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Decay of the Na 2*p* core exciton in sodium halides studied by photoelectron spectroscopy

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The decay of the Na 2*p* core exciton in NaF, NaCl, NaBr, and NaI was investigated by photoelectron spectroscopy with synchrotron radiation. It was observed that the intensities of the valence band and the Auger-electron peak are resonantly enhanced around the excitation photon energy of the Na 2*p* core exciton in NaCl, NaBr, and NaI, while only the Auger-electron peak shows resonant behavior in NaF. These resonant enhancements are interpreted in terms of the nonradiative decay of the Na 2*p* core exciton through the $L_{2,3}$(exciton)-V and $L_{2,3}$(exciton)-VV processes, where $L_{2,3}$(exciton) denotes the initial L_2- or L_3-exciton state and V denotes the final state with a hole in the valence band. The decay probabilities of the Na 2*p* core exciton through these two processes were estimated from the constant-initial-state spectra and the absorption spectra. It was found that the decay through the $L_{2,3}$(exciton)-VV process, where the Na 2*p* core hole forming a core exciton recombines with a valence electron transferring energy to another valence electron, is the predominant nonradiative decay of the Na 2*p* core exciton. The correlation between two valence holes and one bound electron produced in the final state of this core-exciton decay was confirmed by the energy shift of the Auger-electron peak. The decay probabilities of the excited states higher than the core-exciton states were also estimated from the constant-final-state spectra. The result indicates that these higher excited states decay dominantly through the Auger process due to the recombination of the Na 2*p* core hole with the valence electron.

I. INTRODUCTION

The soft-x-ray absorption spectra of alkali halides are characterized by sharp peaks below the threshold. These peaks are generally accepted to be due to the excitation of the core exciton.[1-5] The decay mechanism of the core exciton has been investigated by several groups.[6-14] Arakawa and Williams[6] and the present authors[7] have investigated the radiative decay of the Li 1*s* core exciton in lithium halides by means of the electron excitation and the fluorescence excitation methods, respectively. However, the evidence of the radiative decay of the core exciton, which is due to the recombination of an excited electron with an inner core hole, is not definite, because the emission spectra obtained by electron bombardment change with time, the rate of change depending on the energy and intensity of bombarding electrons,[6] and because the strong resonance scattering of the incident continuous radiation by the exciton and continuum states appears in the emission spectra obtained by the fluorescence excitation method.[7] Beaumont *et al.*[8] have measured the excitation spectra for intrinsic luminescence due to the recombination of self-trapped excitons in NaCl, NaBr, RbCl, and RbBr between 6 and 60 eV, and suggested the competitive relation between luminescence and photoelectron emission processes. Haensel *et al.*[9] and Sugawara and Sasaki[10] have measured photoelectric yield spectra of NaCl and those of the halides of potassium, rubidium, and cesium, respectively, by changing the retarding potential. They have ascribed certain peaks in the yield spectra to the core-exciton decay through the electron-hole recombination with simultaneous excitation of an electron from the valence band to the continuum state, and concluded that this direct recombination is the dominant decay process of the core excitons. However, detailed differences in intensity in adjacent retarding-potential-yield spectra are difficult to determine, so that their studies on the decay processes of the core exciton were restricted in scope. Lapeyre *et al.*[11] have studied the decay of the K 3*p* core exciton in KI by using the constant-initial-state (CIS) and constant-final-state (CFS) modes of operation for obtaining the photoelectron spectroscopy data with synchrotron radiation, and separately identified the Auger and nonradiative direct recombination processes as significant mechanisms in the decay of the K 3*p* core exciton in KI. They have found, as a preliminary estimate, the direct recombination channel to be half as probable as the Auger process.

Recently we have used the CIS and CFS modes of operation, as well as the measurement of the usual energy distribution curve for obtaining the photoelectron spectroscopy data with synchrotron radiation, to obtain the information on the decay process of the Li 1*s* core exciton in lithium halides.[12-14] We have observed the resonant enhancement of the intensities of the valence band and the Auger-electron peak around the excitation photon energy of the Li 1*s* core exciton, and proposed the following two decay processes of the core exciton: (1) a core hole and a photoexcited electron which form the core exciton recombine directly with energy transferred to a valence electron, and (2) the core hole forming a core exciton recombines with a valence electron, transferring energy to another valence electron which is excited to the continuum state. Moreover, it has been suggested that in the final state of the latter decay process two valence holes and one electron can be attracted to one another to result in a bound state which affects the kinetic energy of the Auger electron.

The purpose of the present study is to confirm whether these two decay processes can take place in other alkali halides such as sodium halides, in which the transition from the Na 2*p* level to the bottom of the conduction band is optically allowed and the exciton peak below the threshold in the Na $L_{2,3}$ absorption spectra is the doublet structure resulting from spin-orbit splitting of the Na 2*p* level.[2–5] The present result can also provide useful information on the role of the core exciton in the resonant photoemission phenomena of other substances,[15–19] where conflicting explanations have been reported.

II. EXPERIMENTAL PROCEDURES

Photoelectron spectra 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 about 0.06 eV at the photon energy of 33 eV with 100-μm entrance and 50-μm exit slits and a 1200-groove/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 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 structures in the photoelectron spectrum, very thin samples were prepared *in situ* by evaporation onto gold substrates. The thickness of the samples was estimated to be about 100 Å with an oscillating-quartz thickness gauge. To see the effect of the charging of the samples we measured the Na 2*p* electrons 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 electrons. This peak position did not indicate any energy shift due to the charging of the samples. Thus we believe that the present spectra are not influenced by the charging of the samples.

The base pressure in the sample chamber was about 3×10^{-8} Pa and rose to the 10^{-6} Pa range during evaporation. The pressure in the analyzer chamber was about 4×10^{-9} Pa during measurements. The spectral dependence of the incident radiation onto the samples was determined from the photoelectric yield spectrum of gold.

To discuss the decay of the core exciton and the higher excited states in detail, it is desirable to compare the photoelectron and the absorption spectra which were obtained with the same spectral resolution. Moreover, the absolute values of the absorption coefficient are necessary to evaluate the rate of escape of electrons. The existing results of the absorption spectra[3–5,20–22] are not entirely satisfactory for our purpose, and thus we measured the Na $L_{2,3}$ absorption spectra of all the sodium halides.

The absorption measurements were performed by using synchrotron radiation from a 750-MeV storage ring at the Institute for Molecular Science. A plane-grating monochromator equipped with a Ni-coated cylindrical focusing mirror and a Pt-coated toroidal refocusing mirror was used for the present measurement. The spectral width was about 0.06 eV at the photon energy of 30 eV with a 1200-groove/mm grating and a 100-μm exit slit, which is almost the same as that of the monochromator used for the measurement of the photoelectron spectra. Samples were prepared *in situ* by evaporation onto collodion substrates coated with a thin aluminum foil. The pressure in the sample chamber was about 10^{-5} Pa during the evaporation and dropped immediately to 10^{-7} Pa after the evaporation. The thickness of the samples was measured with an oscillating-quartz thickness gauge calibrated by the Tolansky interferometry to obtain the absorption coefficients.

In order to see the reflection loss of the incident light onto the samples and the effect of inelastic scattering of the photoelectrons, numerical calculations of the reflectivity based on optical constants derived from a Kramers-Kronig analysis of the absorption data were carried out, as well as the computation for the rate of escape of the photoelectrons.

III. EXPERIMENTAL RESULTS

Figures 1–4 show sets of photoelectron spectra of NaF, NaCl, NaBr, and NaI, respectively, which were

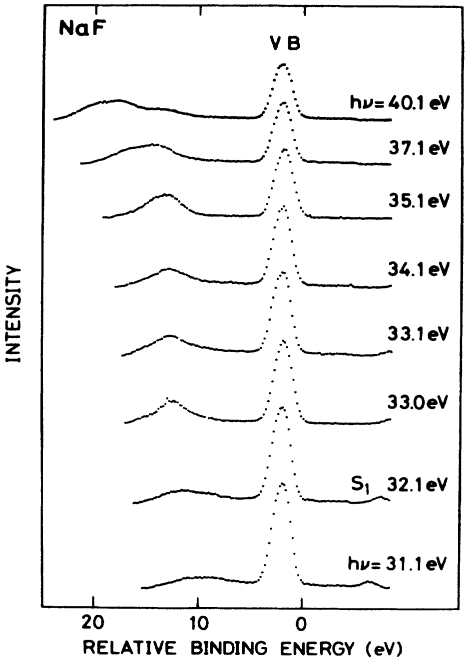

FIG. 1. Set of photoelectron spectra of NaF excited with photon energies around the excitation energy of the Na 2*p* core exciton. S_1 indicates the Na 2*p* electron excited with second-order light. Intensities are normalized to the incident photon flux.

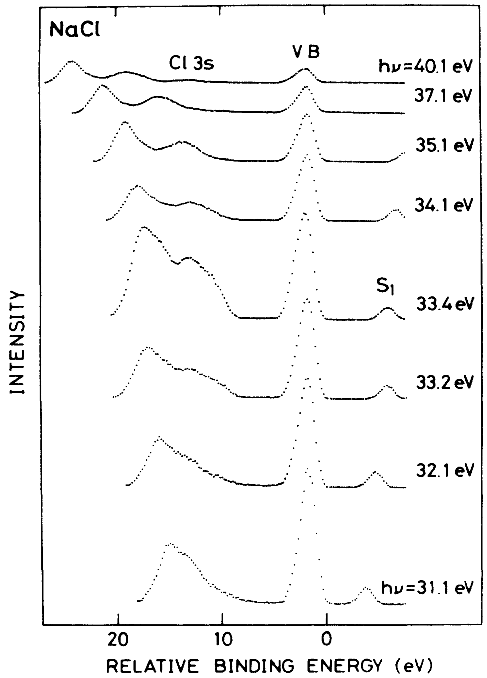

FIG. 2. Set of photoelectron spectra of NaCl excited with photon energies around the excitation energy of the Na 2*p* core exciton. S_1 indicates the Na 2*p* electron excited with second-order light. Intensities are normalized to the incident photon flux.

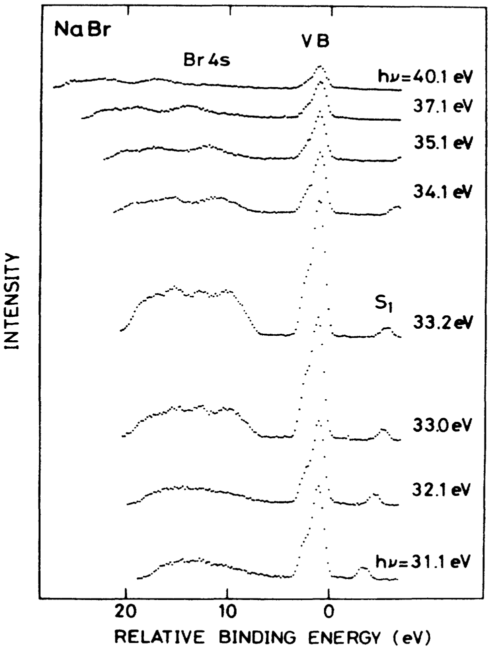

FIG. 3. Set of photoelectron spectra of NaBr excited with photon energies around the excitation energy of the Na 2*p* core exciton. S_1 indicates the Na 2*p* electron excited with second-order light. Intensities are normalized to the incident photon flux.

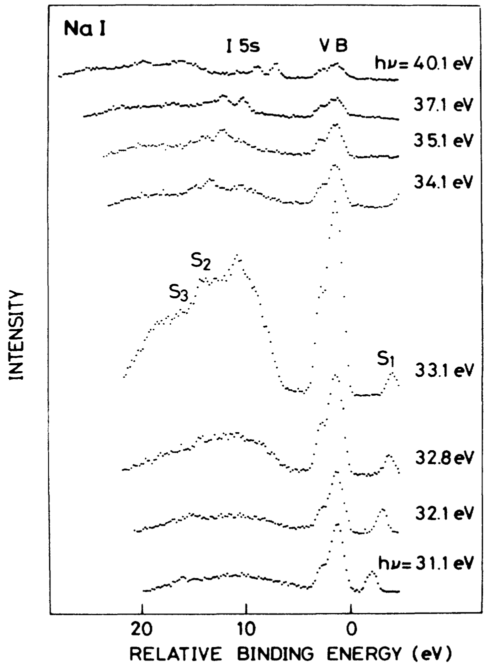

FIG. 4. Set of photoelectron spectra of NaI excited with photon energies around the excitation energy of the Na 2*p* core exciton. S_1, S_2, and S_3 indicate the Na 2*p*, I $4d_{5/2}$, and I $4d_{3/2}$ electrons excited with second-order light, respectively. Intensities are normalized to the incident photon flux.

obtained with various photon energies around the excitation energy of the Na 2*p* core exciton. The binding energies are given relative to the top of the valence band. The ordinate is proportional to the number of photoelectrons per incident photon flux. The peak labeled S_1 is due to the Na 2*p* electron excited by the second-order light, and the peaks labeled S_2 and S_3 in the spectra of NaI are also due to the I $4d_{5/2}$ and $4d_{3/2}$ electrons excited by the second-order light, respectively. The energy position of these peaks indicates that there are no charging effects in the present spectra.

Several photoelectron spectra of sodium halides have been measured with ultraviolet photoelectron spectroscopy (UPS)[23–29] and x-ray photoelectron spectroscopy (XPS).[30–32] The shape of the present valence-band spectrum of NaCl obtained with the excitation photon energy of 31.1 eV is similar to that obtained by Lapeyre *et al.*,[23] which was measured by UPS with $h\nu=30$ eV. The shapes of the present valence-band spectra of NaF and NaBr obtained with $h\nu=40.1$ eV are almost the same as those reported by Poole *et al.*,[24] which were measured with $h\nu=40.81$ eV. On the other hand, the valence-band spectra of the sodium halides obtained by XPS (Ref. 31) are slightly different from the present ones, namely, the FWHM values of the present valence band are smaller than those reported previously.

The valence-band spectrum of NaF shows a single peak, while those of NaCl, NaBr, and NaI consist of a peak and a shoulder on its higher binding-energy side. The binding energies of the peaks and the shoulders in the valence bands are listed in Table I, together with those of the outermost *s* levels of the anions and the Na 2*p* levels. The binding energy of the F 2*s* level in NaF could not be determined since it is close to that of the Na 2*p* level and also the ionization cross section of the F 2*s* electron is much smaller than that of the Na 2*p* electron in the excitation-photon-energy region concerned. The Auger-electron peak is observed in every case when the excitation photon energy is beyond 33 eV. The kinetic energy of the Auger electron in the sodium halides, which was measured with the excitation photon energy of 40.1 eV, is also listed in Table I. The kinetic energy is measured with respect to the top of the valence band for convenience. Another Auger-electron peak is also appreciable at the kinetic energy of about 16.2, 18.3, and 20.2 eV in the spectra of NaCl, NaBr, and NaI, respectively, but it overlaps with the spectra of the inelastically scattered electrons. The energy-loss peak due to the inelastic scattering of the electrons photoexcited from the valence band appears at the binding energy of 13.4 eV in the photoelectron spectra of NaF. According to Scrocco[32] and Best,[33] this energy loss is ascribed to the onset of the interband transition. The energy-loss peak of the same origin appears at the binding energy of 10.2 eV in NaCl, but it is too weak to be clearly observed in the figure.

The Auger-electron peaks are resonantly enhanced at the excitation photon energy of the Na 2*p* core exciton in all the sodium halides. The valence-band spectra of NaCl, NaBr, and NaI are also enhanced around the excitation photon energy of the Na 2*p* core exciton, while the valence-band intensity of NaF does not show such an enhancement. These phenomena are more visual in the CFS spectra with the final state corresponding to the kinetic energy of the Auger electron, and in the CIS spectra with the initial state at the peak of the valence band.

TABLE I. The binding energies of valence band, outermost *s* level of the anion, and Na 2*p* level, as well as the kinetic energies of Auger electrons. Energies are relative to the top of the valence band and are given in electron volts. The energy shift of the Auger-electron peak ΔE_K, the correlation energies U_{VV} and U_{VC}, and the threshold for transition from the Na 2*p* level to the conduction band are also given in electron volts.

	NaF	NaCl	NaBr	NaI
Valence band				
peak	1.9	1.7	1.2	1.2
shoulder		2.7	2.4	2.8
(full width)	(3.8)	(4.0)	(3.4)	(3.8)
Halogen *ns* level		12.7	12.4	10.6
Na 2*p* level	24.7	27.5	27.7	28.8
(FWHM)	(1.9)	(1.5)	(1.3)	(1.2)
$L_{2,3}$-VV	20.2	21.6	23.1	23.8
$L_{2,3}$(exciton)-VV	20.6	22.2	23.5	24.2
ΔE_K	0.4	0.6	0.4	0.4
U_{VV}	0.7	2.5	2.2	2.6
U_{VC}^{a}	1.1	0.9	0.6	0.4
Threshold[b]	36.3	36.0	35.7	35.2

[a] References 37 and 38.
[b] Reference 2.

These are shown in Figs. 5–8 together with the Na $L_{2,3}$ absorption spectra, whose absorption coefficient is given on the right-hand side of the figure. The general feature of the structures and their energy positions in the present Na $L_{2,3}$ absorption spectra agree well with those reported previously,[3–5,20–22] but the detailed intensity distributions of the structures in the present spectra are different from the previous ones. We believe that this difference may be due to the good spectral purity and resolution in the present experiment.

As seen in Figs. 5–8, the CFS spectra show the resonant behavior at 33.1 eV in NaF, at 33.1 and 33.4 eV in NaCl, at 32.95 and 33.2 eV in NaBr, and at 32.8 and 33.1 eV in NaI. The energy position of these peaks and shoulders in the CFS spectra corresponds well to the excitation photon energy of the Na 2*p* core exciton observed in the absorption spectra (33.15 eV in NaF, 33.15 and 33.41 eV in NaCl, 32.95 and 33.23 eV in NaBr, and 32.76 and 33.06 eV in NaI). The FWHM values of the prominent peak in the CFS spectra of NaF, NaCl, NaBr, and NaI are in good agreement with those of the prominent peak in the absorption spectra, while the FWHM value of the lower-energy peak in the CFS spectrum of NaCl is about 0.3 eV, which is about 1.5 times as much as that of the lower-energy peak in the absorption spectrum. In the excitation-photon-energy range above 34 eV, several broad bands appear in the CFS spectra. The prominent band at about 45 eV in the CFS spectrum of NaF is due to the Na 2*p* photoelectron, and such a band appears at about 49, 51, and 53 eV in the CFS spectra of NaCl, NaBr, and NaI, respectively, though it is not shown in the present figures. The peaks at about 35.7 and 36.5 eV in the CFS spectrum of NaI are due to the photoelectrons excited from the I $4d_{5/2}$ and $4d_{3/2}$ levels by the second-order light, respectively. Except these bands, all structures observed in the CFS spectra of the sodium halides coincide well in energy with those in the Na $L_{2,3}$ absorption spectra.

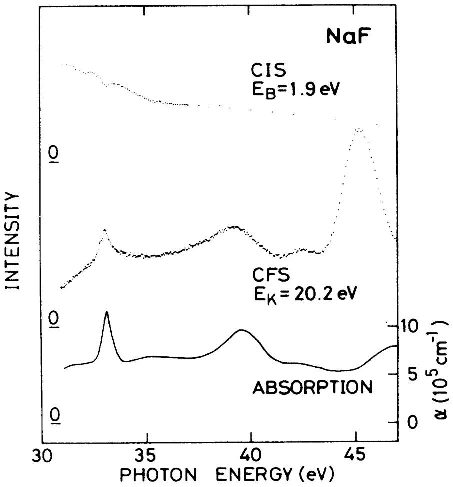

FIG. 5. CIS spectrum measured at the initial binding energy of 1.9 eV, CFS spectrum with the final kinetic energy of 20.2 eV, and the Na $L_{2,3}$ absorption spectrum in NaF.

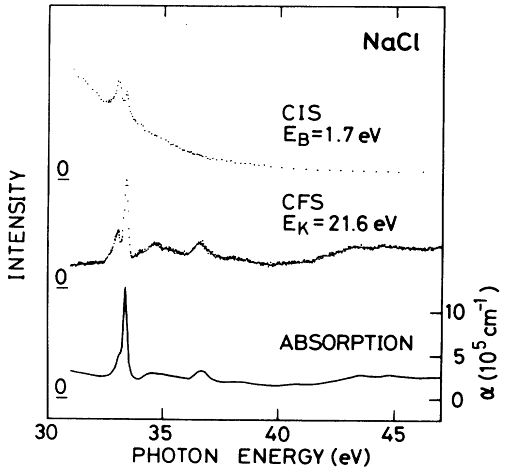

FIG. 6. CIS spectrum measured at the initial binding energy of 1.7 eV, CFS spectrum with the final kinetic energy of 21.6 eV, and the Na $L_{2,3}$ absorption spectrum in NaCl.

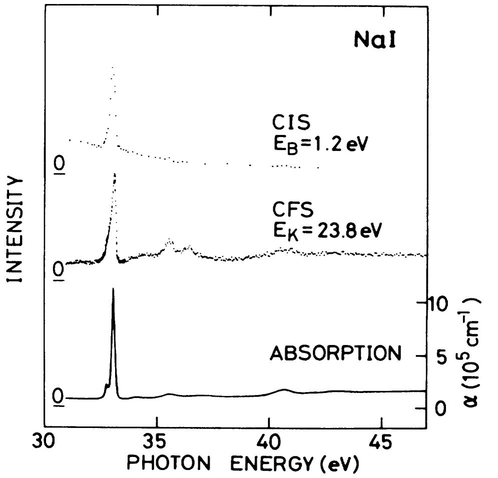

FIG. 8. CIS spectrum measured at the initial binding energy of 1.2 eV, CFS spectrum with the final kinetic energy of 23.8 eV, and the Na $L_{2,3}$ absorption spectrum in NaI.

The CIS spectra show different features from the absorption and CFS spectra. The CIS spectrum of NaF shows no distinct enhancement in the excitation-photon-energy range shown in Fig. 5, but a small dip appears at about 33.2 eV. On the other hand, two prominent peaks appear in the CIS spectra of NaCl and NaBr (at 33.1 and 33.4 eV in NaCl and at 33.05 and 33.2 eV in NaBr), and a shoulder and a prominent peak appear at 32.75 and 33.0 eV, respectively, in the CIS spectrum of NaI. The energy positions of the lower-energy peak of NaBr and the peak of NaI observed in the CIS spectra (33.05 and 33.0 eV) are slightly different from those of the peaks in the absorption and CFS spectra. The FWHM value of the higher-energy peak in the CIS spectrum of NaCl is in good agreement with that of the prominent peak in the absorption spectrum, while the FWHM value of the lower-energy peak in the CIS spectrum of NaCl is about 0.3 eV, which is about 1.5 times as much as that of the lower-energy peak in the absorption spectrum. The FWHM values of the prominent peaks in the CIS spectra of NaBr and NaI could not be determined, since they are not well resolved. Moreover, the intensity ratios of the doublet structures in the CIS, CFS, and absorption spectra are different from one another. In the excitation-photon-energy range above 34 eV, the intensities of the CIS spectra of all the sodium halides decrease monotonously with increasing photon energy. Energy positions of the main structures in the CIS and CFS spectra are given in Table II, together with those in the Na $L_{2,3}$ absorption spectra.

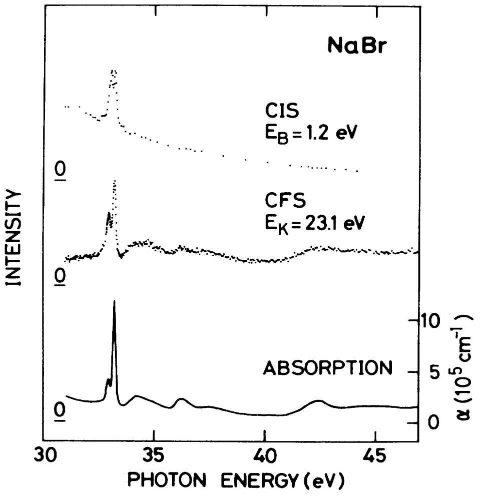

FIG. 7. CIS spectrum measured at the initial binding energy of 1.2 eV, CFS spectrum with the final kinetic energy of 23.1 eV, and the Na $L_{2,3}$ absorption spectrum in NaBr.

IV. DISCUSSION

A. Decay process of the Na 2*p* core exciton

Excitations of the Na 2*p* electrons give rise to prominent absorption structures in sodium halides. It is generally accepted that the threshold for transition from the Na 2*p* level to the conduction band is 36.3, 36.0, 35.7, and 35.2 eV for NaF, NaCl, NaBr, and NaI, respectively, and the structures below the threshold are due to the core excitons.[2] Among these structures, the sharp peaks at 33.15 eV in NaF, at 33.15 and 33.41 eV in NaCl, at 32.95 and 33.23 eV in NaBr, and at 32.76 and 33.06 eV in NaI are due to the creation of the Na 2*p* core exciton at the Γ point in the Brillouin zone.[5] First, we will discuss the decay process of this Na 2*p* core exciton.

As seen in the CIS spectra shown in Figs. 5–8, the valence-band intensity of NaCl, NaBr, and NaI is enhanced around the excitation photon energy of the Na 2*p* core exciton, but there is no distinct enhancement in the CIS spectrum of NaF. On the analogy of the Li 1*s* core exciton in lithium halides,[12,13] this enhancement of the valence-band intensity can be interpreted in terms of

TABLE II. Energy positions (electron volts) of the main structures in the CIS, CFS, and absorption spectra (abs).

				NaF				
CIS	33.2[a]							
CFS	33.1		39.3	42.5	45[b]			
abs	33.15	35.2	39.5	42.5	47.0			
				NaCl				
CIS	33.1	33.4						
CFS	33.1	33.4	34.7	36.6	38.2	40.6	43.3	44.6
abs	33.15	33.41	34.7	36.6	38.2	40.7	43.4	44.7
				NaBr				
CIS	33.05	33.2						
CFS	32.95	33.2	34.2	36.3	37.5	42.4	44.6	
abs	32.95	33.23	34.2	36.3	37.6	42.4	44.7	
				NaI				
CIS	32.75	33.0						
CFS	32.8	33.1	34.2	35.7[c]	36.5[c]	40.7	43.0	
abs	32.76	33.06	34.2	35.5	37.0	40.7	43.0	

[a] Observed as a dip.

[b] Na 2p photoelectron.

[c] I 4$d_{5/2}$ and I 4$d_{3/2}$ photoelectrons excited by the second-order light.

the nonradiative decay of the Na 2p core exciton, where a Na 2p core hole and an electron forming a Na 2p core exciton recombine directly with energy transferred to a valence electron. The final state of this decay process has a configuration involving one hole in the valence band and one electron in the continuum state. Here this decay process of the Na 2p core exciton is called the "$L_{2,3}$(exciton)-V process," where $L_{2,3}$(exciton) denotes the initial L_2- or L_3-exciton state[34] and V denotes the final state with a hole in the valence band. The decay of the core exciton through this process is observed as the enhancement of the valence-band intensity since its final state has the same configuration as that of the direct photoexcitation of the valence electron.

The peaks are clearly observed at the excitation photon energy of the Na 2p core exciton in the CFS spectra, with the final state corresponding to the kinetic energy of the Auger electron of NaF, NaCl, NaBr, and NaI. This resonant behavior of the Auger-electron peak can be interpreted in terms of the Auger decay of the core exciton, where a Na 2p core hole forming a core exciton recombines with a valence electron and the energy is transferred to another valence electron which is excited to the continuum state. The final state of this process has a configuration involving two holes in the valence band, one electron in a bound state, and one electron in the continuum state. This process is called the "$L_{2,3}$(exciton)-VV process."

Previously the present authors have proposed that, in the final state of the core-exciton decay through the K(exciton)-VV process in lithium halides, two valence holes and one electron, which is initially photoexcited from the Li 1s level, can be attracted to one another to result in the bound state which affects the kinetic energy of the Auger electron.[12,13] Thus it is interesting to investigate the energy shift of the Auger-electron peak in the decay process of the Na 2p core exciton through the $L_{2,3}$(exciton)-VV process. To determine the energy position of Auger-electron peaks, we subtracted the components due to the photoelectrons excited from the outermost s level of the anion and the secondary electrons from the raw photoelectron spectra, under the assumption that their intensity ratios to the valence-band intensity are constant in the photon energy region concerned.[35]

The results are shown in Fig. 9. The ordinate of this figure indicates the increment of the kinetic energy ΔE_K

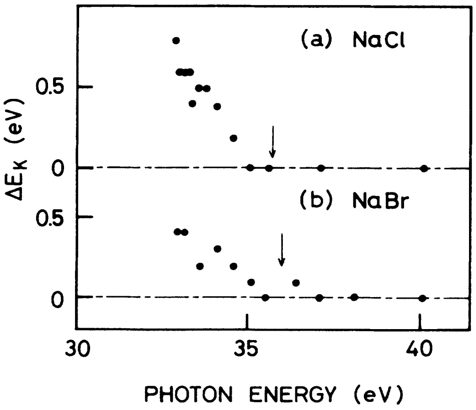

FIG. 9. Peak positions of the main Auger-electron peak of NaCl (a) and NaBr (b) as a function of photon energy. Ordinates indicate the increment of the kinetic energies from the ordinary $L_{2,3}$-VV Auger-electron peak. Arrows indicate the threshold for transition from the Na 2p level to the conduction band (Ref. 2).

from that of the ordinary $L_{2,3}$-VV Auger electron. The arrows in the figure indicate the threshold for transition from the Na $2p$ level to the conduction band.[2] As seen in this figure, the kinetic energy of the Auger electron in the $L_{2,3}$(exciton)-VV process is greater than that of the ordinary $L_{2,3}$-VV Auger electron in NaCl and NaBr. The dependence of the kinetic energy of the Auger electron on the excitation photon energy could not be obtained for NaF and NaI, because the additional peaks due to the secondary electrons or the photoelectrons excited from the I $4d$ levels by the second-order light appear in their spectra. However, the kinetic energies of the Auger electron in NaF and NaI increase from 20.2 to 20.6 eV and from 23.8 to 24.2 eV, respectively, with decreasing the photon energy from 40.1 to 33.1 eV. These results are consistent with the results on lithium halides, that the kinetic energy of the Auger electron produced by the decay of the Li $1s$ core exciton through the K(exciton)-VV process is greater by about 1 eV than that of the ordinary K-VV Auger electrons.[12,13]

Igarashi[36] has calculated a three-body problem involving two valence holes and a single conduction electron in a one-dimensional model. 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 excitation energy of the core exciton. In the cases of sodium halides, the values of the interaction U_{VC} between a valence hole and a conduction electron are estimated to be about 0.4–1.1 eV from the binding energy of the exciton in the optical absorption region.[37,38] Because the values of the valence-band width W are about 3.8, 4.0, 3.4, and 3.8 eV in NaF, NaCl, NaBr, and NaI, respectively (see Table I), the present case is equivalent to the case of $U_{VC}/(W/2)=0.2-0.6$ in his theoretical model. In these values of $U_{VC}/(W/2)$, the deviations of the kinetic energy of the Auger electron from that of an ordinary one are predicted to occur around the excitation photon energy of the core exciton. The theory also predicts that the satellite peak should appear on the lower binding-energy side of the Auger-electron peak. However, such a satellite peak predicted by the theoretical calculation is not clearly observed in the present photoelectron spectra excited either with the photon energy near the excitation energy of the core exciton, or with photon energies away from resonance. In the sodium halides, the values of the correlation energy U_{VV} between two holes in the valence band are estimated to be about 0.7–2.6 eV from the observed binding energies of the Na $2p$ level and the valence band and the kinetic energy of the ordinary $L_{2,3}$-VV Auger electron (see Ref. 12). Since these values of U_{VV} are not so large as those used in the theoretical calculation, it is supposed that the decay of the Na $2p$ core exciton through the $L_{2,3}$(exciton)-VV process is not accompanied by the satellite structure, or the satellite structure becomes so broad as to be buried in the background. Recently Watanabe and Kato[39] have calculated the binding energy of the trion state (two-holes-and-one-electron bound state) to be 0.4–0.8 eV in lithium halides. It should be noticed that this binding energy is close to the increment of the kinetic energy of the Auger electron observed around the excitation photon energy of the core exciton in lithium halides and sodium halides. This implies that the present result on the energy shift of the Auger-electron peak is related to the formation of the two-holes-and-one-electron bound state.

B. Decay probability of the Na $2p$ core exciton

Previously we have estimated the decay probability of the Li $1s$ core exciton in lithium halides.[13] In the following, we will describe the procedure of estimating the decay probability of the core exciton in more detail to discuss the decay of the Na $2p$ core exciton. According to Berglund and Spicer,[40] the intensity of the valence-band photoelectron spectrum $I_{\mathrm{VB}}(h\nu)$ is given by[41]

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

where $r(h\nu)$ is the reflectivity, $n_p(h\nu)$ the flux of incident photon with the energy $h\nu$, K the correction factor having a value between 0.5 and 1, $C(E)$ the threshold function for the electrons with the energy E, $\alpha(h\nu)$ the absorption coefficient, and $l(E)$ the mean free path related to inelastic scattering of electrons. Also $\alpha'_{\mathrm{VB}}(h\nu)$ 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.

When the core excitons are produced by the photoexcitation with the photon energy $h\nu^*$ and subsequently decay through the $L_{2,3}$(exciton)-V process before their migration in the solid, the photoelectron intensity $I_{\mathrm{ex}}(h\nu^*)$ due to the core-exciton decay through the $L_{2,3}$(exciton)-V process can be given with the replacement of $\alpha'_{\mathrm{VB}}(h\nu^*)$ in Eq. (1) by $\alpha'_{\mathrm{ex}}(h\nu^*)P$, 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 $L_{2,3}$(exciton)-V process:

$$I_{\mathrm{ex}}(h\nu^*)\Delta E = A(E)[1-r(h\nu^*)]n_p(h\nu^*) \times \frac{KC(E)}{\alpha(h\nu^*)+1/l(E)}\alpha'_{\mathrm{ex}}(h\nu^*)P\Delta E\ . \tag{2}$$

Therefore, from Eqs. (1) and (2), the probability P is expressed as

$$P=\frac{I_{\mathrm{ex}}(h\nu^*)/I_{\mathrm{VB}}(h\nu^*)}{\alpha'_{\mathrm{ex}}(h\nu^*)/\alpha'_{\mathrm{VB}}(h\nu^*)}\ . \tag{3}$$

It should be noted that the probability P can be definitely determined regardless of the unknown factors such as $r(h\nu^*)$, $A(E)$, K, $C(E)$, $n_p(h\nu^*)$, and $l(E)$ in Eqs. (1) and (2), since these factors do not appear in Eq. (3).

The values of $\alpha'_{\mathrm{ex}}(h\nu^*)$ and $\alpha'_{\mathrm{VB}}(h\nu^*)$ were derived from the absorption spectra and the photoelectron spectrum excited with $h\nu=40.1$ eV, under the assumption that the absorption peak due to $\alpha'_{\mathrm{ex}}(h\nu^*)$ is superposed on the smooth background due to the absorptions from the valence band $\alpha'_{\mathrm{VB}}(h\nu^*)$ and from the outermost s level of the anion $\alpha'_s(h\nu^*)$, and that the ratio of $\alpha'_{\mathrm{VB}}(h\nu^*)/\alpha'_s(h\nu^*)$ is the same as the ratio of the integrated intensities of the valence band and the outermost s level of the anion obtained from the photoelectron spectra excited with the photon energy far from resonance.

Previously[13] we have estimated the value of $I_{\mathrm{ex}}/I_{\mathrm{VB}}$ in Eq. (3) from the ratio of the prominent peak-to-background intensity in the CIS spectra for the Li $1s$ core exciton in lithium halides. In the case of the sodium halides, the absorption coefficients of the L_2-exciton peak are about 2–6 times larger than those of the Li $1s$ core-exciton peak in lithium halides,[42] and thus the quantity related to the electron escape $KC(E)/[\alpha(h\nu)+1/l(E)]$ and reflectivity $r(h\nu)$ in Eqs. (1) and (2) might show some anomaly around the excitation photon energy of the Na $2p$ core exciton.[43] To see these anomalies we carried out the numerical calculations of $KC(E)/[\alpha(h\nu)+1/l(E)]$ by using the observed absorption spectra and the existing results of the mean free path.[44] The result shows that the value of $KC(E)/[\alpha(h\nu)+1/l(E)]$ decreases at the excitation photon energy of the L_2 exciton and its decrements are about 10%, 8%, 7%, and 8% of its maximum value for NaF, NaCl, NaBr, and NaI, respectively.

The reflectivity $r(h\nu)$ in the present experimental arrangement (the angle of incidence is 45° and the electric vector is in the plane of incidence) was calculated numerically with the usual formula[45] by using the optical constants obtained from a Kramers-Kronig analysis of absorption data. The results show that the maximum of $r(h\nu)$ appears on the higher photon-energy side by about 0.1 eV from that of the absorption peak due to the L_2 exciton, and its values are about 0.8%, 5%, 4%, and 2% for NaF, NaCl, NaBr, and NaI, respectively, while other parts of the reflectivity are almost zero.

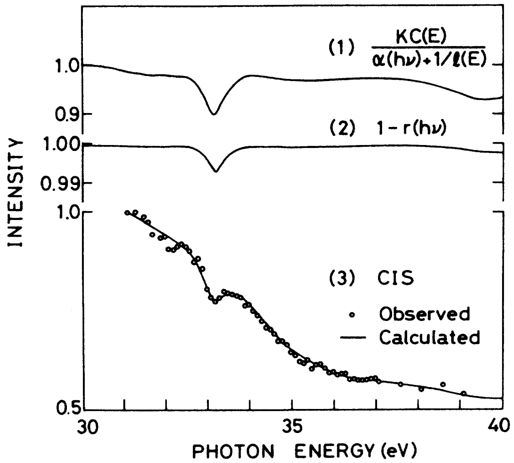

FIG. 10. Comparison of the observed and calculated CIS spectra of NaF. (1) and (2) are numerical calculations of $KC(E)/[\alpha(h\nu)+1/l(E)]$ and $1-r(h\nu)$, respectively. Solid curve (3) indicates the CIS spectrum calculated with Eq. (1), and open points show the observed CIS spectrum. (1) and (3) are given in the arbitrary scales.

The small dip is observed around 33.2 eV in the CIS spectrum of NaF shown in Fig. 5. One might suppose that this dip is an antiresonant minimum due to the Fano-type interaction between a discrete core-exciton state and continuum states.[4,46,47] However, as mentioned above, the rate of escape of electrons shows anomaly around this photon energy, resulting in the decrease of the intensity of the CIS spectrum. Figure 10 shows the comparison of the observed and calculated CIS spectra of NaF (see curve 3). The calculated CIS spectrum (solid curve 3) was obtained with Eq. (1), under the assumption that there is no resonance or antiresonance around the excitation photon energy of the core exciton in NaF. Since the Na $L_{2,3}$ absorption contains three kinds of electronic transition, i.e., the transitions from the valence band, the one from the outermost s level of the anion, and the one from the Na $2p$ level, $\alpha'_{\mathrm{VB}}(h\nu)$ cannot be obtained from the absorption spectra. Thus, $\alpha'_{\mathrm{VB}}(h\nu)$ was approximated to be proportional to the smooth background of the observed CIS spectrum. The value of $l(E)$ was referred to the existing results.[44] The dip depth in the observed CIS spectrum of NaF shown with open points is about 10% of the background intensity, and is almost the same as the decrement of the calculated curve (see curve 3). This result indicates that the anomaly around the excitation photon energy of the Na $2p$ core exciton in NaF is due to the rate of escape of electrons, and thus it is difficult to assign the observed anomaly as the antiresonant minimum which has been observed in the CIS spectra of copper compounds.[48,49] Then we suppose that the decay probability of the Na $2p$ core exciton through the $L_{2,3}$(exciton)-V process is negligible in NaF, and the Na $2p$ hole forming a core exciton is dominantly annihilated through the $L_{2,3}$(exciton)-VV process.

On the other hand, as seen from Figs. 6–8, the intensities of the prominent peaks in the CIS spectra of NaCl, NaBr, and NaI are about 50%, 110%, and 300% of the background intensity, respectively. These values are much larger than the amounts of the anomalies mentioned above. Thus, for these sodium halides, we neglected the anomalies of the quantity related to the electron escape and reflectivity in Eqs. (1) and (2). As mentioned in Sec. III, the energy position and the FWHM value of the prominent peaks in the CIS spectra are slightly different from those of the absorption peaks. This difference may be due to the relaxation process of the core exciton or the effect of the surface exciton, as discussed later. However, we neglected here this slight difference between the CIS and absorption spectra, for simplicity, and derived the decay probability P by using the simple intensity ratio $I_{\mathrm{ex}}/I_{\mathrm{VB}}$ of the prominent peak-to-background intensity in the CIS spectra shown in Figs. 6–8. The values of P, which were estimated for the L_2 and L_3 excitons, are shown in Table III.

The probability P' of the $L_{2,3}$(exciton)-VV process was estimated from the following equation, proposed previously:[13]

$$P' \simeq P\frac{S_{\mathrm{Auger}}}{S_{\mathrm{VB}}}\ , \tag{4}$$

TABLE III. Decay probability of the Na $2p$ core exciton through $L_{2,3}$(exciton)-V and $L_{2,3}$(exciton)-VV processes.

	NaF		NaCl		NaBr		NaI	
	L_2	L_3	L_2	L_3	L_2	L_3	L_2	L_3
L(exciton)-V	0	0	0.11	0.44	0.18	0.82	0.21	0.30
L(exciton)-VV			0.51	0.45	0.31	1.06	0.44	0.46

where S_{Auger} and S_{VB} are the integrated intensity of the Auger-electron peaks due to the $L_{2,3}$(exciton)-VV process and the increase of the valence-band intensity due to the $L_{2,3}$(exciton)-V process, respectively. Here it was assumed that various factors such as $l(E)$, $A(E)$, K, and $C(E)$ are approximately the same between the Auger electron produced by the decay through the $L_{2,3}$(exciton)-VV process and the electron originated from the decay through the $L_{2,3}$(exciton)-V process. The results are also shown in Table III.

Haensel *et al.*[9] have measured photoelectric yield spectra of NaCl by changing the retarding potential and reported that the decay of the Na $2p$ core exciton through the direct electron-hole recombination, which corresponds to the $L_{2,3}$(exciton)-V process, is dominant and Auger decay of the Na $2p$ hole is negligible in NaCl. The present result, however, shows that the probability of the $L_{2,3}$(exciton)-VV process is larger than that of the $L_{2,3}$(exciton)-V process in all the sodium halides. This difference is probable because detailed differences in intensity in adjacent retarding-potential-yield spectra are difficult to determine and their study is restricted in scope.

Previously we found the systematical change in the decay probability of the Li $1s$ core exciton through the K(exciton)-V process in the lithium halides and supposed that its decay probability depends on the delocalization of the valence-band wave function.[13] In the sodium halides, the decay probability through the L_2(exciton)-V process increases in going from fluoride to iodide as in the case of the Li $1s$ core exciton in the lithium halides. Thus, it is suggested that the delocalization of the valence-band wave function plays an important role in the decay processes of the core exciton in the sodium halides as well as the lithium halides.

On the other hand, the probability of the L_3(exciton)-V process does not show the same systematical change as that of the L_2(exciton)-V process, and the probability of the L_3(exciton)-V process is much larger than that of the L_2(exciton)-V process in NaCl, NaBr, and NaI. To interpret the difference in the probability between the L_2(exciton)-V process and the L_3(exciton)-V process, it is considered that the L_2 hole forming a core exciton is annihilated by its relaxation into the L_3 hole. Moreover the relaxation of the core exciton into its relaxed excited state followed by the phonon emission, which has been observed in LiCl and LiBr,[14] is expected in the present case, since the shapes of the valence-band spectra of NaCl, NaBr, and NaI slightly change around the excitation photon energy of the core exciton, and the energy position of the prominent peak in the CIS spectrum of NaI is slightly lower than that of the absorption peak due to the L_2 exciton, as in the case of the lithium halides. These relaxation processes may affect the decay probability of the Na $2p$ core exciton, resulting in the difference in the probability between the L_2(exciton)-V process and the L_3(exciton)-V process.

As another possibility, effects of the surface exciton should be considered, since the mean free path of the photoelectron is about 8–20 Å in the present case.[44] the surface-exciton peaks have been observed on the lower-energy side of the bulk core-exciton peak by a few tenths of an electron volt in the partial yield spectra from a cleaved NaCl (100) crystal surface.[50,51] If the nonradiative decay of such a surface exciton may occur in the present case, it is considered that the extra peaks due to the surface exciton appear on the lower-energy side of the peak due to the decay of the L_2 exciton in the CIS and CFS spectra of the sodium halides, and they overlap with the peak due to the decay of the L_3 exciton. The energy position of the lower-energy peak in the CIS spectrum of NaBr is about 0.18 eV lower than that of the L_2-exciton peak in the absorption spectrum (see Table II), and the FWHM value of the lower-energy peak in the CIS and CFS spectra of NaCl is about 1.5 times as much as that of the L_3-exciton peak in the absorption spectrum. Moreover the total probability of the L_3(exciton)-V process and the L_3(exciton)-VV process in NaBr is in excess of unity. These facts may be explained with the effect of the surface exciton. Thus, in this case, the decay probability for the bulk L_3 exciton should be smaller than the values listed in Table III, because these values have been estimated without taking account of the effect of the surface exciton. However, from the present study alone, it is not clear whether the difference between the decay probabilities estimated for the L_2 and L_3 excitons is caused by the relaxation process of the Na $2p$ core exciton or the effect of the surface exciton. Further investigations, such as the measurement of the angle dependence of the CIS and CFS spectra, are desired.

C. Decay of the higher excited states

Finally we will discuss the decay process of the higher excited states above 34 eV which appear as the broad bands and shoulders in the absorption spectra. According to Pantelides,[2] the absorption structures below the threshold (see Table I) are unequivocally purely excitonic. Nakai *et al.*[3,4] have suggested that the peak, which appears at 39.5, 36.6, 36.3, and 35.5 eV in the Na $L_{2,3}$ absorption spectra of NaF, NaCl, NaBr, and NaI, respectively, is probably due to a metastable exciton superposed on a background of the interband transitions. There are a few proposals to the origin of the structures which are observed above 40 eV in the absorption spectra, but none of them are generally accepted.[2–5,9]

As seen in Figs. 5–8, there is no distinct structure above 34 eV in the CIS spectra of all the sodium halides. On the other hand, the structures of the CFS spectra in the energy range above 34 eV correspond well to those of the absorption spectra (see Table III). These results indicate that an electron excited to the higher excited states above 34 eV decays without having a chance to recombine directly with the Na 2*p* core hole and thus these higher excited states decay through the Auger process due to the recombination of a Na 2*p* core hole with a valence electron.

The decay probability $P''(h\nu)$ of the higher excited states through the Auger process is approximated by using the probability P' of the L_2(exciton)-VV process as

$$P''(h\nu) \simeq P' \frac{I^{\mathrm{CFS}}(h\nu)/I^{\mathrm{CFS}}(h\nu^*)}{\alpha'_{2p}(h\nu)/\alpha'_{\mathrm{ex}}(h\nu^*)} , \tag{5}$$

where $I^{\mathrm{CFS}}(h\nu)$ is the intensity of the CFS spectra at the excitation photon energy $h\nu$ of the higher excited states, and $I^{\mathrm{CFS}}(h\nu^*)$ is the intensity at the excitation photon energy $h\nu^*$ of the L_2 exciton. These values are estimated from CFS spectra after the subtraction of the contribution of the secondary electrons which appears as the background in the raw data. In Eq. (5), $\alpha'_{2p}(h\nu)$ is the part of the absorption coefficient corresponding to the transition from the Na 2*p* core level to the higher excited state, and its value is derived after the subtraction of the components $\alpha'_{\mathrm{VB}}(h\nu)$ and $\alpha'_s(h\nu)$, which are due to the photoexcitation of the valence electron and the outermost *s* electron of the anion, respectively, from the raw absorption spectra. In the estimation, the photon-energy dependence of $\alpha'_{\mathrm{VB}}(h\nu)$ was approximated to be the same as that of the smooth background of the observed CIS spectra and $\alpha'_s(h\nu)$ was assumed to have the same photon-energy dependence as that of $\alpha'_{\mathrm{VB}}(h\nu)$. The result shows that the values of P'' for the higher excitonic state at 34.7 eV in NaCl, 34.2 eV in NaBr, and 34.2 eV in NaI are about 1.0 for all these halides. The values of P'' for the metastable exciton at 36.6 eV in NaCl, 36.3 eV in NaBr, and 35.5 eV in NaI are about 0.9, 1.0, and 1.0, respectively, and those for the higher excited states above 40 eV are 0.9–1.0 for NaCl, NaBr, and NaI. As seen from Fig. 9, the kinetic energy of the Auger electron produced by the decay of the higher excitonic states below the threshold is greater than that of the ordinary $L_{2,3}$(exciton)-VV Auger electron, while the kinetic energy of the Auger electron due to the decay of the excited states higher than the threshold is almost the same as that of the ordinary Auger electron. These results indicate that the higher excitonic states below the threshold and the excited states higher than the threshold may decay dominantly through the $L_{2,3}$(exciton)-VV and ordinary $L_{2,3}$-VV Auger processes, respectively.

V. CONCLUSION

The decay of the Na 2*p* core exciton in NaF, NaCl, NaBr, and NaI was investigated by photoelectron spectroscopy. It was observed that the intensities of the valence band and the Auger-electron peak are resonantly enhanced around the excitation photon energy of the Na 2*p* core exciton in NaCl, NaBr, and NaI, while only the Auger-electron peak shows resonant behavior in NaF. These results were interpreted in terms of the nonradiative decay of the core exciton through the $L_{2,3}$(exciton)-V and $L_{2,3}$(exciton)-VV processes. The dip appearing at about 33.2 eV in the CIS spectrum of NaF was interpreted as being due to the anomaly of the rate of escape of electrons. The important role of the correlation between two holes and one electron in the final state of the core-exciton decay through the $L_{2,3}$(exciton)-VV process, which has been suggested in lithium halides previously,[12,13] was confirmed by the energy shift of the Auger-electron peak in sodium halides. The decay probabilities of the Na 2*p* core exciton through the above two processes were roughly estimated from the CIS and absorption spectra. It was found that the decay through the $L_{2,3}$(exciton)-VV process is the dominant nonradiative decay in the sodium halides. The difference between the decay probabilities estimated for the L_2 and L_3 excitons was ascribed to the relaxation process of the Na 2*p* core exciton or the effect of the surface exciton. It was also observed that in the energy range above 34 eV, the intensities of the CIS spectra of all the sodium halides decrease monotonously with increasing photon energy. The decay probabilities of the higher excited states above 34 eV through the $L_{2,3}$(exciton)-VV or $L_{2,3}$-VV process were estimated to be 0.9–1.0 from the CFS spectra in NaCl, NaBr, and NaI. These results indicate that an electron excited to the higher excited states above 34 eV decays without having a chance to recombine directly with a Na 2*p* core hole.

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[35] This assumption involves implicitly another decay process of the Na 2p core exciton through the $L_{2,3}$(exciton)-M_1, $L_{2,3}$(exciton)-N_1, and $L_{2,3}$(exciton)-O_1 processes for NaCl, NaBr, and NaI, respectively, where a Na 2p core hole and an excited electron forming the core exciton recombine directly with energy transferred to an electron in the outermost s level of the anion. The probability of this decay process is considered to be much smaller than that of the $L_{2,3}$(exciton)-V process by taking account of the intensity ratio of photoelectrons from the outermost s level of the anion to those from the valence band.

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