# Core-Hole Migration and Relaxation Effect in Alkali Halide Excited by Synchrotron Radiation

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Photoluminescence due to radiative transitions between the valence and outermost core bands, in which the Auger process is energetically forbidden, is studied in mixed $Rb_{1-x}Cs_xF$ crystals. The results provide clear evidence that a hole created in the $Rb^+$ $4p$ core band migrates through the crystal, and is trapped at the $Cs^+$ $5p$ core state. The diffusion coefficient of the core holes is estimated to be $1.5 \times 10^{-5}$ $cm^2/s$. Furthermore, a comparison with photoelectron data reveals an important role of relaxation effects in the deexcitation process of core holes.

A conduction electron and a valence hole can move about freely through the volume of a condensed matter. This fact is one of the most important points in solid state physics [1]. On the other hand, when a hole is created in a deep-lying core state, its transport properties have been studied very little. In general, it has been believed that a core hole is not free to move through the crystal. One reason for this is that the core band is narrow or dispersionless, leading to very large effective mass. The other reason is that the core-hole lifetime is very short due to fast Auger decay processes in which the core hole combines with an upper electron by kicking up another electron into an empty state.

The present Letter reports the first finding of the migration of core holes, in which we measured a specific kind of core luminescence, recently found by several groups [2,3], of mixed $Rb_{1-x}Cs_xF$ crystals. Figure 1 shows a schematic energy diagram of this system. The conduction band originates from the $s$ and $d$ states of the $Rb^+$ or $Cs^+$ ions, and the valence band from the $2p$ state of the $F^-$ ions. Below the valence band, there exist two outermost core bands; one is due to the $Cs^+$ $5p$ state and the other to the $Rb^+$ $4p$ state. The former is located 2–3 eV above the latter. In usual cases, the band-gap energy $E_g$ is smaller than the energy difference $E_{VC}$ between the tops of the valence band and the outermost core band. Thus the nonradiative Auger process is predominant for the core-hole decay. However, the reverse relation $E_g > E_{VC}$ is satisfied in both RbF and CsF crystals [3], so that the core hole created in the $Cs^+$ $5p$ or $Rb^+$ $4p$ state is free of the Auger process and combines radiatively with a valence electron. The resulting luminescence has been called "Auger-free (AF) luminescence" [4]. In the present work, we confirm the migration of core holes from $Rb^+$ to $Cs^+$ ions by monitoring host-sensitized AF luminescence. Furthermore, in order to explain a low-energy tail of the AF luminescence band of RbF, partial

relaxations of the outermost core hole and/or the valence electron are introduced. These results must be important in studying fast Auger decay processes, such as an impact-stimulated desorption of atoms or ions from a surface [5], and possibly in developing scintillation detectors for high-energy physics.

We used synchrotron radiation from the electron storage ring UVSOR at the Institute for Molecular Science (IMS) in Okazaki as a light source. The ultraviolet light was monochromatized with a 1-m Seya-Namioka-type monochromator. Crystal ingots of $Rb_{1-x}Cs_xF$ were prepared from the melt in a platinum crucible. Actual Cs
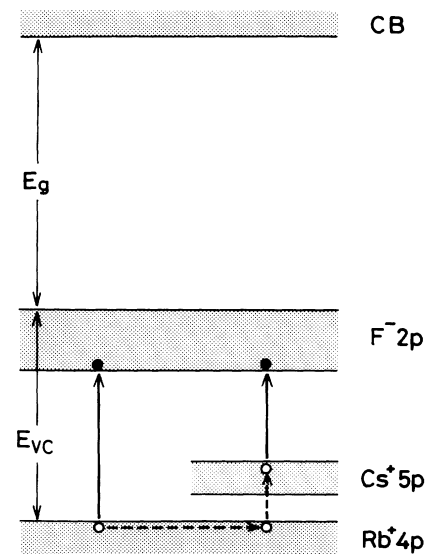


FIG. 1. Schematic energy diagram showing the deexcitation processes of outermost core holes in the mixed $Rb_{1-x}Cs_xF$ system. The radiative transition is indicated by solid arrows, while the migration and trapping are indicated by dashed arrows.

concentration $x$ in the samples was determined by the atomic spectroscopy analysis. The undoped RbF crystal used here contained small amounts of $Cs^+$ ions ($x$ = 0.0008). Luminescence was observed from the irradiated surface of samples with use of a Bausch & Lomb grating monochromator and a Hamamatsu R106UH photomultiplier. The emission spectra were corrected for the spectral response of the detection system, and were given in arbitrary units of photon numbers per unit energy. Lifetime measurements were carried out when the storage ring was operating with a single circulating electron bunch (pulse width, 450 ps; pulse interval, 178 ns). The luminescence decay signals were detected by a microchannel-plate photomultiplier (Hamamatsu R2286U-06) using a time-correlated single-photon counting method.

Figure 2 shows emission spectra of $Rb_{1-x}Cs_xF$ crystals; (a) RbF ($x$ = 0.0008), (b) $x$ = 0.008, (c) $x$ = 0.52, and (d) CsF ($x$ = 1.0). Measurements were made at 295 K under the core-band excitation with 21.0-eV photons. In RbF, an intense band appears at 5.4 eV. This band is ascribed to the interatomic Auger-free transition of the $F^-$ $2p$ valence electron into the $Rb^+$ $4p$ core hole [3].
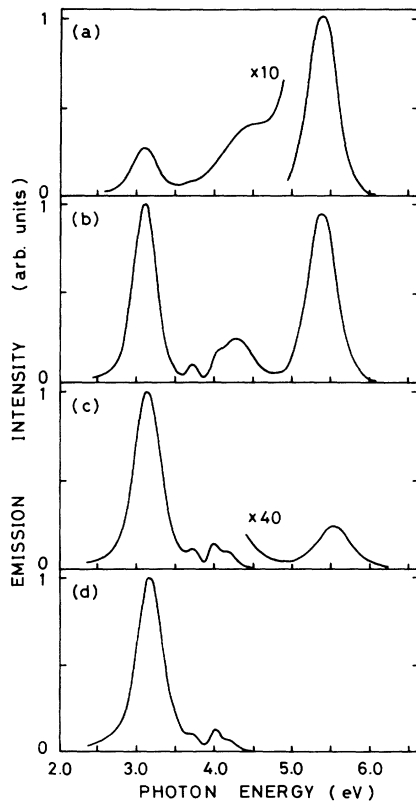
Two weak bands are also found around 3.2 and 4.3 eV on the low-energy side of the 5.4-eV band. In CsF, one can see a dominant band at 3.2 eV and a fine structure around 4.0 eV, both being assigned to the AF luminescence between the $F^-$ $2p$ valence band and the $Cs^+$ $5p$ core level in CsF [3]. From Fig. 2 it is apparent that, when $x$ increases toward 1.0, the 3.2-eV luminescence band grows rapidly at the expense of the 5.4-eV band.

In Figs. 3(a) and 3(b) we present luminescence excitation spectra measured on RbF and CsF, respectively. All of the luminescence bands in RbF have the same excitation threshold at an energy of $17.0 \pm 0.2$ eV. This threshold is located just above the energy of $Rb^+$ $4p$ ($j = \frac{3}{2}$) core excitons and corresponds to the onset of interband transitions from the $Rb^+$ $4p$ level to the conduction band, i.e., $E_g + E_{VC}$ [7]. In the $x$ = 0.008 sample, the excitation spectra for the 3.2- and 5.4-eV bands were identical to those of Fig. 3(a). It is seen from Fig. 3(b) that the 3.2- and 4.0-eV bands in CsF are induced by the photoexcitation above $14.2 \pm 0.2$ eV, in good agreement with the
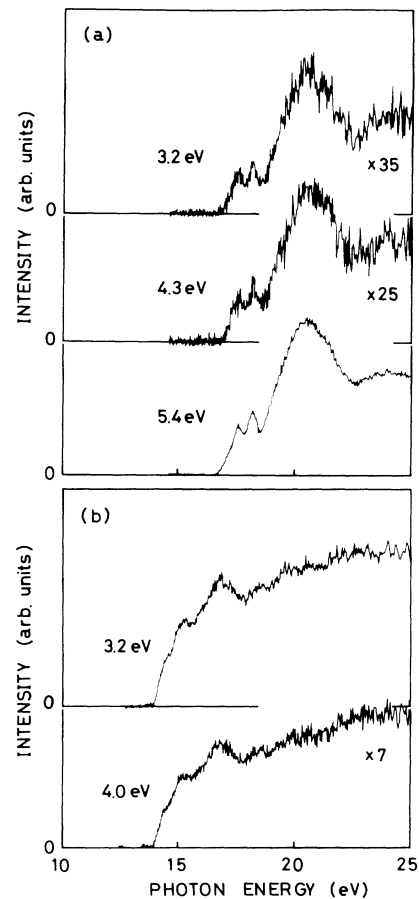


FIG. 2. Emission spectra of mixed $Rb_{1-x}Cs_xF$ crystals measured at 295 K under the core-band excitation with 21.0-eV photons; (a) RbF ($x$ = 0.0008), (b) $x$ = 0.008, (c) $x$ = 0.52, and (d) CsF ($x$ = 1.0). Each spectrum is normalized at the maximum.



FIG. 3. Luminescence excitation spectra taken at 295 K; (a) 3.2-, 4.3-, and 5.4-eV bands in RbF ($x$ = 0.0008), and (b) 3.2- and 4.0-eV bands in CsF ($x$ = 1.0). The $Rb^+$ $4p$ ($j = \frac{3}{2}$) core exciton in RbF and the $Cs^+$ $5p$ ($j = \frac{3}{2}$) core exciton in CsF are located at 16.0 and 13.0 eV, respectively [6].

transition energy from the $Cs^+$ $5p$ level to the conduction band [7]. The excitation spectra obtained in the $x=0.52$ sample showed the same threshold as those of Fig. 3(b).

The decay behaviors of the luminescence bands in RbF are depicted in Fig. 4. These three bands exhibit a slightly nonexponential decay, so that we define the lifetime $\tau$ as a characteristic time at which the initial intensity decreases to $1/e$ value. The 3.2-eV band has a lifetime of $\tau=2.6\pm0.2$ ns, which agrees well with that of the AF luminescence in CsF (not shown). The 5.4-eV band, on the other hand, exhibits the same decay profile as the 4.3-eV band; $\tau=1.4\pm0.2$ ns. The present values of $\tau$ are fairly consistent with the previous data [8].

From the results described above, we understand that the introduction of even small amounts of $Cs^+$ ions into RbF gives rise to a band at 3.2 eV coinciding with the AF luminescence band of pure CsF [9]. It should be stressed that the guest 3.2-eV band does not appear under the $Cs^+$ $5p$ core-level excitation but does under the $Rb^+$ $4p$ core-level excitation, as seen in Fig. 3(a). At first sight, this fact may be somewhat strange in view of our usual experience, in which an impurity-associated luminescence is selectively excited with photons below the intrinsic absorption band due to host crystals. However, in the present case, almost all of the incident photons are absorbed by the host RbF crystal, not by $Cs^+$ impurities, because of the large absorption coefficient of RbF in the core-excitation region. We can, therefore, conclude that

the core hole created in the $Rb^+$ $4p$ band moves through the crystal, and is trapped at the $Cs^+$ $5p$ state during its lifetime [10], to emit the host-sensitized AF luminescence.

In order to analyze the migration of core holes, we adopt the diffusion model [11] for the system of $Rb_{1-x}Cs_xF$. In this case, the total decay rate of a core hole, $1/\tau$, may be represented as a sum of the radiative decay rate at $Rb^+$ sites, $1/\tau_0$, and the energy-transfer rate to $Cs^+$ sites via core-hole diffusion, $4\pi DRn$;

$$\frac{1}{\tau}=\frac{1}{\tau_0}+4\pi DRn, \tag{1}$$

where $D$ is the diffusion coefficient, $R$ is the capture radius of a $Cs^+$ for a core hole, and $n$ is the number of $Cs^+$ ions per unit volume. We neglect here nonradiative recombination channels. In the $x=0.008$ sample, the guest 3.2-eV band is comparable in intensity with the host 5.4-eV band, which means $1/\tau_0=4\pi DRn$ if the quantum efficiency is assumed to be the same for both bands. We thus obtain $D=1.5\times10^{-5}$ $cm^2/s$ by using the values of $\tau_0=1.4\times10^{-9}$ s, $R=1.9\times10^{-8}$ cm [12], and $n=1.8\times10^{20}$ $cm^{-3}$. From this, the diffusion length of a core hole is estimated as $l=(D\tau_0)^{1/2}=15$ Å. That is to say, the core hole is likely to diffuse at random on a few tens of lattice sites in RbF crystals.

From Eq. (1) it is expected that the lifetime $\tau$ of the host luminescence becomes shorter with increasing $n$. This is indeed the case, as shown in Fig. 5. Strictly speaking, the value of $\tau$ of the 5.4-eV luminescence decreases from 1.4 ns ($x=0.0008$) to 1.0 ns ($x=0.008$), which is close to but larger than the expected one ($=1.4\times\frac{1}{2}=0.7$ ns). Such a deviation from the expected
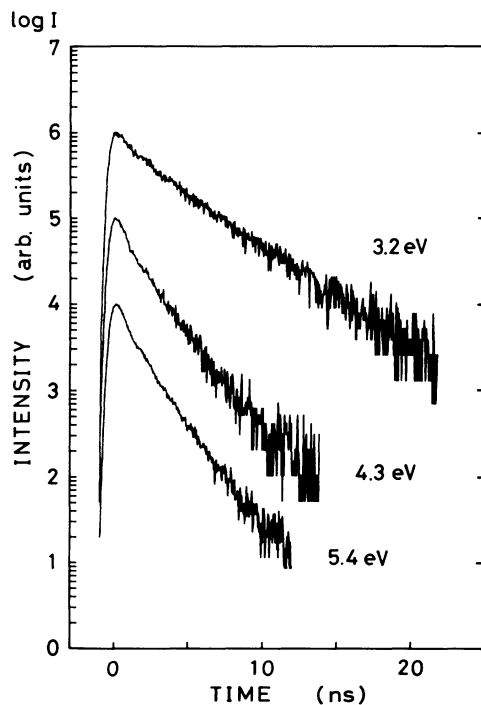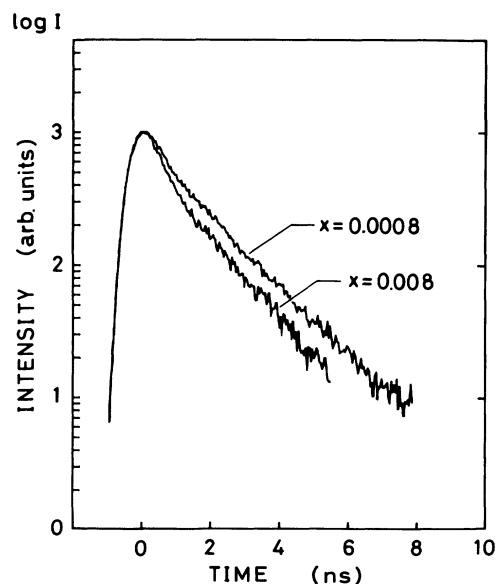


FIG. 4. Decay profiles of the 3.2-, 4.3-, and 5.4-eV bands in RbF ($x=0.0008$) obtained at 295 K under the single-bunch operation of synchrotron radiation at 21.0 eV. The emission intensity is plotted in a logarithmic scale vs time.



FIG. 5. Concentration-dependent changes of the decay profile of the 5.4-eV band in $Rb_{1-x}Cs_xF$ crystals ($x=0.0008$ and 0.008). Both curves are normalized at $t=0$.

value may indicate a contribution of "hot" holes; i.e., the holes transfer their energies to $Cs^+$ ions during the thermal relaxation within the $Rb^+$ core band.

Let us discuss the origin of the 4.3-eV band observed in RbF [Fig. 2(a)]. The 4.3-eV band, which is induced by the core-band excitation above 17.0 eV, has the same lifetime as the 5.4-eV band. The sameness implies that the 4.3-eV band is also linked to AF luminescence of RbF. The energy of emitted photon, $h\nu$, due to AF luminescence is expected as $E_{VC} - \Delta E_V \leq h\nu \leq E_{VC}$ from Fig. 1 [4]. Here, $\Delta E_V$ is the valence-band width. With use of the band parameters, $E_{VC}$ and $\Delta E_V$, which are determined from the photoelectron spectroscopy [13,14], we have $h\nu = 5.2$–$6.8$ eV for RbF and 2.6–4.3 eV for CsF. The agreement between measured and calculated values may be satisfactory in CsF [15]. However, the 4.3-eV band in RbF is located approximately 1.0 eV below the calculated minimum. Such an unexpected low-energy tail of the AF luminescence band has also been observed in $BaF_2$ [16].

In halide crystals it is well known [17] that a hole created in the valence band is self-trapped spontaneously because of the strong coupling with lattice vibrations. In the Auger-free case, the core-hole lifetime is governed by radiative recombination with a valence electron, and is much longer ($\sim 10^{-9}$ s) than the lattice relaxation time (typically $\sim 10^{-13}$ s). Thus a long-lived core hole is also supposed to relax into the self-trapped state [18], from which the low-energy tail luminescence is emitted. If there exists a potential barrier separating the free and self-trapped states, it will be possible to observe the main and low-energy bands simultaneously.

On the other hand, in the efforts to understand a low-energy tail of the soft-x-ray emission band of metals [19,20], the multielectron effect has been shown to be of primary importance. According to this model, when a hole is produced in the core band, it pulls down the valence-electron distribution in its immediate vicinity. As a result, the core hole is filled by an electron having a perturbed wave function, which gives rise to a low-energy tailing of the luminescence band. Further studies both in theory and experiment are required to determine which mechanism is important in the deexcitation process of outermost core holes.

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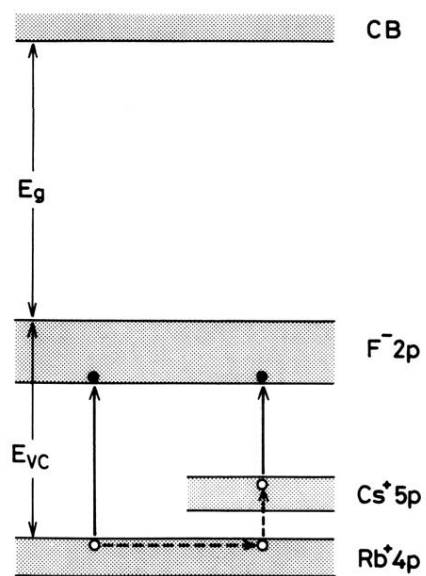[20] R. L. Fink, P. N. First, and C. P. Flynn, Phys. Rev. B 38, 5839 (1988).

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