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Experimental investigation of the origin of the Ti $K\alpha''$ satellites

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The Ti $K\alpha''$ satellite is investigated using a Johann-type spectrometer on the BL15XU undulator beam line of SPring-8 at excitation energies between 4996 and 7000 eV. The intensity of the $K\alpha''$ satellite relative to that of $K\alpha_{1,2}$ exhibits an abrupt jump from 0% to ~1% in a range of 10 eV around an excitation energy of 5010 eV. The energy range to reach saturation is ~500 eV. The creation of spectator holes is implicated to be due to shake-up processes, inducing the emergence of the $K\alpha''$ satellite. The onset energy for the appearance of the satellite is 5011.0 eV ± 0.8 eV, corresponding to the $[1s3p]$ double-ionization threshold energy by a $Z+1$ approximation. The experimental results obtained in this work confirm that the $K\alpha''$ satellite originates from a $3p$ spectator hole, as predicted theoretically by Scott [Phys. Rev. A **34**, 4438 (1986)].

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I. INTRODUCTION

With the advent of third-generation synchrotron-radiation facilities, insertion devices offering tunability and high intensity can now be used, and multielectron transitions in x-ray spectroscopy have begun to receive special attention. Notably, the study of threshold processes is one of the most interesting and fruitful approaches in developing a deeper understanding of atomic and molecular structures and dynamics [1–4].

The multielectron transition processes in $3d$ elements have been studied with great interest from the early days of x-ray spectroscopy. This process can be observed as satellite or hypersatellite peaks in x-ray emission spectra, and as discontinuities in the differential curve of x-ray absorption. The shake process is known as one of the processes, an example of which is the $K\alpha''$ satellite that appears on the high-energy side of the $K\alpha_1$ peak in elements having an atomic number of around 20. In 1936, Parratt measured the $K\alpha''$ spectra of all the $16 \leqslant Z \leqslant 23$ elements (except for Ar) with respect to tube voltage [5]. It was concluded that the origin of the $K\alpha''$ satellite is a $KM \rightarrow LM$ transition, but the subshell contributing to the satellite was not specified. The lack of assignment may be due to the wide spread of the energy distribution of the incident electron beam. In 1986, half a century after Parratt's work, Scott theoretically predicted, using a nonrelativistic single-configuration Hartree-Fock calculation, that a $3p$ spectator hole is the origin of the $K\alpha''$ satellite [6].

It is generally known that when the photon energy is slightly higher than the shake-up or shake-off threshold in the adiabatic region, the sudden approximation is no longer valid and the shake-off probability increases slowly with photon energy. Under these circumstances, the shake-up probability during photoionization is close to the sudden limit even at the energy corresponding to the shake-up threshold [7–9].

Fritsch *et al.* [10] and Sternemann *et al.* [11] have investigated the evolution of the Cu $K\alpha_{3,4}$ and Ge $K\beta'''$ satellites, respectively. Most recently, Galambosi *et al.* studied the dependence of the Cu $K\alpha_{1,2}$ profile on the excitation energy around the $1s$ ionization threshold based on discussion of the contribution of a $3d$ spectator hole [12]. Such work is important because it provides both valuable information regarding the origin of the satellites, and information on how the probabilities of the shake processes are related to the excitation energy.

Experimental confirmation of the $3p$ spectator hole predicted by Scott [6] to be the origin of the evolution of the $K\alpha''$ satellite is therefore of significant interest. In the present work, the dependence of the Ti $K\alpha''$ satellite spectra on the excitation energy is investigated by scanning the excitation energy from onset in the adiabatic region to saturation in the instantaneous approximation limit.

II. EXPERIMENT

Measurements were carried out using the BL15XU undulator beam line of the SPring-8 synchrotron radiation facility of the Japan Synchrotron Radiation Research Institute (JASRI). A monochromatic x-ray excitation source was obtained using a Si(111) double-crystal monochromator with a bandpass of $\delta E/E \sim 10^{-4}$. The flux obtained was greater than 10^{12} photons/s with a spot size of $-1\ \mathrm{mm}^2$. The sample was a pure Ti plate with a thickness of 1 mm. The spectrometer employed had a Johann-type geometry ($\delta E/E \simeq 5 \times 10^{-5}$) with Rowland circle diameter of 1.5 m. The signal was detected using a charge-coupled device (CCD) with a resolution of 1340 × 400 pixels (LCX-400, Roper Scientific). Each pixel of the CCD measured $20 \times 20\ \mu\mathrm{m}^2$, corresponding to

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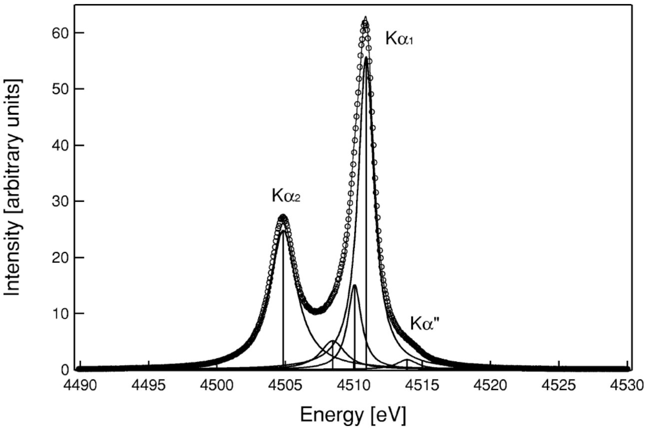

FIG. 1. Measured (open circles) and fitted (solid line) Ti $K\alpha_{1,2}$ spectra and $K\alpha''$ satellite at an excitation energy of 7000 eV.

an active area on the device of 26.8×8.0 mm^2. A Be window of 800 μm thickness was placed in front of the CCD chip to cut visible light and prevent the CCD chip from coming into contact with air. The CCD detector was equipped with Peltier cooler to cool the chip to $-43\,°$C so as to minimize dark current. The surface of the CCD chip touched the Rowland circle tangentially.

In addition to measurements of the Ti $K\alpha$ spectra, the dark current was measured every 3 h. The exposure time for one frame was 10 s; 100 or 200 frames were acquired at each excitation energy, and 100 frames were acquired for dark-current measurement. The contribution from dark current was subtracted appropriately from each spectrum.

The Johann-type spectrometer, equipped with a position-sensitive detector, allowed for measurement of data over the entire energy range investigated without the need to scan the 2θ angle between the sample, analyzing crystal, and detector. A Si(220) crystal was used to analyze x-ray fluorescence. The detector was 26.8 mm in length, corresponding to an effective energy range of $\sim$75 eV at 2θ=91.42°, except the inactive regions at both ends of the CCD chip. This energy range allows the Ti $K\alpha_{1,2}$ and $K\alpha''$ spectra to be measured in only one shot of the CCD at 2θ=91.42°, where the Ti $K\alpha_1$ (4508.4 eV) peak is located at the center of the effective energy range of the detector.

III. DATA ANALYSIS

Five Lorentzians are fitted to the measured Ti $K\alpha$ spectra in Fig. 1. The Lorentzians correspond to $K\alpha_1$, $K\alpha_2$, the $K\alpha_1$ satellite, the $K\alpha_2$ satellite, and the $K\alpha''$ satellite. The two satellites of the $K\alpha_{1,2}$ peaks for copper, as discussed by Deutsch *et al.*, Galambosi *et al.*, and Ito *et al.* [13,12,14], have been suggested to originate from a $[(1s3d)]\rightarrow[(2p3d)]$ transition. In this study, both the position and width of each fitting component were fixed, and only the intensity scale factor was refined in the fit. The fixed values for Lorentzians, except for that of the $K\alpha''$ satellite, were determined by fitting four Lorentzians to the $K\alpha_{1,2}$ spectrum measured at an excitation energy of 4978 eV, at which the spectrum is free from the influence of a satellite caused by a $[1s3p]$ double hole state or resonant Raman scattering. The fixed parameters of the satellite component were determined by fitting Lorentzians to the $K\alpha_{1,2}$ spectra at an excitation energy of 6000 eV, where the satellite is well saturated.

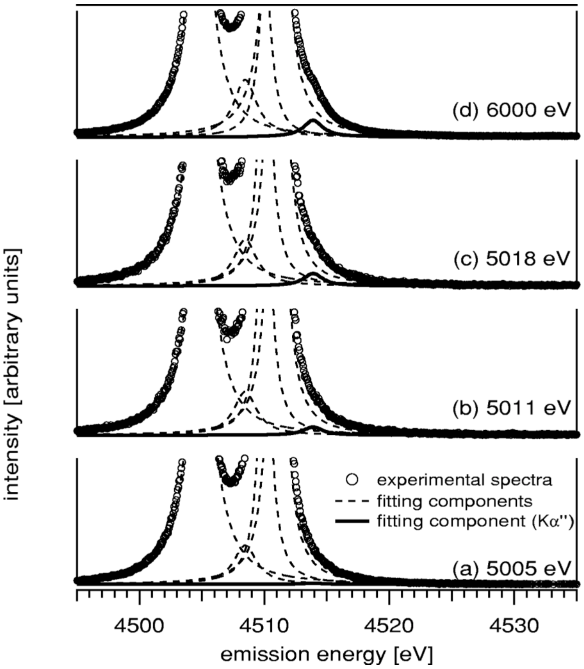

FIG. 2. Evolution of the $K\alpha''$ satellite (solid lines) with increasing excitation energy. The $K\alpha''$ satellite is not observable in (a), where the excitation energy (5005 eV) is the threshold energy of the $[1s3p]$ ionization. The intensity increases when the excitation energy exceeds the threshold (b,c). Evolution ceases when the excitation energy reaches around 5500 eV. The satellite in saturation is shown in (d).

It has been theoretically predicted that the $K\alpha''$ satellite is distributed on not only the high-energy side of $K\alpha_1$, but also between $K\alpha_1$ and $k\alpha_2$ [6]. However, it is difficult to fit a Lorentzian to the latter component of the $K\alpha''$ satellite in the spectra because it is obscured by the valley between $K\alpha_1$ and $K\alpha_2$. The full width at half maximum (FWHM) of the Ti $K\alpha_{1,2}$ peaks in each spectrum were obtained by fitting two asymmetric Lorentzians to each experimental spectrum in order to elucidate the contribution of the satellite to the overall $K\alpha_{1,2}$ spectra.

IV. RESULTS AND DISCUSSION

The results of the fitting for the Ti $K\alpha_{1,2}$ spectra at excitation energies of 5005, 5011, 5018, and 6000 eV are shown in Fig. 2. The Lorentzian corresponding to the $K\alpha''$ satellite is denoted by a solid line in the figure.

The variation in intensity of the satellite with excitation energy obtained by the fitting is shown in Fig. 3. The relative intensity of the $K\alpha''$ satellite compared to the overall $K\alpha_{1,2}$ intensity exhibits an abrupt jump from 0% to $\sim$1% within a range of 10 eV around 5010 eV, as can be seen in Fig. 3. Although the intensity increase ceases at around 5070 eV, the intensity starts to increase again at around 5100 eV and

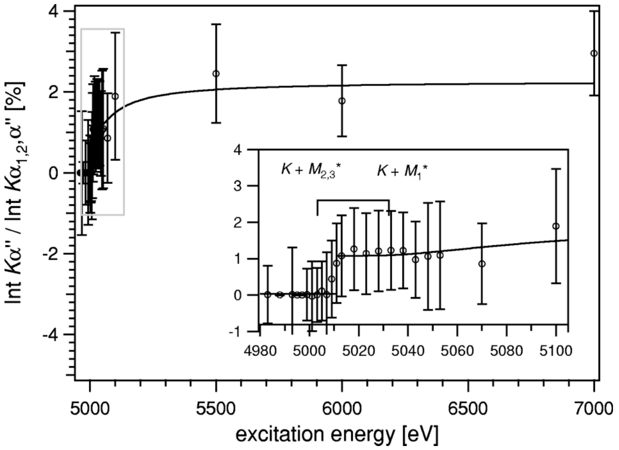

FIG. 3. Intensity of the Ti $K\alpha''$ satellite (open circles) relative to that of the $K\alpha$ lines as a function of excitation energy. The ionization threshold of $K+M^*_{2,3}$ and $K+M^*_1$ (inset) are estimated at a $Z+1$ approximation, where * means the binding energy of the M_i subshell of vanadium ($i=1,2$, and 3). Solid curve represents the result of the fitting using the Thomas model with a step function. Refer to the text for details.

continue to increase up to saturation at around 5500 eV. The relative intensity of the satellite is about 2.5% at saturation.

The solid line in Fig. 3 is the result of fitting to the experimental data using the Thomas model with a step function. The Thomas model [7,8] describes the dependence of the shake-off probability on the excitation energy, and the step function describes the dependence of the shake-up probability. The fitted function is expressed as

$$P(E) = P_{shake\text{-}up}(E) + P_{shake\text{-}off}(E),$$

where E is the excitation energy. $P_{shake\text{-}up}$ is a step function defined by

$$P_{shake\text{-}up}(E) = \begin{cases} C & (E > E_{threshold}), \\ 0 & (E < E_{threshold}), \end{cases}$$

where C is a constant and $E_{threshold}$ is the onset energy of the satellite. P_{Thomas} is expressed as

$$P_{Thomas} = P_\infty \exp\left(- \frac{r^2 E_s^2}{15.32(E - E_{threshold})} \right),$$

where P_∞ is the saturated shake-off probability, r is the distance covered by an outgoing electron, and E_s is the ionization threshold energy of a shaken electron. In the present case, the value of E_s was set to 37.8 eV, corresponding to the ionization threshold energy of a $M_{2,3}$ electron, as determined by a $Z+1$ approximation [15]. The other parameters were refined by the fitting, yielding the following results: $C=1.05\pm0.13$, $P_\infty=1.19\pm0.19$, $r=4.03$ Å ±1.05 Å, and $E_{threshold}=5011.0$ eV ±0.8 eV.

We used a single average threshold energy for calculation convenience because the fitting analysis cannot be executed for more than two threshold ones. Therefore, each transition energy could not be evaluated. The fitting result for $E_{threshold}$ is consistent with the $[1s3p]$ ionization threshold energy of 5004.2 eV obtained by a $Z+1$ approximation.

In the energy region of $[1s3p]$ shake process, below the $3p$ shake-off threshold, only shake-up can occur. The $[1s3p]$ shake-up intensity rises quickly with excitation photon energy in Fig. 3, but not a very fast saturation as predicted in the shake-up process [16]. It reaches 51% about 5 eV above the threshold. This tendency is similar to those previously reported [3,17,18] and may be ascribed to the single and double shake-up states [19,18]. Moreover, as the $[1s3p]$ thresholds are far from the Ti K absorption edge, that is, around 30 eV, it is difficult to consider the resonant Raman scattering associated with $1s^1 \rightarrow 2p^1$ transition.

TABLE I. Probabilities of shake-up and shake-off processes for M shells accompanying ionization of an electron in the K shell in Ti from Dirac-Fock-Slater calculations. n stands for the principal quantum number of the orbital which a skaken M electron jumps into. Column with $n=1(4\leqslant l\leqslant 10)$ is the probability of the shake-up to each shell of $n=1$.

	Initial shells			
Destinations	M_1	M_2	M_3	M_4
$n=4$		6.508×10^{-3}	1.280×10^{-2}	3.085×10^{-2}
$n=5$	7.032×10^{-4}	1.423×10^{-3}	2.811×10^{-3}	7.085×10^{-3}
$n=6$	2.576×10^{-4}	5.628×10^{-4}	1.113×10^{-3}	2.934×10^{-3}
$n=7$	1.243×10^{-4}	2.834×10^{-4}	5.608×10^{-4}	1.532×10^{-3}
$n=8$	6.979×10^{-5}	1.636×10^{-4}	3.239×10^{-4}	9.103×10^{-4}
$n=9$	4.317×10^{-5}	1.033×10^{-4}	2.045×10^{-4}	5.883×10^{-4}
$n=10$	2.859×10^{-5}	6.946×10^{-5}	1.375×10^{-4}	4.035×10^{-4}
Total shake-up	1.227×10^{-3}	9.114×10^{-3}	1.795×10^{-2}	4.430×10^{-2}
Shake-off	6.662×10^{-3}	1.287×10^{-2}	2.551×10^{-2}	2.963×10^{-2}
Total	7.889×10^{-3}	2.198×10^{-2}	4.346×10^{-2}	7.393×10^{-2}

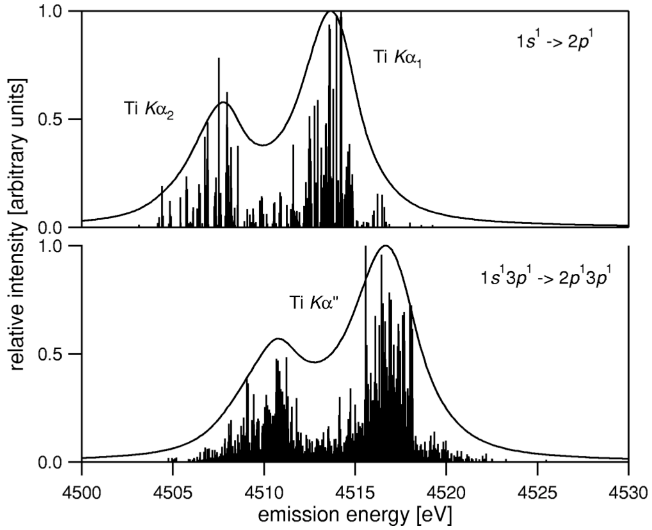

FIG. 4. Intensity distribution of $1s^1 \rightarrow 2p^1$ transitions and $1s^13p^1 \rightarrow 2p^13p^1$ transitions calculated using GRASP code. The solid curve is the convolution using Lorentzians of 1.2 eV width. The intensity is shown relative to the strongest peak.

The probabilities of the shake-up and shake-off processes by which an electron in an $M_i (i=1,\ldots,4)$ subshell is excited and ionized, respectively, were calculated in a manner described by Mukoyama and Ito [9]. The results are tabulated in Table I. The probabilities of the $K+M_{2,3}$ double excitation (or ionization) due to shake-up processes and overall shake processes are $P(M_{2,3})_{\text{(shake-up)}}=2.71\times10^{-2}$ and $P(M_{2,3})_{\text{(shake)}}=6.55\times10^{-2}$, respectively. The ratio of the probability of shake-up processes to that of all shake processes in the $K+M_{2,3}$ double excitation (or ionization) process is given by

$$P(M_{2,3})_{\text{(shake-up)}}:P(M_{2,3})_{\text{(shake)}} \simeq 0.42:1,$$

where $P(M_{2,3})_{\text{(shake-up)}}$ is the sum of probabilities of M_2 and M_3 shake-up processes accompanying K shell ionization, and $P(M_{2,3})_{\text{(shake)}}$ is the sum of probabilities for all shake processes. According to the fitting results, the ratio of the contribution by shake-up processes to all shake processes is approximately $1.05/(1.05+1.19)\simeq0.47\pm0.05$, which is in good agreement with the calculation. This indicates that the contribution of shake-up processes to the $K\alpha''$ satellite intensity is much higher than that for the $K\alpha_{3,4}$ satellite, for which shake-off processes contribute only $\approx$10%.

The intensity distribution profiles of $1s^1 \rightarrow 2p^1$ ($K\alpha_{1,2}$) and the $1s^13p^1 \rightarrow 2p^13p^1$ satellite emission were calculated using GRASP code [20], as shown in Fig. 4. The $1s^13p^1 \rightarrow 2p^13p^1$ satellite spectra lies on the high-energy side of $K\alpha_1$ and between $K\alpha_1$ and $K\alpha_2$, similar to that in Ref. [6]. The calculated and experimental peak positions of $K\alpha_{1,2}$ and the satellites are compared in Table II. We did not directly compare the calculated spectrum with the measured one by putting them on the same figure. The reason for this is as follows: all the possible shake-up processes and the window function of the spectrometer have to be considered in order to make a precise comparison between them. However, it is very difficult to estimate all the shake-up transition energies and to deconvolute the instrumental function from the measured spectrum.

TABLE II. Experimental and calculated emission energies of $K\alpha_{1,2}$ and satellites. Separation is peak top relative energy position of emission line to $K\alpha_1$ line in each case.

Emission line		Energy (eV)	Separation (eV)
Experiment	$K\alpha_1$	4510.8	
	$K\alpha_2$	4505.0	−5.8
	$K\alpha''$	4513.9	3.1
Calculation	$K\alpha_1$	4513.7	
	$K\alpha_2$	4507.8	−5.9
	$K\alpha''$	4516.7	3.0

V. CONCLUSION

The dependence of the intensity of the Ti $K\alpha''$ satellite on the excitation energy was investigated, and it was found that the intensity of the satellite relative to overall $K\alpha$ emission jumps from 0% to ~1% with increasing excitation at around 5010 eV, corresponding to the $[1s3p]$ ionization threshold energy according to a $Z+1$ approximation. The intensity becomes largely saturated by around 5500 eV, at which the relative intensity reaches ~2.5%.

The present results experimentally confirm that the $K\alpha''$ satellite originates from a $3p$ spectator hole, as predicted by Scott. Judging from the variation in intensity of $K\alpha''$, the creation of the $3p$ spectator hole is attributable to shake processes. The probability of the shake processes determined experimentally (2.5%) is less than half the calculated value (6.5%), however, this discrepancy may be smaller considering that one-third of the satellite intensity is probably hidden between $K\alpha_1$ and $K\alpha_2$ in the measured spectra.

The dependence of the satellite intensity on the excitation energy was interpreted by combining the Thomas model (for shake-off) with a step function (for shake-up). The results show that 47% of the $K\alpha''$ satellite is caused by shake-up processes. The ratio of the probability of $[1s3p]$ shake-up processes to all shake processes in the sudden approximation was calculated to be 42%, close to the experimentally determined value of 47%. This agreement indicates that, for $3d$ elements, the shake-up processes are more important in the creation of a $3p$ spectator hole than that of a $2p$ spectator hole accompanying ionization of a $1s$ electron.

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