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Photoelectron spectroscopic study of decay process of Li 1*s*—core exciton in LiF

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The decay process of the Li 1*s*—core exciton in LiF was investigated by means of photoelectron spectroscopy. The enhancement of the intensities of the valence band and the Auger peak was observed at the photon energy corresponding to the excitation energy of the Li 1*s*—core exciton. Two nonradiative decay processes of the core exciton, *K*(exciton)-*V* process and *K*(exciton)-*VV* process, were proposed to interpret the resonant behavior in the constant-initial-state spectrum with the initial state at the peak of the valence band and in the constant-final-state spectrum with the final state corresponding to the kinetic energy of the Auger electron. It was also suggested that, in the *K*(exciton)-*VV* process, which is a predominant nonradiative decay process in LiF, the excited electron in a bound state affects the kinetic energy of the Auger electron.

I. INTRODUCTION

The fundamental absorption spectra of alkali halides are characterized by sharp exciton peaks near the threshold. The decay mechanism of the exciton has been investigated by many authors,[1] and there are several decay channels in which the exciton loses its energy radiatively or nonradiatively; edge emission, luminescence of self-trapped excitons, creation of the Frenkel defects, interaction with phonons or impurities, and so on.

In contrast, with regard to the core exciton which appears below the threshold energy in the soft-x-ray absorption spectra, several groups[2–6] studied its decay mechanism with different methods and suggested possible decay processes. Arakawa and Williams[2] measured the emission spectrum of lithium halides with electron bombardments and ascribed one of the observed peaks to the radiative decay of a core exciton. However, the intensity distribution of the soft-x-ray spectra of the halides depends appreciably on the energy and intensity of bombarding electrons and changes rapidly with time. Aita *et al.*[3] tried to investigate the presence of the radiative decay of a core exciton in the soft-x-ray emission spectra of LiF produced by the fluorescence excitation method. 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 continuum radiation by the exciton and continuum state. Haensel *et al.*[4] and Sugawara and Sasaki[5] measured photoelectric yield spectra of NaCl and those of the halides of potassium, rubidium, and cesium, respectively, by changing the retarding potential. They discussed several decay mechanisms of the core exciton and identified certain peaks in the yield spectra as being due to the core-exciton decay through electron-hole recombination with simultaneous excitation of another electron from the valence band to continuum state. In principle, the information on the decay processes of core excitons is implicit in the family of the yield spectra measured at closely spaced retarding potentials. In practice, however, detailed differences in intensity in adjacent retarding-potential-yield spectra are difficult to determine, so that the studies on the decay processes of core excitons have been restricted in scope. Lapeyre *et al.*[6] measured the photoelectron spectra of KI and ascribed the peak in the constant initial state (CIS) and constant final state (CFS) spectra to the direct recombination decay and Auger decay of the core exciton, respectively. However, the decay processes of the core exciton do not become clear from their experiment, because the peaks of the secondary electrons in the photoelectron spectrum overlap with the Auger peak due to the core-exciton decay.

The purpose of the present study is to obtain the information on the decay process of the core exciton in alkali halides by means of photoelectron spectroscopy. Lithium fluoride is selected for discussion because its 1*s* core exciton appears in the photon-energy region suitable for the present experiment. Furthermore, the results obtained in the present study might provide information on the resonant photoemission phenomena which have attracted recent attention.[7]

II. EXPERIMENTAL

The data were obtained with an ultrahigh-vacuum photoelectron spectrometer. 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, and it was monochromatized with a 2-m grazing incidence monochromator of a modified Rowland-mount type. 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 energy distribution of the emitted electrons was measured with a double-stage electrostatic energy analyzer of the cylindrical mirror type. The analyzer resolution was constant with full width at half maximum (FWHM) of 0.8 eV.

Since charging of the samples can result in a shift and broadening of the structures in the photoelectron spectrum, very thin samples were evaporated onto gold *in situ*. The base pressure in the sample chamber was about 3×10^{-7} Pa and rose to 10^{-6} Pa range during evaporation. The pressure in the spectrometer was about 3×10^{-8} Pa during measurements. The thickness was estimated to be about 100 Å with an oscillating quartz thickness gauge. No charging effects such as the shift and broadening of the structures were found in the observed photoelectron spectra. The spectral dependence of the incident radiation on the samples was determined from the photoelectric yield spectrum of gold.

III. EXPERIMENTAL RESULTS

Figure 1 shows a set of photoelectron spectra of LiF obtained with various excitation photon energies around the energy of the Li 1*s*—core exciton. The binding energies are given relative to the top of the valence band. The ordinate is proportional to the photoelectrons per incident photon. The spectrum obtained with the excitation photon energy of 57 eV is the same as that reported by Gudat *et al.*,[8] which was measured with the photon energy of 120 eV in the binding-energy range of 0—30 eV. In addition to the valence band and the F 2*s* band located at 24.5 eV, structures are observed around 18 and 27 eV which may arise from secondary processes such as plasmon excitations.[8—10] Moreover, the Auger peak is observed at the relative kinetic energy of about 42 eV when the excitation photon energy is beyond 61 eV. The energy scale of the kinetic energy is presented relative to the top of the valence band for convenience. The intensity of the Auger peak shows the maximum at the excitation photon energy of 61.9 eV, which corresponds to the energy of the core exciton. At this photon energy, the intensity of the valence band has also the maximum. These phenomena are more visual in the CIS spectrum with the initial state at the peak of the valence band and in the CFS spectrum with the final state corresponding to the kinetic energy of the Auger electron. They are shown in Fig. 2 together with the Li *K* absorption spectrum of LiF obtained by Haensel *et al.*[11] As seen in this figure, the CIS and CFS spectra show the resonant behavior at 61.9 eV, which is the energy of the Li 1*s*—core exciton. The peak in the CIS and CFS spectra has the same FWHM of 1 eV as the core-exciton peak in the absorption spectrum, while the background intensity is different among these three spectra. In the photon-energy region above 64.5 eV, the structure in the CFS spectrum corresponds to that in the absorption spectrum although the 67-eV peak due to the direct photoexcitation from the F 2*s* level overlaps with the CFS spectrum. In the CIS spectrum no clear peaks are evident in the same energy region.

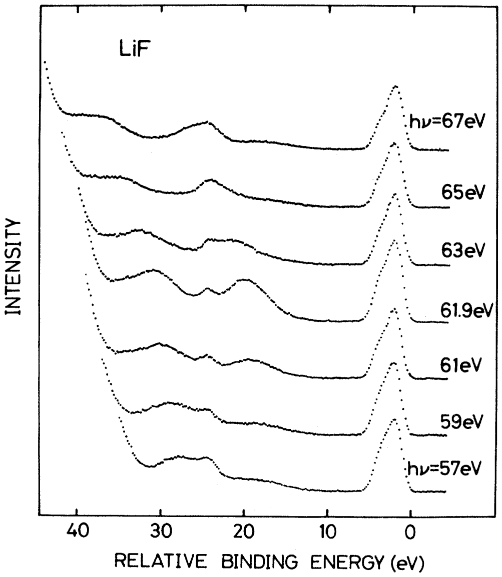

FIG. 1. Set of photoelectron spectra of LiF excited with photon energies around the excitation energy of the Li 1*s*—core exciton. Intensities are normalized to the incident photon.

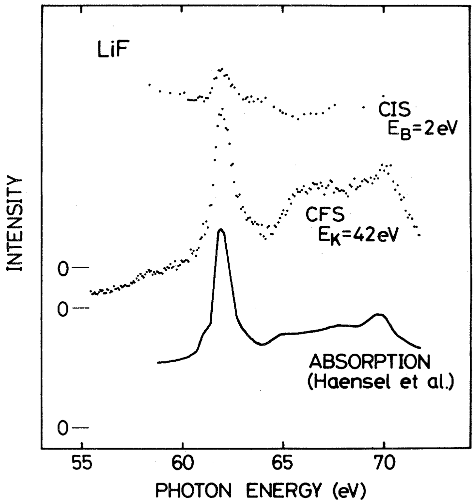

FIG. 2. CIS and CFS spectra of which initial binding energy and final kinetic energy are 2 and 42 eV, respectively, and also the Li *K* absorption spectrum obtained by Haensel *et al.* (Ref. 11).

IV. DISCUSSION

As mentioned in Sec. I, the decay mechanism of the core exciton was investigated by several groups and following decay processes have been proposed[2—6,12]: (a) radiative recombination, (b) thermal decay via exciton phonon scattering, (c) nonradiative decay due to direct recombination of electron and hole, and (d) Auger decay resulting in two excited electrons and two holes. Among them, processes (c) and (d) contribute to photoemission. Thus these processes will be discussed in detail and further analyses of these processes will be presented in order to interpret the present experimental results.

A Li 1*s*—core hole and an electron which form a Li 1*s*—core exciton may recombine directly with the energy being transferred to a valence electron. This decay process corresponds to process (c) mentioned above and is shown schematically in Fig. 3(a). The final state of this process has a configuration involving one hole in the valence band and one electron in the continuum state. This process is 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 state with

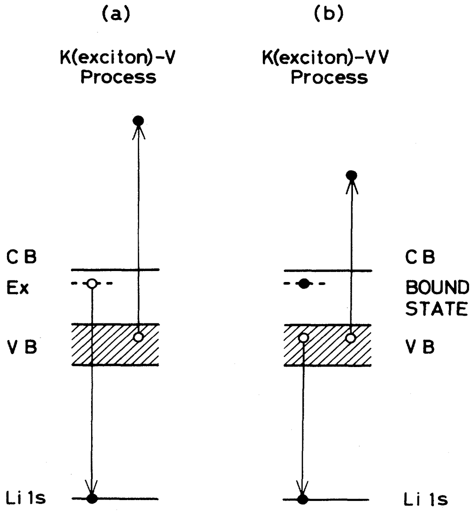

FIG. 3. Schematic illustrations of nonradiative decay processes of the Li 1s—core exciton. (a) K(exciton)-V process of which the final-state configuration involves one hole in the valence band and one electron in the continuum state. (b) K(exciton)-VV process of which the final-state configuration involves two holes in the valence band, one electron in the bound state, and one electron in the continuum state. The arrows show one of the possible electronic transitions resulting in the final-state configuration.

a hole in the valence band. Since the final-state configuration is the same as that in the direct photoexcitation from the valence band, the experimental evidence of the K(exciton)-V process of the core-exciton decay will be observed as a resonance enhancement in the CIS spectrum with the initial state at the peak of the valence band. In fact, the resonant behavior at the energy of the core exciton is clearly seen in Fig. 2, even though it is about one fifth of the background intensitv.

Process (d) is called the "K(exciton)-VV process" and is shown schematically in Fig. 3(b). The Li 1s—core hole forming a core exciton can recombine with a valence electron, and the energy is transferred to another valence electron which is excited to the continuum state. Then, the final state has a configuration involving two holes in the valence band, one electron in a bound state, and one electron in the continuum state. The evidence of this process will be observed in the CFS spectrum at the kinetic energy of the Auger electron. As seen in Fig. 2, the prominent peak appears at 61.9 eV in the CFS spectrum which corresponds to the energy of the Li 1s—core exciton. At $h\nu=61.9$ eV, the shakeup process accompanying the K(exciton)-V process or the direct photoexcitation from the valence band also leaves the system in the same final configuration as that of the K(exciton)-VV process, and these two processes are indistinguishable. However, the satellite structures due to nonresonant shakeup, which have been observed in Ni,[13] Cu,[14] and GaP,[15] for example, are not appreciable in the photoelectron spectra of LiF with excitation photon energy below 61 eV and above 64 eV. The energy position and the FWHM of the 61.9-eV peak in the CFS spectrum are in good agreement with those of the absorption spectrum. The shakeup process probably makes a smaller contribution to the core-exciton decay than the K(exciton)-VV process in LiF, even though the shakeup process may exist.

Previous authors have not taken the initially photoexcited electron into consideration in process (d).[4–6] Its role in the decay process of the core exciton has not been clearly understood yet. Now, the present authors would stress that at the final state of the K(exciton)-VV process, one electron is bound to some level below the conduction band but not in the continuum state. In order to clarify this point, the valence band, its secondaries, and the F 2s band were subtracted from the raw photoelectron spectra numerically, on the assumption that their intensity ratios do not depend on the photon energy in the energy region concerned. The spectrum obtained with the excitation photon energy of 80.7 eV was used as a reference for subtraction. The difference photoelectron spectra, which mean the Auger spectra produced with various excitation photon energies, are shown in Fig. 4. The energy position of the Auger peak in the difference photoelectron spectra with photon energies of 72 and 64.5 eV is in good agreement with the broken line, which shows the energy position of the Auger peak in the raw photoelectron spectrum with the excitation photon energy of 80.7 eV. This result indicates that when the excitation photon energy is larger than the threshold of the Li 1s—to—conduction-band transition [64.4 eV (Ref. 16)], the excited electron acts as a free elec-

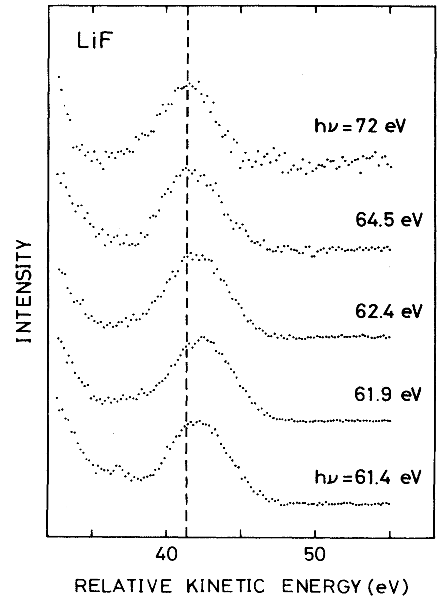

FIG. 4. Auger spectra derived by the subtraction of the valence band, its secondaries, and the F 2s band from the raw photoelectron spectra. The photoelectron spectrum obtained with the photon energy of 80.7 eV was used as the reference for the subtraction. The intensity of the Auger peak around 42 eV is normalized. The broken line shows the energy position of the Auger peak appearing in the raw photoelectron spectrum excited with the photon energy of 80.7 eV.

tron and the Auger electron is that in the ordinary Auger process (K-VV transition), in which the final state has two holes in the valence band and two electrons in the continuum state. In this case, Auger electrons are ascribed to the annihilation of the Li 1s—core hole. The kinetic energy of the K-VV Auger electron E_K is given by[17]

$$E_K = E_B(K) - 2E_B(V) - U_C ,$$

where $E_B(K)$ and $E_B(V)$ denote the binding energies of the K and valence electrons, respectively, and U_C denotes the correlation energy due to the hole-hole interaction. From the one-electron binding energies [$E_B(K) = 50.6$ eV and $E_B(V) = 2$ eV] and the kinetic energy ($E_K = 41.4$ eV), which are obtained in the present experiment, one can obtain $U_C = 5.2$ eV.

On the other hand, when the photon energy is around the energy of the Li 1s—core exciton, the kinetic energy of the Auger peak is different from that of the K-VV Auger peak. The peak position in the difference photoelectron spectra with 62.4-, 61.9-, and 61.4-eV excitation shifts to higher kinetic energy side by the amount of 0.6—0.9 eV as seen in Fig. 4. This result cannot be interpreted in terms of the Auger decay model suggested previously by Sugawara and Sasaki[5]; they considered that an electron forming a core exciton moves to the bottom of the continuum state, and the Auger electron is expected to have the kinetic energy $E_K' = E_K - E_b$, where E_b is the binding energy of the core exciton. The present authors propose here that the electron photoexcited to the core-exciton state is bound to some level below the bottom of the continuum state at the final state of the decay process and screens effectively[15] the two holes in the valence band, thus reducing the correlation energy U_C from 5.2 to 4.3 eV. Therefore, the resonant behavior of the CFS spectrum at the kinetic energy of the Auger electron is due to the core-exciton decay through the K(exciton)-VV process, in which the final state has two holes in the valence band, one electron in the bound state, and one electron in the continuum state. Details of the bound state are not clear at the present stage, but it is supposed that two holes and one excited electron can be attracted to one another to result in such a bound state and that the change of the correlation energy is attributed to the additional Coulomb attraction due to the presence of the bound electron.

It is worthwhile noting that the ratios of the two decay processes of the core exciton are not the same among alkali halides. As seen in Fig. 1, the intensity of the Auger electrons due to the K(exciton)-VV process is much larger than the increase of the valence-band intensity which is due to the K(exciton)-V process. Lapeyre *et al.*[6] have reported that in KI the direct recombination process which corresponds to the K(exciton)-V process is half as probable as the Auger process, which corresponds to the K(exciton)-VV process. On the other hand, Haensel *et al.*[4] and Sugawara and Sasaki[5] reported that the decay through direct electron-hole recombination is dominant in NaCl and in the halides of potassium, rubidium, and cesium, and the Auger decay is negligible in these halides. The ratios of the two processes might contain more information on the decay processes of the core exciton, and further analysis of the probability of the two decay processes in LiF is under way.

In conclusion, the present photoelectron spectra of LiF show the resonant behavior at the energy of the Li 1s—core exciton and this result can be 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. It is also shown that the K(exciton)-VV process is a predominant nonradiative decay process in LiF and that this process is different from the ordinary K-VV Auger process. The excited electron is supposed to be in the bound state and plays an important role in the energy of the Auger electrons.

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[1] See, for example, a review article by Ch. B. Lushchik, in *Excitons,* edited by E. I. Rashba and M. D. Sturge (North-Holland, Amsterdam, 1982), p. 505.

[2] E. T. Arakawa and M. W. Williams, Phys. Rev. Lett. 36, 333 (1976).

[3] O. Aita, K. Tsutsumi, K. Ichikawa, M. Kamada, M. Okusawa, H. Nakamura, and T. Watanabe, Phys. Rev. B 23, 5676 (1981).

[4] R. Haensel, G. Keitel, G. Peters, P. Schreiber, B. Sonntag, and C. Kunz, Phys. Rev. Lett. 23, 530 (1969).

[5] H. Sugawara and T. Sasaki, J. Phys. Soc. Jpn. 46, 132 (1979).

[6] G. J. Lapeyre, A. D. Baer, J. Hermanson, J. Anderson, J. A. Knapp, and P. L. Gobby, Solid State Commun. 15, 1601 (1974).

[7] L. C. Davis and L. A. Feldkamp, Phys. Rev. B 23, 6239 (1981).

[8] W. Gudat, C. Kunz, and H. Peterson, Phys. Rev. Lett. 32, 1370 (1974).

[9] D. M. Roessler and W. C. Walker, J. Phys. Chem. Solids 28, 1507 (1967).

[10] F. C. Brown, C. Gähwiller, A. B. Kunz, and N. O. Lipari, Phys. Rev. Lett. 25, 927 (1970).

[11] R. Haensel, C. Kunz, and B. Sonntag, Phys. Rev. Lett. 20, 262 (1968).

[12] G. W. Rubloff, Phys. Rev. B 5, 662 (1972).

[13] C. Guillot, Y. Ballu, J. Paigné, J. Lecante, K. P. Jain, P. Thiry, R. Pinchaux, Y. Pétroff, and L. M. Falicov, Phys. Rev. Lett. 39, 1632 (1977).

[14] M. Iwan, F. J. Himpsel, and D. E. Eastman, Phys. Rev. Lett. 43, 1829 (1979).

[15] T.-C. Chiang and D. E. Eastman, Phys. Rev. B 21, 5749 (1980).

[16] S. T. Pantelides, Phys. Rev. B 11, 2391 (1975).

[17] P. H. Citrin, J. E. Rowe, and S. B. Christman, Phys. Rev. B 14, 2642 (1976).