PHYSICAL REVIEW B VOLUME 19, NUMBER 6 15 MARCH 1979

Study of the self-trapped exciton and F-center formation on a picosecond time scale in KBr

J. M. Ortega*
Naval Research Laboratory, Washington, D.C. 20375

(Received 6 July 1978)

We have studied optical absorption at 694 nm in KBr, on a picosecond time scale, after two-photon excitation by a 347-nm pulse. We have measured an F-center rise time of (15 ± 10) psec in the temperature range 300–660 K. The self-trapped exciton exhibits more complicated creation kinetics, with population of its lower state delayed by about 60 psec. In addition, we discuss a model of F-center production involving the free exciton as the precursor state.

The production of excitons in many alkali halides gives rise to a number of phenomena: (i) the so-called edge luminescence due to the free exciton (FE) itself which has been observed so far only in the iodides,[1,2] and (ii) the growth of a transient self-trapped exciton (STE) whose decay is responsible for the so-called intrinsic luminescence.[3,4] In addition, the STE exhibits several transient absorption bands.[5] (iii) another phenomenon is the production of Frenkel defects in the crystal, i.e., the F-H pair.[6]

Although many explanations have been proposed in particular for the F-center production mechanism,[7-9] these phenomena and their relationship are not yet clearly understood, needing thus more experimental information.

Since the states involved in the experimental study of these phenomena are mainly highly excited states with very short lifetimes, one of the best ways of obtaining information about them is to use time-resolved optical spectroscopy in the picosecond range. These techniques have been extensively developed in the past few years[10] and have already been successfully applied to such systems,[11-13] showing, in particular, that the F-center rise time is of the order of 10^{-11} sec in several alkali halides. However, it is difficult to be able to measure the kinetics of more than one species in the same alkali halide at the same temperature and with an experimental time resolution compatible with the characteristic time constants involved. This has been done only in KI (Ref. 13), where only "incomplete" or "unstable" F centers were observed simultaneously with the STE, which we shall compare further with our results.

Hence the purpose of this work was to measure the creation kinetics of the F center and STE in the same alkali halide and at the same temperature. In addition, we will discuss, in view of the results, the possibility for the free exciton to be

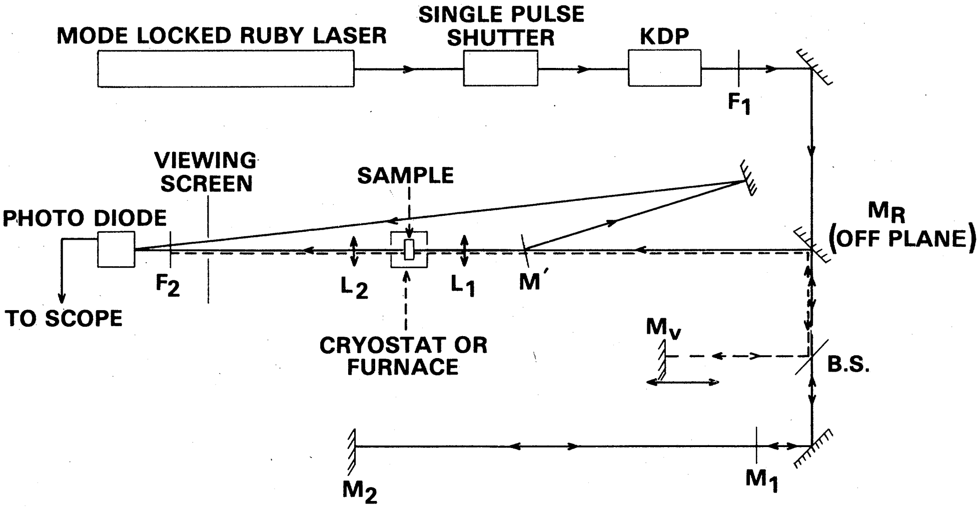

FIG. 1. Apparatus for measurement on a picosecond time scale of absorption at 694 nm following two-photon excitation at 347 nm. The auxiliary white source used to look at the sample surface is not shown.

the precursor of the *F* center in the Frenkel defect production mechanism.

I. EXPERIMENTAL

The experiment consists in measuring the absorption of a sample at various delays after excitation by means of a mode locked ruby laser. The probe beam was obtained by selecting a single pulse from the mode locked ruby laser, and the excitation was provided by two-photon absorption in the sample of the second harmonic, spatially delayed, of the unattenuated probe beam.

Since the principle of the measurements was basically the same as the one used by Bradford *et al*[11] we will describe it only briefly (Fig. 1): A single pulse of 694 nm emanated from a mode locked ruby laser followed by a single pulse shutter. A second ruby rod, flashlamp pumped, was used as light amplifier. The light conversion into the second harmonic (347 nm) was achieved through a potassium dihydrogen phosphate crystal. The 694-nm beam, strongly attenuated by filter F_1, and the 347-nm beam were then separated by passing through the dichroic beam splitter BS. The uv beam was then reflected back by mirror M_v whose position was adjustable in the range of $-60-+250$-psec optical delay of the probe pulse. The red pulse was reflected back by the semitransparent mirror M_1, which gave the probe pulse, and by the mirror M_2 which gave a second probe pulse delayed by 11 nsec. All the pulses passed once more through the beam splitter BS, ensuring a good attenuation of the undesirable wavelength, and were reflected by mirror M_R toward the sample. M_1, M_2, and M_R back reflections were slightly misaligned with the incident beam so that M_R was a totally reflecting mirror positioned outside the incident beam. Both beams were focused into the sample by the chromatic fused silica lens L_1. Lens L_2 was used for refocusing the red light on the photodiode and for making an enlarged image (×50) of the first surface of the crystal on a viewing screen, with the aid of an auxiliairy white light. This enlargement allowed direct control of the adjustment of the system, since in KBr the induced coloration, as well as the 694-nm light, can be seen visually. A replica of the pulses sent by M_1 and M_2 was taken by the pellicle reflector M' and directed toward the detector. A filter F_2 stopped the remaining uv light. Finally, the red interrogation pulses were recorded with the fast vacuum photodiode and a Tektronix 7904 oscilloscope. The uv pulse has been also recorded. The level of light amplification has been adjusted so that the maximum optical density obtained was about unity.

The quantity of interest is the ratio between optical density for an optical delay Δ between the probe and exciting pulses $[D(\Delta)]$ and the optical density for the fixed delay 11 nsec $[D(11\text{ nsec})]$ versus the delay Δ. Let G_1 and G_2 be the intensity of the pulses sent by mirrors M_1 and M_2 through the sample and G_1' and G_2' the intensity of the pulses reflected by mirror M'. G_1°, G_2°, $G_1'^\circ$, and $G_2'^\circ$ label the intensity of the pulses for a shot where no uv light is sent toward the sample. Then

$$D(\Delta) = \log\left(G_1' G_1^0 / G_1 G_1'^0\right),$$
$$D(11\text{ nsec}) = \log\left(G_2' G_2^0 / G_2 G_2'^0\right).$$

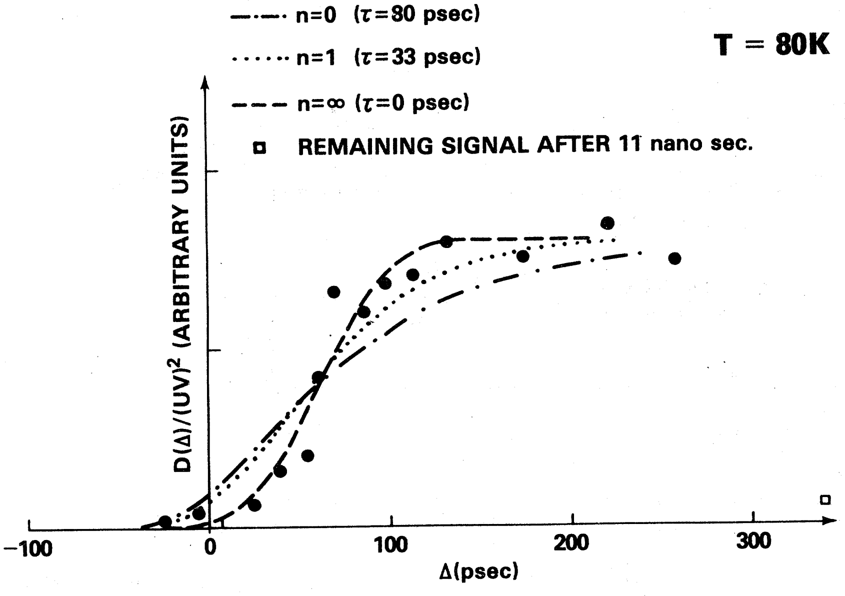

FIG. 2. Optical density at 694 nm vs delay, Δ, after the 347-nm pulse, at 80 K. The units are arbitrary since we used the square of intensity of the uv pulse as a reference (see text).

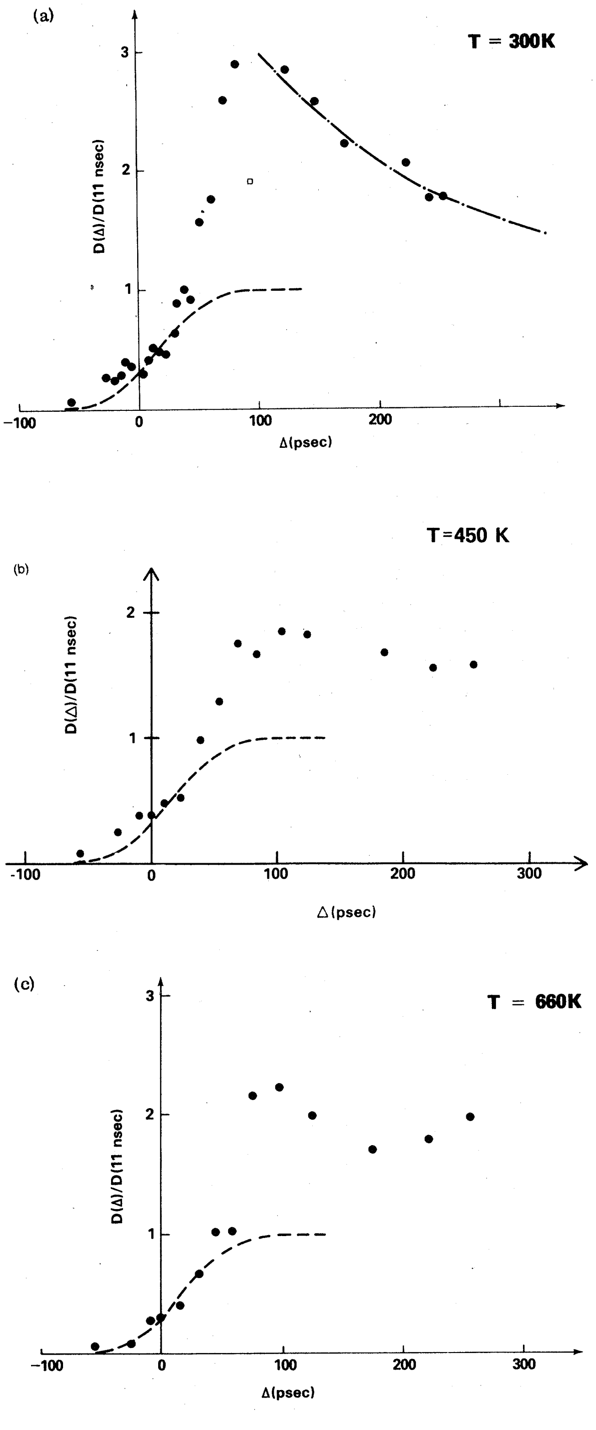

FIG. 3. Fractional optical density $D(\Delta)/D(11\text{ nsec})$ at 694 nm vs delay, Δ, after the 347-nm pulse. The dashed curve is a best-fit convolution of pulse shapes for the stable part (after 11 nsec) of the optical density with an exponential form for defect production, yielding $\tau_F \simeq 15$ psec (see text). (a) At 300 K. The dot-dashed line is a best fit with a single decaying exponential for the STE decay, yielding $\tau_{\text{STE}} \simeq 160$ psec; (b) at 450 K; (c) at 660 K.

The average half width of the pulse duration was 45 psec (± 15 psec) as measured by an Electrophotonics (1974) streak camera.

The zero delay coincidence has been measured in the same way as Bradford *et al.*[11] did. The uncertainty for this position corresponds to less than 5 psec.

In displaying the experimental results (Figs. 2 and 3), we have not drawn error bars around the plotted points, although each of them is an average over several data points, since there is no way of calculating the absolute error. For example, we have shown in Fig. 3(a) an aberrant point which is the result of the measurement for $\Delta = 100$ psec. This seems to be due to a greater amount of uv light than the average we had at the time of this measurement, influencing the relative amounts of *F* center and STE. Then the relative amounts which can be deduced from the data should be regarded as probably unreliable and depending upon the experimental conditions.

II. RESULTS

In order to observe both the STE and *F*-center kinetics, we worked with KBr samples so that the 694-nm wavelength overlaps both the STE and *F* bands. In fact, the 694-nm wavelength is located well inside one of the STE absorption bands,[5] although it is on the high-energy edge of the *F* band. Thus a strong temperature dependence in the amount of the observed *F* centers was observed.

At 80 K only about 8% of the absorption measured at $\Delta \simeq 100$ ps remains after 11 nsec. Thus in this case, the error over $D(11\text{ nsec})$ becoming of the order of 50%, we have plotted $D(\Delta)$ over the square of the magnitude of the uv pulse, since the uv absorption by the sample is a two-photon process. Since the lifetime of the *F* center at this temperature is greater than a few nanoseconds, as we verified it at higher temperatures, the resulting absorption has been attributed to the STE. The STE lifetime at $T \simeq 80$ K, deduced from the remaining absorption after 11 nsec, is 4 nsec (± 1 nsec).

The time dependence of the growth of the STE has an unusual shape (Fig. 2). Such a "delayed" process has been already observed by Faust *et al.*[14] in nitromethane photolysis on the nanosecond time scale. They interpreted this effect as arising from a decay, from the exciton to the lower STE state in our case, through n intervals among $(n+1)$ intermediate levels having roughly the same time constant τ_n (otherwise, the process is dominated by the longer time constant). This has been studied theoretically by Williams *et al.*[12] For n equal time constants they found that the observed absorption $K(t)$ should obey the form

$$K(t) = 1 - P_n(t)\exp(-t/\tau_n),$$

$$P_n(t) = \sum_{j=0}^{n} \frac{1}{j!}\left(\frac{t}{\tau_n}\right)^j .$$

These authors have also developed theoretical expressions describing the convolution of any kinetics with the exciting and probe pulse shapes. We have used them for pulse widths of 50 psec each and a final optical density of 0.5. The computerized results are plotted in Fig. 2 for $n=1$ (no intermediate state), $n=2$ (one intermediate state), and $n=\infty$. In this last case it can be shown that the time dependence is simply a single step delayed by a certain amount of time t_d such that:

$$n\tau_n = t_d \quad \text{even when } n \to \infty .$$

Thus t_d is an adjustable parameter.

In these plots the lifetime has been adjusted so that the curves are reaching the point where the optical density is 0.4 times the final density for the same delay Δ. The curves (Fig. 2) show that although our experiment is not accurate enough to tell us what is the exact number of levels involved in the formation of the STE triplet ground state, there are at least several of these intermediate levels.

At room temperature [Fig. 3(a)] some stable F centers in the range of 11 nsec appear. In addition, the STE, now unstable within this time range, are still exhibiting clearly the same behavior as at 80 K. We have fitted [Fig. 3(a)] the F-center growth kinetic, i.e., the beginning of the experimental curve, by a single exponential convoluted with the excitating and probe pulse. This leads to a creation time τ_F of $\tau_F = (15 \pm 10)$ psec.

We have also fitted [Fig. 3(a)] the decaying STE absorption by a single exponential, leading to a STE decay time of (160 ± 20) psec.

At 450 K [Fig. 3(b)] we obtained basically the same behavior of both species except that the STE seems not to be decaying. This effect can be understood by looking at the data taken at higher temperature (660 K). It appears [Fig. 3(c)] that a third growing species is now observed. At 450 K the amount of this third species is such that the end of the curve looks flat, although at 660 K it is clearly growing. Meanwhile, the behavior of the F center and STE remain unchanged.

This last component is probably due to some preexisting traps in the crystal which would be filled by freed electrons when the F center and STE become unstable with the increasing temperature. This trapping time would decrease from a few nanoseconds,[9] at room or lower temperatures, to a few hundreds of picoseconds at high temperature. However, we have done no experimental search in order to clarify further this question.

We have estimated the lifetime of the STE at 660 K as (50 ± 20) psec. The lifetimes of the STE measured at 80, 300, and 660 K account for an activation energy for the STE nonradiative decay process of about 35 meV, which is in very good agreement with the value (37 meV) determined by luminescence techniques.[15] This agreement confirms our assignment to the STE of the absorption observed at 80 K.

Thus our data obtained at various temperatures show that in KBr the F center has a creation time of about 15 psec and is temperature independent, in the error range (± 10 psec.). The lower STE formation is delayed by about 60 psec. This delay is probably due to some excited electronic levels lying between the electronic state reached by two-photon absorption of the uv pulse and the final lowest triplet STE state. Another possibility, that the STE and F-centers formations could be anticorrelated, will be discussed in Sec. III.

This result of a delayed STE formation is not in contradiction with previous measurements. In KI Suzuki and Hirai[13] have observed complex kinetics involving rapidly growing and decaying F centers followed by the growth of the STE absorption band. They interpreted the STE behavior by a single exponential growth. However, it seems that their experimental curves could be fitted as well by slower-decaying F centers followed by the rise of "delayed excitons." In this case the delay would be about 150 psec at 4 K. The situation seems to be quite the same in NaBr where Williams *et al.*[12] have performed such measurements. The delay would then be around 30 psec. We are then led to the conclusion that the heavier the alkali halide, the longer the STE delay. This would explain why these authors[12] did not observe such a kinetic in NaCl, the time scale of the phenomenon being then too small in regard to the time resolution allowed by mode locked Nd:YAG laser pulses. A delay in the lowest STE formation is thus likely to be a general phenomenon in alkali halides.

III. DISCUSSION

It has been generally assumed until now[7-9] that the precursor of the F center was an excited state of the STE. However, our experiment, showing that the F center and the relaxed STE have different paths of formation, together with other experiments we will discuss in this section, suggests that the relaxed STE and the F center could have essentially different precursors. In this section we will focus on the possibility for the free exciton (FE) to be the F-center precursor. We will first discuss the experimental features of the process from this point of view and then give a qualitative basis of what could be a FE mechanism of *F*-center production.

There have been many theoretical[7-9] and experimental[16] works on the primary process of *F*-center creation. At first we will recall two of them which seem quite contradictory and with which any *F*-center creation model will have to deal.

(i) Tanimura and Okada[17] have shown, in KBr, that the precursor of the *F* center is apparently mobile although the precursor of the relaxed STE is not. We want to point out that this implies immediate self-trapping, in some excited STE states, for the excitons or electron hole pairs, which will give rise to the lower STE state. Thus the delay we have observed for its formation is an intrinsic effect and is not due to the release of electrons from shallow traps in the crystal.

(ii) It has been shown experimentally by Williams[18] and Keller and Patten[19] that the *F* center can be created from some excited state of the STE.

The Tanimura and Okada experiment suggests that the mobile FE is the precursor of the *F* center. The second set of experiments, on the other hand, pleads for a STE state as the *F*-center precursor. But then some excited states of the STE, in which, as we have shown experimentally, the STE was remaining for a time long in regard to the *F*-center rise time, would have to be not mobile. An another excited state of the STE, precursor of the *F* center, would have to be.

This apparent contradiction can be solved by the assumption that there is a tunnel effect allowing the excited STE to come back to the free exciton. Moreover, this assumption is consistent with the thermal dependence of the process that we will discuss now.

Williams *et al.*[12] have shown that in KCl the *F*-center production yield approaches unity with increasing temperature, and that it can be associated at high temperature with a thermal energy of 75 meV. They interpreted this effect by supposing that nearly all of the excitons, existing in an excited state, would give rise to close *F*-*H* pairs, some of them being unstable or incomplete, and recombining on a time scale shorter than 46 psec. If one attempts to apply such a model to alkali halides other than KCl having higher efficiency for the STE luminescence,[15] or if one extrapolates the *F*-center production yield in KCl toward unity with increasing temperature, then it is implied that the $F+H$ recombination produces luminescent STE states.[9,12] In this case the STE precursor would be the same as the *F*-center one, in contradiction with the experiment[17] of Tanimura *et al.* in KBr. Furthermore, Kabler and Williams[9] have pointed out that in KI the measured values of the potential barrier and of the involved phonon frequency could not account for the observed *F*-center rise time. In addition, the rise time would not be temperature independent as it seems to be after our and Suzuki and Hirai[12,13] experiments.

These effects can be explained by assuming that

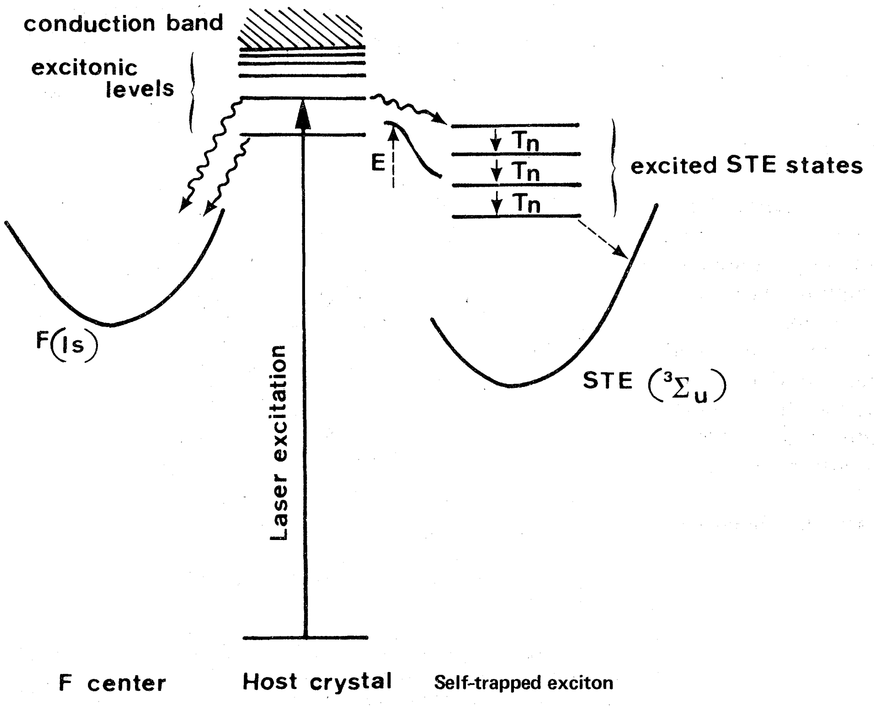

FIG. 4. Schematic sketch of the electronic levels involved in the STE and *F*-center formation proposed paths. These processes are indicated by sinusoidal arrows (↝). The potential barrier of energy *E* is roughly drawn (see text). For clarity the level spacings are unrealistic.

this potential barrier lies, in fact, in the excited states of the exciton allowing the excited STE to return to a FE state (Fig. 4). Such a barrier, between the FE and the STE, has been already suggested by Mott and Stoneham.[20] However, this barrier cannot account for the observed delay of the lowest STE since we have shown that its kinetics is not a single exponential. In fact, this barrier is most likely to be overcome by the hot exciton, unless for excitation in the first exciton band,[15,21] and to be effective between the excited STE states and the FE. For some reasons the unrelaxed FE could not be self-trapped after the initial stage, after the experiment[17] of Tanimura and Okada. Then the situation would be the following: The hot exciton, created by the excitating pulse, splits immediately toward the relaxed FE states and the STE. The F-center creation mechanism starts during the fast relaxation of the FE, although the STE remains for a certain time, a few tens of picoseconds in KBr, in excited states.

These excited states of the STE are likely to diffuse toward the FE through the potential barrier (Fig. 4). This would give the observed temperature dependence of the F-center creation yield. In addition, the rise time would no longer be dominated by the tunneling process, since it can occur only as long as the STE excited states are populated.

The lifetime associated with this tunneling process would be

$$\frac{1}{\tau_t}=\nu_0\exp(-E/kT);$$

at 1000 K in KCl, it gives

$$\tau_t\simeq 0.5\ \text{psec};$$

with $E=75$ meV (Ref. 12) and $\nu_0=6\ 10^{12}$ cps (Ref. 9) (LO frequency).

Thus a lifetime of the relevant transient STE states of a few picoseconds would account for an F-center creation yield dominated by a thermally activated process, but only at high temperature as observed experimentally,[12] and approaching unity near 1000 K. The F-center rise time would then be temperature independent and determined mainly by the intrinsic time for the FE to relax nonradiatively. Hence the existence of a STE → FE tunneling process is consistent with all the aforementioned data.

The existence of the free exciton has been recently established[1,2] by observation of its luminescence. However, the weakness of this luminescence requires a very fast quenching process. The assumption of a potential barrier between the relaxed first excitonic state and the STE, depleting the FE population, leads[2] to radiative decay probabilities (10^5–$4\ 10^7$ sec^{-1} in the iodides) which seem much weaker than the expected ones ($\sim 10^9$ sec^{-1}) for such transitions. Thus another nonradiative channel should exist. The F-center production mechanism, which occurs in the picosecond time range, would be this nonradiative channel in our model. It would be predominant for higher states of the FE, since no luminescence is observed then.

This does not exclude the possibility of other nonradiative paths leading back to the unperturbed crystal. In particular, in KI a very fast secondary process, as shown experimentally by Suzuki and Hirai,[13] quenches the F-center production at low temperature. The quenching of the F-center production efficiency at very low temperature ($T<4$K) in KCl (Ref. 22) could be also related to this effect.

A possible way for the FE production mechanism of the F center can be explained qualitatively as follows: The $F+H$ pair production occurs through a nonradiative decay channel of the exciton which transfers its energy to the surrounding ions. Expelling a halogen atom from its normal lattice site requires, in an STE model of the F-center production,[7-9] coupling of the STE with translational and/or rotational modes of vibration, although the STE is expected to be mainly coupled with stretching or breathing modes, as is the F_2 center in alkali halides.[23] More generally speaking, it is difficult to understand how the crystal symmetry can be broken by a highly symmetric defect like the FE or the STE, unless the STE itself would not be symmetric as it has been re-

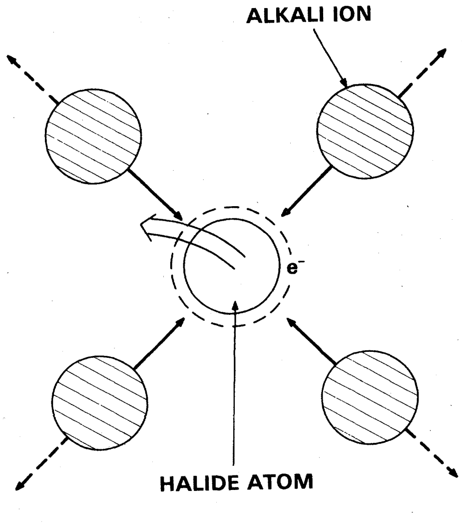

FIG. 5. Schematic sketch of the physical situation, involving a breathing mode on the defect site, likely to expel a halide atom from its normal lattice position.

cently suggested.[24] On the other hand, a totally symmetric relaxation, i.e., having the crystal symmetry of the ions surrounding a FE, is likely to expel the halogen atom (Fig. 5). Such a relaxation would make its equilibrium position unstable and make it escape along the path of least resistance.

This process can be seen as follows: Once the process has started, the electron, being subjected to the electric field of the surrounding alkali ions and to the Pauli repulsion against entering the space occupied by the halogen atom, has more room to expand into the vacancy since the halogen atom has begun to move. Then some new electronic levels are available for the electron allowing the process of nonradiative transitions to continue. In other words, the energy of some electronic levels, including the final 1*s* state of the *F* center, are lowered by the move of the halide atom and are helping this atom to move further since the surrounding ions get more energy as the process goes on and more nonradiative transitions take place. It is then a kind of cooperative phenomenon which avalanches once triggered. The phenomenon could be more easily triggered when exciting higher in energy than the first excitonic band. This could explain why the edge luminescence appears only when excited in this band. However, the process could be triggered even when exciting in this band,[25] since light in the excitonic range cannot be absorbed without, at least, three-body interactions involving a phonon of the crystal.[26] Impurities could also play this role.[27]

Furthermore, Kabler and Williams[9] have shown that the state corresponding to a $F^{+}+H^{-}$ pair is lower in energy than the $F+H$ pair state. Our model would explain why the final product of the process is the $F+H$ pair: Expelling the halogen atom requires the electron to occupy successively many electronic levels. These levels are spatially located in the vacancy freed by the halogen atom, which leads automatically to the 1*s* *F* center state as the final level.

IV. SUMMARY

In the experimental part of this paper we have shown that in KBr the formation of the lower STE triplet state is "delayed." Its creation path seems to involve intermediate STE levels between the initial state, obtained by uv excitation of the crystal, and the observed final state. Its time dependence looks roughly like a step delayed by about 60 psec. The *F* center has a simpler time dependence which can be fitted by a single exponential involving a rise time of (15 ± 10), seemingly constant between 300 and 660 K.

In the theoretical part we have presented a model of *F*-center production involving the free exciton as the *F*-center precursor. Such a model is able to take into account the main experimental features of the process, at least as well as the models, involving the STE as the precursor, which have been previously proposed.[7-9] Thus the exact nature of the *F*-center production mechanism requires further experimental investigation.

ACKNOWLEDGMENTS

The author wishes to thank Dr. M. N. Kabler for welcoming him in his laboratory and for many helpful discussions. He is also very indebted to Dr. R. T. Williams for many advices and discussions throughout this work. The author would like to acknowledge the support by the NRL, the CNRS (France), and a NATO fellowship.

---

*Present address: E. S. P. C. I. 10, rue Vanquelin 75231, Paris, France.

[1] Ch. Luskchik, I. Kuusmann, P. Liblik, N. Lushick, T. Soovik, and A. Ratas, International Conference on Luminescence, Tokyo, 1975, p. 170 (unpublished).

[2] H. Nishimura, C. Ohhigashi, Y. Tanaka, and M. Tomura, J. Phys. Soc. Jpn. 43, 157 (1977).

[3] M. N. Kabler, Phys. Rev. 136, A1296 (1964).

[4] R. B. Murray and F. J. Keller, Phys. Rev. 137, A942 (1965).

[5] R. T. Williams and M. N. Kabler, Phys. Rev. B 9, 1897 (1974).

[6] See, for example, M. N. Kabler, in *Proceedings of the NATO Advanced Study Institute on Radiation Damage Processes in Materials*, Corsica, 1973, edited by C. H. S. Dupuy (Noordhoff, Leyden, 1975), p. 171.

[7] N. Itoh and M. Saidoh, J. Phys. Colloq. 34, C-901 (1973).

[8] Y. Toyozawa, *Proceedings of the Fourth International Conference on Vacuum Ultraviolet Radiation Physics*, Hamburg, 1974, edited by E. E. Koch, R. Haensel, and C. Kunz (Pergamon, Vieweg, 1974), p. 137.

[9] M. N. Kabler and R. T. Williams, Phys. Rev. B 18, 1948 (1978).

[10] See, for example, *Ultrashort Light Pulses*, edited by S. L. Shapiro (Springer-Verlag, New York, 1977).

[11] J. N. Bradford, R. T. Williams, and W. L. Faust, Phys. Rev. Lett. 35, 300 (1975).

[12] R. T. Williams, J. N. Bradford, and W. L. Faust (unpublished).

[13] Y. Suzuki and M. Hirai, J. Phys. Soc. Jpn. 43, 1679 (1977).

[14] W. L. Faust, L. S. Goldberg, T. R. Royt, J. N. Bradford, R. T. Williams, J. M. Schnur, P. G. Stone, and R. G. Weiss, presented at the Topical Meeting on Picosecond phenomena (Hilton Head, S. C., 1978) (unpublished).

[15] M. Ikezawa and T. Kojima, J. Phys. Soc. Jpn. 27,

1551 (1969).

[16] See, for example, Ref. 9 and N. Itoh, J. Phys. Colloq. C 7, p. C7-27 (1976).

[17] K. Tanimura and T. Okada, Phys. Rev. B 13, 1811 (1976).

[18] R. T. Williams, Phys. Rev. Lett. 36, 529 (1976).

[19] F. J. Keller and F. W. Patten, Solid State Commun. 7, 1603 (1969).

[20] N. F. Mott and A. M. Stoneham, J. Phys. C 10, 3391 (1977).

[21] M. P. Fontana, Phys. Rev. Lett. 37, 789 (1976).

[22] T. Karazawa and M. Hirai, J. Phys. Soc. Jpn. 40, 169 (1976).

[23] M. Hirai and K. Hashijume, J. Phys. Soc. Jpn. 24, 1059 (1968).

[24] D. Block, Y. Merle d'Aubigne, and A. Wasiela, Abstracts of the International Conference on Defects on Insulating Crystals (Gatlinburg, Tenn., 1977), p. 46 (unpublished).

[25] See, for example, Ch. B. Lushchik, I. K. Vitol, and M. A. Elango, Sov. Phys. Solid State 10, 2166 (1969).

[26] J. J. Hopfield, Phys. Rev. 112, 1555 (1958).

[27] M. Maki, N. Nagasawa, and M. Hirai, Solid State Commun. 17, 1409 (1975).