

Relationship between OH^- defect reorientation rates and the quenching of the F -center luminescence in alkali halides

Laércio Gomes

Instituto de Pesquisas Energéticas e Nucleares, Comissão Nacional de Energia Nuclear, São Paulo, Caixa Postal 11049, Pinheiros, 05422-970 São Paulo, Brazil

Fritz Luty

Physics Department, University of Utah, Salt Lake City, Utah 84112

(Received 5 May 1995)

We extend in this work the previously obtained results that the presence of sufficient amounts of statistically distributed OH^- defects in KCl drastically quench the F -center luminescence, photoconductivity, and excited state (F^*) lifetime $\tau(F^*)$. The extension to three new host materials (KBr, RbCl, RbBr) will test whether the OH^- reorientation rate (τ_{reor}^{-1}) plays the decisive role in this strong OH^- dipole F^* -center interaction effect. While for the earlier studied host KCl above 10 K, the OH^- reorientation is extremely high [$\tau_{\text{reor}}^{-1}(\text{OH}^-) > 10^{10} \text{ sec}^{-1}$], KBr, RbCl, and RbBr have at 10 K dipolar reorientation times long compared to the radiative F -center lifetime, $\tau_{\text{reor}}(\text{OH}^-) \gg \tau(F^*)$. Under temperature increase, however, the OH^- dipolar reorientation rates speed up drastically, so that one reaches the opposite condition $\tau_{\text{reor}}(\text{OH}^-) \ll \tau(F^*)$. We find indeed that in these materials, the F luminescence is nearly fully efficient and of long lifetime below 15 K but becomes quenched drastically and short in lifetime when increasing the OH^- reorientation rate with the temperature. Quantitative analysis shows that the OH^- reorientation time must be about four orders of magnitude shorter than the radiative F^* lifetime, in order to fully quench the F luminescence. In contrast to these statistically distributed F -center and OH^- defect systems, aggregated pairs of both defects [$F_H(\text{OH}^-)$ defects] show in all hosts, nearly independent of temperature, very strong luminescence quenching. All these results are analyzed and discussed within dynamical OH^- reorientational models.

I. INTRODUCTION

In our previous work we have shown that the electronic processes in the relaxed excited F -center (F^*) state of KCl become drastically changed by the presence of high (10^{-3} – 10^{-2}) concentrations of OH^- defects in the host. All three measured characteristic F^* quantities—the luminescence, the photoionization (photoconductivity), and the total time needed for one optical cycle—decrease systematically and strongly with increasing OH^- doping. In quenching (additively colored) crystals with statistical F -center and OH^- distribution the observed behavior could be fitted to a phenomenological model, involving total luminescence and photoionization quenching for a critical distance $R_c \leq 5$ lattice parameters (a) between F -center and OH^- defects. In contrast to these drastic effects on the relaxed excited F -center behavior by the presence of OH^- defects within $R_c \leq 5a$ the absorption spectrum of the F center is (besides a very slight 2–3% broadening effect) not perturbed at all by the statistically distributed OH^- defects.

Our quantitative interpretation in the previous paper¹ for this drastically different perturbation of OH^- defects on the F -center absorption and emission behavior was based on the fact that the F -center wave functions are rather compact during the absorption process, while the relaxed excited F^* state assumes a rather wide spatial extension, causing strong overlap and interaction with the

OH^- defect even five lattice parameters away. The main basic question, however, still remains unanswered: why and how does this perturbed relaxed excited F -center and OH^- defect “interactive state” produce such a short lifetime and high efficiency for nonradiative deexcitation of the excited F electron back into the F ground state?

An attractive and interesting speculation raised at the end of paper¹ is the question whether the drastic OH^- effect on the F nonradiative deexcitation is due to a static or a dynamic (reorientational) effect of the large OH^- electric dipole moment on the F center. One can assume that if the positive end of the OH^- dipole is directed towards the nearby F^* center, the electric dipole field works attractively on the excited F^* state; in contrast to this, the negative OH^- dipole and oriented towards the F center should more repel the F^* electron back towards the vacancy. Rapid reorientation between these two dipole orientations can modulate the interacting excited F state and cause its nonradiative deexcitation process.

The experiments in the first paper were performed quantitatively only in KCl, in which OH^- dipoles reorient extremely rapidly² ($\tau_{\text{reor}} \leq 10^{-10} \text{ sec}$ at $T > 10 \text{ K}$ where all experiments were performed). In order to test this question about the significance of the OH^- reorientation for the F luminescence quenching, we extend these measurements in this work to three more host materials (KBr, RbCl, and RbBr), which—at least at low temperature—are known to have much slower OH^- re-

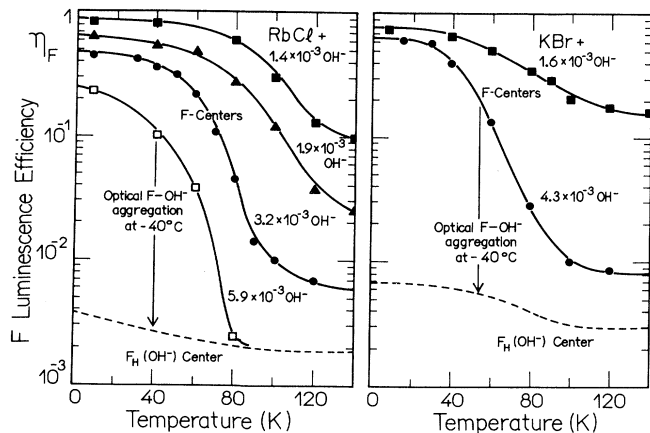


FIG. 1. Temperature dependence of F luminescence efficiency in OH^- doped $\text{RbCl}:\text{OH}^-$ (1.4×10^{-3} , 1.9×10^{-3} , and 3.2×10^{-3} mol fraction) and $\text{KBr}:\text{OH}^-$ (1.6×10^{-3} and 4.3×10^{-3}) in the quenched case (solid lines). The aggregated case, $F_H(\text{OH}^-)$ center, is represented by broken lines.

orientation rates so that at 10 K the OH^- reorientation time is in fact longer than the normal excited F -center luminescence lifetime. These experiments will yield significant and clear answers to the above raised question.

Besides the study of statistically distributed (i.e., nonassociated) F and OH^- defects, we have shown¹ that weak F light irradiation in $\text{KCl}:\text{OH}^-$ at -30°C leads to the conversion of the normal F band into a strongly broadened and red-shifted "perturbed F band," which can only have been formed by association of the F center to an OH^- defect. Electron-nuclear double resonance experiments³ have shown that in the $F_H(\text{OH}^-)$ center in KCl the F center and OH^- molecule occupy (200) neighboring positions. These " $F_H(\text{OH}^-)$ " defects in KCl show—compared to the statistically distributed F and OH^- defects—an even stronger "total" decrease of the F luminescence and photoionization, even in crystals with

lower OH^- doping. We will include in this paper measurements on the $F_H(\text{OH}^-)$ defects in KBr , RbCl , and RbBr —both on their absorption structure and their emission properties. It is evident that for this closely associated F -center- OH^- pair, both the nature and wave function of the excited F_H electron, and the normal reorientation properties of isolated OH^- defects could be drastically changed by the strong interaction of this defected pair.

II. EXPERIMENTAL TECHNIQUES AND APPARATUS

The single crystals of different OH^- dopings were grown in the Utah Crystal Growth Laboratory. The actual OH^- content in the samples was determined by IR or UV measurements of the vibrational or electronic OH^- absorption, using the quantitative calibrations from Ref. 4. Absorption measurements were performed in a Cary-Varian model 17 DX spectrometer. Emission measurements were performed using a tunable dye laser pumped by Ar^+ or Kr^+ ion laser excitation, and a cooled PbS detector with appropriate filter or a grating monochromator for detection. Emission lifetimes were measured by the time dependence of the luminescence signals excited by a pulsed excimer pumped dye laser system of 10 ns duration. The transient signals were detected by using a photomultiplier tube of S1 type cathode and analyzed by using a type cathode and analyzed by using an rapid oscilloscope.

III. EXPERIMENTAL RESULTS

We extended in this work the investigation of the quenching effect on the F type emission from F centers in the presence of high concentrations of the OH^- defect in various alkali halides—i.e., KBr , RbCl , and RbBr . This investigation was done always in additively colored crystals, which at first have been freshly quenched from high temperature and immediately cooled without light exposure to low temperature. In the first type of system used

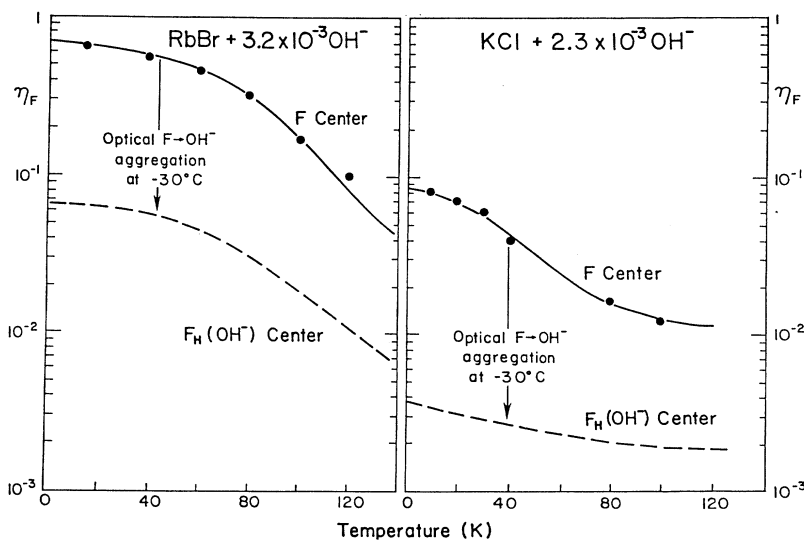


FIG. 2. Temperature dependence of F luminescence efficiency in OH^- doped $\text{RbBr}:\text{OH}^-$ (3.2×10^{-3} mol fraction) and $\text{KCl}:\text{OH}^-$ (2.3×10^{-3} mol fraction) in the quenched case (solid lines). The aggregated case, $F_H(\text{OH}^-)$ center, is represented by broken lines.

in our experiments we worked with crystals containing statistically distributed F centers and OH^- defects—i.e., in the quenched stage. Figures 1 and 2 (solid lines) show how the F luminescence of quenched F centers in KCl, KBr, RbCl, and RbBr depends on OH^- doping and temperature. Evidently, even in this only slightly reduced “quenched” case, the presence of nonassociated $F\text{-OH}^-$ defects produces for both cases high F luminescence efficiency at low temperature, but drastic reduction of this efficiency under the increase of the temperature (to about 10^{-2} quantum efficiency).

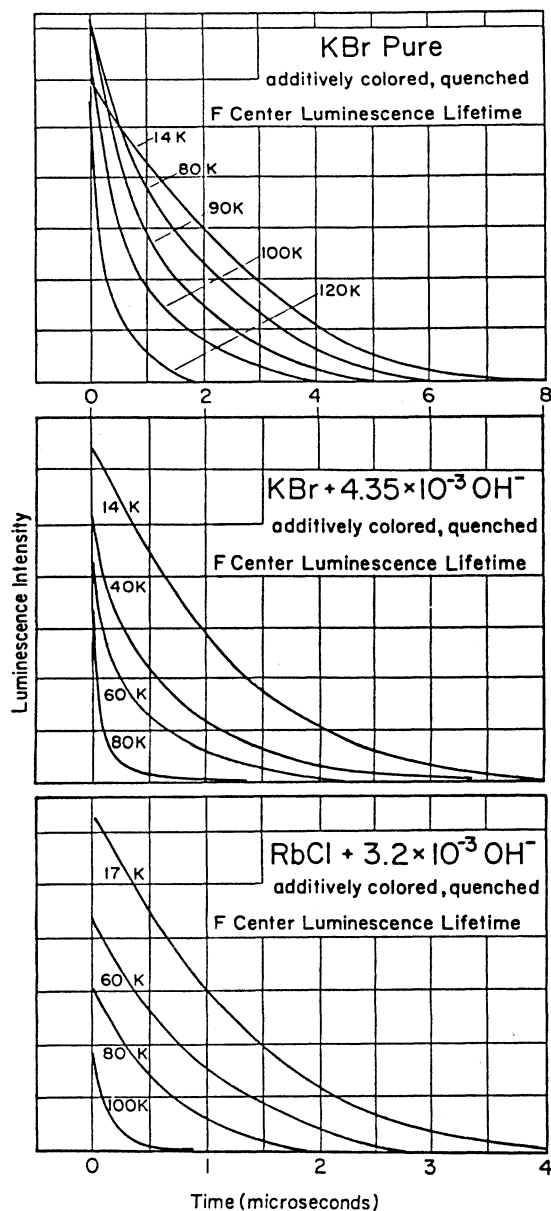


FIG. 3. The time dependence of the F luminescence signal excited by a pulsed laser of 10 nsec of time duration and tuned at the main F absorption band in pure and OH^- doped KBr and RbCl crystals at several temperatures for the nonaggregated case.

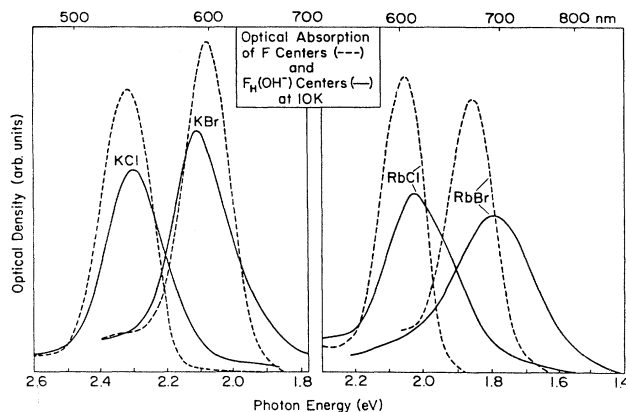


FIG. 4. Absorption band of F centers in several OH^- doped hosts (KCl, KBr, RbCl, and RbBr) measured at 10 K. The solid line represents the absorption band of the nonaggregate system. The dashed line represents the absorption of the $F_H(\text{OH}^-)$ center produced by appropriate optical aggregation.

In all these and the following cases, the F luminescence efficiencies were obtained by comparing the “perturbed” F luminescence in doped crystals with the normal F luminescence intensity from F centers in the pure host lattice with the same F concentration and temperature. The results shown in Fig. 2 for both hosts, $\text{KCl}:\text{OH}^-$ and $\text{RbBr}:\text{OH}^-$, are partially in contrast. While in $\text{RbBr}:\text{OH}^-$ the F luminescence intensity is slightly reduced to 70%, in $\text{KCl}:\text{OH}^-$ it is only 8.5% when $T \rightarrow 0$ K. On the other hand, the F luminescence in $\text{RbBr}:\text{OH}^-$

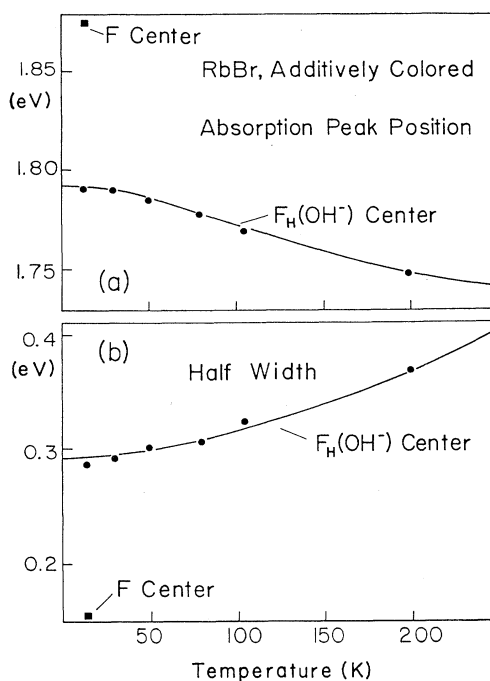


FIG. 5. Temperature dependence of peak position (a) and half width (b) of $F_H(\text{OH}^-)$ absorption in RbBr.

has a much stronger temperature effect (70→4 %) than is exhibited by $\text{KCl}:\text{OH}^-$ (8.5→1 %). It is important to mention that in all the OH^- doped hosts studied in the "quenched" case, the F absorption band (measured at 10 K) does not show any perturbation compared to the F band measured in the pure crystal. For this case of quenched system—statistically distributed F and OH^- defects—we also measured the time resolved decay of the F -center luminescence at several temperatures for KBr and RbCl both doped with high OH^- concentration and in pure KBr for comparison (Fig. 3). Pure KBr shows—as is well known—up to 90 K, only a slight decrease of the integrated luminescence and lifetime. In contrast to this, KBr and RbCl doped with OH^- show a reduction of lifetime and gradual decrease of the F emission intensity with the temperature increase from 10 to 100 K. This effect is also in good agreement with the observation of the strong decrease of F luminescence efficiency with the temperature increase exhibited in Fig. 1.

The second type of system used in our experiments consisted of the same colored OH^- doped crystals which, however, after quenching (and initial low-temperature measurements) were illuminated with rather small doses of visible light at -30°C . This very controlled aggregation step, in all the hosts here investigated, does not produce the normal intrinsic F aggregate centers, F_2 and F_3 , but a broadening and redshifting in the F band (at 10 K) as is indicated in Fig. 4 (solid lines) for four host materials. In all these cases, the F center forms an $F\text{-OH}^-$ defect pair, called $F_H(\text{OH}^-)$ center, which exhibits (in all the host lattice here investigated) a very strong quenching of the F emission, basically independent of the temperature, as is shown in Figs. 1 and 2 (broken lines). KCl ,

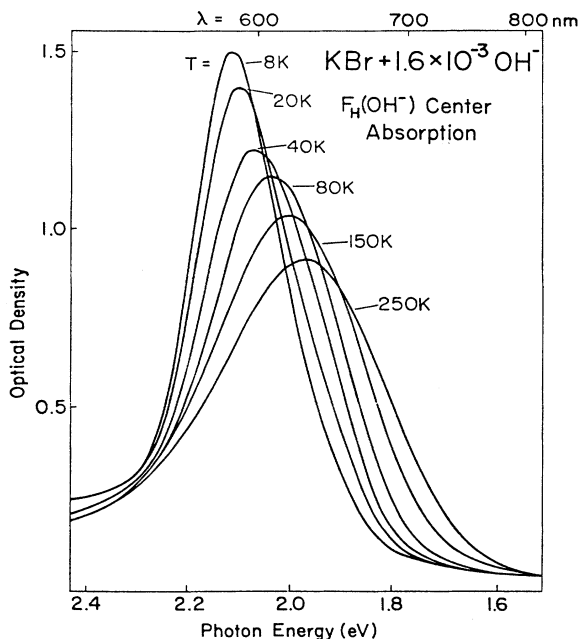


FIG. 6. Spectral dependence of $F_H(\text{OH}^-)$ absorption band in KBr at several temperatures.

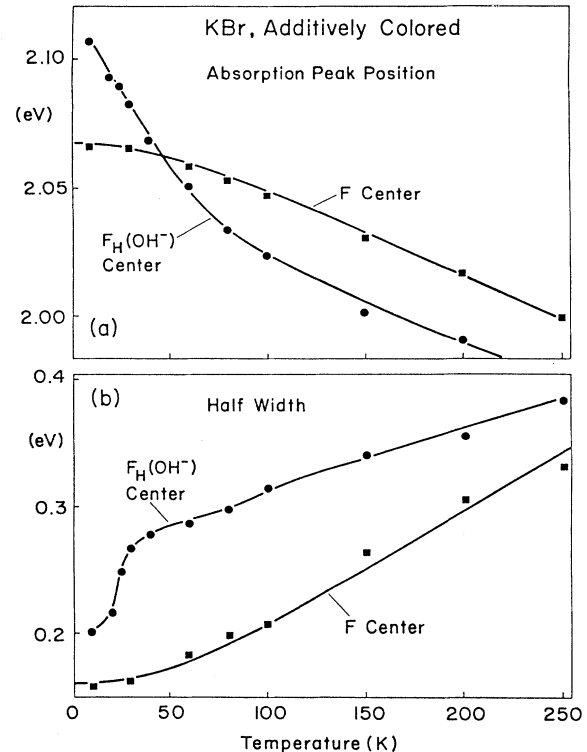


FIG. 7. Temperature dependence of peak position (a) and half width (b) of $F_H(\text{OH}^-)$ absorption in KBr .

RbCl , and RbBr exhibit a similar "normal" behavior: a redshift and broadening of the $F_H(\text{OH}^-)$ compared to the normal F band, with both effects gradually increasing with the increase of the lattice parameter (Fig. 4). As shown for one of these normal examples, the temperature dependence of the peak position and halfwidth (RbBr in Fig. 5) is very smooth and monotonic, like for the F band. $F_H(\text{OH}^-)$ absorption in KBr , however, shows a different and abnormal behavior same as was observed in $\text{Kl}:\text{OH}^-$.⁵ At low temperature it is—as the only case—shifted to high energies compared to the F band and it has nearly the same width as the F band. Its spectral band position and width—originally measured in Fig. 6—shows unusually strong low-temperature variations. A plot of these quantities (in comparison to that of the F center) as a function of temperature shows a very strong blueshift and narrowing effects in the low-temperature range (10–50 K) as is shown in Fig. 7. Above this temperature, the band becomes more "normal" like the other $F_H(\text{OH}^-)$ absorptions: redshifted and considerably wider than the F band. This abnormal behavior of $F_H(\text{OH}^-)$ absorption in KBr is produced by the gradual freezing of the system into one of the two possible configurations having the OH^- dipole parallel (type I) or perpendicular (type II) to the neighboring F center at temperatures below 10 K.⁵

IV. DISCUSSION

It is evident from our previous results in KCl (Ref. 1) that a long distance and strong interaction exists between

these two types of defects, F and OH^- centers. This interaction does not affect the F -center absorption but very much affects the electronic process following the absorption in the F excited state. In this work we have extended the investigation of this process to three different host materials to check out the strength of the interaction under the OH^- reorientation rate variation. Of course one can modify this reorientation rate either by changing the temperature or the host lattice—we did that by both ways. Also here we have studied, for that implication, only the most interesting and simple case of high OH^- concentrations (in the range from $3\text{--}5 \times 10^{-3}$ mol fraction) where most of the F centers have an OH^- defect inside of the critical radius of $5a$ (a equals lattice parameter), as was previously determined in KCl.

In this case, the main contribution for the F luminescence quenching due to the OH^- dipole effects comes from the temperature that is directly responsible for the variation of the OH^- reorientation rate. Figure 8 describes the observed phenomenological correlation between the OH^- dipole reorientation time and the measured F luminescence efficiency with the temperature for several hosts. It is very important to note that the F luminescence is about 50% efficient ($\eta_F \approx 0.5$) in RbBr, KBr, and RbCl, when the OH^- reorientation rate has a value around $2 \times 10^7 \text{ sec}^{-1}$, which is about ten times the F radiative transition rate in these hosts. Of course this condition happens at different temperatures depending on the host: $T \approx 15 \text{ K}$ for RbCl, $T \approx 25 \text{ K}$ for KBr, and $T \approx 70$ for RbBr.

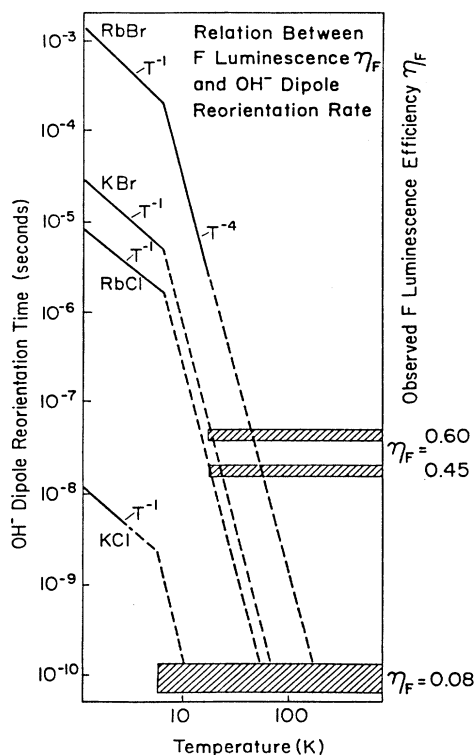


FIG. 8. Observed correlation between the OH^- dipole reorientation time and the measured F luminescence efficiency with the temperature for several hosts (RbBr, KBr, RbCl, and KCl).

The F luminescence efficiency drastically decreases to 8% ($\eta_F \approx 0.08$) by increasing the OH^- reorientation rate up to 10^{10} sec^{-1} , assuming the T^4 dependence verified for the OH^- reorientation rate at low temperature ($2\text{--}12 \text{ K}$)² is a good approximation for the high-temperature range. This particular rate value achieved in KCl at 10 K, and in KBr, and RbCl around 80 K introduces a very efficient nonradiative deexcitation process in the excited F center leading to a very low F luminescence efficiency ($\eta_F \approx 0.08$).

In the following part of the discussion we will analyze this strong temperature effect on the F luminescence efficiency in a more quantitative way for the RbCl host. Using the experimental data of Fig. 1, it was possible to obtain the luminescence efficiency (η_F) of F centers for the RbCl crystal as a function of the OH^- concentration at several fixed temperatures. These results are exhibited in Fig. 9 where is shown not a $\ln \eta_F \propto n(\text{OH}^-)$ dependence as was first determined in KCl,¹ but the following relation:

$$\ln \eta_F \propto [n(\text{OH}^-) - n^*(\text{OH}^-)],$$

where $[n(\text{OH}^-) - n^*(\text{OH}^-)]$ refers to the concentration of those OH^- defects that really participate in the quenching effect. The straight line behavior obtained for RbCl crystals have η_F value equal to unity not when $n(\text{OH}^-)$ approaches zero as was observed in KCl, but at a sizable $n^*(\text{OH}^-)$ value around 10^{-3} for the cases when $T < 120 \text{ K}$. η_F has an exponential dependence on $n(\text{OH}^-)$ as was first determined in KCl using a statistical model¹ to average the luminescence efficiency of F centers in the presence of randomly distributed OH^- defects. In the case of KCl, the best results were obtained by using a step function for the F luminescence efficiency with a

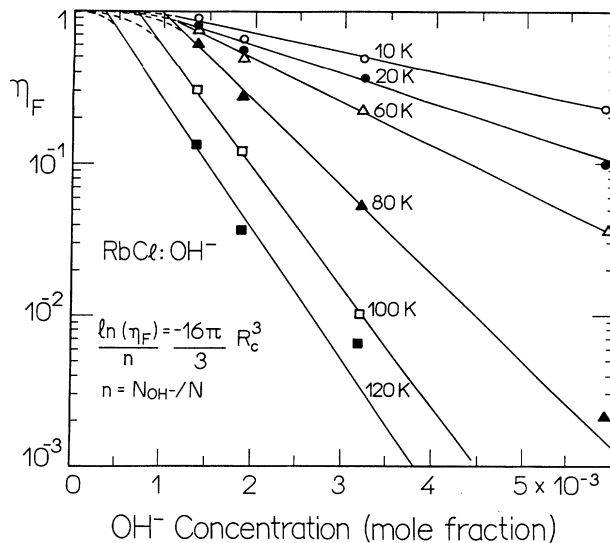


FIG. 9. Measured F luminescence efficiency (η_F) in RbCl as function of OH^- concentration in the range of $(1\text{--}6) \times 10^{-3}$ mol fraction, at several temperatures (10, 20, 60, 80, 100, and 120 K). The solid lines represent the best fit obtained using Eq. (2) from the step function model.

critical distance (R_c). In that model, the total F luminescence efficiency was given by

$$\eta_F = \exp \left[- \left[\frac{16\pi}{3} \right] R_c^3 n(\text{OH}^-) \right], \quad (1)$$

where $n(\text{OH}^-)$ is the concentration (mol fraction) of OH⁻ defects that really participate in the quenching effect and R_c is the critical distance in units of lattice parameter a .

In order to make Eq. (1) more general, we should have in mind that the $n(\text{OH}^-)$ in Eq. (1) represents the concentration of OH⁻ defects participation in the quenching process of F luminescence. After measuring different hosts than KCl, we realize that might not be true that all the OH⁻ defects participate in the quenching of F centers at high OH⁻ doping level. There is always a partial amount of nonparticipating OH⁻ defects related with $n^*(\text{OH}^-)$. A more general expression for η_F should be given by the following equation:

$$\eta_F = \exp \left[- \left[\frac{16\pi}{3} \right] R_c^3 [n(\text{OH}^-) - n^*(\text{OH}^-)] \right]. \quad (2)$$

By using Eq. (2) to fit the measured F luminescence efficiency in RbCl as a function of OH⁻ concentration, using the data exhibited in Fig. 9, we got the $n^*(\text{OH}^-)$ and R_c values at different temperatures (see Table I).

These results show that $n^*(\text{OH}^-)$ value approaches 10^{-4} in RbCl when the temperature gets higher than 120 K. Only at such higher temperature the RbCl system works like the KCl system where $n^*(\text{OH}^-) \approx 0$. Another important observation is that the critical radius of F -OH⁻ interaction depends on the temperature and approaches a minimum value $R_{c0} = 3.08(a)$ when $T \rightarrow 0$ K.

We know from earlier works that for high OH⁻ concentrations ($\approx 10^{-3}$), the elastic and electric interaction between the dipoles strongly "blocks" their reorientational motion.⁶ Even in a randomly distributed system the number of blocked OH⁻ dipoles would increase at higher concentrations due to the long distance of the dipole-dipole interaction of OH⁻ defects, producing a nonparticipating OH⁻ concentration, $n^*(\text{OH}^-)$, that must be subtracted from the total OH⁻ concentration. Only that concentration difference is able to quench the total F luminescence.

In order to show this concentration effect on the reori-

TABLE I. The critical radius values and $n^*(\text{OH}^-)$ obtained by using Eq. (2) for RbCl:OH⁻. R_c is given in unity of lattice parameter.

T (K)	R_c	$N^*(\text{OH}^-)$
10	3.08	9.88×10^{-3}
40	3.39	9.88×10^{-3}
60	3.73	9.88×10^{-3}
80	4.28	9.88×10^{-3}
100	4.54	6.00×10^{-3}
120	4.76	1.50×10^{-3}
130	4.79	$< 1 \times 10^{-4}$

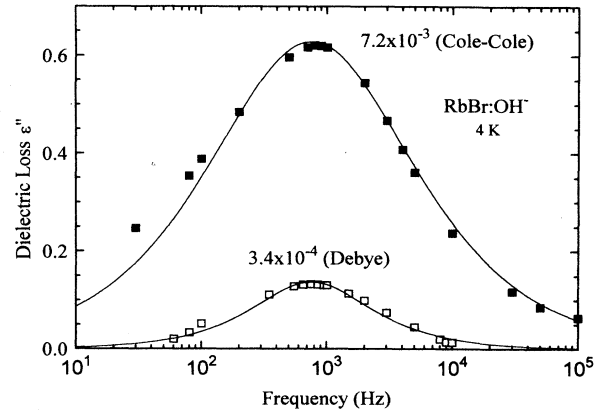


FIG. 10. Dielectric loss ϵ'' versus frequency for RbBr crystals doped with low (3.4×10^{-4} mol fraction) and high (7.2×10^{-3} mol fraction) OH⁻ ions, measured at 4 K. The low concentration crystal exhibits a pure paraelectric dipole behavior (Debye model) (solid line). In the high concentration case, the dipoles obey a Cole-Cole model (solid line), where α_{CC} is 0.305.

entational motion (tunneling) of OH⁻ dipoles, we measured the dielectric losses (ϵ'') of two RbBr samples doped with low (3.4×10^{-4} mol fraction) and high (7.2×10^{-3}) OH⁻ concentrations and for KBr doped with 2.85×10^{-3} . RbBr and KBr hosts were chosen because their reorientation rates (at 4 K) meet the frequency range of the used equipment (10 – 10^5 Hz). The capacitance and conductance of the samples were measured with a General Radio Precision Capacitance Measurement System type 1621 in the three terminal configuration to shield the capacitance of the leads. The system was operated in the 10 – 10^5 Hz range of frequencies and at amplitudes in the 1.5–15 V voltage range. Figures 10 and 11 show the dielectric losses (ϵ'') as function of the voltage frequency. The solid lines represent the best fitting obtained using a Debye (for low RbBr

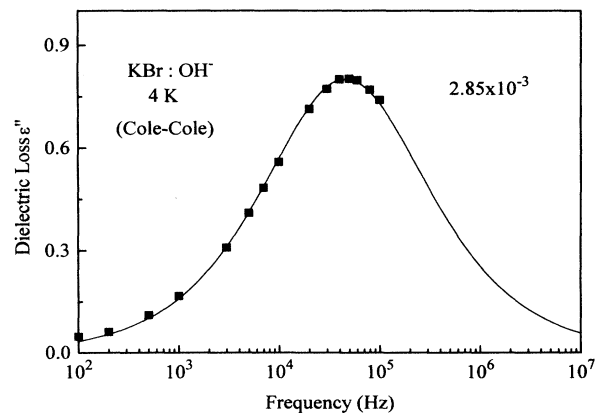


FIG. 11. Dielectric loss ϵ'' versus frequency for KBr doped with 2.85×10^{-3} mol fraction of OH⁻ ions, measured at 4 K. The solid line represents the best fitting using a Cole-Cole model where α_{CC} is 0.3154.

OH⁻ doping) and a Cole-Cole model⁷ for RbBr and KBr with high OH⁻ dopings. It is seen that in the low OH⁻ concentration crystal (3.4×10^{-4} mol fraction), the dipoles reorient with a unique time constant (τ_{reor}) equal to $[1/(2\pi f_{\text{max}})]$, where f_{max} corresponds to the frequency peak of the dielectric loss curve obtained using the Debye law. By increasing the OH⁻ concentration in the order of 10^{-3} mol fraction, the dipole reorientation time has a symmetric distribution centered at τ_0 which is coincident with the reorientation time obtained for low concentration (see Fig. 10). In that case of high OH⁻ concentration, the dielectric loss curves, measured for RbBr and KBr (solid lines of Figs. 10 and 11), follow a Cole-Cole model with α_{CC} equal to 0.3057 for RbBr and 0.3154 for KBr. In that case the OH⁻ relaxation time distribution is given by

$$G(s) = \left[\frac{1}{2\pi} \right] \frac{\sin(\alpha_{\text{CC}}\pi)}{\cosh[(1-\alpha_{\text{CC}})s] - \cos(\alpha_{\text{CC}}\pi)},$$

where $s = \ln(\tau_{\text{reor}}/\tau_0)$. This distribution is exhibited in Fig. 12, from where it is seen as the same width for both RbBr and KBr crystals.

The dielectric loss area $A(\epsilon'')$ is proportional to $(n_{\text{OH}} p^2 / KT)$, where n_{OH} is the concentration of OH⁻ dipoles, p is the dipole strength ($e\text{\AA}$), K is the Boltzmann constant, and T is the temperature. Theoretically one must expect a ratio between the two dielectric loss areas, $[A(\epsilon'')_{\text{HIGH}} / A(\epsilon'')_{\text{LOW}}]$, equal to 21.3 which is the OH⁻ concentration ratio between the two RbBr crystals used. On the other hand, we found a small value equal to 11.5. It means that only 54% of available OH⁻ dipoles contributes to the dielectric loss ϵ'' (the remaining OH⁻ dipoles were blocked by dipole-dipole interaction) in high OH⁻ doped RbBr.

Concerning now the temperature effects on F luminescence efficiency which shows a temperature-dependent critical radius, the following microscopic assumption was tentatively made to clarify the physical essence of this interaction. Let us assume now that the total nonradiative probability induced in the F excited state by the ac elec-

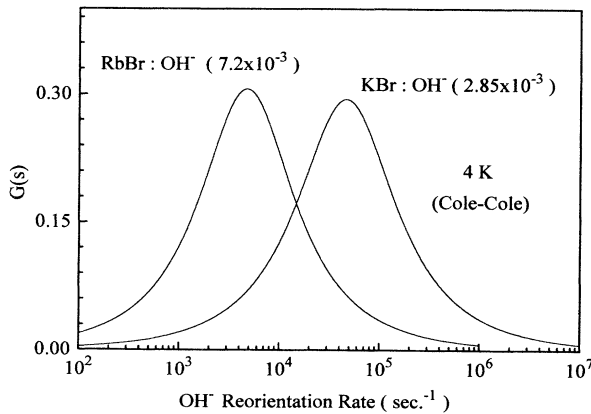


FIG. 12. Relaxation time distribution of OH⁻ dipoles obtained from the Cole-Cole model for RbBr doped with 7.2×10^{-3} OH⁻ mol fraction and KBr (2.85×10^{-3}) at 4 K. $\alpha_{\text{CC}} = 0.3057$ for RbBr and 0.3154 for KBr.

tric field of the OH⁻ defect—situated at distance R from the F center—can be divided in two parts due to the following distinct effects; i.e., $P_{\text{nr}} = P_{\text{lf}} + P_{\text{hf}}$.

(i) A low frequency term (P_{lf}) due to the induced nonradiative probability at lower temperatures when $\tau_{\text{reor}} \geq \tau_{\text{rad}}$.

(ii) A high frequency term (P_{hf}) due to the F -center deexcitation induced by the temperature-dependent reorientation rate ($\propto T^4$) of the OH⁻ dipole when $\tau_{\text{reor}} \ll \tau_{\text{rad}}$.

In the case of high frequency, the attempt frequency (preexponential factor) must be governed by a power law (aT^b) dependence since this determines the dipole reorientation rate of OH⁻ (Refs. 2 and 8) and consequently the maximum position of the OH⁻ reorientation rate distribution, $G(s)$, verified in the case of high OH⁻ concentrations ($\geq 10^{-3}$).

The total probability of nonradiative F -center deexcitation (P_{nr}), induced by an OH⁻ defect, as a function of distance R , should be given by

$$P_{\text{nr}} = (f_0 + aT^b) \exp \left[-\frac{AR}{R_{c0}} \right], \quad (3)$$

where R_{c0} is the critical radius of the interaction at $T \approx 0$ K. The a , b , and A parameters are obtained from the best fit of the data. f_0 is the temperature-independent preexponential factor obtained from the relation between τ_{rad} and A . This relation is obtained by using the condition that $P_{\text{nr}} = \tau_{\text{rad}}^{-1}$ in Eq. (3) when $R = R_{c0}$ (at $T = 0$ K). It implies that $\tau_{\text{rad}}^{-1} = f_0 \exp(-A)$.

The temperature-dependent critical radius was derived from the present model using the true condition that $P_{\text{nr}} = \tau_{\text{rad}}^{-1}$ (or $\eta_{\text{rad}} = 0.5$) when $R = R_c$ at temperature $T > 0$ K, in Eq. (3). It gives the following expression:

$$\tau_{\text{rad}}^{-1} = (f_0 + aT^b) \exp \left[-\frac{AR_c}{R_{c0}} \right]$$

or

$$R_c = R_{c0} \left[1 + \frac{\ln \left[\frac{f_0 + aT^b}{\tau_{\text{rad}}^{-1}} \right]}{A} \right], \quad (4)$$

where R_{c0} , A , a' , and b are the parameters which can be obtained from the best fit. Using the R_c values from Table I on Eq. (4), we got the values of these parameters (shown in Table II), where $a = a' \exp(A)$. Note that

TABLE II. Parameter values obtained from the best fit of data using Eq. (4) from the present model where $R_c = R_c(T)$, for RbCl and KCl systems. R_{c0} is given in unity of lattice parameter.

KCl:OH ⁻				
R_{c0}	f_0	A	a	b
4.04	$1.25 \times 10^{15} \text{ sec}^{-1}$	20.39	$1.63 \times 10^{11} \text{ sec}^{-1} \text{ K}^{-3}$	3.0
RbCl:OH ⁻				
R_{c0}	f_0	A	a	b
3.076	$1.35 \times 10^{10} \text{ sec}^{-1}$	9.0	$6338 \text{ sec}^{-1} \text{ K}^{-4}$	4.0

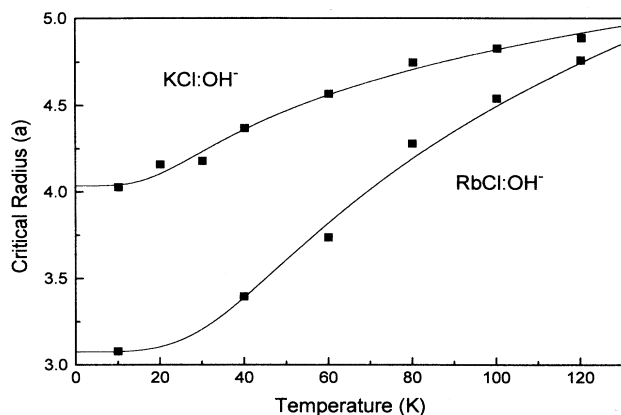


FIG. 13. Temperature behavior of the mean critical distance (R_c) of $F\text{-OH}^-$ interaction in RbCl, and KCl crystals for the nonaggregated case. The solid lines represent the best fit obtained using Eq. (4) from the present model. The parameter values are listed in Table II.

$f_0 = 1.35 \times 10^{10} \text{ sec}^{-1}$ was obtained using $f_0 = \tau_{\text{rad}}^{-1} \exp(A)$, where $\tau_{\text{rad}}^{-1} = 1.66 \times 10^6 \text{ sec}^{-1}$ for RbCl. The theoretical behavior of R_c , predicted by Eq. (4), gives the solid line of Fig. 13 which is in good agreement with the experimental values. This model explains well the temperature behavior of the critical radius for the nonradiative induced F -center deexcitation.

Now substituting Eq. (4) in Eq. (2), one gets the temperature dependence of the F -center luminescence efficiency. Both the theoretical (solid lines) and experimental data (η_F) agree very well for RbCl doped with several OH^- concentrations at several temperatures, as seen in Fig. 9. In all the calculations for the temperature range up to 80 K, we used $n^*(\text{OH}^-) = 9.88 \times 10^{-3} \text{ mol fraction}$. At temperatures higher than 80 K, $n^*(\text{OH}^-)$ deviates from this constant value towards zero.

Also, we calculate the critical radius R_c of $F\text{-OH}^-$ interaction in KCl doped with $2.3 \times 10^{-3} \text{ OH}^-$ at several temperatures, using the F luminescence efficiency [$\eta_F(T)$] data from Fig. 2. Using Eq. (2) one can obtain the following expression for $R_c(T)$:

$$R_c(T) = \left[\frac{-3 \ln \eta_F(T)}{16\pi \Delta N} \right]^{1/3},$$

where $\Delta N = [n(\text{OH}^-) - n^*(\text{OH}^-)]$ with $n^*(\text{OH}^-) \approx 0$. The calculated R_c values for the KCl system are shown in Fig. 13. Using Eq. (4) derived from the present model, we obtained the solid line of Fig. 13 corresponding to the best fit of R_c data as a function of the temperature in KCl. In Table II we show the fitted parameters obtained for both RbCl and KCl systems for comparison.

V. SUMMARY

In this paper we have proposed a microscopic probability for the nonradiative F -center deexcitation due to the $F\text{-OH}^-$ interaction which includes two effects from the ac electric field of OH^- dipoles actuating in the preexponential factor as an attempt frequency to the back return of the excited F electron into the ground state. This interaction produces two distinct terms for the nonradiative probability: low and high frequency terms. Using the condition that both microscopic probabilities of perturbed F center, the radiative (τ_{rad}^{-1}) and the nonradiative (P_{nr}), have identical values when $R = R_c$, we could get a theoretical expression for the temperature dependence of the critical radius of that interaction. Using that law, the R_c values were fitted to the model allowing us to obtain the attempt frequency constants that turn out to be proportional to T^4 for RbCl:OH⁻ and proportional to T^3 for KCl:OH⁻ systems in the temperature range investigated. These observations are in agreement with what has been experimentally observed for the reorientation rate of isolated OH^- defects in RbCl and RbBr at 10 K.² The theory of one- and two-phonon reorientation rates of paraelectric OH^- defects in alkali halide crystals predicts also a T^3 and $T^{4.5}$ dependence at about 10 K.⁸

Considering this fact, one must conclude that the temperature-dependent reorientation rate of the OH^- defect produces an ac electric field which repels the F^* electron back to the F ground state with a nonradiative probability strongly dependent on the temperature due to the external dipole reorientational effects.

ACKNOWLEDGMENT

Financial support from the Saõ Paulo State Science Foundation (FAPESP) is acknowledged.

¹L. Gomes and F. Luty, Phys. Rev. B **30**, 7194 (1984).

²S. Kapphan and F. Luty, Solid State Commun. **8**, 349 (1970).

³M. Jordan, H. Sothe, J. M. Spaeth, and F. Luty (unpublished).

⁴B. Fritz, F. Luty, and J. Anger, Z. Phys. **174**, 240 (1963).

⁵G. Baldacchini, S. Botti, U. M. Grassano, L. Gomes, and F.

Luty, Europhys. Lett. **9**, 735 (1989).

⁶L. Gomes and F. Luty (unpublished).

⁷K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).

⁸B. G. Dick and D. Strauch, Phys. Rev. B **2**, 2200 (1970).