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Temperature dependence of the nonradiative decay of the Na 2*p* core exciton in sodium halides

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The photoelectron and absorption spectra of NaF, NaCl, NaBr, and NaI were measured at room temperature and liquid-nitrogen temperature (LNT) to investigate the decay of the core exciton. The constant-initial-state (CIS) spectra with the initial state at the peak of the valence band of NaCl, NaBr, and NaI at LNT show two peaks around the excitation energy of the Na 2*p* core exciton, but the energy difference between these two peaks does not correspond to the spin-orbit splitting of the Na 2*p* core level. The higher-energy peak, which appears at the same photon energy and shows the same temperature dependence as those of the prominent exciton peak in the absorption spectrum, was interpreted as originating from the decay of the bulk-core exciton. On the other hand, the lower-energy peak, whose energy position does not coincide with that of the core-exciton peak in the absorption spectrum, was attributed to the decay of the surface-core exciton. In the case of NaF the CIS spectrum obtained at LNT shows the dip at the excitation energy of the Na 2*p* core exciton and the broad peak on the lower-energy side of the dip. This newly observed broad peak was attributed to another Na 2*p* core exciton distinct from the well-known Na 2*p* core exciton.

I. INTRODUCTION

Recently, we investigated the nonradiative decay processes of the Li 1*s* core exciton in lithium halides[1–3] and the Na 2*p* core exciton in sodium halides[4,5] by using resonant photoemission, which has been introduced by Lapeyre *et al.*[6] to study the nonradiative decay processes of the K 3*p* core exciton in KI. In these measurements the observed intensities of the valence band and the Auger-electron peak are resonantly enhanced around the excitation photon energy of the core exciton. To explain these phenomena the following two decay processes of the core exciton were proposed:[1,4] a core hole and a photoexcited electron, which form the core exciton, recombine directly with energy transferred to a valence electron. This process is called the "*K* (exciton)-*V* process" for lithium halides or the "$L_{2,3}$ (exciton)-*V* process" for sodium halides, where *K* (exciton) or $L_{2,3}$ (exciton) denotes the initial state with the *K* hole or the $L_{2,3}$ hole accompanied by a bound electron (core exciton), and *V* denotes the final state with a hole in the valence band. This process gives rise to the resonant enhancement of the constant-initial-state (CIS) spectrum with the initial state at the peak of the valence band around the excitation photon energy of the core exciton, because the final state of this process has the same configuration as that of the direct photoexcitation from the valence band at the excitation photon energy of the core exciton, and the CIS spectrum shows the intensity of the initial state versus the excitation photon energy as shown schematically in Fig. 1(a). In the second process, which is shown schematically in Fig. 1(b), the core hole forming a core exciton recombines wih a valence electron, transferring energy to another valence electron which is excited to the continuum state. This process is called the "*K* (exciton)-*VV* process" or the "$L_{2,3}$ (exciton)-*VV* process" and gives rise to enhancement in the constant-final-state (CFS) spectrum with the final state corresponding to the kinetic energy of the Auger electron, because the CFS spectrum shows the electron intensity with a fixed kinetic energy versus the excitation photon energy. The decay probabilities of these two decay processes were estimated from the photoelectron spectra and the absorption spectra,[2,4] and it was

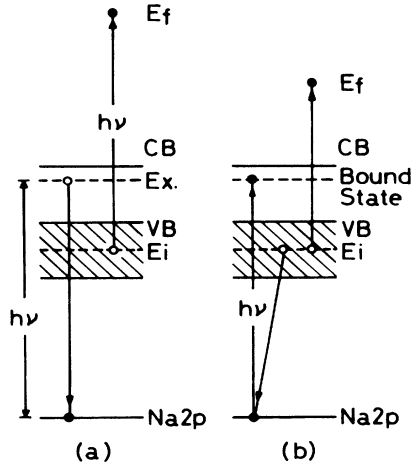

FIG. 1. Schematic illustration of nonradiative decay process of the Na 2*p* core exciton. (a) $L_{2,3}$ (exciton)-*V* process of which the final-state configuration involves one hole in the valence band and one electron in the continuum state. The kinetic energy of the resonant electron is the same as the primary valence emission. (b) $L_{2,3}$ (exciton)-*VV* process of which the final-state configuration involves two holes in the valence band, one electron in a bound state, and one electron in the continuum state. E_i and E_f indicate the initial state and the final state of photoelectrons, respectively. The tunability of synchrotron radiation is necessary for distinction of the two decay processes of the core exciton.

suggested that the decay probability of the latter process is greater than that of the former one both in lithium halides and in sodium halides. Moreover, it was found that the kinetic energy of the ejected electron in the latter process is slightly larger than that of the ordinary Auger electron.

In the course of the study on NaCl and NaBr, however, the extra peak, whose energy position does not coincide with that of the exciton peak in the absorption spectrum, was observed on the lower-energy side of the main peak, whose energy position coincides with that of the exciton peak in the absorption spectrum, in the CIS spectra with the initial state at the peak of the valence band of NaCl and NaBr, and the energy position and the profile of this extra peak depend strongly on the incident angle of exciting light on the sample surface.[5] This extra peak was attributed to the nonradiative decay of the surface-core exciton.[5] In the case of the NaI only a broad single peak was found in the CIS spectrum on the slightly lower-energy side of the core-exciton peak in the absorption spectrum. On the other hand, the CIS spectrum of NaF shows no distinct enhancement at the excitation photon energy of the Na $2p$ core exciton, but a shallow dip appears at that energy.[4] Origin of this dip was interpreted as being due to the anomaly of the rate of escape of electrons on the assumption that the decay probability of the Na $2p$ core exciton through the $L_{2,3}$ (exciton)-V process is zero in the case of NaF, and the observed anomaly was well simulated by the calculation.[4]

The transition, often referred to as surface-core excitons, has been observed in several materials[7–13] with the photoelectron spectroscopy or soft-x-ray absorption spectroscopy. The energy of the excitation to the surface state in III-V compound semiconductors has been estimated with several models,[14–16] but for ionic crystals, the relative energy of the surface-core excitons to the bulk ones has not been clearly explained yet.

The present study is concerned with the temperature dependence of the CIS and CFS spectra of sodium halides. The Na $L_{2,3}$ absorption spectra of sodium halides show the sharp and intense peaks due to the formation of the core exciton,[17–21] and these peaks shift by about 0.1 eV to the higher-energy side upon cooling the specimen from room temperature (RT) to liquid-nitrogen temperature (LNT).[19] However, we expect that the surface-core exciton would show the different temperature dependence from that of the bulk-core exciton. Moreover, we anticipate that the peak due to the decay of the surface-core exciton in the CIS spectrum is well resolved from the peak due to the decay of the bulk-core exciton at LNT, because the width of the bulk-exciton peak observed at LNT is narrower than that observed at RT in the absorption spectrum.

II. EXPERIMENTAL PROCEDURE

Photoelectron spectra at RT and LNT 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 0.03 eV at the photon energy of 33 eV with 50-μm slits and a 1200-groove/mm grating. The energy distribution of the photoelectrons 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. In the case of the CIS measurements the retarding potential between the specimen and the electron-energy analyzer was synchronously swept with the photon-energy scan of the monochromator. Also, the CIS spectra were constructed from a set of valence-band spectra excited at different photon energies. Good agreement was obtained in these CIS spectra measured by the different methods.

Specimens were prepared *in situ* by evaporation onto gold substrates at room temperature. After the evaporation no heat treatment was made and the spectra were measured immediately after evaporation. The thickness of the specimens was estimated to be about 100 Å with an oscillating-quartz thickness gauge. Spectral profiles did not change in scans after irradiation for several hours as compared with that in the first scan.

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 incident radiation on the specimens was determined from the photoelectric yield spectrum of gold.

The absorption measurements at RT and LNT were performed by using synchrotron radiation from a 750-MeV storage ring at the Institute for Molecular Science. A detailed description of the experimental procedure has been shown elsewhere.[4]

III. EXPERIMENTAL RESULTS

The CIS spectra with the initial state at the peak of the valence band, and the CFS spectra with the final state corresponding to the kinetic energy of the Auger electron, were measured for sodium halides at RT and LNT. The results are shown in Figs. 2–5 for NaF, NaCl, NaBr, and NaI, respectively, together with the respective absorption spectra. The spectra shown by dashed lines and solid lines were obtained at RT and LNT, respectively. These spectra were obtained with the normal incidence of exciting light, namely, were excited by the parallel component of the electric field vector of incident light. The intensity of the CIS spectra at RT and LNT is normalized around the photon energy of 34 eV for the covenience of the direct comparison of the increment of the valence-band intensity. The intensity of both CFS spectra is also normalized around the photon energy of 34 eV.

The absorption spectra of NaCl, NaBr, and NaI show a double peak around 33 eV, though in NaF only a single peak is seen in the absorption spectrum. These absorption peaks shift to the higher energy by about 0.1 eV and become narrower when the specimens are cooled. The origin of these peaks have been attributed to the creation

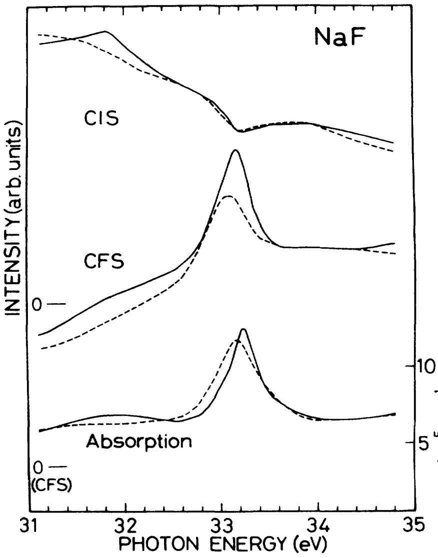

FIG. 2. CIS spectrum with the initial state at the peak of the valence band, CFS spectrum with the final state corresponding to the kinetic energy of the Auger electron, and Na $L_{2,3}$ absorption spectrum of NaF. Solid lines and dashed lines represent the spectra obtained at LNT and RT, respectively.

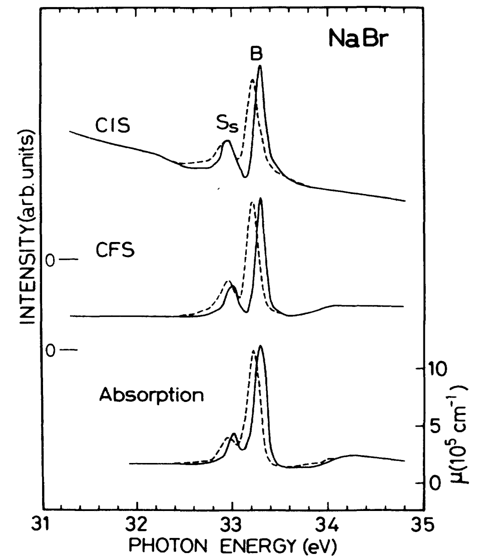

FIG. 4. CIS spectrum with the initial state at the peak of the valence band, CFS spectrum with the final state corresponding to the kinetic energy of the Auger electron, and Na $L_{2,3}$ absorption spectrum of NaBr. Solid lines and dashed lines represent the spectra obtained at LNT and RT, respectively.

of the Na 2p core excitons[17–22] at the Γ point in the Brillouin zone,[18] though the intensity ratio of the lower energy peak to the main peak is very different from the expected branching ratio of 2/1. According to the Onodera and Toyozawa theory,[23] this difference has been interpreted with intermediate coupling scheme, since the spin-orbit splitting of the Na 2p level and the energy of the exchange interaction between an electron and a hole of the core exciton are comparable in sodium halides.[18,19]

The CFS spectra are resonantly enhanced around the excitation photon energy of the Na 2p core exciton in all the sodium halides. This fact shows that the core exciton

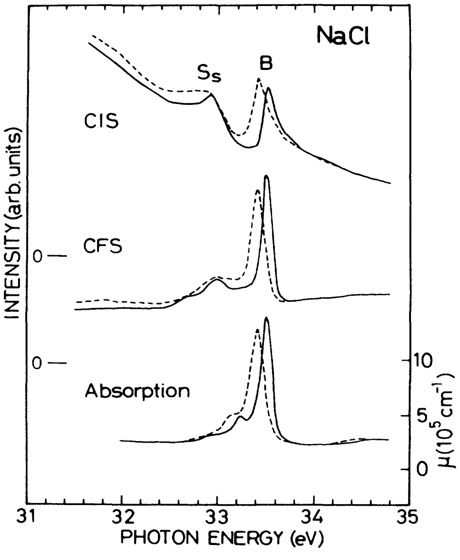

FIG. 3. CIS spectrum with the initial state at the peak of the valence band, CFS spectrum with the final state corresponding to the kinetic energy of the Auger electron, and Na $L_{2,3}$ absorption spectrum of NaCl. Solid lines and dashed lines represent the spectra obtained at LNT and RT, respectively.

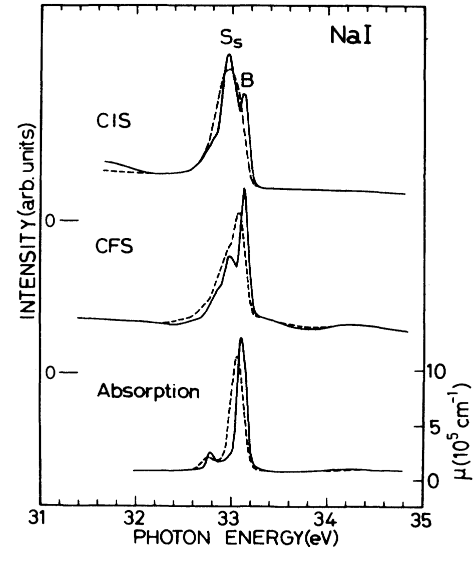

FIG. 5. CIS spectrum with the initial state at the peak of the valence band, CFS spectrum with the final state corresponding to the kinetic energy of the Auger electron, and Na $L_{2,3}$ absorption spectrum of NaI. Solid lines and dashed lines represent the spectra obtained at LNT and RT, respectively.

decays through the $L_{2,3}$ (exciton)-VV process as discussed in previous papers.[4,5] The energy position of the most intense peak B in NaCl, NaBr, and NaI agrees with that of the L_2-core exciton peak[24] in the respective absorption spectra, though in NaF the peak of the CFS spectrum is located at a slightly lower energy position than that of the exciton peak in the absorption spectrum. The FWHM values of the most intense peak B in the CFS spectra of NaCl and NaBr are in good agreement with those of the prominent peaks in the respective absorption spectra. However, the lower-energy peak in the CFS spectrum of NaCl does not coincide in energy with that in the absorption spectra and does not show the distinct energy shift upon cooling the specimen to LNT, while the position of the lower-energy peak of NaBr coincides with that of the absorption peak. In the case of NaI the CFS spectrum obtained at RT shows a single peak, but the cooling of the specimen splits this peak into two components. The energy position of the higher-energy component B in the CFS spectrum coincides with that of the higher-energy peak in the absorption spectrum at LNT, but the lower-energy one is located at the photon energy corresponding to the valley between the two peaks observed in the absorption spectrum at LNT.

The feature of the CIS spectra is different from that of the absorption and CFS spectra. The CIS spectra of NaF show no distinct enhancement at the excitation photon energy of the Na $2p$ core exciton, but a shallow dip appears at this energy. This dip was interpreted as being due to the anomaly of the rate of escape of electrons and the reflection loss of the incident light on the surface of the specimens on the assumption that the decay probability of the Na $2p$ core exciton through the $L_{2,3}$ (exciton)-V process is zero.[4] Upon cooling the specimen of NaF to LNT, a broad peak is clearly observed around 32 eV in the CIS, CFS, and absorption spectra though at RT this peak is buried in the background. On the other hand, the CIS spectra of NaCl, NaBr, and NaI are resonantly enhanced around the excitation photon energy of the core exciton, and thus it is considered that the $L_{2,3}$ (exciton)-V process clearly occurs in these substances.

In the case of NaCl and NaBr the main peak B of the CIS spectra at RT is located at the same energy position as that of the prominent peak of the respective absorption and CFS spectra, and shows the same amount of the energy shift as that observed in the absorption and CFS spectra when the specimens are cooled. On the other hand, the position of the lower-energy peak in the CIS spectra is different from that in the absorption spectra and no distinct energy shift is observed upon cooling the specimens to LNT. In the case of NaI a single peak is observed in the CIS spectra obtained at RT, and this peak splits into two components upon cooling as in the case of CFS spectra. The energy position of the higher-energy component at LNT well coincides with that in the absorption spectrum at LNT, though there is no peak in the absorption spectrum to coincide in energy with the CIS peak at RT. In the case of the lower-energy component at LNT, however, no corresponding peak is seen in the absorption spectrum at LNT.

IV. DISCUSSION

It is well known that unannealed alkali halide films contain high densities of point defects.[25,26] The irradiation of the vacuum ultraviolet can also generate these defects on the surface by a photochemical process.[27] Gallon *et al.*[28,29] have shown that the F-center electron can actually participate in Auger decay of shallow core holes in LiF. In the present study, however, no spectral change was observed in scans after irradiation for several hours. Then, we can probably rule out the possibility of participation by point defects.

Previously we measured the incident-angle dependence of the CIS and CFS spectra of sodium halides.[5] The results on NaCl are shown in Fig. 6. The CIS spectrum indicated by a solid line in Fig. 6 shows a peak S_p at 33.1 eV and a peak B at 33.4 eV which agrees well with the Na L_2 core-exciton peak of the absorption spectrum. In this case the incident angle of light on the sample surface was 45°, namely, the angle between the electric field vector of incident light and the sample surface was set at 45°. On the other hand, the spectrum indicated by a dashed line in Fig. 6, which was excited with the normal incident light with the electric field vector parallel to the sample surface, shows a new peak S_s at 32.8 eV and the peak S_p disappears in this condition. Moreover, the intensity of the peaks S_s and S_p reduced in the CIS spectra of NaCl with contamination. These polarization and surface-sensitive behavior suggest that the peaks S_s and S_p do not reflect bulk properties but surface properties. Similar incident-angle dependences were found in the CIS and CFS spectra of NaBr and NaI. A detailed description has been shown elsewhere.[5]

These surface-sensitive structures show different temperature dependences in energy from the bulk-derived structures as seen in Figs. 3–5. On the contrary, the higher-energy peak in the CIS spectra obtained at RT and LNT is observed at the same energy position as that of the main peak in the respective absorption spectra, and

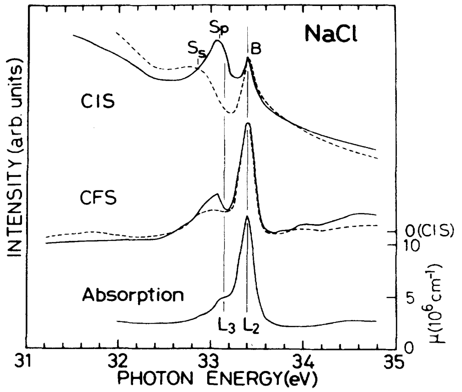

FIG. 6. CIS and CFS spectra of NaCl obtained at the incident angles of 0° (dashed lines) and 45° (solid lines), and the Na $L_{2,3}$ absorption spectrum at RT. Vertical lines are drawn at the L_2- and L_3-core exciton peaks.

its width in the CIS spectra agrees approximately with that of the main peak in the absorption spectrum. Thus, the higher-energy peak in the CIS spectra can be attributed to the nonradiative direct recombination of the bulk-core exciton.

Rehder *et al.*[10] have measured the partial-yield spectra from the (100) surface of a cleaved NaCl crystal and found that the spectral feature depends strongly on the polarization of incident light and the lower-energy peaks in the spectra disappear upon contamination of the surface. These surface-sensitive peaks have been interpreted as being due to the surface-core excitons.[10,11] They have also found the similar peak in the total yield spectrum of a thin evaporated film of NaCl to that observed in the spectrum of the (100) surface of the single crystal and attributed this peak to the surface-state feature since thin films of NaCl form microcrystals with cubic symmetry.[30]

It is known that the deposited thin films of NaCl form microcrystals with strong preferred orientation.[30] We examined preferred orientation in thin films of NaCl and NaBr evaporated on gold substrates with the x-ray diffraction method, and found that the films of NaCl show only the preferred orientation of the ⟨001⟩ and ⟨011⟩ directions, and those ⟨001⟩ and ⟨011⟩ axes extend within ±7.5° and ±13°, respectively, around the normal of the sample surface.[5] In the case of NaBr the preferred orientation of the thin film was the ⟨001⟩ and ⟨111⟩ directions and their axes extend within ±5° and ±6.5°, respectively, around the normal of the sample surface.[5] These facts mean that even the surface of the evaporated films might exhibit more or less the surface properties similar to that of a single crystal.[5]

The energy position of the surface-core exciton relative to the bulk-core exciton has been discussed by Henrich *et al.*[31] for a MgO. According to them, there is a large gradient of the Madelung potential at the surface of the ionic insulator which gives rise to a strong electric field perpendicular to the surface. This field causes the electronic states of the Na^+ ion to split in a manner similar to the Stark splitting. The Stark effect causes the 3*s* state to the downward energy shift and one of the 2*p* states, whose eigenfunction is directed to the parallel, to the external electric field, to the upward energy shift. However, this upward energy shift of the 2*p* core state is negligibly small to be observed,[31] and then only a surface-core exciton should be observed in the lower-energy region of the bulk one owing to the downward energy shift of the 3*s* state of the surface ion, and may not show any dependence of its energy position on the incident angle of exciting light on the sample surface.

Let us consider the excitonic states at the (001) surface. In the surface layer of the (001) surface each sodium ion is surrounded by four halogen ions and only one halogen ion in the direction perpendicular to the surface. Thus, the electrons around the Na^+ ion in the surface layer are influenced by the crystal field of the C_{4v} symmetry rather than the O_h symmetry in the bulk, and this field splits the Na 2*p* states into two levels. We estimate the difference of this crystal field of the C_{4v} symmetry from the O_h field in the bulk by assuming that each neighboring ion is a point charge.[32] The result is

$$V' = -\frac{e^2}{a}\left[1+\frac{r\cos\theta}{a}-\frac{r^2}{2a^2}+\frac{3}{2}\frac{r^2\cos^2\theta}{a^2}+\cdots\right], \tag{1}$$

where a is the distance between the cation and the anion, and r and θ are the distance from the central Na^+ ion to an electron in question, and the polar angle from the ⟨001⟩ axis, respectively. The first term causes the downward energy shift of each level from that in the bulk state by the same amount. A similar equation of the distorted potential will be obtained for the anion site. The first term of this equation for the anion causes the upward energy shift for levels of the anion. These energy shifts give rise to the reduction in the surface-band gap resulting from the smaller Madelung potential at the surface. According to the Levine and Mark approach[33] this reduction of the surface-band gap at the (001) surface is estimated to be about 0.37, 0.33, and 0.26 eV for NaCl, NaBr, and NaI, respectively. Therefore, each level of Na^+ ion at the surface shifts downward and levels of the anions shift upward by a half of the above values, respectively. However, the transition energy from the Na 2*p* to Na 3*s* levels at the surface, which corresponds to the core-exciton transition, does not change from that in the bulk even though the surface-band gap becomes narrower.

The second term in Eq. (1) causes the Stark splitting mentioned above. The third and fourth terms remove the degeneracy of the 2*p* states and split them into two levels. In estimating this splitting, we used the wave function of the hydrogenlike atom.[34] The result shows that the eigenvalue belonging to the 2*p* wave function perpendicular to the surface plane is lowered by $18e^2a_0^2/(a^3Z^2)$ from that belonging to the wave function parallel to the surface plane, where a_0 is the Bohr radius and Z is an effective charge seen by the Na 2*p* electrons. Thus, two kinds of surface-core excitons are expected on the lower-energy side of the excitation photon energy of the bulk-core exciton. One of them is formed with the Na 2*p* wave functions in the direction perpendicular to the surface (S_p surface-core exciton) and can be excited with incident light whose electric vector perpendicular to the surface (*p*-polarized light). The other is formed with the Na 2*p* wave functions parallel to the surface (S_s surface-core exciton) and can be excited with incident light with the electric vector parallel to the surface (*s*-polarized light). This surface-core exciton is located on the lower-energy side of the S_p surface-core exciton as shown in Fig. 6.

Similar polarization behavior is expected for the (011) surface. Though the situation for this surface is somewhat different from that for the (001) surface, two kinds of the Na 2*p* states are expected from simple consideration for the symmetry of the coordination in this surface. One of them responds to only *s*-polarized light and the other responds to both *s*- and *p*-polarized light. Thus, even in this case two surface-core excitons are expected though the energy positions of these surface-core excitons may be a little different from those observed at the (001) surface. However, the CIS spectrum of NaCl shows only one peak on the lower-energy side of the bulk-exciton peak as seen in Fig. 3. Therefore, the energy positions of the surface-core excitons formed at the (011) surface may not be so different from those formed at the (001) surface.

The energy positions of the surface-core excitons at the (001) surface are calculated. In the calculation the effective charge Z was determied by Slater's rule,[34] and it was assumed that the distance between the cation and the anion at the surface is the same as that in the bulk. The results are given in Table I together with the observed values. The observed values are rather approximate ones, because in the case of the spectra obtained at the incident angle of 45°, the spectra should show both of the S_p and the S_s surface-core excitons. However, the peak S_p is clearly seen in the spectra obtained at 45° between the peak positions of the S_s surface-core exciton and the bulk-core exciton. Thus, we take the energy position of the S_p surface-core exciton as the peak position of the S_p peak.

The calculated values of the energy difference between the bulk-core exciton and the S_s surface-core excitons are larger than the observed ones by a factor of 3–5. On the contrary, the calculated values of the distance between two surface-core excitons are smaller than the observed ones.

The reasons for the discrepancies between the calculated and observed values may be supposed as follows: (1) the wave functions used for the calculations are rather approximate, (2) the effective charges are not determined precisely, and (3) the sodium and halogen ions are not the point-charge completely. However, the systematic change of the energy position of the surface-core excitons among sodium halides is well explained in the present model. For example, since energy due to the Stark effect (second term) varies inversely with the square of the lattice constant which increases with going from NaCl to NaI and decreases upon the cooling, the energy separation between the bulk- and surface-core excitons decreases with going from NaCl to NaI and increases at LNT. This expectation is good in agreement with the present experimental results shown in Figs. 3–6 and Table I. Moreover, since the energy separation between the S_s and S_p excitons depends on the inverse cube of the lattice constant, it must decreases with going from NaCl to NaI. This is the reason why the CIS and CFS spectra of NaI show the single peak at RT.

It is worthwhile noting that the magnitude of the enhancement of the excitation energy of the core exciton is somewhat different between the CIS spectra with the different initial states. For example, the CIS spectra of NaCl and NaBr with the initial state at the shoulder in the valence-band spectrum are more enhanced at the excitation energy of the core exciton than those with the initial state at the peak of the valence-band spectrum, while in the case of NaI the peak of the valence band is more enhanced than the shoulder. These facts suggest that an electron at some singular points in the Brillouin zone is selectively excited with the annihilation of the core exciton as observed in LiCl and LiBr.[3] In the case of sodium halides, the broadening of the valence-band spectra at the excitation energy of the core exciton is not observed in contrast to the case of lithium halides. This fact means that the relaxation of the Na 2p core exciton during the decay through the $L_{2,3}$ (exciton)-V process is too slow or is too small to be observed with the present experimental resolution of the electron-energy analyzer.

It is interesting whether or not the change of the nonradiative decay probability of the bulk-core exciton through the L_2 (exciton)-V process is observed in the spectra when the specimens are cooled from RT to LNT. It turned out that the decay probabilities at RT and LNT due to the L_2 (exciton)-V process are almost the same for NaCl and NaBr, within experimental accuracy, after the calculations were followed through following the same procedure as that described in previous papers.[2,4]

Finally, we consider the spectra of NaF. The spectra in Fig. 2 show different features from those of the other sodium halides. The CIS spectrum shows the dip instead of the peak at 33.2 eV, and the FWHM value of the Na 2p core-exciton peak in the absorption spectrum is very broad as compared with that in the other sodium halides. Moreover, the broad peak seems to grow clearly at about 31.8 eV in the CIS spectrum when the specimen is cooled. The CFS and absorption spectra at LNT also show the broad peak at the same energy. Thus, this peak may originate in the bulk state instead of the surface state.

The calculation of the energy bands suggests that the bottom of the conduction band is at the Γ point and has s-like character.[35] Also, it is generally accepted that the threshold from the Na 2p level to the bottom of the conduction band is 36.3 eV at RT for NaF, and the structures below the threshold are due to the core excitons.[22] The sharp peak at 33.2 eV in the absorption spectrum has been assigned to the Na 2p core exciton at the Γ point in the Brillouin zone.[18]

The valence band of NaF is mainly composed of the 2p state of the F^- ion, and the shallow core levels are the F

TABLE I. The energy difference between the bulk-core exciton and the S_s surface-core excitons, $\Delta(\text{bulk}-S_s)$, and the splitting energy between the surface-core excitons, $\Delta(S_p-S_s)$. All values are given in electron volts.

	$\Delta(\text{bulk}-S_s)$		$\Delta(S_p-S_s)$	
	Calc.	Obs.	Calc.	Obs.[a]
NaCl	1.40	0.60	0.06	0.24
NaBr	1.25	0.30	0.05	0.12
NaI	1.06		0.04	

[a] Reference 5.

2s level and the Na 2p level. Pantelides[22] has estimated the threshold from the F 2s level to the bottom of the conduction band to be 34.7 eV at RT from the x-ray photoemission and optical band-gap data. Therefore, one of the possibilities of the origin of the peak at 31.8 eV in the absorption spectrum is that this peak is caused by the transition from the F 2s level to the excitonic state below the conduction band. If this is the case, the peak at 31.8 eV in the CIS spectrum would be ascribed to the nonradiative direct recombination of the F 2s hole and the excited electron which form the F 2s core exciton.

Another possibility is that the newly observed peak at 31.8 eV originates from another Na 2p core exciton. If the Na 2p core exciton observed at 33.2 eV is not so stable and can easily relax to the stable state, i.e., the Na 2p core exciton at 31.8 eV, this process causes the broadening of the linewidth of the well-known exciton peak at 33.2 eV and disturbs the direct recombination decay of this core exciton. Thus, the dip at 33.2 eV in the CIS spectrum of NaF is interpreted as being due to the lack of the $L_{2,3}$ (exciton)-V process in cooperation with the anomalies of the reflectivity of the incident light on the sample, and the short escape depth of the photoelectron in this energy region. Moreover, since this relaxation leaves the core hole in the Na 2p states unchanged, the $L_{2,3}$ (exciton)-VV process can be observed as the enhancement of the CFS spectrum at 33.2 eV. Therefore, this assignment of the newly observed structure at 31.8 eV explains consistently the structures appearing in the absorption, CIS, and CFS spectra at this time.

V. SUMMARY

The CIS, CFS, and absorption spectra of NaF, NaCl, NaBr, and NaI were measured at RT and LNT. The resonant enhancement of the intensity of the valence band and the Auger-electron peak is observed around the excitation energy of the Na 2p core exciton in NaCl, NaBr, and NaI, while in NaF only the Auger-electron peak shows the resonant behavior in this energy region. The CIS spectrum of NaF shows the dip at the Na 2p core-exciton peak observed in the absorption spectrum. The peak was newly observed in the CIS and absorption spectra of NaF on the lower-energy side by about 1.5 eV than the well-known core-exciton peak. The CIS spectra of NaCl, NaBr, and NaI at LNT show two peaks around the excitation energy of the Na 2p core exciton, but the energy difference between these two peaks does not correspond to the spin-orbit splitting of the Na 2p level. The higher-energy peak, which appears at the same photon energy and shows the same temperature dependence as those of the prominent exciton peak in the absorption spectrum, was interpreted as originating from the decay of the bulk-core exciton. On the other hand, the lower-energy peak, whose energy position does not coincide with the core-exciton peak in the absorption spectrum, was attributed to the decay of the surface-core exciton. The origin and the energy positions of the surface-core exciton were interpreted in terms of the distortion of the symmetry at the surface from the O_h symmetry in the bulk. It was found that the decay probabilities of the Na 2p core exciton through the $L_{2,3}$ (exciton)-V process at RT and LNT are comparable in NaCl and NaBr. The newly observed peak on the lower-energy side of the well-known exciton peak in the CIS and absorption spectra of NaF was attributed to another Na 2p core exciton distinct from the well-known core exciton.

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