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Formation of the self-trapped exciton via thermally induced defect reactions in alkali halides

K. Tanimura* and T. Okada
Department of Nuclear Engineering, Osaka University, Yamada-kami, Suita 565, Japan
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Low-temperature thermoluminescence has been studied in KBr, NaCl, and KI by means of emission-spectrum measurements of glow peaks and of detailed analysis as to the quantitative correlation between emission intensities and the amount of reacted defects. It is found that the luminescence center is the self-trapped exciton which results in both σ and π emissions in these salts below 100 K and that the self-trapped exciton is produced at the temperature where the annihilation of the F center takes place. It is, however, shown that the recombination between F and H centers can excite only the lowest triplet exciton in KBr. The quantum yield of the exciton formation by F-H recombination is estimated less than 0.03. The energetic correlation between the exciton and the F-H pair state in the defect-annihilation process in KBr is discussed.

I. INTRODUCTION

Lattice-defect production by radiolysis in alkali halides involves the conversion of electronic-excitation energy into lattice energy in the form of defects of the Frenkel type. The exciton has been known to be the most important candidate in this process, and the photochemical process of F-H pair formation has been studied extensively.[1]

Annihilation of lattice defects through their recombination, on the other hand, restores perfect lattices, which is accompanied by the release of stored energy. Recent study by the present authors[2] has shown that thermally triggered recombination between neutral Frenkel pairs can result in so-called thermoluminescence (TL) below room temperature.[2] This result clearly indicates that the stored energy, or the formation energy, in the form of lattice defects is converted into the electronic-excitation energy which is responsible for the emission. Thus the thermoluminescent process has the opposite aspect to color-center formation. It should be stressed that in the case of nonactivated crystals there is no extrinsic origin for emissions such as the emission from an activating impurity which has been shown to be the main luminescence center in KCL:Tl-type crystals.[3] The thermoluminescence center in pure materials, therefore, should be an intrinsic excited state which is formed through color-center reactions (the term "intrinsic TL" may describe appropriately the concerned luminescence phenomena).

Tanimura *et al.*[4] and Purdy and Murray[5] have shown that emission from the self-trapped exciton (STE) can be excited as thermoluminescence in KBr and KCl at low temperatures below 100 K, although the mechanism of exciton formation via defect reactions has not been well established. Detailed study of low-temperature TL in alkali halides, therefore, not only makes clear the mechanism of intrinsic TL, but provides us with useful information as to the relationship between lattice defects and STE's.

In this paper, we study the luminescent phenomena concerning NaCl, KBr, and KI crystals through measurements of emission spectra of glow peaks and detailed analysis as to the quantitative correlations between the intensity of glow peaks and the amount of reacted defects. The most important findings here are the following:

(1) The thermoluminescence centers in these materials are the STE's at least at low temperatures.

(2) Recombination between F-H pairs in KBr creates only the lowest STE triplet state which is responsible for π emission.

II. EXPERIMENTAL

Single crystals of KBr, NaCl, and KI were obtained from Harshaw Chemical Co. Specimens with a thickness of 1.0 ± 0.02 mm were placed in a cryostat, cooled by thermal conduction, and were irradiated by x rays generated with a Toshiba x-ray tube (AFX-61A-W) through a KBr filter with a thickness of 0.2 mm, to promote uniform coloration. The temperature of the sample was measured by an Au:Fe vs Chromel thermocouple, and controlled automatically by using a programmable temperature controller (Shinku Riko HPC-5000VL). The heating rate of 3.4 K/min was kept constant during isochronal annealing from 5 to 110 K. The optical absorption was measured with a Shimazu-SV50A spectrophotometer. A simultaneous recording of the glow curve and of the optical-density change at the F-band maximum of a given sample was made in order to get correlations between these quantities with least ambiguity. A grating monochromator with a tungsten filament lamp was

used as a light source. The monochromatic light was incident on the specimen, and the emerging light was measured with an HTV R-207 photomultiplier through appropriate glass filters. TL in this measuring system was detected by an HTV R-292 photomultiplier cooled with liquid nitrogen through a grating monochromator at a proper wavelength. Since the peak position and the half width of the F band do not depend sensitively on temperature at least from 10 to 60 K, the obtained optical-density change of the F band can represent the concentration change. A xenon arc lamp (Ushio UXL-500D) was used with glass filters as an exciting light source. In the measurement of the emission spectra of glow peaks, scanning in the wavelength range from 200 to 700 nm was done within 10 sec, so that a full emission spectrum could be obtained while the sample warmed up about 0.6 K. Simultaneous monitoring of the glow curve made it possible to obtain the TL spectra at the maximum of the respective glow peaks where change in TL intensities within scanning time was the smallest (less than 2%). All emission spectra were corrected for monochromator dispersion and photomultiplier response.

III. EXPERIMENTAL RESULTS

Figure 1 shows the glow curve measured at 230 nm (top) and the relative change in the F-center concentration (bottom) during isochronal annealing of an NaCl sample, x ray irradiated at 6 K. Glow peaks appear at 16, 21, and 37 K where the F center has correspondingly annealing stages. Similar results for KBr are shown in Fig. 2. The glow curve measured at 280 nm is shown in the upper part, and the relative changes in concentration of the F and H centers are shown in the bottom part respectively. A strong glow peak has its maximum at 29.5 K and peaks with TL intensities about two orders of magnitude weaker appear in the temperature region from 35 to 50 K. At the temperature where glow peaks take place, F and H centers decay thermally, as for NaCl, which is shown in Fig. 1. No thermoluminescent glow was observed below 22 K, at which the temperature most of the charged Frenkel pairs consisting of F^+ and I centers disappeared. The glow curve of irradiated KI was also measured, although the changes in F-center concentration could not be determined because of poor colorability at 6 K. The main glow peak was found to appear at 76 K and peaks with very weak intensities to appear at 22, 30, 40, and 56 K. The results for KI are essentially the same as those obtained previously.[6]

The solid, broken, and dash-dot lines of Fig. 3 represent the emission spectra of thermoluminescence obtained at glow peaks: at 16 K for NaCl, at 29.5 K for KBr, and at 76 K for KI, respectively. It is evident that the emission bands are the same as those of the intrinsic luminescence

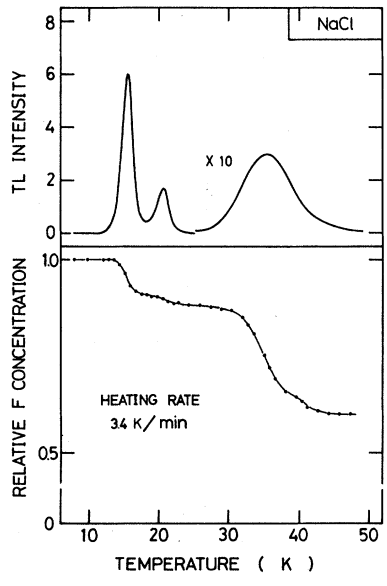

FIG. 1. Simultaneously measured thermoluminescence glow curve and the annealing curve of the F center in NaCl. Top: A constant-wavelength glow curve measured at 230 nm. Bottom: relative F-center concentration change during isochronal annealing.

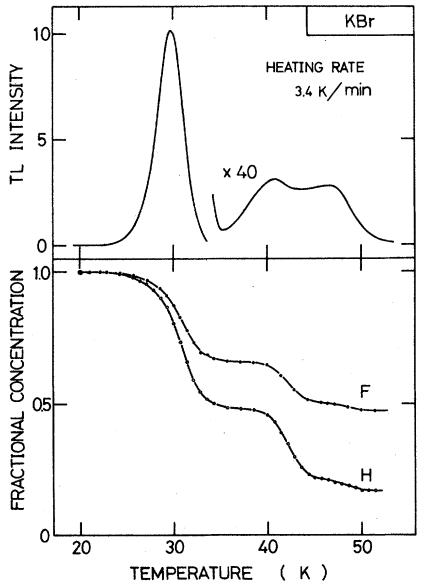

FIG. 2. Top: A constant-wavelength glow curve measured at 280 nm. Bottom: Relative concentration changes of F and H centers during the isochronal annealing.

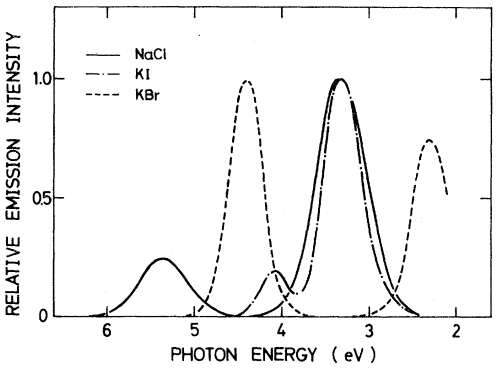

FIG. 3. The emission spectra of glow peaks at 16 K for NaCl, at 29.5 K for KBr, and at 76 K for KI, respectively.

in the respective salt, although the ratio of σ to π emission intensities is not exactly the same as that due to x-ray excitation at similar temperatures. It has been confirmed that in other glow peaks of these salts the same emission bands are observed.

In order to find the correlation between the emission intensity of a glow peak and the concentration of annihilated F and H centers, detailed measurements were made in the case of KBr. In Fig. 4 are shown the TL intensities of the glow peak at 29.5 K at the σ and π emission-band maxima as a function of the total amount of H center decayed at the corresponding annealing stage. The total amount of decayed H center, which is abbreviated as Δn_H, was controlled by changing the degree of coloration at 6 K. It was observed that the decrement of the F center in this stage has a linear relationship to that of the H center. The shape of the glow peak measured at 520 nm (the π component) was dependent, although slightly, on Δn_H: the temperature giving the maximum TL intensity shifted towards a higher value with increasing Δn_H. Such a change could not be detected in the σ-omission component. The intensity of the σ emission is saturated for large Δn_H. On the other hand, that of the π emission continues to increase as seen in Fig. 4. This difference in behavior between σ and π emission suggests that the formation of each STE state has its origin in different reactions.

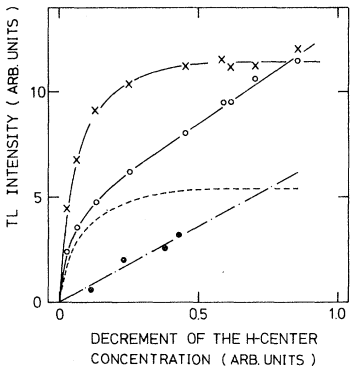

FIG. 4. Maximum TL intensities of the $\sigma(x)$ and $\pi(o)$ emission components of the glow peak at 29.5 K, as a function of the decrement of the H-center concentration at the first stage in as-irradiated specimens. By decrement of the H center is meant the difference in optical density before and after the stage. TL intensities are corrected for monochromator dispersion, photomultiplier response, and self-absorptions due to color centers. Broken and dash-dot curves represent the two resolved components of the π-emission glow peak. The solid circles show the maximum TL intensity of the π emission in V_K-free specimens (see text). The heating rate is 3.4 K/min for all measurements.

Measurements were also made on changes in the height and shape of glow peaks caused by F-band excitation. We observed both σ and π emissions upon F-band excitation of as-irradiated KBr. This result confirms that the V_K center is destroyed by capturing F electrons released by the F-band excitation.[7] The H absorption band was also bleached by the prolonged optical illumination.

Figure 5 shows the TL intensity of the σ-emission component at the maximum of the 29.5-K peak as a function of Δn_H which, in this experiment, was changed by controlling the time interval of the F-light illumination after x-ray irradiation with a fixed dose. It is clear that the TL intensity in such samples exhibits a dependence on Δn_H different from that in the as-irradiated ones shown in Fig. 4. No essential differences were observed in the shape of the σ-emission glow peak between optically bleached and as-irradiated samples. The result that the maximum TL inten-

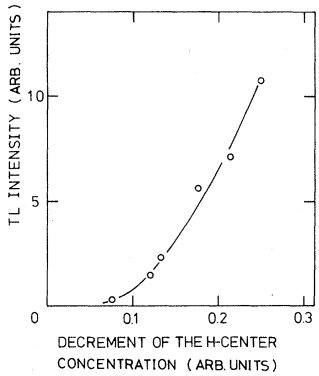

FIG. 5. Maximum TL intensity of the σ emission of the 29.5-K glow peak as a function of the decrement of H-center concentration which was controlled by changing the time interval of F-light illumination for a sample irradiated with a fixed x-ray dose.

sity of the σ-emission component is not uniquely determined for a fixed decrement of the H center indicates that the excitation of this component is not directly correlated to the recombination of the H center with the F center.

In Fig. 6 we compare the glow peaks of the π component of a low x-ray dose as-irradiated specimen with that of a specimen illuminated with F light after x-ray irradiation at a considerable high dose.[8] It is evident that glow peaks in such samples have distincting different shapes and peak positions: The glow peak in the optically illuminated sample peaks at 30.5 K, whereas that in the as-irradiated one, as mentioned above, peaks at 29.5 K. The intensity of the π emission of the glow peak in the optically bleached sample where few V_K centers are contained was measured as a function of Δn_H. The result is shown in Fig. 4 by solid circles; the intensity is proportional to Δn_H. It is, therefore, clear that two components are superposed in the π emission of the glow peak around 30 K. Subtracting the linearly increasing component (shown by solid circles) from the π-emission intensity of the glow peak in as-irradiated specimens gives a component shown by the broken curve in Fig. 4. The resolved component, exhibiting saturation, shows the following properties: (i) the dependence of the intensity on Δn_H is similar to that of the σ omission; (ii) the ratio of the saturating intensity I_s to that of the σ emission is essentially the same as in the emission spectrum of the intrinsic luminescence excited by x rays at similar temperatures.

Emission-spectrum measurement was also made for the glow peak as 102 K in KBr : 0.10-mole% Na. This glow peak has already been studied and has been identified as being due to the recombination of an H center freed from an Na^+ ion with an F center.[2] In contrast to the case of glow peaks below 77 K, the spectrum consists of a single band which is the same as the π-emission band in KBr. No emission bands having higher energy were observed in this glow peak.

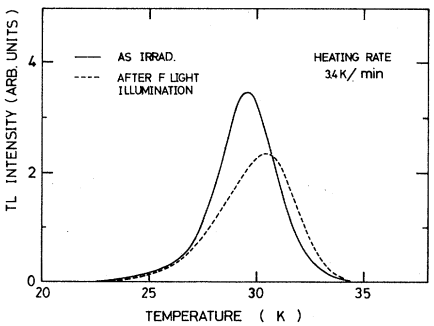

FIG. 6. Glow curves of the π-emission component near the first stage in KBr. The solid curve is the curve of a low x-ray dose as-irradiated sample, and the broken one is the glow curve of a V_K-free specimen.

IV. DISCUSSION

Among the results described in the preceding section, one of the most important findings is that the thermoluminescence center at low temperatures in pure or nonactivated crystals is the self-trapped exciton, at least for the materials studied here. This fact shows that the self-trapped exciton also plays the central role in the thermoluminescence of pure salts. The important feature is that such intrinsic excited states are formed via thermally induced reactions of color centers created by ionizing radiation.

There have been several works on low temperature TL in alkali halides.[9,10] In these works where no emission-spectrum measurements were made, the emission has been attributed to the decay of the H center, mainly on the basis of the fact that the H center decays in the temperature region where glow peaks appear. In general, the decay of the H center results in the formation of other interstitial-type centers through interaction with other imperfections or the annihilation of the interstitial atom through its recombination with the F center. It is the latter reaction that causes the release of the stored energy. Then the glow peak which is originated from the decay of the H center should satisfy the relation

$$I(T)=\gamma\eta(-dn_F/dT), \tag{1}$$

where n_F is the F-center concentration, and γ and η are the formation and luminescence efficiencies of the excited state responsible for TL emission, respectively. According to this equation, the shape of the glow peak is the same as that of the first derivative of the annealing curve of the F (and H) centers with respect to temperature, and the total number of photons emitted is in proportion to the concentration of the F centers annihilated at a given stage.

In view of the above arguments, one notes that the present results, especially on the quantitative correlation between the amount of the decayed H and F centers and the TL intensity, indicate that the formation of the exciton as the thermoluminescence center does not occur through a single process of recombination of H and F centers. Below we give a detailed analysis of the relationship between the glow peaks of the σ and π components and the decay of the F and H centers, in order to make clear the origin of the formation of the self-trapped exciton.

A. Reactions responsible for exciton formation

The decay of the H center at the first stage around 30 K has been assigned mainly to the recombination of correlated pairs of F and H centers, the reaction kinetics of which is of the first-order type.[11] Figure 7 shows the least-square fit of a first-order rate equation for the present results on isochronal annealing of F and H centers. The best fit is obtained with values of 2.8×10^5 sec^{-1} and 0.042 eV for the pre-exponential factor and the activation energy, respectively. These parameter values are slightly different from those obtained by Saidoh and Itoh, although it is confirmed that the first stage of H-center annealing is described by the first-order kinetics. Equation (1) for this stage then can be written as

$$I(T) = \gamma \eta n_H (s/\beta) \exp(-E/kT), \qquad (2)$$

where s, E, and β are the pre-exponential factor, the activation energy, and the heating rate, respectively. The maximum TL intensity in this case should be proportional to the decrement of F and H centers, when the emission originates from F-H recombination.

From the results shown in Fig. 4, the height of the σ-emission band at the glow-peak maximum at 29.5 K does not have a linear correlation with Δn_H.[12] This result indicates that the second excited state of the STE is not formed directly by recombination of F and H centers. The excitation of the σ emission may be due to some indirect reactions of the H center and/or to a reaction of other defects which occurs at a similar temperature. It has been shown in the previous section that the σ emission of the glow peak having a saturating nature is quite sensitive to F-band excitation prior to heating which destroys mainly the V_K center in the sample. This fact shows the close correlation of the σ-emission band of the glow peak to the radiation-induced V_K center. It has also been demonstrated that the thermally stimulated conduction-electron current also occurs around temperatures where the glow peaks are excited,[9] although the excitation mechanism of such conduction electrons has not been made clear. Then it may be reasonable to attribute the origin of the σ emission to the recombination of a V_K center with such an electron. Recombination results in the formation of an STE with sufficient energy to (give) σ emission. The saturating property of the σ-emission intensity may come from the limited concentration of the V_K center created by irradiation or of the electrons capable of being excited.[10]

In the case of π emission of the glow peak, two components are resolved: one with dependence on Δn_H which parallels the σ emission and the other having a linear correlation with the amount of F and H centers annihilated. This linear relationship suggests that the component originates from the recombination of neutral Frenkel pairs, since one consequence of Eq. (1) is satisfied. We check here another one by comparing the shape of the π-emission component of the glow peak having linear relationship with Δn_H to the first derivative for H-center annealing. Since the η of the π emission is dependent on temperature above K,[13] the shape of the glow peak should be compensated in terms of η for an accurate representation of the concentration of the states formed at each temperature. In Fig. 8 the thus corrected shape of the glow peak is compared with Eq. (2) for the same values of the parameters as in Fig.

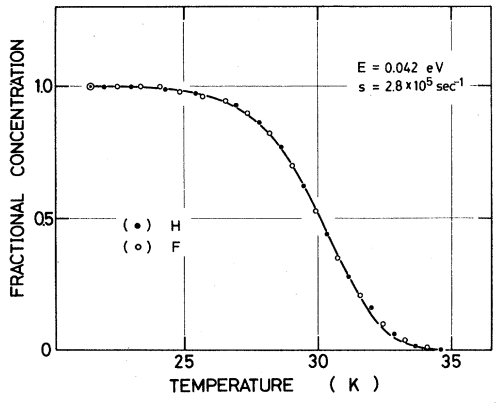

FIG. 7. The least-square fit of a first-order reaction equation to the first annealing stage of the F and H centers in KBr. The solid curve shows the calculated result using the parameter values indicated in the figure.

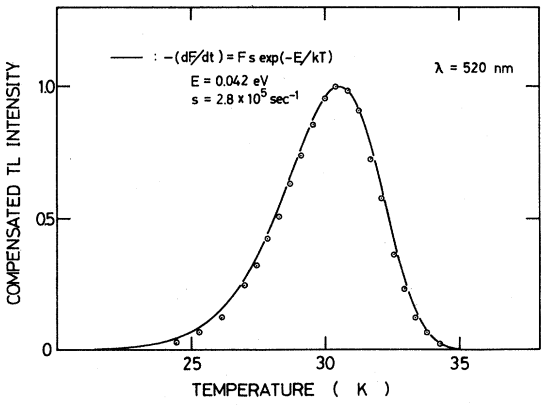

FIG. 8. Comparison of the glow peak of the π component in a V_K-free specimen with the first derivative of the annealing curve of the F center. The TL intensity of the glow peak is corrected in terms of the temperature dependence of the luminescence efficiency using the results of Karasawa and Hirai (Ref. 13).

7. One can see good agreement between both quantities. It can be therefore concluded that the linearly increasing component of the π emission is due to recombination of F and H centers at the first annealing stage.

This conclusion is further confirmed by the experimental results shown in Fig. 9. In this figure it is shown that only the π emission is excited by the recombination of the H center with an F center, the former one being freed from the trap of an Na^+ impurity ion. Taking into account the temperature dependence of the luminescence efficiencies of σ and π emissions, the σ-emission intensity is two orders of magnitude stronger than the intensity of the π emission around 100 K, upon one-photon excitation of pure KBr.[14] The result that only π emission is observed in a 102-K glow peak therefore provides further support for the conclusion that recombination of a neutral Frenkel pair can only excite the lowest triplet state of the STE $(V_K e)_\pi$.

B. Defect-annihilation energetics in KBr

The above results and discussions have revealed that the state of the pair of F and H centers is energetically higher than $(V_K e)_\pi$, but lower than the second excited singlet state $(V_K e)_\sigma$ in KBr. One of the important conclusions which can be deduced from this finding concerns the formation energy E_F of an F-H pair, which is of great importance in the defect-formation mechanism in alkali halides. Below we discuss the energetic correlation between the self-trapped exciton and the F-H pair state in the defect-annihilation process in KBr.

This process can be represented schematically by the two-dimensional configuration-coordinate diagram of Fig. 10, which is analogous to that of color-center formation given by Itoh and Saidoh.[15] The 1s exciton band is situated at 6.8 eV, and the

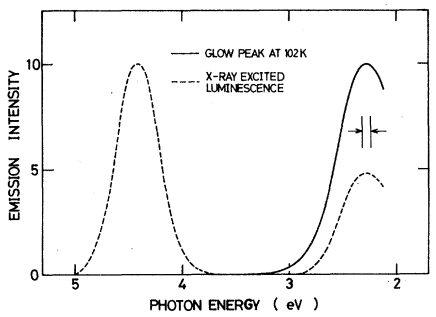

FIG. 9. Emission spectrum of the glow peak at 102 K due to the recombination of the H center thermally freed from the trap of an Na^+ ion in KBr: 0.10-mole% Na. The x-ray-excited emission spectrum at 6 K is also shown for comparison.

transition energy of the π emission is 2.27 eV in KBr.[14] Assuming that the energy spent by nonradiative relaxation is the same for both the initial and final states,[16] and taking into account that the exchange energy of the lowest excited state of the exciton is small,[17] one can estimate the minimum of $(V_K e)_\pi$ to be 4.4 eV. The corresponding energy of $(V_K e)_\sigma$ is higher by 1.6 eV than that of $(V_K e)_\pi$.[18] Then, we can determine E_F in KBr as

$$4.4 < E_F < 6.0 \text{ eV}.$$

The experimental result that the recombination of a charged Frenkel pair of F^+ and I centers is not luminescent then indicates that the formation energy of this pair is smaller than 4.4 eV in KBr. This is consistent with theoretical results of Schulze and Hardy.[19]

It should be pointed out that the quantum efficiency of the creation of $(V_K e)_\pi$ through recombination of F and H centers is considerably smaller than unity, although the formation is energetically possible. We estimate that the formation efficiency of the lowest triplet state of the STE, γ, by F-H recombination relative to that of the electron–V_K-center recombination, is about 0.1 or less, based on the following results and considerations. During F-band excitation of an as-irradiated specimen, an abrupt drop of F-center concentration of about $0.1n_0$, where n_0 is the initial concentration of the F center, was observed within several minutes. In this time interval, the intensity of the σ emission excited by the F light was reduced to the noise level of our detection system, so that $0.1n_0$ may roughly represent the V_K-center concentration in this sample. The bleached sample was then warmed, and the π-emission intensity of the glow peak at the first stage was measured. The maximum TL intensity of the π emission was $0.38I_s$, where I_s is the saturated value of the π emission defined in Fig. 4. The decrement of the F center was about $0.4n_0$ at this stage. Provided that I_s is due to all the present V_K centers, the relative value of γ is roughly 0.1. Clearly this value is considered to be the upper limit, since it may not be all the V_K centers that are responsible for the π emission of the saturating component of the glow peak. In KBr, the ratio of the total emission intensity of π emission to that of σ emission is about 0.5 in the spectrum excited by x rays at the lowest temperature.[20] Then, the γ of the V_K-center–electron recombination is not greater than 0.3. The γ of the F-H recombination is, therefore, estimated to be less than 0.03.

The considerably small value of γ suggests the presence of a potential barrier at the transition state from the F-H pair into $(V_K e)_\pi$. As discussed by Itoh *et al.*,[21] the origin of the barrier may be

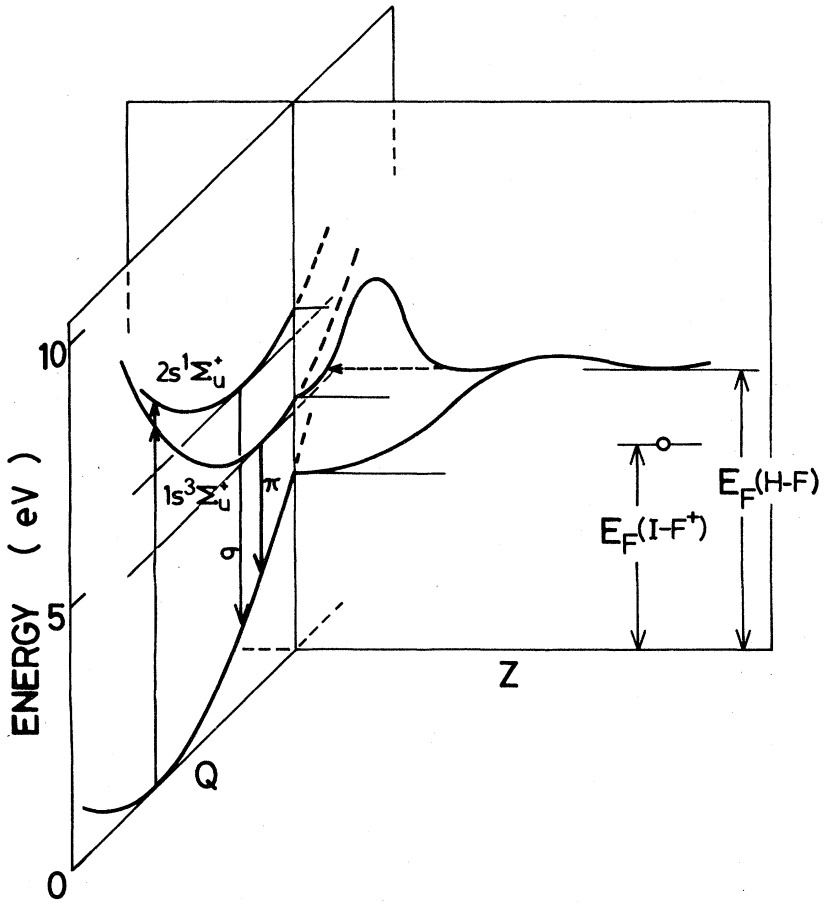

FIG. 10. Schematic configuration-coordinate curves for the defect-annihilation process in KBr. The coordinate Q represents the displacement along the Br-Br direction in $(V_K e)$, and the coordinate Z represents approximately the location of the center of the Br_2^- in the interstitial site. The ordinate shows approximately the energy of the state. The intersection of two planes may take place at a Q value larger than that giving the minimum of $(V_K e)$, since the Br_2^- in the H center has the smaller internuclear distance.

the overlap of the π electron of the Br_2^- and the s electrons of the K^+ ions associated with the F center. By such a potential, most of the formation energy in the form of the F-H pair may be released nonradiatively in the defect-annihilation process.

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*Present address: Crystalline Materials Science, Nagoya University, Nagoya, Japan.

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