

$\text{YAlO}_3:\text{Ce}^{3+}$ also exhibits the apparent narrowing of emission band. The Figure 2 depicts Ce^{3+} concentration dependent FWHM (Full Width at Half Maximum) of 370 nm emission band. As can be seen in Figure 2, the band narrowing is more pronounced as the concentration of Ce^{3+} in YAlO_3 is increased. The foregoing observations positively support that two emission bands in $\text{YAlO}_3:\text{Ce}^{3+}$ is closely related to Ce^{3+} ions in YAlO_3 host.

The Ce^{3+} sites in YAlO_3 have been proposed⁷ and conjectured⁸, but the supporting arguments are less convincing. The YAlO_3 has perovskite structure same as SrTiO_3 and the existing polyhedra are YO_{12} , YAl_8 and AlO_6 in this structure. The ionic radii of Ce^{3+} , Y^{3+} and Al^{3+} are 0.94 Å, 0.92 Å and 0.51 Å respectively. Thus the more probable Ce^{3+} sites in YAlO_3 are YO_{12} and YAl_8 polyhedra where Ce^{3+} is substituted for Y^{3+} from the ionic radii argument. It is generally accepted that the UV emission band in $\text{YAlO}_3:\text{Ce}^{3+}$ is originated from the occupied site of Ce^{3+} in YO_{12} polyhedron. The green emission center in $\text{YAlO}_3:\text{Ce}^{3+}$ has not been established to date. Mares *et al.*⁸ reported the green emission band in $\text{YAlO}_3:\text{Ce}^{3+}$. They also suggested that the possible occupied site of green emission of Ce^{3+} in YAlO_3 is YAl_8 polyhedra without any positively convincing arguments. The Ce^{3+} related green emission band was disappeared when YAlO_3 was codoped with Nd^{3+} , Cr^{3+} and Ce^{3+} .⁸ This observation suggested that many types of polyhedra, *i.e.*, YAl_8 , CeAl_8 , and NdAl_8 , could be formed when Nd^{3+} , Cr^{3+} and Ce^{3+} ions were codoped in YAlO_3 . Thus energy transfer between ions, $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ and $\text{Ce}^{3+} \rightarrow \text{Cr}^{3+}$, could be possible and the energy transfer between ions was man-

ifested with disappearing of green emission band. The above rationale supports that the origin of green emission band site of Ce^{3+} in YAlO_3 is YAl_8 polyhedron where Ce^{3+} is substituted for Y^{3+} .

In summary, we investigated the emission characteristics of $\text{YAlO}_3:\text{Ce}^{3+}$ and the origin of Ce^{3+} related green emission band site in $\text{YAlO}_3:\text{Ce}^{3+}$ has been established as YAl_8 polyhedron. In other words, the cerium is substituted for yttrium such that CeAl_8 polyhedron can be formed and cerium in this site is the origin of green emission band in $\text{YAlO}_3:\text{Ce}^{3+}$.

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Superfast Transfer via Crossover of F Electronic Energy to OH^- Vibration in RbCl

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Since Dexter, Klick, and Russell reported a crossover mechanism which provides a criterion for the nonradiative quenching of simple impurity centers,¹ the fate of an electronically excited F center in alkali halides has been studied as one of the typical cases.¹⁻³ The relaxed excited F (F^*) centers in rubidium and potassium halides have a strong luminescence with a microsecond-long lifetime at cryogenic temperatures, while those in lithium and sodium halides have a poor luminescence.^{4,5} This remarkable difference in the two types of hosts can be explained by the difference in crossover energy barriers from the relaxed excited state to the crossing point of the excited and ground state potential curves.¹ However, the luminescence in KCl , in which the barrier is too high for effective crossover, is reported^{6,7} to decrease by the concentration increase of doped molecular

defects such as OH^- and CN^- . F_H formation, association of F center with a molecular defect, makes F absorption broader and lower in energy and quenches F luminescence drastically.⁸ Vibrational emission and anti-Stokes Raman scattering from molecular defects observed after F center excitation indicate that the electronic excitation energy of an F center transfers into the stretching vibrational mode of a molecular defect.⁹⁻¹¹

The energy transfer rate in randomly distributed crystals is varied very much, depending on transfer distance, temperature and host.⁸⁻¹² However, the superfast transfer component in aggregated crystals is much the same, regardless of concentration, isotope, and host.¹³ This superfast recovery, resulting from the deactivation of an excited F-molecular defect pair, is achieved by the lattice relaxation¹⁴ of the ex-

cited F center immediately followed by energy transfer to the molecular defect.¹³

This note presents another strong evidence and a schematic explanation to the previous report¹³ that the energy transfer in an $F_H(OH^-)$ center, associated pair of F and OH^- , takes place *via* curve crossover tunneling mechanism. The curve crossing between the OH^- -vibrationally excited but electronically ground state of an F_H center and the excited state brings down the crossover barrier enormously so that the energy transfer *via* crossover process occurs instantly even in RbCl at cryogenic temperatures.

Experimental procedures were already reported in detail.¹³

Results and Discussion

Any fast quenching of F excitation by OH^- in randomly distributed RbCl is not observable at studied short time windows and cryogenic temperatures (Figure 1(a)), while the superfast deactivation component becomes predominant in aggregated samples (Figure 1(b)-(d)). The results in Figure 1 are consistent with the negligible quenching of F luminescence by OH^- in randomly distributed RbCl crystals and with drastic quenching in aggregated crystals at 10 K.⁸ As already reported,¹³ the superfast component results from the lattice relaxation of $F_H(OH^-)$ upon excitation, immediately followed by energy transfer from the F^* electronic state to OH^- vibrational states. We emphasize that vibrational emission and anti-Stokes Raman scattering⁹⁻¹¹ from molecular defects after F excitation are the observations made after the event of the energy transfer already completed *via* this superfast process. In the remaining

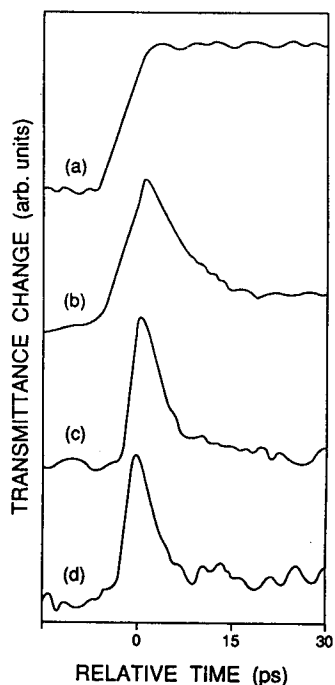


Figure 1. Bleach recovery kinetic profiles, pumped and monitored at 590 nm, of F absorption in OH^- -doped (1.4×10^{-3}) RbCl at various temperatures. The F centers in (a) are randomly distributed, while those in (b)-(d) are optically aggregated. The respective sample temperatures in (a), (b), (c) and (d) are 10, 10, 25, and 50 K.

part of this report we will focus rather on explaining the mechanism and nature of the energy transfer in an $F_H(OH^-)$ center based on the temperature-varied kinetic profiles given in Figure 1.

The full widths at half the maximum of the temporal instrument response function for the kinetic profiles of Figure 1(b)-(d), estimated as twice the times from the half-rise to the peak, are 6.2, 2.9 and 2.9 ps respectively. The deconvoluted recovery times of the superfast component from the temporal instrument response functions are 4.2 ps at 10 K, 3.4 at 25 K, and 2.9 ps at 50 K. The recovery is not only superfast as comparable to the lattice relaxation in alkali halides¹⁴ but also nearly temperature-independent. Although this recovery time is similar to the instrument response time, the superfast recovery component is definitely not resulting from pump scatter or any coherent artifacts between the pump and probe beams since a superfast recovery component is never observable in any samples that are not expected to have any superfast recoveries as in Figure 1(a).

The origin of this ultrafast and almost temperature-independent deexcitation of $F_H(OH^-)$ excitation at cryogenic temperatures, the nature of the electronic interaction between F^* and OH^- , and the mechanism of the energy transfer are well explained by the schematic configurational coordinate diagram of Figure 2. Upon optical excitation an $F_H(OH^-)$ center undergoes lattice relaxation in a few picoseconds,¹⁴ forming the configurationally relaxed excited state. Energy transfer from the lattice-vibrationally relaxed excited state without OH^- -vibrational excitation into one of vibrational states $v = 1-3$ of the paired OH^- in the configurationally unrelaxed F ground state occurs *via* curve crossover tunneling mechanism (see arrows in Figure 2). The curve crossing between the OH^- -vibrationally excited

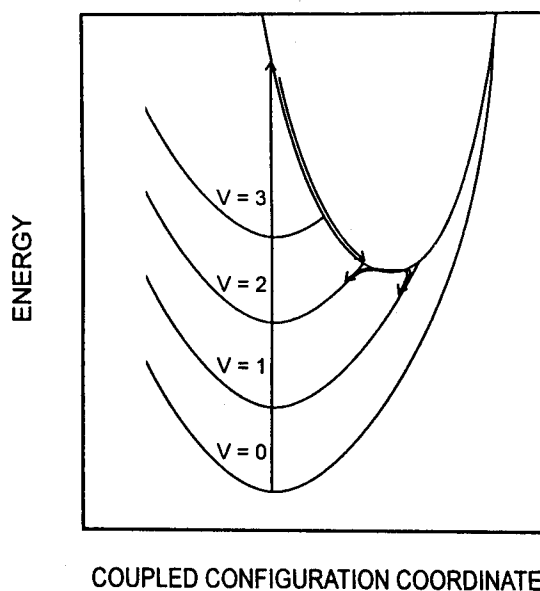


Figure 2. Schematic configurational coordinate diagram to explain the configurational relaxation and following superfast energy transfer *via* crossover of F electronic excitation at 590 nm ($= 17000 \text{ cm}^{-1}$) to OH^- -vibrational ($\nu = 3650 \text{ cm}^{-1}$) levels in optically aggregated RbCl. Note that only one of the two p orbital lobes in the excited parabolic curve separated by a nodal plane is shown to focus our explanation on crossover.

but F-electronically ground state of an $F_H(OH^-)$ center and the OH^- -vibrationally unexcited but F-electronically excited state drastically lowers the crossover barrier from the relaxed excited state to the crossing point of the F center potential curves even in RbCl as illustrated in Figure 2. The unassociated F^* center in RbCl is known to have the barrier that is too high to relax nonradiatively *via* crossover.^{4,5} The perturbation by tunneling process may even further eliminate the effective potential barrier¹⁵ so that the energy transfer *via* crossover process occurs nearly instantly even at cryogenic temperatures. The almost independence in temperature of the superfast recovery time suggests that the major part of F absorption bleach recovery time is the lattice-vibrational relaxation time rather than the crossover time. It seems that the associated F and OH defects in an $F_H(OH^-)$ center behave, in a sense, much like a supermolecule, in which the energy levels of each component species are no longer independent. The nature of electronic interaction in the energy transfer between the paired defects is electron exchange.

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Theoretical Studies on the Photochemical Reaction of Monofunctional Psoralen Derivatives with Thymine

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Psoralen derivatives has been actively investigated both with regard to their ability to act as dermal photosensitizing agents and as a useful tool for studying the structure and dynamics of nucleic acids.^{1,2} Monofunctional derivatives of the psoralen type have two photoreactive sites, the 3,4 and 4',5' double bonds. In the presence of 356 nm light monoadducts with pyrimidine bases are found, *i.e.*, C⁴-cycloaddition products involving the 5,6 double bond of pyrimidine bases are formed.^{3,4} Moreover DNA cross-links are detected by several methods, including the melting and renaturation pattern of treated DNA bases.⁵ It is assumed that the 3,4 and 4',5' double bonds of monofunctional derivatives of psoralen are both involved in the formation of cross links between pyrimidine bases of opposite DNA base strands. Their Photosensitizing activity has been related to their ability to form a covalent linkage with the pyrimidine bases of DNA upon UV-A irradiation for treatment of several skin diseases.⁶

The photoreactive sites in allopsoralen (AlloPs), carbethoxypsoralen (CEOP) and pyridopsoralen (PyPs) are the 3,4 (pyrone) and 4',5' (furan) bonds. As the 3,4 mono-adduct does not absorb near UV. light, the 4',5' adducts is the intermediate involved in the formation of cross links.⁷ Their biological properties have been attributed to their ability to photoreact with nucleic acids. It appears that the genotoxic effects, as well as the therapeutically important antiproliferative effects, are due mainly to their capacity to induce photoconjugation to DNA bases.

We now describe for the postulation and photoadduct of the clinically important monofunctional psoralen with thymine, chosen as a model⁸⁻¹⁰ for the pyrimidine base in DNA with which the psoralen derivatives probably bonds. Many efforts have been expended to develop psoralen derivatives which permit only monofunctional photobinding with DNA bases and thereby diminish undesirable side ef-