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Decay process of Li 1*s* core exciton in lithium halides studied by photoelectron spectroscopy

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The decay process of the Li 1*s* core exciton was investigated by measuring the photoelectron spectra of LiCl and LiBr. It was observed that the valence-band spectrum as well as the Auger peak is enhanced at photon energies close to the excitation energy of the Li 1*s* core exciton. To explain these phenomena the following two processes were proposed: A Li 1*s* core hole and an excited electron which form the Li 1*s* core exciton may recombine directly with energy transferred to a valence electron. In this case, the valence-band photoelectron spectrum is resonantly enhanced at the photon energy close to the excitation energy of the core exciton, since the final state of this process is the same as that of the direct photoexcitation from the valence band. In the second process, the Li 1*s* core hole forming a core exciton recombines with a valence electron transferring energy to another valence electron which is excited to the continuum state. This process results in an enhancement of the Auger-electron peak. The decay probability of the Li 1*s* core exciton through these two processes was estimated from the photoelectron spectra and the Li *K* absorption spectra. It was found that the latter process is a predominant decay process in lithium halides.

I. INTRODUCTION

The decay mechanism of the exciton in the optical absorption region has been investigated by many authors,[1] whereas, with regard to the core exciton, only several groups[2–7] have studied its decay mechanism with different methods. We have tried to investigate the radiative decay of the core exciton in the emission spectrum of LiF produced by a fluorescence excitation method.[3] However, the evidence of the radiative decay of the core exciton is obscure owing to the presence of the strong resonance scattering of the incident continuous radiation by the exciton and continuum states.

Recently, we measured photoelectron spectra of LiF with the photon energy near the excitation energy of the Li 1*s* core exciton to obtain the information on the decay process of the core exciton. We observed the enhancement of the intensities of the valence band and the Auger-electron peak at the photon energy of the excitation energy of the Li 1*s* core exciton.[7] To explain these phenomena the following processes were proposed: (1) A Li 1*s* core hole and an excited electron which form the Li 1*s* core exciton may recombine directly with energy transferred to a valence electron. This process was called the "*K*(exciton)-*V* process," where *K*(exciton) denotes the initial state with the *K* hole accompanied by a bound electron (core exciton) and *V* denotes the final state with a hole in the valence band. Since the final state of this process is the same as that of the direct photoexcitation from the valence band, the valence-band photoelectron spectrum is resonantly enhanced at the photon energy of the excitation energy of the core exciton. (2) The Li 1*s* core hole forming a core exciton recombines with a valence electron transferring energy to another valence electron which is excited to the continuum state. This process is called the "*K*(exciton)-*VV* process" and results in an enhancement of the Auger-electron peak. Moreover, it was observed that the kinetic energy of the Auger electron in this process is slightly larger than that in the ordinary *K*-*VV* Auger process.

The purpose of the present study is to confirm whether these two decay processes can take place in other lithium halides such as LiCl and LiBr and, in particular, to observe the occurrence of the energy shift of the Auger peak in the *K*(exciton)-*VV* process. Since the ionicity, the band width, and the binding energy of the core exciton of these materials vary systematically in going from LiF to LiBr, we expect the strength of the resonance enhancement to reflect the systematic change of these natures. We are also interested in estimating the probability of these two nonradiative decay processes among lithium halides.

II. EXPERIMENTAL

Photoelectron spectra were observed with an ultrahigh vacuum photoelectron spectrometer with a 2-m grazing incidence monochromator of a modified Rowland-mount type. 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. The spectral width was 0.2 eV at the photon energy of 60 eV with 80-μm slits and a 1200 grooves/mm grating. The photoelectron energy was measured with a double-stage cylindrical mirror analyzer. The analyzer resolution was constant with a full width at half maximum (FWHM) of 0.4 eV.

Since charging of the samples can result in a shift and broadening of the photoelectron spectrum, studies were made on thin films which were evaporated onto gold substrates *in situ* in a separately pumped sample chamber. The base pressure in the sample chamber was about 4×10^{-8} Pa and rose to a 10^{-6} Pa range during evaporation. The pressure in the analyzer chamber was about 7×10^{-9} Pa during measurements. The spectral dependence of the radiation incident on the samples was determined from the photoelectric yield spectrum of gold.

III. RESULTS

Figure 1 shows a set of photoelectron spectra of LiCl obtained with various photon energies around the excitation energy of the Li 1*s* core exciton. The binding energies are measured relative to the top of the valence band. The ordinate is proportional to the number of photoelectrons per incident photon flux. The spectrum obtained with the photon energy of 57.1 eV shows the presence of a peak and a shoulder in the valence band at binding energies of 1.4 and 3.0 eV, respectively, and also of the Cl 3*s* level at 11.7 eV. The shape and width of the valence-band spectrum are similar to those obtained by Poole *et al.*[8] with the photon energy of 40.81 eV. In addition to the valence band and the Cl 3*s* level, three Auger-electron peaks are observed when the photon energy is higher than 59 eV. The relative kinetic energies of these Auger peaks are about 47, 42, and 37 eV in the spectrum excited at 66.1 eV photons. The kinetic energy is measured with respect to the top of the valence band for convenience. The Auger peak with the kinetic energy of 47 eV is about ten times more intense than the other two Auger peaks. All of these Auger peaks are enhanced at the photon energy of 60.7 eV, which is the excitation energy of the Li 1*s* core exciton. Around this photon energy, the valence-band spectrum is also enhanced. These phenomena are more visual in the constant-initial-state (CIS) spectrum with the initial state at the peak of the valence band and in the constant-final-state (CFS) spectrum with the final state corresponding to the kinetic energy of the Auger-electron peak at 47 eV. They are shown in Fig. 2 together with the Li *K* absorption spectrum of LiCl obtained by Haensel *et al.*[9]

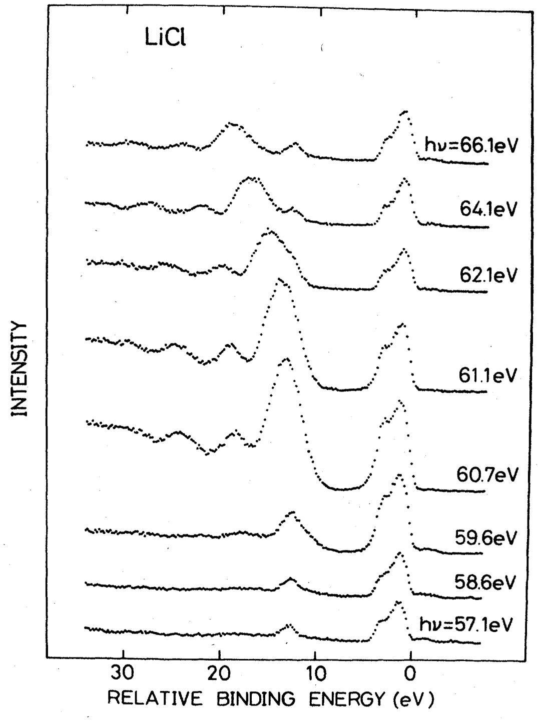

FIG. 1. Set of photoelectron spectra of LiCl excited with photon energies around the excitation energy of the Li 1*s* core exciton. Intensities are normalized to the incident photon flux.

As seen in this figure, the CIS spectrum shows two peaks around the excitation energy of the Li 1*s* core exciton. The energy position of the main peak of the CIS spectrum is 0.2 eV lower than that of the CFS and the absorption spectra. The other peak observed at 59.4 eV is located at the low-energy tail of the core-exciton peak in the absorption spectrum.

The CFS spectrum also shows resonant behavior at the photon energy of 60.7 eV. The structures in the CFS spectrum coincide with those in the absorption spectrum, except for the peak at 59.4 eV. The main peak in the CIS and the CFS spectra has the same FWHM of 0.8 eV as that of the core-exciton peak in the absorption spectrum, while the lower-energy peak in the CIS spectrum has a considerably narrower FWHM of 0.4 eV.

Figure 3 shows a set of photoelectron spectra of LiBr obtained with various photon energies around the excitation energy of the Li 1*s* core exciton. The spectrum obtained with $h\nu = 57.1$ eV shows two peaks in the valence band at 1.5 and 3.4 eV and the Br 4*s* level at 13.2 eV. The width of the valence band is the same as that reported by Poole *et al.*[8] which was obtained with the photon energy of 40.81 eV. However, the intensity ratios of the two peaks in the valence band are slightly different from each other. In addition to the valence band and the Br 4*s* level,

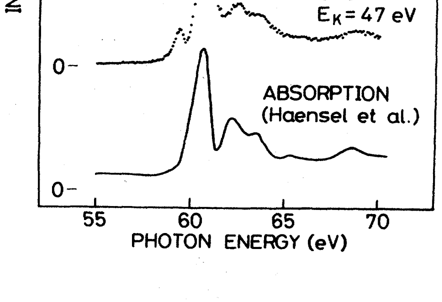

FIG. 2. CIS spectrum measured at the initial binding energy of 1.4 eV, CFS spectrum with the final kinetic energy of 47 eV, and the Li *K* absorption spectrum obtained by Haensel *et al.* (Ref. 9).

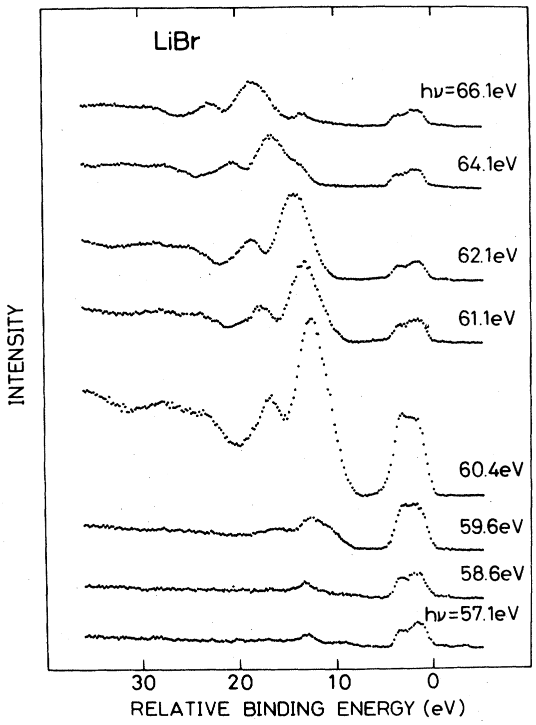

FIG. 3. Set of photoelectron spectra of LiBr excited with photon energies around the excitation energy of the Li 1*s* core exciton. Intensities are normalized to the incident photon flux.

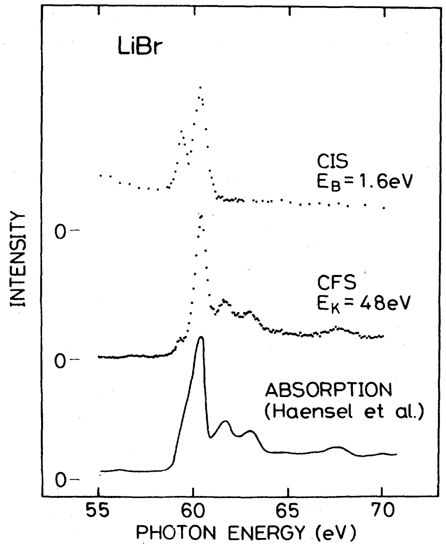

FIG. 4. CIS spectrum measured at the initial binding energy of 1.6 eV, CFS spectrum with the final kinetic energy of 48 eV, and the Li *K* absorption spectrum obtained by Haensel *et al.* (Ref. 9).

the Auger peaks are observed at the kinetic energies of about 48, 43, and 33 eV in the spectrum obtained with $h\nu=66.1$ eV, and these Auger peaks are also observed when the photon energy is higher than 59 eV. The intensity of the valence band changes more drastically than the case of LiCl when the photon energy is varied around the excitation energy of the Li 1*s* core exciton, 60.4 eV. At this photon energy the Auger peaks also exhibit resonant behavior. In LiCl and LiBr the energy position of the Auger peaks in the spectra obtained with the photon energy near the excitation energy of the Li 1*s* core exciton is slightly different from that obtained with higher photon energies as in the case of LiF.[7]

Figure 4 shows the CIS spectrum with the initial state at the peak of the valence band, the CFS spectrum with the final state corresponding to the kinetic energy of the Auger-electron peak at 48 eV, and the Li *K* absorption spectrum of LiBr obtained by Haensel *et al.*[9] As seen in this figure, the CIS spectrum shows two peaks at 59.3 eV and 60.3 eV. The lower-energy peak is located at the tail of the core-exciton peak in the absorption spectrum, and the energy position of the main peak is 0.1 eV lower than that of the Li 1*s* core exciton of LiBr. The FWHM of the main peak is 0.8 eV, while that of the lower-energy peak is 0.5 eV. The CFS spectrum shows resonant behavior at 60.4 eV, the excitation energy of the core exciton, and the structures in this spectrum correspond well to those in the absorption spectrum except for the peak at 59.3 eV. The FWHM of the main peak in the CFS spectrum is 0.8 eV, which is narrower than that in the absorption spectrum.

IV. DISCUSSION

As seen in Figs. 2 and 4, the valence-band and the Auger spectra are enhanced close to the photon energy of the excitation energy of the Li 1*s* core exciton in LiCl and LiBr. This indicates that the *K*(exciton)-*V* process and the *K*(exciton)-*VV* process, both of which were proposed for LiF previously,[7] are also the main channels of the nonradiative decay process of the core exciton in these lithium halides.

It should be noticed that the extra peak is observed on the lower-energy side of the main peak in the CIS and the CFS spectra of LiCl and LiBr. Pantelides[10] has indicated that the exciton observed in the Li *K* absorption spectra of lithium halides should be formed by a band which has *p*-like character. On the other hand, calculated energy bands suggest that the minimum of the conduction bands has *s*-like character.[11] Fields *et al.*[12] have measured the electron energy-loss spectrum of LiF using samples of a single crystal and observed the *s*-like core exciton at 61 eV in addition to the *p*-like exciton. Stott *et al.*[13] have measured the Li *K* partial yield spectrum of LiF and assigned the shoulder at 61 eV to the *s*-like exciton. Therefore, the extra peak observed on the lower-energy side of the decay peak of the *p*-like exciton in the CIS and the CFS spectra of LiCl and LiBr can be ascribed to the nonradiative decay of the *s*-like core exciton. If this is the case, the peak due to the decay of the *s*-like exciton should be also observed at about 61 eV (Refs. 12 and 13) in the CIS spectrum of LiF. However, since the enhancement of the valence-band spectrum due to the decay of the core exciton is very weak in LiF compared with that in LiCl and LiBr, the nonradiative decay of the *s*-like exciton may not be observed in the case of LiF. If the extra peak is due to the decay of the *s*-like exciton, its binding energy is estimated to be 2.9 eV and 2.5 eV for LiCl and LiBr, respectively, from the values of the excitation threshold, 62.3 eV and 61.8 eV (Ref. 10), of the Li 1*s* electron.

As another possibility, effects of the surface exciton should be considered, since the mean free path of the photoelectron has a minimum in the energy region concerned. Lapeyre and Anderson[14] have observed the surface core exciton in the CIS spectrum with the initial state at the valence band of GaAs. Saile *et al.*[15] have measured the absorption spectra of rare-gas solids with the thickness of 30—40 Å and observed the contribution of the surface exciton on the lower-energy side of the bulk one. In this case the linewidth of the surface exciton is considerably narrower than that of the bulk one. In the present CIS spectra the FWHM of the lower-energy peak is about half as much as the main peak. Therefore, these observations may suggest the possibility that the lower-energy peak is due to the surface exciton. However, from the present study alone, it is not clear whether the lower-energy peak in the CIS and the CFS spectra is caused by the *s*-like exciton or the surface exciton. To clarify this problem, other experimental results such as the measurement of the inelastic electron scattering as a function of the momentum transfer with single-crystal samples are desired for LiCl and LiBr.

To understand the *K*(exciton)-*VV* process, we attempted to determine the energy position of the Auger peak. Unfortunately, the photoelectron peak excited from the outermost *s* level of the anion overlaps with the Auger peak obtained at the photon energies close to the excitation energy of the Li 1*s* core exciton. Thus, we subtracted the peak arising from the *s* level of the anion from the raw photoelectron spectra by assuming that the intensity of the *s*-level peak is constant when the photon energy is varied in the region from 57 to 64 eV. Figure 5 shows the results of the peak positions of the Auger electron for LiF (a), LiCl (b), and LiBr (c). The ordinate of the figure indicates the increment of the kinetic energies from those of the ordinary *K*-*VV* Auger electron. The arrows in the figure indicate the transition energy from the Li 1*s* level to the bottom of the conduction band.[10] In the excitations of the Li 1*s* electron to the core-exciton states, the Auger peak shifts upward by about 1 eV from the kinetic energy of the ordinary one, whereas the shift is not observed clearly in the excitations to the continuum states. In other words, the kinetic energy of the Auger electron in the *K*(exciton)-*VV* process is greater than that of the ordinary Auger electron in lithium halides.

Energy shifts of the Auger peak are known as the post-collision interaction (PCI) in gaseous materials.[16-18] In the case of the PCI, the Coulomb repulsion between a "slow" photoelectron receding from the atom and a "fast" Auger electron emitted in the decay of that atom can produce an upward shift of the kinetic energy of the observed Auger electrons. For example, it has been reported in Xe gas that the shift of the Auger peak due to the PCI is about 0.3 eV at the ionization threshold of the core level[17] and is still observed with the excitation energies up to several hundreds of electron volts above the threshold.[18]

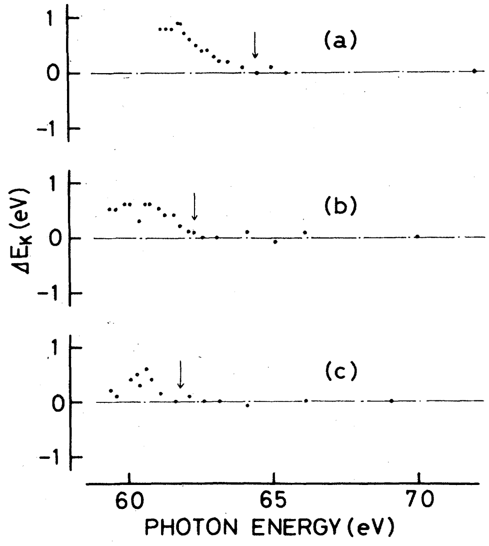

FIG. 5. Peak positions of the main Auger peak of LiF (a), LiCl (b), and LiBr (c) as a function of photon energy. Ordinates indicate the increment of the kinetic energies from the ordinary *K*-*VV* Auger peak. Arrows indicate the transition energy from the Li 1*s* level to the bottom of the conduction band (Ref. 10).

In solid substances there have been several reports on the Auger shift near the threshold energy.[5,7,19-22] Thuler *et al.*[19] have measured the resonance photoemission near the photothreshold of the $3p$ core level for Cu, Cu_2O, and CuO and observed that the $M_{2,3}$-$M_{4,5}M_{4,5}$ Auger peak does not show evidence of an energy shift near the threshold. Miller and Chiang[20] have reported a shift of Auger peak due to the PCI near the La $4d$ threshold of lanthanum compounds. Sugawara and Sasaki[5] have measured the photoelectric yield spectra of halides of potassium, rubidium, and cesium and considered that the electron forming a core exciton makes transition to the bottom of the conduction band when the core exciton undergoes the Auger decay. In their model, the Auger electron is expected to have a smaller kinetic energy than that of the ordinary Auger electron by the amount of the binding energy of the core exciton. In the present case, the upward energy shift of the Auger peak is observed in lithium halides when the photon energy is below the excitation energy of the Li 1*s* electron to the bottom of the conduction band, as seen in Fig. 5. When the Li 1*s* core exciton decays through the *K*(exciton)-*VV* process, the final state consists of two holes in the valence band, one electron in a bound state, and one electron in the continuum state. Therefore, the results discussed above suggest that the correlation energy among two holes and a bound electron in the final state plays an important role in the present case.

Recently, Igarashi[23] has calculated a three-body problem involving two holes and a single conduction electron. From his results, it is considered that the kinetic energy of the Auger electron deviates from that of the ordinary Auger electron when the photon energy is near the threshold for the core-exciton formation. This result seems to support the present conclusion in regard to the shift of the Auger peak. However, he has also suggested that the satellite peak should appear on the lower binding-energy side of the Auger peak by taking account of the screening of the conduction electron. This peak coexists with the Auger peak when the interaction between a valence hole and a conduction electron, U_{VC}, is not zero. When the correlation energy U_{VV} between two holes in the valence band is large, this satellite becomes sharp due to the formation of a true three-particle bound state. In the present case, U_{VV}'s are estimated to be between 3.5 and 5.2 eV in lithium halides from the binding energies of the Li 1*s* level and the valence band and the kinetic energy of the Auger electron (see Ref. 7), and U_{VC}'s are estimated to be about 0.4—1.0 eV from the binding energies of the exciton in the optical absorption region.[24–27] The values of the valence-band width W are about 5.1, 4.8, and 4.6 eV in LiF, LiCl, and LiBr, respectively. Thus, the present case is equivalent to the cases of $U_{VV}/(W/2)=0.7-2$ and $U_{VC}/(W/2)=0.2-0.4$ in the theoretical model. However, the satellite structure predicted by the theoretical calculation is not clearly observed in the present photoelectron spectra, as shown in Figs. 1 and 3. Therefore, it is still an open question whether the decay of the core exciton through the *K*(exciton)-*VV* process in lithium halides is not accompanied by the satellite structure, or the satellite structure becomes broadened and is buried in the background in the present case.

Next we consider the decay probability of the Li 1*s* core exciton through the *K*(exciton)-*V* process and the *K*(exciton)-*VV* process. According to Berglund and Spicer,[28] the photoelectron spectrum having energies between E and $E+\Delta E$ is given by

$$R(E)\Delta E=\frac{KC(E)n_p(h\nu)\alpha'(E)\Delta E}{\alpha(h\nu)+1/l}\ , \tag{1}$$

where K is the correction factor having a value between 0.5 and 1, $C(E)$ the threshold function, l the mean free path related to inelastic scattering of electrons with the energy E, $n_p(h\nu)$ the incident flux of photons with the energy $h\nu$, and $\alpha(h\nu)$ the absorption coefficient of the specimen. Also, $\alpha'(E)$ is the part of $\alpha(h\nu)$ due to electronic transitions from the occupied states to continuum states between E and $E+\Delta E$. Thus, the photoelectron spectrum of the valence band, I_{VB}, is expressed as

$$I_{\mathrm{VB}}\Delta E=\frac{A(E)KC(E)n_p(h\nu)}{\alpha(h\nu)+1/l}\alpha'_{\mathrm{VB}}(h\nu)\,\Delta E\ , \tag{2}$$

where $\alpha'_{\mathrm{VB}}(h\nu)$ is the part of the absorption coefficient due to the electronic transition from the valence band and $A(E)$ is the detection efficiency determined by the experimental conditions. The photoelectron intensity due to the *K*(exciton)-*V* process I_{ex} can be written, similar to Eq. (2), as

$$I_{\mathrm{ex}}\Delta E=\frac{A(E)KC(E)n_p(h\nu)}{\alpha(h\nu)+1/l}\alpha'_{\mathrm{ex}}(h\nu)P\,\Delta E\ , \tag{3}$$

where $\alpha'_{\mathrm{ex}}(h\nu)$ is the part of the absorption coefficient due to the formation of the core exciton and P is the decay probability of the core exciton through the *K*(exciton)-*V* process. Therefore, from Eqs. (2) and (3), the probability P is expressed as

$$P=\frac{I_{\mathrm{ex}}/I_{\mathrm{VB}}}{\alpha'_{\mathrm{ex}}(h\nu)/\alpha'_{\mathrm{VB}}(h\nu)}\ . \tag{4}$$

It should be noticed that all of the unknown factors such as $A(E)$, K, $C(E)$, $n_p(h\nu)$, and l do not appear in Eq. (4) and the probability P can be determined experimentally. The value of $I_{\mathrm{ex}}/I_{\mathrm{VB}}$ is estimated from the ratio of the main peak to background intensity in the CIS spectra shown in Figs. 2 and 4. On the other hand, the value of $\alpha'_{\mathrm{ex}}(h\nu)/\alpha'_{\mathrm{VB}}(h\nu)$ cannot be simply estimated from the absorption spectra alone, since the absorption below the Li 1*s* core excitation energy contains two kinds of electronic transitions, i.e., the transition from the valence band to the conduction band and the one from the outermost *s* level of the anion to the conduction band. Thus, the value of $\alpha'_{\mathrm{ex}}(h\nu)/\alpha'_{\mathrm{VB}}(h\nu)$ is derived from the absorption spectra obtained by Haensel *et al.*[9] and the photoelectron spectrum excited with the photon energy below 58 eV, under the assumption that the ratio of the integrated intensities of the valence band and the outermost *s* level observed in the photoelectron spectrum is the same as the ratio of the absorption coefficients $\alpha'_{\mathrm{VB}}(h\nu)/\alpha'_s(h\nu)$, where $\alpha'_s(h\nu)$ is the part of the absorption coefficient due to the electronic transition from the outermost *s* level.

Under the assumption that the escape functions and the mean free path of the Auger electron via the *K*(exciton)-*VV* process are approximately the same as those of the photoelectron excited directly from the valence band, the decay probability P' of the *K*(exciton)-*VV* process is also expressed as follows:

$$P'\simeq P\frac{S_{\mathrm{Aug}}}{S_{\mathrm{VB}}}\ . \tag{5}$$

Here, S_{Aug} and S_{VB} are the integrated intensity of the Auger peaks due to the *K*(exciton)-*VV* process and the increase of the valence-band intensity due to the *K*(exciton)-*V* process at the photon energy equal to the Li 1*s* core exciton, respectively. The results are given in Table I (Ref. 29).

The decay probability of the *K*(exciton)-*V* process increases systematically in lithium halides when the atomic number of the anion is increased. Since the ionicity of these substances decreases in going from LiF to LiBr (Ref. 30), it is supposed that the decay probability depends

TABLE I. Decay probability of the Li 1*s* core exciton through the *K*(exciton)-*V* process and the *K*(exciton)-*VV* process at the photon energy of the core-exciton peak. All quantities are given in units of percent.

	LiF	LiCl	LiBr
K(exciton)-*V*	9	14	19
K(exciton)-*VV*	47	43	81

on the delocalization of the valence-band wave function from LiF to LiBr.

The decay probability subject to the K(exciton)-VV process may contain some ambiguity in the estimation of the intensity of the Auger electron S_{Aug}. Moreover, other nonradiative decay channels via the outermost s level of the anions, i.e., the K(exciton)-$M_1(N_1)$ process, the K(exciton)-$M_1(N_1)V$ process, and so on, contribute to the spectra in the energy region concerned. Therefore, the values in the lower row of Table I are not definite ones but qualitative ratios of the decay probability between the K(exciton)-V process and the K(exciton)-VV process among lithium halides.

The decay probability of the K(exciton)-VV process in lithium halides is a few times larger than that of the K(exciton)-V process. The present result is different from the results reported by Haensel *et al.*[4] and Sugawara and Sasaki.[5] They reported that the decay through direct electron-hole recombination, which corresponds to the K(exciton)-V process, is dominant in NaCl and in the halides of potassium, rubidium, and cesium, and that the Auger decay, which corresponds to the K(exciton)-VV process, is negligible in these halides.

It is worthwhile noting that the shape of the valence band of LiCl and LiBr changes in the photon-energy region where the K(exciton)-V process is observed in the CIS spectrum. The shoulder at the binding energy of 3.0 eV in the photoelectron spectra in Fig. 1 is about half as much as the main peak when the excitation photon energy is below 58.6 eV or above 62.1 eV. On the other hand, its intensity rises up to 80% of the main peak at the excitation energy of the core exciton. This tendency is more clear in the case of LiBr. The higher binding-energy peak of the valence band has about 60% intensity of the lower-energy peak away from resonance, while at resonance it is more intense than the lower-energy peak. Moreover, the energy difference between two peaks is slightly reduced at resonance. The change of the valence-band shape under the K(exciton)-V process might contain more information on the decay process of the core exciton, and further analyses of this point are under way.

Finally, as seen in Figs. 2 and 4, the CIS spectra show no structure when the photon energy is beyond 61 eV, in contrast to the CFS and the absorption spectra. This indicates that the Li 1s core exciton decays through the K(exciton)-V process but the electron photoexcited into the conduction band can scarcely recombine with the Li 1s hole. In other words, the enhancement of the CIS spectra is the experimental evidence of the existence of the core exciton below the absorption threshold.

In conclusion, the present photoelectron spectra of LiCl and LiBr show the resonant behavior around the photon energy of the excitation energy of the Li 1s core exciton, and this result is interpreted in terms of the two decay processes of the Li 1s core exciton, the K(exciton)-V process and the K(exciton)-VV process. In LiCl and LiBr, the extra peak is observed on the low-energy side of the main peak in the CIS and the CFS spectra, and this peak may be ascribed to the s-like exciton or the surface exciton. The decay probability of the Li 1s core exciton through two processes is roughly estimated, and it is shown that the K(exciton)-VV process is the predominant decay process in lithium halides and that the decay probability of the K(exciton)-V process increases systematically when the atomic number of the anion is increased. The kinetic energy of the Auger electron due to the K(exciton)-VV process is about 1 eV larger than that of the ordinary K-VV Auger electron. It suggests that the correlation energy in the configuration involving two holes in the valence band and the electron bound to them results in an important role for the kinetic energy of the Auger electron in lithium halides.

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[29] In the case of LiBr, the shape of the valence band changes when the excitation photon energy is changed around the energy of the Li 1s core exciton, as discussed later. We used two different ways to determine the probability P: (a) a simple intensity ratio $I_{\mathrm{ex}}/I_{\mathrm{VB}}$ obtained from the CIS spectrum, and (b) an integrated intensity ratio $S_{\mathrm{ex}}/S_{\mathrm{VB}}$ of the valence band. The results obtained with both methods agree to within ±5%. The estimation of the decay probabilities through the K(exciton)-V process and the K(exciton)-VV process is strongly dependent on the absorption spectra. So we have attempted to estimate the probability by using the data obtained by F. C. Brown, C. Gähwiller, A. B. Kunz, and N. O. Lipari [Phys. Rev. Lett. **25**, 927 (1970)]. The results show similar dependence on substances. However, the probabilities are a few times larger than those shown in Table I, and the total probabilities of two processes are in excess of 100% for all samples measured here. Therefore, we did not use the values obtained from their data.

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