Resonant Double Excitation Observed in the Near-Threshold Evolution of the Photoexcited F $K\alpha$ Satellite Intensity in NaF

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We present a precise measurement of the photoexcited F $K\alpha$ satellite intensity's evolution for NaF from $[1s2p]$ double excitation threshold to saturation. A direct comparison between the observed evolution and the x-ray absorption spectrum was successfully made, and the contribution of multi-electron transitions to the absorption spectrum was clearly resolved for the first time. A resonancelike feature observed in the near-threshold evolution is attributed to the $[1s2p]3p^2$ resonant double excitation as confirmed by calculations.

With the advent of recent synchrotron radiation (SR) sources, a study of multielectron processes, e.g., shakeup (SU) single ionization or shakeoff (SO) double ionization, accompanying the innershell photoionization has received special attention as a powerful method to investigate intra-atomic *e-e* correlations especially near their thresholds [1–3]. In such experiments, the intensities of x-ray satellite or hypersatellite lines are measured as a function of exciting photon energy by x-ray emission spectroscopy (XES). The measured intensity's evolution of these satellite lines was compared with predictions based on the analytic Thomas model [4]. The continuous intensity rise from zero at threshold indicates that the origin of multiple vacancy production for core electrons in innershell photoabsorption of medium-Z atoms is a pure SO process.

On the other hand, the multielectron contribution due to the SU process is evidently seen in the x-ray absorption near edge structure (XANES) spectra [5]. In the sub-keV region, a rich phenomenology concerning both the multi-electron processes and the chemical effects is expected especially for valence electrons in the solid-state target; furthermore, the relative importance of the SU process increases and deviations from the Thomas model is expected. It can be studied by soft x-ray emission (SXE) spectroscopy [6] where the existence of spectator vacancies influences the valence-to-core as well as the core-to-core x-ray emission [7,8]. In order to study such processes, ionic fluorine compounds are an intriguing class of materials.

In the soft x-ray region, x-ray absorption spectra have been measured for various fluorine compounds, e.g., F-K XANES of alkali [9], alkaline-earth [10], and $3d$ transition-metal [11] fluorides, to study their electronic structure. The obtained F-K XANES spectra were compared with short-range order multiple scattering calculations [9,10]. Although theoretical calculations have shown

qualitative agreement in gross spectral features, they do not take into account the contribution of multielectron processes which must be considered above their threshold. Thus, if we precisely measure the satellite intensity's evolution in compounds for which rich structures are observed in XANES, we can study and characterize the contribution of multielectron transitions.

While most of the early work on F $K\alpha$ emission [12–15] has studied the chemical bonding effects reflected in the x-ray satellite spectra of various fluorides, Rubensson *et al.* [7] investigated multielectron correlation effects in CaF_2 by SXE spectroscopy using SR. More recently, Uda *et al.* [16] have measured the evolution of photoexcited F $K\alpha$ satellite intensity in CaF_2. They have shown the existence of a small bump in the evolution curve and ascribed it to resonance in multielectron excitation, although the number of data points in their experiment is not enough to discuss fine structure of the evolution curve. Thus, it was felt important to measure the evolution of satellite lines more precisely for valence-to-core transitions in a fluoride and compare it with XANES spectra as well as multiconfiguration cluster calculations in order to identify the origin of the observed features. In this Letter, we study the F-K absorption and the F $K\alpha$ emission spectra of a highly ionic fluorine compound NaF. The high-resolution SR induced spectra show clear evidence for multielectron transitions and a resonance-like feature observed near threshold is attributed to a resonant double excitation as calculated from a cluster model including on-site Coulomb interactions and multiplet splitting.

The experiments were performed at the undulator beam line of BL-2C at Photon Factory, KEK. The F-K absorption spectrum was measured by means of the total photon yield (TPY) method using a photodiode. The $K\alpha$ emission spectra were measured as a function of exciting photon-energy using an SXE spectrometer [17]. The

sample used was single-crystalline NaF, which is a stable ionic insulator crystallizing in the NaCl structure. No correction was made for self-absorption and detector efficiency because the range of energies spanned by the F $K\alpha_{1,2}$ to $K\alpha L^2$ x rays, where $K\alpha L^n$ denotes a configuration with a single K vacancy and nL vacancies, is small. The energy scale of the SXE spectrum was calibrated using the geometrical parameter and the energy of the $K\alpha_{1,2}$ emission reported in the literature. The accuracy of the energy scale for emission spectra was estimated to be about ± 0.2 eV. The calibration of exciting photon energy was carried out by measuring the kinetic energies of $4f$ photoelectrons emitted from the Au surface.

Figure 1 shows the spectral variation of the F $K\alpha$ emission for NaF with excitation energies starting from the near onset of $[1s2p]$ double excitation, which can be calculated to be about 706.7 eV by the $Z + 1$ approximation [18], to energies high enough above the threshold, where square brackets indicate hole states. As can be seen in this figure, the spectral shape in the region of $K\alpha L^1$ ($K\alpha'$, $K\alpha_3$, and $K\alpha_4$) satellite lines is very sensitive to the excitation energy. The relative intensity ratio between $K\alpha_3$ ($[1s2p]^3P \to [2p^2]^3P$) and $K\alpha_4$ ($[1s2p]^1P \to [2p^2]^1D$) drastically changes in the excitation energy range between 712.4 and 720.4 eV. Above 720.4 eV, the $K\alpha_4/K\alpha_3$ intensity ratio converges to almost the unity. At excitation energies above 750 eV, although it is not
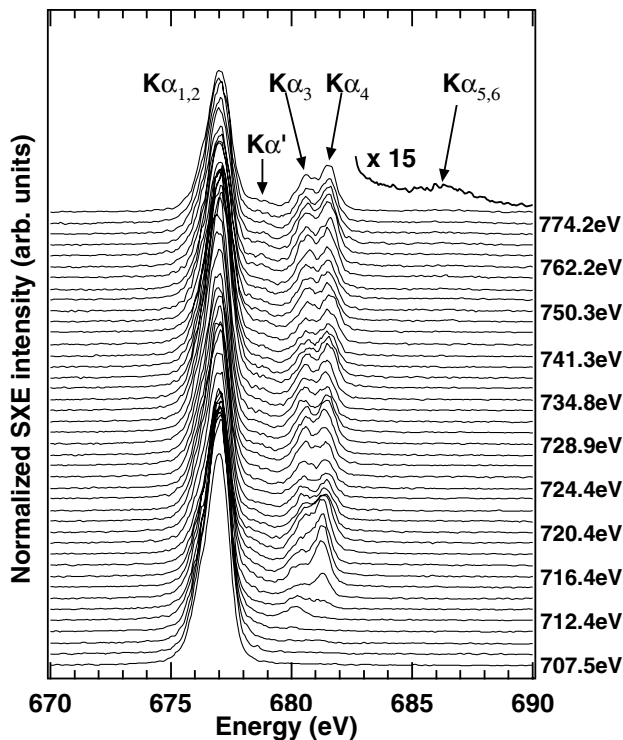
clearly visible in Fig. 1, a small hump was observed at around 685 eV corresponding to the emission energies of the $K\alpha_{5,6}$ ($K\alpha L^2$) group. Here the peak intensities and the centroid energies of $K\alpha_{1,2}$, $K\alpha L^1$, and $K\alpha L^2$ lines were carefully determined by means of least-squares fitting procedures. The obtained energies, i.e., 680.5 ± 0.5 ($K\alpha_3$), 681.4 ± 0.5 ($K\alpha_4$), and 685.8 ± 0.6 ($K\alpha_{5,6}$) eV, are in good agreement with previous data [14,15]. The energy 678.5 ± 0.5 eV for the $K\alpha'$ line ($[1s2p]^1P \to [2p^2]^1S$) was experimentally determined for the first time.

All the obtained peak intensities are normalized by the accumulation time and incident photon flux monitored by the drain current of the refocusing mirror. Resultant normalized SXE yields are plotted in Fig. 2 together with the F-K XANES spectrum (upper solid line). As can be seen in the figure, the energy dependence of the total SXE yields (open circles), where $total$ SXE $= K\alpha_{1,2} + K\alpha L^1 + K\alpha L^2$, resembles the absorption spectrum reasonably well. The curve of the $K\alpha L^1$ yields (open triangles) reflects the excitation function of $[1s2p]$ double excitation, while the closed circles demonstrate the F-K absorption spectrum free from the contribution of multielectron transitions. Furthermore, it is noteworthy that the energy of the peak in the $K\alpha L^1$ yield curve at 718.4 eV coincides with that of the dip in the $K\alpha_{1,2}$ yield curve. The peak at 718.4 eV is ascribed to the resonant double excitation, e.g., $[1s2p]3p^2$ configuration, as discussed in terms of atomic calculations using the Hartree-Fock method by Uda et $al.$ [16]. They have observed a similar resonancelike feature around 715 eV, although it appeared as a small bump, in the evolution of the $K\alpha L^1$ satellite of F in CaF_2.
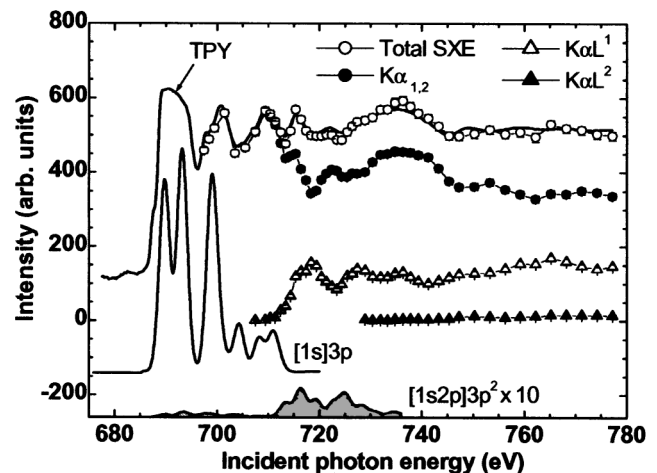

FIG. 1. Spectral variation of the F $K\alpha$ emission for NaF. Typical energies of the exciting photons are indicated beside each spectrum.

FIG. 2. The F-K absorption spectrum (upper solid line) of NaF measured by the TPY method. The normalized SXE yields are plotted as a function of the exciting photon energy for comparison. Theoretical fluorescence XANES spectra for the $[1s]3p$ single excitation (lower solid line) and the $[1s2p]3p^2$ double excitation (solid line with shade) are also presented.

In order to understand and confirm the origin of the observed features, we have calculated the F-K fluorescence XANES spectra in terms of coherent second-order optical processes based on the formulation described in Ref. [20]. In the calculations, the ground state was assumed to be $2p^6$ electronic configurations, i.e., F^- ions. This is in line with the fact that the valence electrons are mostly F $2p$ character because of high Pauling bond ionicity 0.909 of NaF [12]. The intermediate states and final states of the dipole transition are linear combinations of $1s^1 2p^6 3p^1$ and $1s^1 2p^5 3p^2$ configurations, and $1s^2 2p^5 3p^1$ and $1s^2 2p^4 3p^2$ configurations, respectively. The Slater integrals and the spin-orbit coupling constants were calculated by Cowan's Hartree-Fock program [21] and then the Slater integrals were scaled down to 80%. In order to calculate the spectrum, we have adopted the F $3p$ partial density of state (pDOS) obtained by molecular orbital (MO) calculations with the DV-$X\alpha$ method [22] using a cluster model with O_h symmetry. Gaussian broadening due to the experimental resolution was taken into account. In Fig. 2, the lower solid curve represents the excitation of the $1s$ electron into the $3p$ states forming the unoccupied t_{1u} MO, and the solid line with shading shows the double excitation of $1s$ and $2p$ electrons, namely, the $[1s2p]3p^2$ state. This $[1s2p]3p^2$ curve shows the structure below the threshold of $[1s2p]$ double excitation. This is caused by the energy window used to calculate the fluorescence XANES which covers not only the satellite lines, but also the Lorentzian tail of the diagram lines. Although the calculated XANES spectra represent a rather sharp structure, a gross feature of the experimental spectrum is reproduced fairly well, especially near the onset of $[1s2p]3p^2$ double excitation. Therefore we attribute the structure at 718.4 eV to be the $[1s2p]3p^2$ resonant double excitation.

Figure 3(a) shows the evolution curve of the $K\alpha L^n / K\alpha_{1,2}$ intensity ratio for F in NaF from the $[1s2p]$ double excitation threshold to energies high enough to produce $[1s2p^2]$ triple vacancy states. This figure shows clearly the resonance at 718.4 eV. Previous measurements and calculations for the intensity ratio are also plotted in the figure [12–15]. In all of these previous measurements, the incident energies of photons or electrons were high enough above the ionization threshold and the values of intensity ratio can be considered to be those in the sudden limit, corresponding to the asymptotic value in the present experiment. These intensity ratios reflect the $K + L$ shake probabilities for F atoms in NaF. The evolution curve for the $K\alpha L^1$ satellite intensity is not smoothly increasing as a function of exciting photon energy, but has rich structure. This feature is completely different from previous work on the evolution of x-ray satellites [1–3]. In previous studies, except for the work by Sternemann *et al.*, they have measured the satellite lines arising from core-to-core transitions in medium-Z atoms. In such cases, the dominant mechanism of mul-
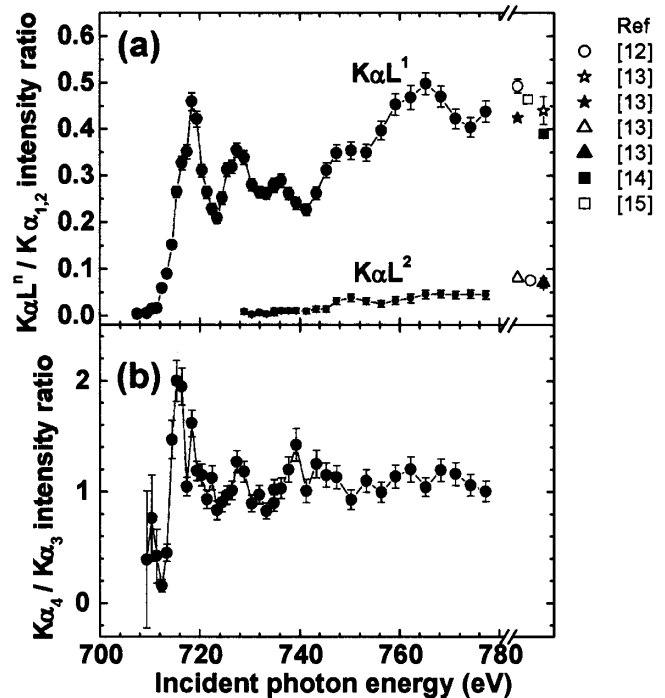

FIG. 3. (a) Evolution curves for the $K\alpha L^n / K\alpha_{1,2}$ intensity ratio together with the previous measurements and the calculations. (b) The $K\alpha_4 / K\alpha_3$ intensity ratio as a function of the excitation energy.

tiple ionization is due to the SO process, where inner-shell multielectron excitation and x-ray emission processes are not affected much by the chemical environment. On the other hand, since the F $K\alpha$ emission in NaF arises from the valence-to-core transition, the SU mechanism plays an important role, and the excitation and emission processes must be significantly affected by solid-state band-structure effects. The multiple excitation to the unoccupied MOs may have larger probability than in the case when only core electrons are excited. There is no information, however, about the difference in the near-threshold photon-energy dependence of SU versus SO processes suitable for the present study. Therefore, we refer to the experimental results of SU and SO probabilities accompanying the K-shell photoionization for atomic neon. The values of SU and SO probabilities measured using monochromatized x rays ($h\nu = 1487$ eV) are 9.1% [23] and 15.8% [24] relative to single excitation, respectively. Although we cannot extract the SU probability from the present study, we could estimate the total $K + L$ shake probability to be 31% in the sudden limit using the relationship between the transition probability and the relative intensity [25].

As mentioned previously, the evolution of the spectral shape between 712.4 and 720.4 eV for the $K\alpha L^1$ region is quite sensitive to the excitation energy. In Fig. 3(b), the $K\alpha_4 / K\alpha_3$ intensity ratios are plotted against the exciting photon energy. This behavior is completely different from
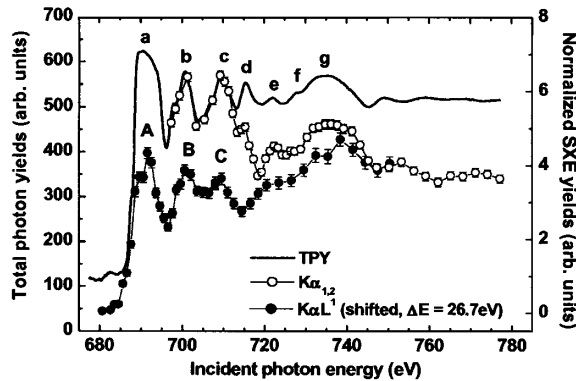
FIG. 4. The F-K absorption spectrum (thick solid line) of NaF compared with the evolution curves for the normalized SXE yields for $K\alpha_{1,2}$ and $K\alpha L^1$ lines. The $K\alpha L^1$ satellite intensity's evolution was shifted in energy axis by 26.7 eV to the lower energy side.

the case of the Cu $K\alpha_{3,4}$ linear growth model [1]. We see an abrupt growth of the $K\alpha_4$ line in comparison with the $K\alpha_3$ line starting several eV above the $[1s2p]$ double excitation threshold. This trend is apparently concerned with a selective excitation to the term dependent $[1s2p]$ double vacancy state near the threshold. According to the atomic calculation by multiconfiguration Dirac-Fock method using the GRASP code [26], the lowest double vacancy state is $[1s2p]^3P_2$ and the $[1s2p]^1P_1$ state locates at around 3.2 eV above that state. Therefore we could only observe the $K\alpha_3$ line just above the threshold and see the abrupt growth of the $K\alpha_4$ line from the $[1s2p]^1P_1$ threshold. When the excitation energy is high enough above the threshold of $[1s2p]$ double vacancy production, the $K\alpha_4/K\alpha_3$ intensity ratio converges to constant value because it should depend only on the statistical population of $[1s2p]$ states. This saturation value is strongly dependent on the chemical bonding as was pointed out by Demekhin and Sachenko [27].

In Fig. 4, we present the F-K absorption spectrum together with the energy-shifted $K\alpha L^1$ satellite intensity's evolution (closed circles) and the yield curve of $K\alpha_{1,2}$ lines (open circles). The shift energy $\Delta E = 26.7$ eV is in fairly good agreement with the theoretical energy difference 23.6 eV between the $[1s]3p$ single excitation and the $[1s2p]3p^2$ double excitation as shown in Fig. 2. Figure 4 clearly demonstrates the evidence of the suggestion by Brown et al. [28]. In their Cl$^-$ $L_{2,3}$ absorption spectrum of NaCl, they ascribed peaks observed at about 10 eV above the threshold to the replicas caused by double electron excitation. It is apparent that the spectral shape and the energies of the peaks a, b, and c resemble very much the spectral range between A and C. Thus, the structure A–C, which originates in the excitation to multiply excited states in the continuum, is a replica of the structure a–c. This is due to variations in the density of

states which allows the core electrons to excite just like single electron excitation. This would give rise to resonances in the close-lying normal-monopole SU excitations. This conclusion is supported by the calculation for F $3p$ pDOS shown in Fig. 2. Thus, the spectral region between d and g definitely contains the contribution of multielectron processes. In conclusion, the evolution curve by XES can be used to separate the contributions of the single and double excitation processes in XANES spectra.

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