [Eq. (6)] in the $\tilde{F}^*$ state, which is 2–3 orders of magnitude shorter than the radiative lifetime τ_r. The measured quantum efficiencies η_r and τ_0 values then yield for the radiative lifetime

$$\tau_r(\mathrm{NaBr})=\frac{\tau_0}{\eta_r}=\frac{3.3\times10^{-10}}{2\times10^{-3}}=1.6\times10^{-7},$$
$$\tau_r(\mathrm{NaI})=\frac{\tau_0}{\eta_r}=\frac{10^{-11}}{5\times10^{-3}}=2\times10^{-8} \tag{8}$$

with τ expressed in units of sec.

These are much more reasonable values for radiative lifetimes compared to the ones which would follow for the crossover model [Eq. (5)], a fact which lends strong support to our general model. The values obtained in Eq. (7) are still lower than typical τ_r values for F centers in other hosts.[13] However, the accuracy of the model used and its parameters should not be overestimated. The attempt frequency ν in Eq. (3) is unknown and was chosen to be at the same "reasonable" value as found for KCl. The real value could easily deviate from this by up to an order of magnitude. The absolute fluorescence quantum efficiency [Eq. (6)] was experimentally determined only within a factor of $2-3$, and any temperature dependence of the nonradiative transition rate $(\tau_{\mathrm{nr}})^{-1}$ was neglected. Within all these uncertainties, the values in Eq. (8) appear very reasonable.

For comparison with data outside this work, only a few results on NaBr are available in the literature. Bosi[14] reported in 1976 the absence of F luminescence in NaBr, which is explainable in view of the very small efficiency we found. He observed, however, a weak photoconductivity, the temperature dependence of which yielded a gap energy of $\Delta E = 0.135$ eV. In a later work by Bosi *et al.*,[15] a new value of $\Delta E = 0.078$ eV was obtained and a weak luminescence at energies above 1 eV in colored NaBr was investigated in terms of its lifetime properties, and was found to consist mostly of a quick component ($\tau = 23$ nsec) and less than 8% of a long (1000 nsec) component. The large quick component was attributed to M centers, the weak slow component to F centers. This tentative assignment, the absence of any spectral absorption or emission data in Ref. 15, and the fact that the investigated luminescence—by the cutoff of the multiplier—was located at unknown energies (>1 eV) outside or at the highest energy end of our observed spectra, make comparison to our data virtually impossible.

We now consider the second perturbation to the simple F-center system and its electron processes; the introduction of *high F-center concentrations,* i.e., interaction effects among F centers. We discuss this again first for the normal F centers [Fig. 14(a)]. Under increase of the F-center density, the full quantum efficiency of F-center emission becomes gradually reduced ("concentration quenching of the F luminescence").[16] A possible explanation of this effect assumes that for close-lying F centers (distance <13 lattice parameters), the electron can tunnel into the neighboring F center (process 14 in Fig. 14) forming an F' state, and subsequently will tunnel into the $\tilde{F}_0$ state [process 15 in Fig. 14(a)]. This two-step (14) (15) process through an intermediate F' state thus presents in high concentrated F systems a nonradiative competing process which reduces the F emission (3). The validity of this model was tested and confirmed by spin-polarization experiments,[8] in which the process (14) could be quenched by a magnetic field and the emission process (3) was accordingly increased.

For high F-center densities in NaI and NaBr we found under optical F excitation at low temperatures a high efficient conversion into F' centers (Figs. 5 and 6), showing that the electron-transfer process (14) works in these materials too. Contrary to the normal F-center systems, however, the F' centers formed in this way are not short lived, but were found to be completely stable (tested up to 24-h holding time). Apparently *the back-tunneling* $F' \rightarrow \tilde{F}_0$ *process (15) does not work in* NaBr and NaI. This is not surprising in view of the very special spectral F' features observed in these systems: While in normal F-center systems the F' optical transition lies on the low-energy side of the F band, the F' transition nearly coincides with the F band in NaBr (Fig. 4) and lies even at the high-energy side of the F band in NaI (Fig. 3). We therefore must conclude that the F' level lies much deeper in these materials [Fig. 14(b)] compared to the normal alkali halides [Fig. 14(a)]. Simple considerations about the various energies involved show, in fact, that in NaBr and NaI *the* F' *level lies deeper than the* $\tilde{F}_0$ *level,* so that the tunneling process (15) is no longer possible in this material. The extremely high F' absorption energy and the stable F' formation by the tunneling process (14) are therefore completely consistent.

A third important point which we must consider is the fact that F-center luminescence is present not only due to excitation of the optical cycle (3), but also due to the recapture of electrons into previously ionized F centers (processes 10, 11). We discuss this again first for the normal F centers. It was shown by detailed measurements[7] that the same spectral emission as the normal F luminescence is emitted in this capture process, i.e., that *electron capture of the vacancy occurs via the relaxed excited state* $\tilde{F}^*$. The temperature dependence of this electron-capture luminescene could be exactly accounted for by the competing (ionization and radiative) processes which are effective in this state.[7] With increasing temperature, an increasing number of F centers become ionized, so that under constant light irradiation an increasing dynamic F':F equilibrium is created. As a consequence, an increasing ratio of the observed luminescence under temperature increase is due to the "capture luminescence" compared to the "optical-cycle luminescence."

This leads to an important consequence for radiationless transition, which so far has been overlooked in the discussion of the crossover model. This model has been considered only for the direct optical-cycle luminescence in terms of the crossing point X. For the recapture luminescence, we would have to construct in Fig. 1 another potential curve for the ionized F state. While the exact nature of this curve is now known, three features are predictable:

(a) Its minimum of energy should lie by the amount ΔE (= thermal ionization energy) above the minimum $\tilde{F}^*$ of the excited F-state curve.

(b) Its minimum should lie close to the Q_2 configuration of the F^* curve, because the electron-phonon interaction in the $\tilde{F}^*$ state (very spreadout wave function) and the F_{ion} state (electron removed) should be similar.

(c) Owing to the same reason (b), the shape of the F_{ion} curve should be similar to that of the $\tilde{F}^*$ center.

It is evident that within the crossover model, the efficiency of the recapture luminescence (at low temperatures) must always have a full efficiency. The conduction electrons (which are not "hot," but in thermal equilibrium) lie at the minimum of F_{ion} curve; this minimum, by the above arguments (a),(b),(c), lies very close to the $\tilde{F}^*$ minimum. No crossing is possible in this relaxed situation with the ground-state curve, and luminescence should always occur.

In our NaBr and NaI experiments, we create under constant light irradiation into the overlapping F and F' bands a high dynamic F':F ratio, i.e., a high ratio of recapture to direct-excitation luminescence, under two conditions. For *dilute* F systems at *higher* temperatures [due to thermal ionization (5)] and for *concentrated* systems at *all* temperatures [due to the tunneling reaction (14) and constantly repeated optical ionization (16) of the formed F' centers]. Nevertheless, the experimentally observed luminescence efficiency is in both cases *not* increased by the added capture luminescence. This discards again the crossover model, while our assumption of a strong nonradiative deexcitation process (3*b*) in the relaxed excited state predicts the *same* quenching for directly excited and recaptured luminescence, in agreement with experiment.

We finally must ask the question, if the observed spectral features of the NaBr and NaI emissions can be accounted for. In Fig. 16(b) we show with the straight line the empirical trend of observed emission energies for various alkali halides, based on the dielectric effective-mass model.[13] The low-energy emission peaks observed in NaBr and NaI fall quite well on this line, while the high-energy peaks give the same trend but lie about 0.2 eV above the line. This gives support to the assumption that we are dealing with a genuine F luminescence, but leaves open the question for the double structure of the luminescence.

We propose the following model to explain the observed features: The low-energy emission is the F luminescence from the relaxed excited state $\tilde{F}^*$. The higher-energy emission is a luminescence, only present in the recapture processes, which occurs from a higher-lying level either directly from the bottom of the conduction band or from a higher-level F state, as observed in Kondo and Kanzaki's double-excitation experiment.[17] This extra emission has a low efficiency because it occurs from a "hot" situation in a higher state which is not relaxed into the minimum at $\tilde{F}^*$. It is quite possible that this weak higher-energy luminescence is present in normal F-center systems also whenever recapture processes take place. Its observation, however, is completely impossible due to the overlap with the (2 – 3 orders of magnitude stronger) broad F emission from the relaxed excited state. In NaI and NaBr, where the latter is reduced by a competing non-radiative process by 2 – 3 orders of magnitude, this extra recapture luminescence becomes observable. This interpretation is in agreement with the observed features, interrelations, and variations of the two luminescence effects. The high-energy luminescence should be relatively increased whenever we increase the amount of recapture processes relative to the direct excitation processes. This can be achieved in three ways:

(i) With *rising temperature*, the F':F ratio increases under constant irradiation and the recapture processes increase. We indeed observe an increase of the high-energy luminescence at the expense of the low-energy luminescence in NaI (Figs. 9 and 10) and similar effects in NaBr.

(ii) *Increase of the F concentration*, which increases the recapture processes due to the transfer reaction (14) $F \rightarrow F'$, leads for both NaI (Fig. 8) and NaBr (text) to a strong increase of the high-energy relative to the low-energy luminescences.

(iii) *Auxiliary strong F-light illumination* (Fig. 12) shifts the $F \rightarrow F'$ equilibrium, increasing the recapture processes and the corresponding luminescence ratio.

The observed excitation spectra for both luminescence effects (Fig. 11) reflect the fact that they are a mixture of direct excitation and recapture effects which are excited and initiated in dynamic F: F' equilibrium in both the F and F' band. The excitation spectra, corresponding to composite F and F'

curves, show higher efficiencies for the high-energy luminescence in the F'-band region (particularly in the high-density sample, because F' excitation initiates relatively more recapture processes). We see that qualitatively all these observed features are well in agreement with out two-emission model. Indications for the possible existence of a second relaxed excited-state configuration of F centers in alkali halides have been obtained by Winnacker *et al.* in spin-resonance measurements.[18]

The three basic results from this work provide important consequences and challenges for theoretical treatments and further experimental work.

(1) Our results contradict the model of a crossover reaction during relaxation, and instead give evidence for a strong nonradiative reaction occurring after relaxation from the relaxed excited state. One of the predictions of the crossover model is the occurrence of a wavelength-dependent emission efficiency under variation of the excitation across the F absorption band, in systems with comparable energies of the F and X point in Fig. 1 (e.g., for NaCl). This effect, which never has been observed experimentally for F centers, is obviously not existent in our model. Within the configuration coordinate model, our postulated nonradiative process can be visualized as a tunneling-type process from the minimum of the excited-state curve ($\widetilde{F}^*$) horizontally through the barrier to point B on the ground-state curve (Fig. 1). As the condition for a low-lying crossing point (X) is parallel to the condition of a small height and width of the barrier, it is not astonishing that the Dexter *et al.* criterion may still approximately classify and order different systems in terms of their nonradiative deexcitation properties. The physical justification for the tunneling $\widetilde{F}^* \rightarrow B$ process is based on the fact that the adiabatic approximation (which represents the $\widetilde{F}^*$ state as a product of vibrational and electronic states) is not strictly valid due to the Q dependence of the electronic wave function, so that this constructed product state is not truly a stationary one. Nonradiative decay processes, based on this limitation of the applicability of the adiabatic approximations, have been considered in theoretical work by Kubo and Toyozawa,[19] Honda and Tomura,[20] and the extended work of Stumpf and his co-workers.[21] The F-center data in NaI and NaBr now supply testing material for these theories. On the experimental side, lifetime measurements in the spectral range of the weak F emissions of NaI and NaBr will be the most crucial final test between the crossover and tunneling model.

(2) The experiments in this work clearly identify the band at 2.4 eV in NaI as due to the two-electron F' centers. Both the *position* of the F' band (on the *high*-energy side of the F band) and its rather narrow symmetric *shape* are unusual features compared to the usual broad, unsymmetric low-energy F' absorption in other alkali halides. The shape of the band suggests that optical absorption does not lead directly into conductive states but into a bound singlet state of the system, which becomes autoionized after lattice relaxation. [The latter is necessary to account for the full temperature-independent ionization probability, Fig. 5(a).] It remains as a challenge to the theory to verify and understand the strongly enhanced binding of the two electrons in the F' center of NaI compared to other host crystals. As a key to a possible understanding, one may consider the somewhat related phenomena of negative alkali halide molecules, which have recently been studied both theoretically and experimentally.[22] The second electron at an F' center may be regarded in an LCAO picture to be bound in the $(\mathrm{NaI})^-$ states of the NaI molecules surrounding the defect. For the Li and Na fluorides and chlorides (the only studied systems), sizable energies ($E = 0.3 - 0.7$ eV) binding the extra electron to the molecules are found. The observed pronounced increase of E from the fluorides to the chlorides could—if it extrapolates as a trend—lead to high E values for LiI and NaI, which may reflect in parallelism a large binding energy of the F' electron in crystals of these materials. On the experimental side, *spin-polarization experiments* (quenching the formation of the two-electron singlet states[8]) are the most decisive ones to test the proposed F'-center model for the 2.4-eV band in NaI and NaBr. These experiments are presently under way with positive results.[23]

(3) The third challenge to the theory is an account and understanding of a higher excited state from which a second F luminescence may occur, as speculated from the results in this work. For the experiment, it will be a challenge to test if in "normal" F centers (with high efficient luminescence from the relaxed excited state) a *weak higher-energy luminescence* component becomes added whenever electron recapture processes at the ionized F center are present. As F-center ionization and recapture processes can be "switched on and off" at low temperature with an electric field by field ionization,[7] such an experiment could, for instance, be performed with a high-field modulation technique in a highly sensitive way.

Note added in proof. After completion of this manuscript, we became aware that investigations similar to those reported here on *F* centers in NaBr and NaI have been done by Takiyama and coworkers in LiCl, a system for which quenching of the *F* luminescence is predicted by the Dexter *et al.* criterion [J. Phys. Soc. Jpn. 44, 1627 (1978); Phys. Status Solidi B 99, K97 (1980)]. The obtained results and conclusions in LiCl, however, are quite different from ours.

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