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Core-exciton decay and change in the valence-band spectra of LiCl and LiBr

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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. The drastic change in the shape of the valence-band spectra was observed in accordance with the enhancement of the intensity when photon energies are varied around the excitation energy of the Li 1*s* core exciton. This change is attributed to the nonuniform distribution of the lithium-derived states in the valence band. To interpret the broadening of the valence-band spectra, it is proposed that the core exciton relaxes during the decay transferring its energy to a valence electron.

I. INTRODUCTION

Resonant photoemission has been observed for various *d*- and *f*-band metals[1–5] and their compounds,[6–10] semiconductors,[11–13] and ionic crystals.[14–16] The technique of the resonance photoemission uses the fact that the coupling between different photoexcitation channels changes the spectral shape and/or intensity of the valence-band photoemission when the excitation-photon energy is varied around a core absorption edge. Most measurements using this technique have been applied to enhance weak emissions, such as 3*d* (Ref. 8) shake-up satellite in Ni (Refs. 1–3) and to separate emissions of different valence states in mixed-valence materials.[9,10]

In semiconductors and ionic crystals the resonance due to the decay of the core exciton occurs near the excitation-photon energy of the core exciton.[11–16] Previously, we measured photoelectron spectra of lithium halides with the photon energies near the excitation energy of the Li 1*s* core exciton and observed the enhancement of intensities of the valence band and the Auger-electron peak.[15,16] These enhancements have been interpreted in terms of the *K*(exciton)-*V* process and the *K*(exciton)-*VV* process, where *K*(exciton) denotes the initial state with *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 states of these processes are different from each other, we could easily separate these two decay processes of the core exciton from each other in the case of lithium halides.

In this study, we report changes in the valence-band spectra of LiCl and LiBr in more detail. The changes will be discussed with the *K*(exciton)-*V* decay process of the Li 1*s* core exciton,[15,16] in which the Li 1*s* core exciton directly recombines, transferring its energy to a valence electron.

II. EXPERIMENTAL PROCEDURE

The experiment was performed by using synchrotron radiation from a storage ring at the Institute for Solid State Physics of the University of Tokyo as a light source. A double stage cylindrical mirror analyzer and a modified Rowland-mount monochromator were used to obtain photoelectron spectra. The total spectral resolution (i.e., combined monochromator and electron-energy analyzer resolutions) was about 0.4 eV. The base pressure in the sample chamber was about 4×10^{-8} Pa and rose to a 10^{-6} range during evaporation. The pressure in the analyzer chamber was about 7×10^{-9} Pa during measurements.

Since charging of samples can result in a shift and a broadening of the structures in the photoelectron spectra, studies were made on thin films which were evaporated onto gold substrates *in situ*. To see the effect of the charging of the samples we measured the Li 1*s* electron excited by the second-order light from the monochromator (with a photon energy twice as much as the first-order photon energy) simultaneously with the valence electron. This peak position did not indicate any energy shift due to the charging of the samples. Thus, we believe the spectrum is not influenced by the charging of the samples in the present case.

III. RESULTS AND DISCUSSION

Figures 1 and 2 show a set of photoelectron spectra of LiCl and LiBr, respectively, obtained with various excitation-photon energies around the Li 1*s* threshold. The excitation energies are given on the right-hand side of each spectrum. The binding energies are measured relative to the top of the valence band. The intensity of the spectra is normalized to the incident photon flux. The intensity of the valence band is enhanced around the photon energies of the excitation energy of the Li 1*s* core exciton, i.e., 60.7 eV for LiCl and 60.4 eV for LiBr. This enhancement has been interpreted in terms of nonradiative decay of the core exciton through the *K*(exciton)-*V* process[15,16] which leaves a hole in the valence band and an electron in the continuum state after the annihilation of the core exciton. The final state of this process is the same as that of the direct photoexcitation of the valence band.

The valence-band spectra of LiCl have a prominent peak *A* and a shoulder *B* around 1.4 and 3.3 eV at first sight, respectively. It is noted from the detailed observation of Fig. 1 that the shape of the valence-band spectra varies in the photon-energy region where the *K*(exciton)-*V*

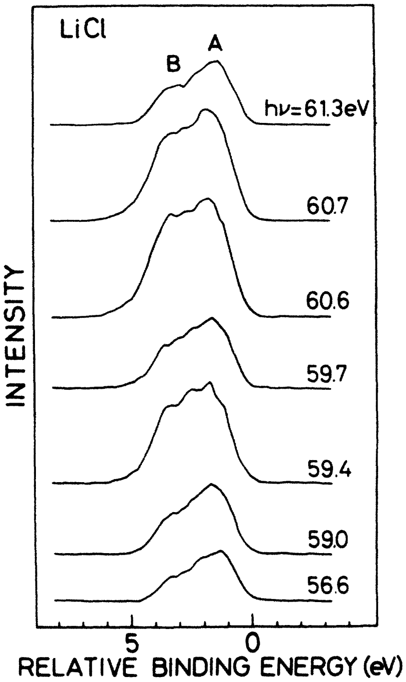

FIG. 1. Set of photoelectron spectra of the valence region of LiCl excited with photon energies around the excitation energy of the Li 1*s* core exciton. Intensities are normalized to the incident photon flux.

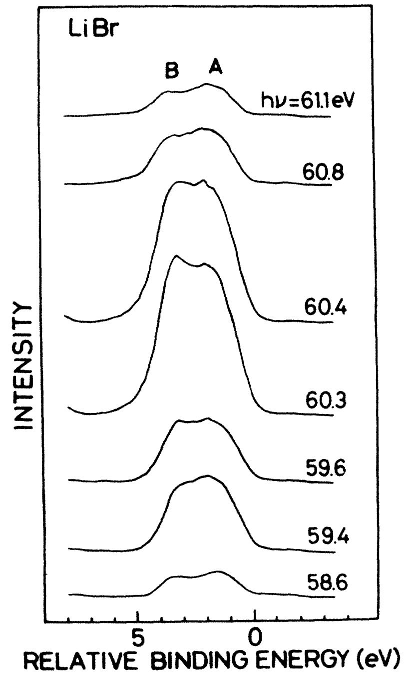

FIG. 2. Set of photoelectron spectra of the valence region of LiBr excited with photon energies around the excitation energy of the Li 1*s* core exciton. Intensities are normalized to the incident photon flux.

process is observed. For example, the intensity of the shoulder *B* is about half as much as that of the peak *A* when the excitation energy is below 59 eV and above 61.3 eV. On the other hand, its intensity rises up to 80% of the peak *A* at resonance, i.e., at the excitation energy of the core exciton. More drastic changes in the spectral profile occur in LiBr as shown in Fig. 2. The valence-band spectra of LiBr clearly show two peaks *A* and *B* in all the spectra. The higher binding-energy peak *B* has about 60% intensity of the lower energy peak *A* away from resonance, while at resonance the former is more intense than the latter. Moreover, the energy difference between the two peaks is reduced from 1.8 to 1.3 eV at resonance, and the bandwidth is wider at resonance than that observed away from resonance.

It is well known that the charging of the samples also causes the broadening and the shift of the observed spectra. However, there were no charging effects in the present case as mentioned above, and therefore, the broadening and the change in the shape of the valence-band spectra are caused by the intrinsic character originating from the electronic structure of the specimen.

Pong and Smith[17] have measured the photoelectron spectra of LiCl with the excitation energies below 21.1 eV. These spectra also show two peaks in the valence band, but the peak on the higher binding energy side is more intense than that on the lower energy side in contrast with the present results. It implies that the spectral profile depends on the excitation-photon energy. Such dependence is caused by different intensity changes in each structure in the spectra, i.e., by different dependence of the photoionization cross sections of the constituent character of each band on the photon energy. Freeouf *et al.*[18] have studied this dependence of gold in the photon energy range between 15 and 90 eV using synchrotron radiation. They showed that for $h\nu \leqq 30$ eV the spectra of the valence band are strongly modulated by matrix elements, whereas above this photon energy the spectra reflect structures in the one-electron density of states. In fact, the spectral profile of the valence band of LiCl and LiBr, which was reported by Poole *et al.*[19] using the excitation-photon energy of 40.81 eV, is similar to that of the present spectra obtained with the photon energies below 56.6 eV and above 61.3 eV. In the present case the spectral profile of the valence-band spectra varies in the limited energy range, i.e., between 59 and 61.3 eV, where the Li 1*s* core exciton is observed in the absorption spectrum. Therefore, the change in the spectral profile in this energy range should be related to the photoexcitation of the core exciton and its successive decay through the K(exciton)-V process, and not to the matrix elements and the joint density of states.

A clear view of the change in the spectral profile under the K(exciton)-V process is shown in Fig. 3, where the valence-band spectrum of LiCl obtained with the excitation-photon energy of the Li 1*s* core exciton ($h\nu = 60.7$ eV) is shown by the dotted line, and the solid line represents the spectrum taken at 56.6 eV which is far below the Li 1*s* threshold. The intensities of these spectra are normalized at the binding energy of 1.4 eV, at which the main peak is observed in the valence-band spectra

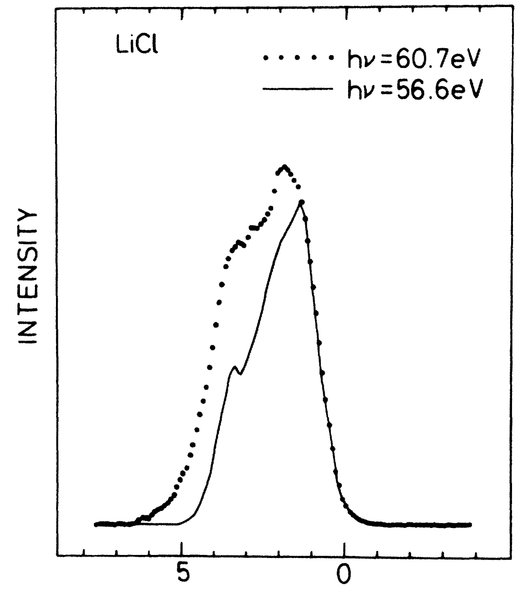

FIG. 3. Comparison of the spectral profile of LiCl measured below the onset of the Li 1*s* absorption (56.6 eV) with that taken at resonance (60.7 eV). Dotted and solid lines indicate the spectra taken at 60.7 and 56.6 eV, respectively. Linear background was subtracted from both spectra.

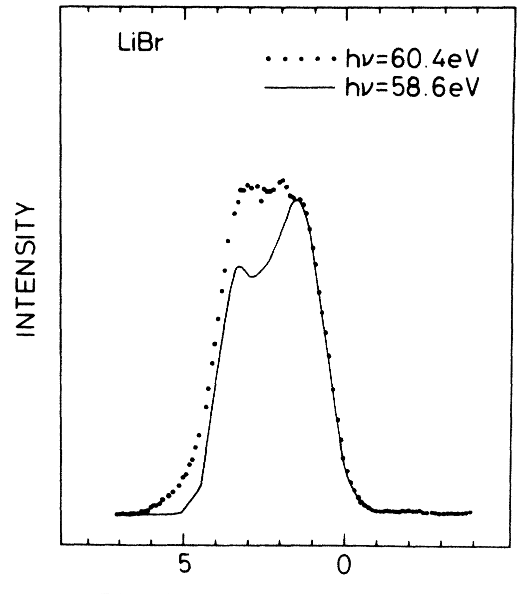

FIG. 4. Comparison of the spectral profile of LiBr measured below the onset of the Li 1*s* absorption (58.6 eV) with that taken at resonance (60.4 eV). Dotted and solid lines indicate the spectra taken at 60.4 and 58.6 eV, respectively. Linear background was subtracted from both spectra.

measured with the photon energies below 56.6 and above 61.3 eV, after a linear background has been subtracted. When the photon energy coincides with the core-exciton peak observed in the absorption spectrum, the main peak in the valence-band spectrum of LiCl appears on about 0.5 eV higher binding-energy side of that measured with the photon energy of 56.6 eV, while the shoulder *B* is located at almost the same binding energy. Moreover, the spectrum taken at resonance extends to the higher binding-energy side, while the shape on the lower binding-energy side of the spectrum coincides well with that of the spectrum taken away from resonance. The peak shift and broadening of the spectra are observed only when the photon energies are close to the excitation energy of the Li 1*s* core exciton.

Similar comparison between the spectra of LiBr is given in Fig. 4. The spectrum measured with the photon energy of the core-exciton peak is shown by the dotted line, and the solid line represents the spectrum measured with the photon energy of 58.6 eV which is below the onset of the Li 1*s* absorption. Two new peaks can be recognized at 2 and 3.1 eV in the spectrum taken at resonance ($h\nu=60.4$ eV). Moreover, the spectrum extends to the higher binding-energy side. The change in the spectral profile clearly occurs under the *K*(exciton)-*V* process in LiBr.

The present results mentioned above suggest that the probability of the excitation of each valence electron due to the *K*(exciton)-*V* process is not the same as that due to the direct photoexcitation of this valence electron, and an electron existing at some singular points of the valence band is selectively excited at the annihilation of the core exciton. Thus, we subtracted the spectrum measured with the photon energy of 56.6 eV for LiCl or 58.6 eV for LiBr, which is below the onset of the Li 1*s* absorption, from the raw spectra measured with the photon energies close to the excitation energy of the core exciton. This procedure leads us to a better understanding of at what singular points of energy bands electrons are selectively excited through the *K*(exciton)-*V* process. The results of LiCl and LiBr are shown in Figs. 5 and 6, respectively.

In these figures the energy bands calculated by Kunz[20] with nonrelativistic self-consistent Hartree-Fock theory are also shown. The difference spectra of LiCl show two new peaks at about 1.9 and 2.8 eV which are labeled *C* and *D*, respectively. The peak *C* seems to correspond to the X'_5 state, while there is no singular point corresponding to the peak *D* in the calculated energy bands. In the case of LiBr the difference spectra show two new peaks labeled *C* and *D* whose binding energies are 2.0 and 3.1 eV, respectively. The peaks *C* and *D* may correspond to the X'_5 and X'_4 states, respectively. The singular points corresponding to the peaks *A* and *B* in the spectra of LiCl and of LiBr are not seen in the calculated energy bands. Thus, these peaks may arise from the other singular points where the calculation is not carried out by Kunz.[20] These results give direct suggestion that the states at *X* and some points in the *k* space are more enhanced than that at the Γ point when the core exciton annihilates through the *K*(exciton)-*V* process.

It is well known that the valence band of the lithium halides is mainly composed of *p* states of the halogen ion. According to Pauling[21] the covalency of these substances increases in going from LiF to LiBr. In other words, the amount of the mixing of the states derived from the lithium ion into the valence band increases with increasing the atomic number of the halogen ion. This amount might affect the probability of the energy transfer from the core exciton to a valence electron when the core exciton annihilates through the *K*(exciton)-*V* process, since the Li 1*s* core exciton is essentially of Frenkel type localized at the lithium site. In fact, the probability of the *K*(exciton)-*V* process among the various decay processes of the Li 1*s* core exciton increases in going from LiF to LiBr (Ref. 16). Therefore, the results discussed above suggest that the lithium-derived states are not uniformly distributed in the valence band, mainly composed of *p* character derived from the halogen ion, and the mixing seems to be little at the Γ point (see Figs. 5 and 6).

Next, we consider the broadening of the valence spectra caused by the *K*(exciton)-*V* process. The full width at half maximum (FWHM) of the valence-band spectrum may be estimated experimentally with better accuracy than the full width of the valence band because of the uncertainty of the boundaries between the valence band and background intensity. However, the FWHM has less significance, since the spectral profile of the valence band of lithium halides is largely asymmetric as seen in Figs. 1 and 2. Thus, we measured the full width at 10% of the maximum of the valence spectra. The results are plotted in Figs. 7(a) and 7(b) for LiCl and LiBr, respectively. The Li *K* absorption spectra of LiCl and LiBr obtained by Haensel *et al.*[22] are also shown with the solid line for reference.

The widths of the valence spectra are broadened about 0.8 and 0.7 eV for LiCl and LiBr, respectively, at the photon energies close to the core-exciton peak, and this increment of the bandwidth is only observed in the photon-energy region where the intensity of the valence spectrum is enhanced due to the *K*(exciton)-*V* process. It should be noted that the broadening of the width is only observed on the higher binding-energy side of the valence spectra as mentioned above. These results lead to the direct suggestion that the energy transferred to a valence electron during the *K*(exciton)-*V* process is the same as, or less than the excitation energy of the core exciton. In other words, the core exciton causes some relaxation during the decay transferring its energy to a valence electron.

The optical properties and nonradiative decay of the core exciton may be dominated by the strong coupling of the electron with lattice modes of various frequencies and symmetries around the core exciton.[23] This complex situation can be enormously simplified by assuming that the

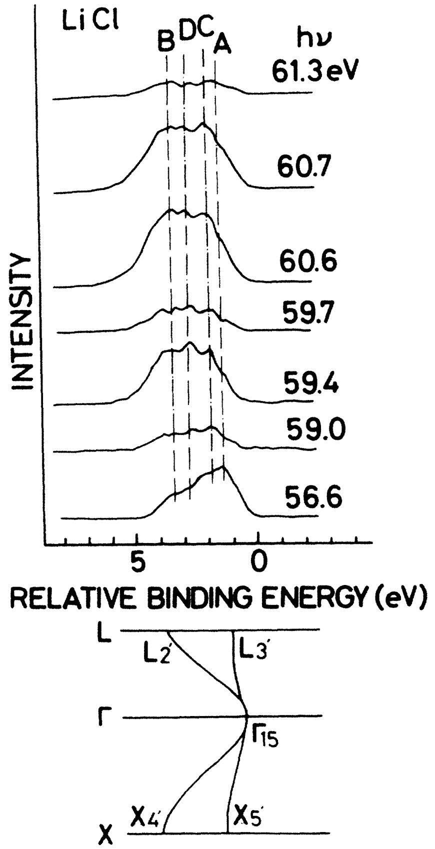

FIG. 5. Difference spectra of LiCl. Difference spectra were obtained with subtracting the spectrum taken at 56.6 eV from each raw spectrum. Raw spectrum taken at 56.6 eV and the energy bands calculated by Kunz (Ref. 20) are also shown.

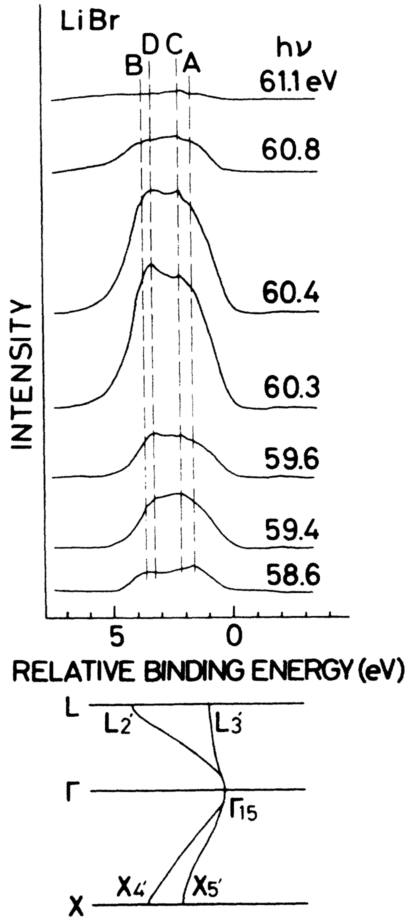

FIG. 6. Difference spectra of LiBr. Difference spectra were obtained with subtracting the spectrum taken at 58.6 eV from each raw spectrum. Raw spectrum taken at 58.6 eV and the energy bands calculated by Kunz (Ref. 20) are also shown.

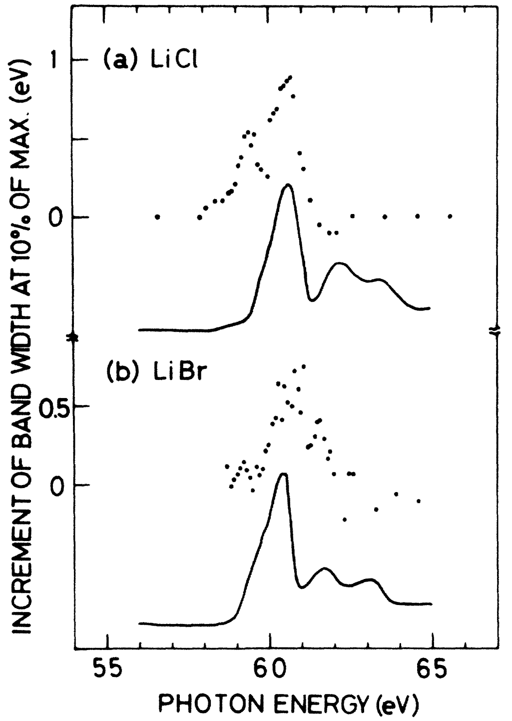

FIG. 7. Increment of the valence-band width at 10% of the maximum for (a) LiCl and (b) LiBr. Li *K* absorption spectra of LiCl and LiBr obtained by Haensel *et al.* (Ref. 22) are also shown by the solid lines.

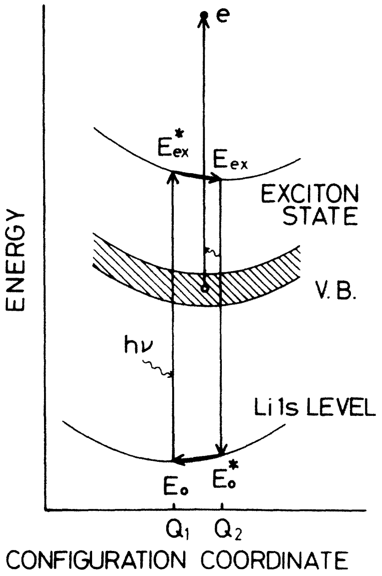

FIG. 8. Schematic energy diagram for the Li 1*s* level and exciton states of lithium halides as a function of the configuration coordinate *Q*.

essential electron-phonon coupling can be described by a single mode *Q* of a fixed frequency value. This leads to a representation in which the energy of each electronic state depends on the "configuration coordinate" *Q*, as illustrated in Fig. 8. Soft x-ray absorption transfers the electron from the minimum of the ground-state curve (E_0; Li 1*s* level) into the nonequilibrium excited state $E^*_{\rm ex}$ (core-exciton state) in a Frank-Condon transition, producing the core exciton. If rapid relaxation occurs with phonon emission, this changes the configuration to the new value Q_2 and brings the system into thermal equilibrium at the relaxed excited state $E_{\rm ex}$. The transition after this relaxation should occur between $E_{\rm ex}$ and E^*_0 transferring the energy to a valence electron, and subsequent relaxation from E^*_0 to E_0 follows it. Because the system might not reach so rapidly the relaxed excited state, the energy transferred to the valence electron during the annihilation of the core exciton through the *K*(exciton)-*V* process is the same as, or less than the creation energy of the core exciton (namely, between $E^*_{\rm ex}-E_0$ and $E_{\rm ex}-E^*_0$).

The maximum energy of the relaxation is roughly estimated to be about 0.8 and 0.7 eV for LiCl and LiBr, respectively. The experimental suggestion of the relaxation of the Li 1*s* core exciton during its decay has been reported by Arakawa and Williams.[24] They have measured the soft x-ray emission spectra of lithium halides and reported that the emission band due to the radiative decay of the core exciton appears on the lower energy side of the absorption peak. These facts suggest that the Li 1*s* core exciton in lithium halides relaxes during the radiative or nonradiative decay.

It is noted that the bandwidth has a maximum at about the photon energy corresponding to the excitation energy of the core exciton and decreases with increasing the photon energy to the threshold of the conduction band. This result suggests that the electron excited to the higher energy states of the core exciton, i.e., *ns* and *np* exciton states ($n \geqq 2$), does not simply relax to the lowest relaxed excited state of the core exciton, because if the *ns* or *np* core exciton relaxes to the lowest relaxed excited state of the 1*s* exciton (namely, $E_{\rm ex}$), the observed bandwidth is expected to monotonously increase and has a maximum at the photon energy corresponding to the excitation energy into the bottom of the conduction band as the excitation-photon energy is increased. Therefore, in order to explain the present results shown in Fig. 7, it might be considered that the *ns* or *np* core exciton will relax into its own relaxed state. However, details of this point are still not understood.

In summary, the valence-band spectra of LiCl and LiBr were measured with the photon energies around the excitation energy of the Li 1*s* core exciton, and the following results are obtained. The shape and the width of the valence spectrum vary in accordance with the enhancement of the intensity when the photon energies are close to the excitation energy of the core exciton. These changes are attributed to nonuniform distribution of the lithium-derived states in the valence band and to the relaxation of the core exciton during the decay through the *K*(exciton)-*V* process.

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