Observation of Interatomic Radiative Transition of Valence Electrons to Outermost-Core-Hole States in Alkali Halides

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Excitation spectra of visible luminescence in CsF (2.5–5.6 eV), CsCl (3.9–6.0 eV), CsBr (4.4–6.2 eV), and RbF (2.6–6.2 eV) have been measured at room temperature with use of synchrotron radiation for the energy range up to 40 eV. It is shown that the excitation thresholds of these luminescence bands are located at the transition energies from the outermost-core band to the conduction band. This fact provides direct evidence for the radiative decay of valence electrons into outermost core holes in which the Auger decay process is energetically impossible in these materials.

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A hole created in a deep-lying core state is usually filled by an electron coming from some higher state. The difference in binding energy between these two states is either released as an x-ray photon or transferred to another bound electron which is ejected to the continuum state, known as an Auger electron. For outer core states, the Auger decay process is the more probable one and the radiative transition probability becomes small, being less than 0.1.[1] This situation has been well recognized in many materials, since the difference in binding energy between the two states is generally larger than the binding energy of upper bound electrons. Hence, it is difficult to observe fluorescence arising from the core decay, and many studies have been reported on Auger-electron emission.[2-4]

However, there are some peculiar ionic crystals in which the Auger process is energetically forbidden. Band-structure calculations[5,6] for ionic crystals show that the conduction band originates from the excited *s* and *d* states of the positive ions and the valence bands from the filled *p* states of the negative ions. The wave functions of the valence bands are considerably localized on the negative-ion sites. Below the valence bands, there are outermost-core bands originating from the filled *p* states of the positive ions. The onset of transitions from the outermost core states to the conduction band is located at about 21, 18, and 14 eV for K, Rb, and Cs halides, respectively.[7] If 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-hole state ($E_g < E_{vc}$), an interatomic Auger electron will be emitted nonradiatively[2-4] (hereinafter referred to as type A). On the other hand, if $E_g > E_{vc}$, a photon will be emitted with high efficiency (type L).

In this Letter, we report the first direct evidence of the luminescence due to interatomic radiative transitions of valence electrons to outermost core holes in type-L alkali halides, such as CsF, CsCl, CsBr, and RbF. In this work we propose the term "Auger-free luminescence," emphasizing that this transition emits photons without ejecting Auger electrons. Auger-free luminescence should have an excitation threshold at the energy $E_g + E_{vc}$, since the transition from the outermost core states to the filled valence band is not possible.

In the present experiments, synchrotron radiation from the 750-MeV electron storage ring UVSOR at the Institute for Molecular Science, Okazaki, was used as a light source. Vacuum-ultraviolet light from the storage ring was monochromatized with a 1-m Seya-Namioka–type monochromator. Its bandpass was about 0.8 nm, which corresponds to 0.03 eV at a photon energy of 20 eV. A LiF crystal was used as an order-sorting filter. Crystals of CsCl, CsBr, and CsI used in the present experiments were grown in a halogen atmosphere from the melt by the vertical Bridgman method. Powdered CsF and RbF were pressed and mounted on the sample holder in an atmosphere of dry nitrogen. The luminescence emitted from the sample was viewed along a line perpendicular to the beam through a sapphire window, and was focused by a fused-silica lens on the entrance slit of the analyzing monochromator (Shimadzu Bausch & Lomb). The signal was detected in the spectral range 200–600 nm with an R585 (Hamamatsu Photonics) photomultiplier. The bandwidth of the analyzing monochromator was fixed with a resolution of 5 nm for measurements of emission spectra and 20 nm for measurements of excitation spectra. The emission spectra were not corrected for the spectral response of the detecting system.

The solid curves in Fig. 1 show typical emission spectra of CsF, CsCl, CsBr, and RbF measured at room temperature under 21.4-eV photon excitation, corresponding to the interband transition from the outermost core band to the conduction band. The emission spectra of CsCl and CsBr obtained under valence-band excitation are

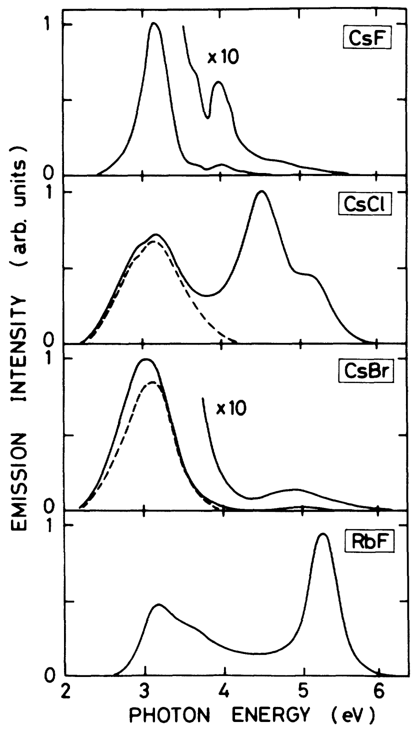

FIG. 1. Emission spectra (solid curves) of CsF, CsCl, CsBr, and RbF measured at room temperature under 21.4-eV photon excitation, corresponding to the interband transition from the outermost-core band to the conduction band. Dashed curves: emission spectra obtained under 8.9- (for CsCl) and 10.9-eV (for CsBr) photon excitation, corresponding to valence-band excitation.

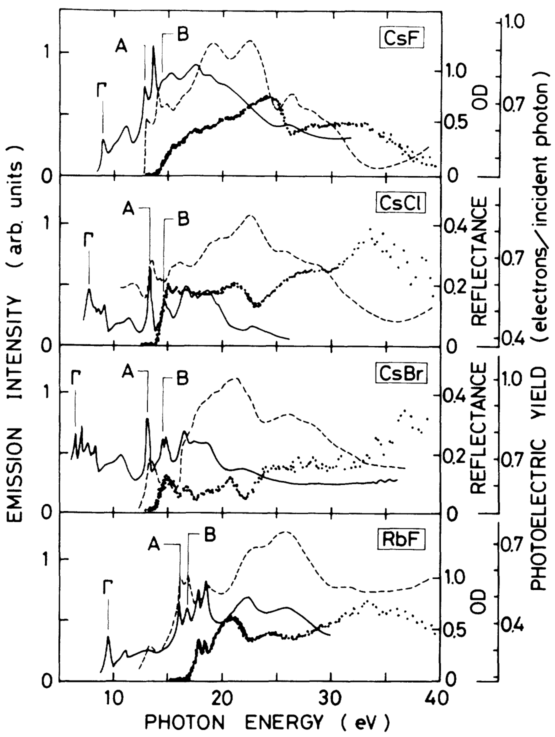

FIG. 2. Excitation spectra (dotted lines) for the 3.2-eV band (CsF), 4.5-eV band (CsCl), 4.9-eV band (CsBr), and 5.3-eV band (RbF). Photoelectric yield spectra (Ref. 8) (dashed curves), and absorption (Ref. 9) or reflectivity spectra (Ref. 10) (solid curves) are also shown for reference. Γ indicates the peak positions of the valence excitons, and A and B correspond to the core excitons of $j=\frac{3}{2}$ and $j=\frac{1}{2}$, respectively.

also shown by dashed curves. No detectable photons were observed in CsF and RbF under valence-band excitation. Our results for three Cs halides are in good agreement with those of cathodoluminescence reported by Valbis, Rachko, and Yansons.[8]

In Fig. 2 we present the excitation spectra for the 3.2-eV band (CsF), 4.5-eV band (CsCl), 4.9-eV band (CsBr), and 5.3-eV band (RbF), together with photoelectric yield spectra,[8] and absorption[9] or reflectivity spectra.[10] In CsF the excitation spectrum for the 4.0-eV band was practically the same as that for the 3.2-eV band. Similar situations were also observed for the 4.5- and 5.1-eV bands in CsCl, and for the 3.3- and 5.3-eV bands in RbF. The most outstanding feature of the excitation spectra is that the threshold energies do not depend on halogen elements, but on alkali elements; the threshold energy E_{th} of CsF, CsCl, and CsBr is 14.1 ± 0.2 eV, and that of RbF is 17.0 ± 0.1 eV. These values are in good agreement with the transition energies from the outermost core states of the respective positive ions to the conduction band, and are summarized in Table I.

The observed threshold energies strongly suggest that the mechanism for the luminescence of interest here is due to Auger-free interatomic transitions of electrons from X^- np halogen valence bands ($n=2$, 3, and 4 for $X=$F, Cl, and Br, respectively) to the Cs^+ $5p$ or Rb^+ $4p$ holes. On the other hand, the low-energy components of CsCl and CsBr cannot be linked to Auger-free luminescence, since they are also excited efficiently under valence-band excitation.[12]

Evidence in support of the above identification of Auger-free luminescence comes from photoemission data. According to our interpretation, it is expected that one incident photon in the energy region above E_{th} should produce one photoelectron for the crystals of type L, while it should produce one photoelectron and one Auger electron for the crystals of type A. Thus, there should be a difference in the photoelectric yield between these two types L and A. The photoemission data measured by Sugawara and Sasaki[3] clearly show that the maximum absolute yields in the region of photon energies above E_{th} are smaller than unity for the crystals of type L, while they are larger than unity for the crystals of type A. These observations support our interpretation mentioned above.

TABLE I. Summary of parameters relevant to Auger-free luminescence in alkali halides. All values are in electronvolts. The experimental uncertainties for the range of emission spectra are 0.3 eV for the upper limit and 0.1 eV for the lower limit. The calculation contains uncertainties of 0.3 eV.

			Peak positions	Energy range of emission spectra		
Crystal	E_g	E_{vc}	of emission bands	Measured	Calculated	E_{th}
CsF	9.8[a]	4.3[a]	3.2, 3.7, 4.0, 4.1, 4.7	2.5–5.6	2.6–4.3[b] (1.5)–4.4[a]	14.1 ± 0.2
CsCl	8.3[a]	5.8[a]	4.5, 5.1	3.9–6.0	4.0–5.8[b] 3.4–5.9[a]	14.1 ± 0.2
CsBr	7.3[a]	6.6[a]	4.9	4.4–6.2	4.4–6.2[b] 3.6–6.6[a]	14.1 ± 0.2
RbF	10.3[a]	7.4[a]	3.3, 5.3	2.6–6.2	4.3–7.4[a]	17.0 ± 0.1

[a] Reference 7.

[b] Reference 11.

In an auxiliary experiment, luminescence decay curves following the 90.115-MHz bunch of the electron storage ring were determined by a single-photon counting method. The Auger-free luminescence was confirmed to have decay times shorter than 5 ns. On the other hand, it was observed that the low-energy components in CsCl and CsBr have long decay times (> 10 ns).

The energy range of emitted photons $h\nu$ due to the Auger-free luminescence is calculated as $E_{vc} - \Delta E_v < h\nu < E_{vc}$ by the assumption that the outermost core holes have sufficient time to relax to the upper part of the band before the radiative transition. Here, ΔE_v is the valence-band width. Table I shows calculated values of $h\nu$, by use of band parameters, E_{vc} and ΔE_v, which are determined by photoelectron spectroscopy.[7,11] The agreement between the measured and calculated values is good for three Cs halides, by consideration of the upper limit of 6.2 eV for our emission measurements. We thus believe that the radiative transition occurs through the same band structure as determined by photoelectron spectroscopy.

In RbF, the measured lower limit of the emission spectrum is located approximately 1.7 eV below the calculated one. In order to explain this low-energy shift, it will be necessary to introduce some relaxation of the outermost core-hole state and/or the valence-band state. The interesting part of this work is that the low-energy shift is observed only in RbF, and not in CsF, CsCl, and CsBr.[12] Crystals of both RbF and CsF are of the NaCl structure, and CsBr crystallizes in the CsCl structure. Therefore, there is no clear correlation with the crystal structure. Further theoretical studies are required on this problem.[13]

The thresholds for the Auger-free luminescence are clearly above the energies of the core excitons Cs^+ $5p$ $(j=\frac{3}{2}) \rightarrow \Gamma_1$ in Cs halides, and Rb^+ $4p$ $(j=\frac{3}{2}) \rightarrow \Gamma_1$ in RbF, respectively, as shown in Fig. 2. The photoelectric yield spectra show well-defined peaks around core-excitation transitions. These facts suggest that the core exciton decays efficiently through Auger-electron emission.

Since E_{th} corresponds to the interband transition energy from the outermost-core band to the conduction band, the binding energy E_{cb} of the core excitons at Γ_1 can be calculated as $E_{cb} = E_{\text{th}} - E_{xc}$. Here, E_{xc} is the energy of core excitons observed in the optical spectra. By use of the values of E_{xc} obtained by Saito,[14] E_{cb} is evaluated to be 1.1, 0.8, 0.9, and 1.0 eV for CsF, CsCl, CsBr, and RbF, respectively. These values of Cs halides are larger than the binding energies of valence-band excitons at Γ_1, i.e., 0.6, 0.5, and 0.5 eV for CsF, CsCl, and CsBr.[11] This is consistent with a suggestion that the core excitons should be more strongly bound than the corresponding valence excitons since the core hole in alkali ions is not effectively screened by the valence-electron cloud, which lies almost completely on the halogen ions.[15]

It is interesting here to see whether Auger-free luminescence can be observed in crystals of $E_{vc} > E_g > E_{vc} - \Delta E_v$. This condition is fulfilled in CsI, where the Auger-free luminescence is expected to appear in the range of 4.4–5.6 eV (Ref. 7) or 5.2–5.6 eV (Ref. 11). Under γ-ray excitation of CsI, we have found a luminescence of 3.5–5.0 eV peaking at 4.1 eV at room temperature.[16] This band, however, was not excited under valence-band excitation nor under outermost-core-band excitation. Further studies of this band are needed.

In conclusion, our data give a convincing demonstration of Auger-free luminescence due to interatomic radiative transition of the valence electrons to the outermost core holes in materials where $E_g > E_{vc}$. It would be of interest to extend the present work in directions leading to the finding of other materials showing Auger-free luminescence, for example, KF, BaBr_2, BaCl_2, and BaF_2.[17]

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