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Photoelectron spectroscopic study of the decay process of excited 4*d* states in cesium halides

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The nonradiative decay of excited 4*d* states in CsCl and CsBr was investigated by photoelectron spectroscopy with use of synchrotron radiation. It was observed that the intensities of the Auger-electron peak and Cs 5*p* photoelectron peak are resonantly enhanced around the Cs 4*d* excitation energy, while the valence-band intensity is not clearly enhanced. The enhancements are interpreted in terms of two decay processes, the direct recombination and the Auger decay processes, of excited 4*d* states. It is shown that excited 4*d* states in CsCl and CsBr decay dominantly through the $N_{4,5}$-$O_{2,3}O_{2,3}$ Auger process, and the probability of the direct-recombination decay with the energy transferred to Cs 5*p* electrons is estimated to be 2–8 %, by using constant-initial-state and absorption spectra.

I. INTRODUCTION

Through the years, there have been many studies on absorption spectra of atoms or ions with nuclear charge $Z=54-70$ in the region of 4*d* excitation.[1–15] The absorption spectra are characterized by huge peaks with widths ranging from 15 to 70 eV and weak sharp lines with widths of several tenths of an electron volt. The huge peaks are interpreted in terms of delayed onsets of $4d \rightarrow \varepsilon f$ transitions for lighter elements ($Z \leq 54$), while for heavier elements ($Z \geq 56$) the observed absorption peaks arise from the $4d \rightarrow nf$ discrete transitions which are autoionized into the continuum. On the other hand, the sharp lines are interpreted in terms of multiplet structures due to transition $4d \rightarrow 4f$.[4] However, the sharp lines as well as the strong peaks are not completely interpreted within an atomic picture, and should be explained by taking account of the delocalization of excited 4*d* states in the compounds.[12,15] The purpose of the present study is to know the decay process and the degree of localization of excited 4*d* states by means of photoelectron spectroscopy. We choose *Cs* halides as our samples in the course of our study, because cesium ($Z=55$) is on the border line between the two cases for *f* wave-function collapse mentioned above.

II. EXPERIMENTAL PROCEDURES

Synchrotron radiation from an electron storage ring at the Institute for Solid State Physics of the University of Tokyo was used as a light source for photoemission measurements, and the spectral width was about 0.18 eV at a photon energy of 90 eV. The electron-energy-analyzer resolution was constant with a full width at half maximum of 0.4 eV.

The absorption measurements were performed by using synchrotron radiation from a 750-MeV storage ring (UVSOR) at the Institute for Molecular Science. The spectral width was about 0.18 eV at a photon energy of 90 eV. A filter of a metallic samarium was used to reduce higher-order light from the monochromator. Samples were prepared *in situ* by evaporation onto collodion substrates coated with a thin aluminum film. The thickness of samples was measured with an oscillating-quartz thickness gauge to obtain absorption coefficients.

III. EXPERIMENTAL RESULTS

Figure 1 shows photoelectron spectra of CsCl and CsBr, which were obtained with excitation-photon energy

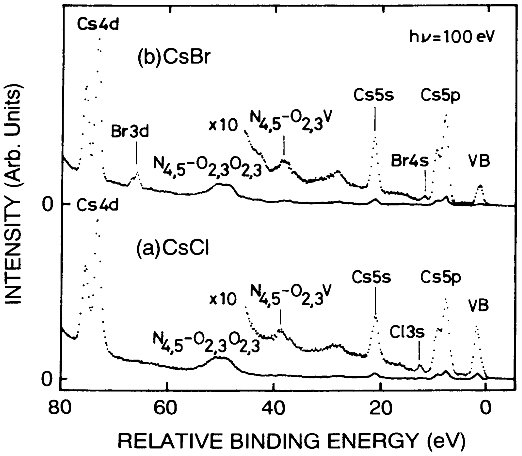

FIG. 1. Photoelectron spectra of CsCl and CsBr obtained with excitation-photon energy of 100 eV. The binding energy is given relative to the top of the valence band.

of 100 eV. The present valence-band spectra of CsCl and CsBr are similar in shape to those obtained by Poole *et al.*[16] and Smith and Pong,[17] who used the excitation-photon energy of 40.81 eV. Binding energies of the valence band and the inner core levels in the energy-distribution curves are listed in Table I, as well as the kinetic energies of the $N_{4,5}$-$O_{2,3}O_{2,3}$ Auger electrons, where $N_{4,5}$ denotes the initial N_4 or N_5 hole state and $O_{2,3}$ denotes the final O_2 or O_3 hole state. The binding energies and the kinetic energies were measured with respect to the top of the valence band for convenience.

Figures 2 and 3 show the constant-initial-state (CIS) spectra with the initial states at the peak of valence band and Cs $5p_{3/2}$ level (VB CIS and $5p$ CIS), and the constant-final-state (CFS) spectra with the final state at the kinetic energy of the $N_{4,5}$-$O_{2,3}O_{2,3}$ Auger-electron peaks in CsCl and CsBr, respectively. The Cs $N_{4,5}$ absorption spectra are also shown for comparison, whose absorption coefficients are given on the right-hand side of the figures. The absorption spectrum of CsCl shows peaks or shoulder at 78.5 (*A*), 80.2 (*B*), 82.5 (*C*), 85 (*D*), 88.5 (*E*), 93.2 (*F*), 96.3 (*G*), 101.2 (*H*), and 107.5 (*I*) eV, while that of CsBr shows peaks or shoulders at 80 (*B*), 82.3 (*C*), 85.2 (*D*), 88 (*E*), 93 (*E*), 96.2 (*G*), 101.7 (*H*), and 108.2 (*I*) eV. The present absorption spectra of CsCl and CsBr agree well with those reported previously,[1] but the present value of the absorption coefficient is slightly different from the previous one. This difference may be due to the experimental accuracy in measuring the sample thickness.

The CFS spectra and the $5p$ CIS spectra in both substances also show weak peaks or shoulders corresponding to the absorption structures. Intensity distributions of the CFS and absorption spectra coincide with each other, while the intensity distribution of the $5p$ CIS spectrum is much different from that of the absorption spectrum. The strongest maximum of the $5p$ CIS spectra, for instance, is observed at peak *F*, while the absorption maximum is located at peak *I*. The VB-CIS spectrum of CsCl decreases monotonously with increasingly photon energy,

TABLE I. The binding energies of valence band and inner core levels, as well as the kinetic energies of Auger electrons observed at an excitation photon energy of 100 eV. Energies are relative to the top of the valence band and are given in electron volts.

	CsCl	CsBr
Valence band	1.7	1.6
Cs $5p_{3/2}$	7.4	8.0
Cs $5p_{1/2}$	9.2	9.6
Halogen *ns*	12.2	11.9
Cs $5s$	21.1	21.2
Br $3d_{5/2}$		65.7
Br $3d_{3/2}$		66.8
Cs $4d_{5/2}$	72.8	73.1
Cs $4d_{3/2}$	75.1	75.4
$N_{4,5}$-$O_{2,3}V$	61.4	61.6
$N_{4,5}$-$O_{2,3}O_{2,3}$	49	49.2
	51.2	51.4

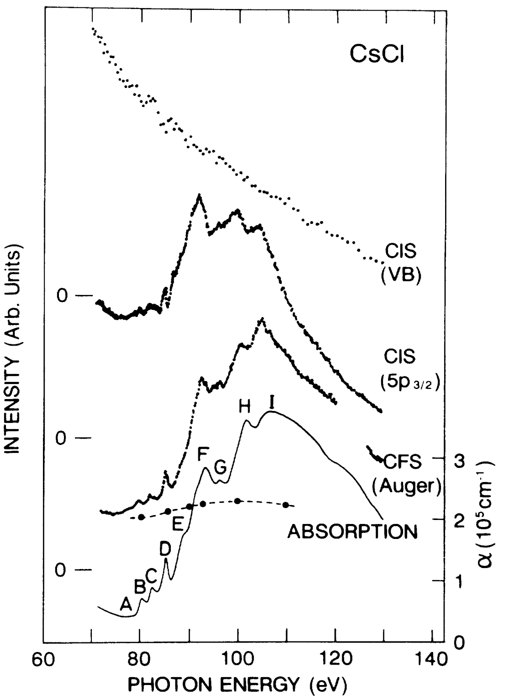

FIG. 2. Valence-band CIS, Cs $5p_{3/2}$ CIS, CFS, and absorption spectra of CsCl. Solid circles in the CFS spectrum show the background intensities derived from photoelectron spectra, and the broken line is the guide to the eyes. The absorption coefficient is given on the right-hand side of the figure.

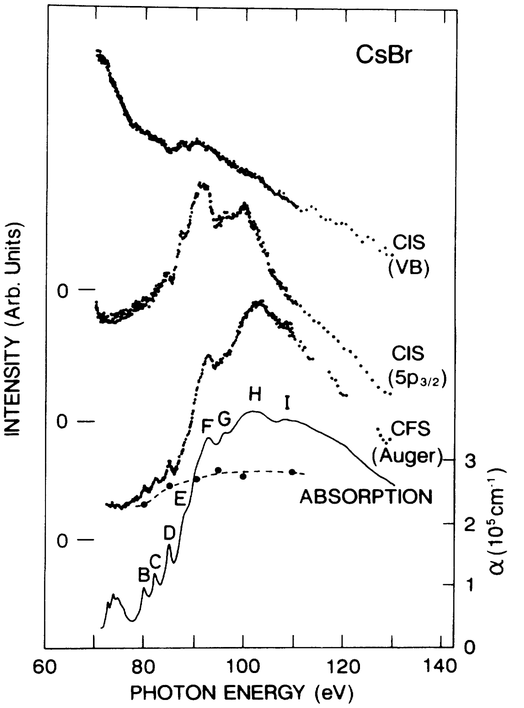

FIG. 3. Valence-band CIS, Cs $5p_{3/2}$ CIS, CFS, and absorption spectra of CsBr. Solid circles in the CFS spectrum show the background intensities derived from photoelectron spectra, and the broken line is the guide to the eyes. The absorption coefficient is given on the right-hand side of the figure.

while that of CsBr shows small peaks around 87 and 91 eV, which correspond to the absorption maxima E and F, respectively. The structure due to the Br $M_{4,5}$ absorption is seen at about 72.5, 73.5, 74.5, and 75.5 eV in the absorption spectrum, but this is beyond present interest.

IV. DISCUSSION

Cardona *et al.*[1] have investigated the Cs $N_{4,5}$ absorption spectra of Cs halide films by using synchrotron radiation, and attributed peak A to the forbidden exciton, and peaks F and G to double excitation ($4d$ and $5p$ electrons are excited simultaneously by a single photon). Radler and Sonntag[5] have found a close correspondence between the Cs $4d$ spectra of molecular and crystalline CsCl and ascribed the absorption peak A to transitions to states mainly originating from Cs^+ $6s$ level and peaks B and C to transitions to final states with Cs^+ $6p$ parentage. They also assigned peak D to the transition of f levels localized within the potential barrier around the Cs^+ core, while Connerade[10] has theoretically shown that Cs^+ has a collapsed f wave function associated with $4d \rightarrow 4f$, εf giant resonance.

As seen in Figs. 2 and 3, the enhancement of the Cs $5p$ photoelectron intensity is clearly observed in CsCl and CsBr. This enhancement can be interpreted in terms of the $N_{4,5}$-$O_{2,3}$ decay process of excited Cs $4d$ states, where a Cs $4d$ hole and an excited electron recombine directly with the energy transferred to a Cs $5p$ electron. The CFS spectra with the final state at the $N_{4,5}$-$O_{2,3}O_{2,3}$ Auger-electron peak are also enhanced in both substances. This enhancement can be interpreted in terms of the $N_{4,5}$-$O_{2,3}O_{2,3}$ decay process of excited Cs $4d$ states: a Cs $4d$ hole and a $5p$ electron recombine with the energy transferred to another $5p$ electron which is excited into the continuum. In addition to the decay processes mentioned above, excited $4d$ states can decay nonradiatively through the $N_{4,5}$-O_1 and $N_{4,5}$-$O_{2,3}V$ processes. The probabilities of these decay processes are less than those of the $N_{4,5}$-$O_{2,3}$ and $N_{4,5}$-$O_{2,3}O_{2,3}$ processes, respectively.

Strictly speaking, the CFS spectra contain the background due to the inelastic scattering of Cs $5p$, Cs $5s$, halogen s, and valence-band photoelectrons. The solid circles shown in Figs. 2 and 3 show the background intensities derived from photoelectron spectra obtained with various excitation-photon energies, and the broken lines are guides to the eyes. As seen in the figures, the background intensity is smooth more than the Auger-electron intensity, an then it does not change drastically the spectral feature of the observed CFS spectra. It should be noted that the spectral features of the CFS and the absorption spectra are very similar with each other. This indicates that excited $4d$ states of CsCl and CsBr decay dominantly through the $N_{4,5}$-$O_{2,3}O_{2,3}$ process.

In contrast, the spectra feature of *Cs*-$5p$ CIS spectra is much different from that of the absorption spectra. This means that the decay probability of each excited $4d$ state is not constant over Cs $N_{4,5}$ excitation energy region. Previously we[18–20] have proposed an equation for the probability of the decay through direct recombination between a core hole and an excited electron and showed that the branching ratio between different decay processes is dependent on the localization of the valence and the conduction electrons. Here, we will apply the equation to obtain the decay probability, P, of excited $4d$ states through $N_{4,5}$-$O_{2,3}$ process in CsCl and CsBr as follows:

$$P = \frac{\Delta I_{5p}(h\nu)/I_{5p}(h\nu)}{\alpha_{4d}(h\nu)/\alpha_{5p}(h\nu)} , \tag{1}$$

where ΔI_{5p} and I_{5p} are the increment of the Cs $5p$ photoelectron intensity due to the $N_{4,5}$-$O_{2,3}$ process and the Cs $5p$ photoelectron intensity without any resonant enhancement, respectively. Also α_{4d} and α_{5p} are parts of the absorption coefficient due to the formation of excited $4d$ states and due to transition from Cs $5p$ level to the continuum, respectively. The values of α_{4d} and α_{5p} were derived from the absorption spectra and the photoelectron spectra excited with 75-eV photon, under the assumption that the absorption peak due to α_{4d} is superposed on the smooth background due to the absorptions from the valence band α_{VB}, the outermost s level of the anion α_s, the $5p$ levels of cesium α_{5p}, and the $5s$ level of cesium α_{5s}, and that the ratios of α_{VB}, α_s, α_{5p}, and α_{5s} are the same as the ratios of the integrated intensities of each peaks in the photoelectron spectrum obtained with the photon energy of 75 eV.

The estimated values of decay probability of excited $4d$ states through the $N_{4,5}$-$O_{2,3}$ process are 2–5 % for CsCl and 4–8 % for CsBr. The maximum value is obtained for peak F, and the values of about 4% and 7% are estimated for peak D in CsCl and CsBr, respectively. The values for the other structures are 2–3 % for CsCl and 4–6 % for CsBr. These results indicate that the absorption peaks D and F are attributed to transitions to a little more localized states among various excited $4d$ states in CsCl and CsBr.

Peak D in CsCl and CsBr has been assigned to the transition from the $4d$ level to the collapsed f state of Cs^+.[5,11] The present result is consistent with the assignment, since the collapsed f state is localized within the potential barrier. Cardona *et al.*[1] have proposed that the 93-eV peak corresponding to peak F in the absorption spectra of cesium halides is due to the double excitation of $4d$ and $5p$ electrons with a single photon.[21,22] However, it is hard to interpret the enhancement of the $5p$ CIS spectra at peak F in terms of the decay of the double excited states, because simultaneous deexcitation of two excited electrons is required to transfer their energy to Cs $5p$ electron, and because the enhancement of the $5p$ CIS spectra is not so large for peak G which has been assigned to a spin-orbit mate of peak F. Also, the peaks assigned to the double excitation in the Na $L_{2,3}$ absorption spectra of sodium halides do not show any enhancement of the CIS spectra.[20] We suppose that peak F may be due to $4d^9 5f^1$ state hybridized with $4d^9 4f^1$ state from the analogy of the structures in the giant absorption of BaF_2,[12] where the f-wave-function collapse is larger than in cesium halides.

The decay probabilities of the shoulder or peaks A, B, and C are about 2–3 % for CsCl and those of peaks B

and *C* are about 4–5 % for CsBr. This is consistent with the idea that these absorption peaks are attributed to transitions to 6*s* ad 6*p* levels,[1,5] since they are less localized than *f* levels. In contrast, no evidence supporting the forbidden exciton is obtained for peak *A*.

The VB CIS of CsCl is not enhanced around Cs 4*d* excitation energy region, and the enhancement of the VB-CIS of CsBr is very small. These indicate that excited Cs 4*d* states scarcely decay with the energy transferred to valence electrons. The small enhancement of the valence-band intensity of CsBr is considered to be due to the mixing of the cesium and bromine wave functions in the valence and/or conduction bands. This is consistent with the fact that the ionicity of bromine ion is smaller than that of chlorine ion.

Chiang *et al.*[23] have observed the much larger shift of the N_5-$O_{2,3}O_{2,3}$ ($^1S_0$) Auger-electron energy for Cs$^+$ in CsCl than that for X and I$^-$ in KI, supporting the *f*-wave-function collapse for Cs$^+$. As shown in Fig. 4, the shift of Auger-electron energy is observed in the photon energy range from 85 to 95 eV, but the energy shift is not observed above 100 eV, where the decay probability through the $N_{4,5}$-$O_{2,3}$ process is very low. This energy shift may be interpreted in terms of the two-hole-and-one-electron bound state (trion state),[18–20] since besides an ejected Auger electron the final state configuration of the $N_{4,5}$-$O_{2,3}O_{2,3}$ process involves two holes in the Cs 5*p* level and an initially photoexcited electron which is localized well within the potential barrier of the Cs$^+$ core.

Recently, Auger-free luminescence has been observed in cesium halides.[24] Since the Auger-free luminescence is due to the radiative transitions of electrons from the valence band to the next deeper outermost 5*p* core holes of Cs$^+$, it is interesting to discuss the relation between the Auger-free luminescence and the final states after the decay of excited 4*d* states. Kubota, MacDonald, and Munro[25] have measured the excitation spectra of Auger-free luminescence in CsCl and CsBr between 50 and 140 eV, and found that the excitation spectra of Auger-free luminescence are anticorrelated with respect to the absorption spectra, and the lifetime of the luminescence shows a minimum around 108 eV, where the absorption maximum appears. They considered the difference of 5*p* hole states between the surface layer and the bulk to interpret the results, although the definite conclusion has not been obtained. The final state after the decay through the $N_{4,5}$-$O_{2,3}O_{2,3}$ process has two holes at the Cs 5*p* level, and the $N_{4,5}$-$O_{2,3}$ process produces a hole at the Cs 5*p* level, while the initial state for the Auger-free luminescence has a hole at the Cs 5*p* level. Thus, it is simply considered that the Auger-free luminescence occurs after the $N_{4,5}$-$O_{2,3}$ process of excited 4*d* states. This should contribute to the enhancement of the Auger-free luminescence. Also if a single two-hole state produced by the $N_{4,5}$-$O_{2,3}O_{2,3}$ process changes to two one-hole states, the intensity of the Auger-free luminescence should be increased up to about two times as that obtained below Cs 4*d* threshold, and the lifetime of the luminescence should be constant over Cs 4*d* excitation energy. This is not the case. Thus, we propose that the two-hole state produced by the $N_{4,5}$-$O_{2,3}O_{2,3}$ process cannot be easily decomposed into two one-hole states, resulting in the anticorrelated feature of the excitation spectra and the reduction of the lifetime. Further investigations, however, are necessary to interpret quantitatively the relation between the nonradiative decay of excited 4*d* states and the radiative decay of the 5*p* hole state.[26,27]

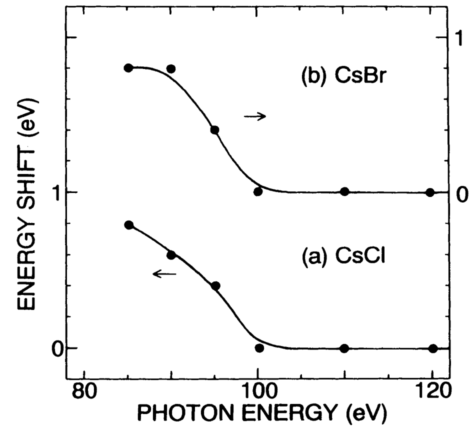

FIG. 4. Energy shifts of the $N_{4,5}$-$O_{2,3}O_{2,3}$ Auger-electron peaks in CsCl and CsBr. The increments of the energy relative to the kinetic energy obtained with photon energy of 100 eV are shown.

In conclusion, the nonradiative decay of excited 4*d* states in CsCl and CsBr was investigated by photoelectron spectroscopy. It was observed that the CFS and the 5*p* CIS spectra are resonantly enhanced around Cs $N_{4,5}$ excitation energy, while the VB-CIS spectra are not clearly enhanced. The enhancements were interpreted in terms of $N_{4,5}$-$O_{2,3}$ and $N_{4,5}$-$O_{2,3}O_{2,3}$ decay processes of excited 4*d* states. It was found that excited 4*d* states in CsCl and CsBr decay dominantly through the $N_{4,5}$-$O_{2,3}O_{2,3}$ process. The decay probability of excited 4*d* states through the $N_{4,5}$-$O_{2,3}$ process was estimated to be 2–8 %, by using the 5*p* CIS and the absorption spectra. The spectral feature of the 5*p* CIS spectrum was found to be much different from that of the Cs $N_{4,5}$ absorption spectrum, indicating that the degree of localization of excited 4*d* states is not constant over the Cs $N_{4,5}$ absorption region.

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