Electron Dynamics Probed by Time-Resolved Hard X-ray Photoelectron Spectroscopy

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We have realized element-specific pump-probe time-resolved hard X-ray photoelectron spectroscopy (TR-HAXPES) for the study of ultrafast electron dynamics in condensed matter. TR-HAXPES has been applied for the first time to determine the temporal evolution of space-charge effects on Ti 1s core-level photoelectron spectra of SrTiO₃ at the SACLA X-ray free electron laser facility. We found that the temporal evolution of Ti 1s kinetic energy shifts can be well explained by a mean-field model for the electron propagation in the vacuum. We also report preliminary results of a real-time laser-assisted valence-transition in YbInCu₄, observed by measuring Yb 3d_{5/2} core-level HAXPES spectra at BL19LXU of SPring-8, under ON/OFF conditions of an optical pump-laser. We observed drastic changes in intensities of the Yb²⁺ and Yb³⁺ spectral components induced by pump-laser irradiation.

Key words: electron dynamics, time-resolved measurement, HAXPES

1. INTRODUCTION

Hard X-ray photoelectron spectroscopy (HAXPES) is nowadays well known as one of the most powerful methods to investigate the bulk electronic structure of condensed matter owing to its intrinsic advantages, *i.e.* surface insensitivity and large probing depth, compared with PES using ultraviolet or soft X-ray radiation [1,2]. In order to extend the capability of HAXPES for studying transient electronic states of bulk samples on the femtosecond to sub-nanosecond time scale, we have been making efforts to realize time-resolved (TR) HAXPES using (ultra)short-pulsed high-brilliance X-ray sources, such as the X-ray free electron laser (XFEL) facility SACLA [3] and the 27m-long undulator beam-line BL19LXU of SPring-8 [4]. Very recently, we have developed a single-shot CCD-based data acquisition system suited for TR-HAXPES and demonstrated its effectiveness by measuring core-level photoelectron spectra from solid targets at SACLA and SPring-8 [5].

As a first major step to apply TR-HAXPES to the element-specific study of electron dynamics in materials, we have carried out systematic studies of time-resolved space-charge effects, *i.e.* energy shifts and broadenings

of core-level photoelectron spectra, as functions of incident power density and the delay between pump- and probe-pulses at the SACLA XFEL facility. We have also performed preliminary experiments at BL19LXU of SPring-8 for the real-time observation of laser-assisted valence-transition in YbInCu₄ by measuring Yb 3d_{5/2} HAXPES spectra.

In this paper, we briefly describe these experiments and also discuss future prospects of TR-HAXPES for materials science.

2. EXPERIMENTAL

Experiments were carried out at two different (ultra)short-pulsed high-brilliance X-ray sources, namely, BL3 of SACLA and BL19LXU of SPring-8. At the SACLA XFEL facility, the HAXPES apparatus was installed in the experimental hutch EH2. The lens axis of the hemispherical electron energy analyzer R4000-10kV (VG SCIENTA) was in the horizontal plane, at a right angle to the XFEL-beam direction. The target material was a single-crystalline La-doped SrTiO₃ (STO) chip. We measured the Ti 1s HAXPES spectra of the STO target with the ordinary sweep mode using 8.005 keV

monochromatic XFEL-radiation with $\Delta E \sim 1$ eV. The pulse duration was about 30 fs and the repetition-rate was 10 Hz. The average XFEL power was adjusted to be less than 1 $\mu\text{J}/\text{pulse}$ by using Si thin-plate filters. The diameter of the XFEL-beam was about 0.6 mm at the target position. The XFEL-beam was introduced to the target material in a grazing incidence geometry. The pump-laser beam of 400 nm wavelength was incident on the target collinearly with the XFEL-beam. The beam size of the pump-laser was about 0.7 mm and the repetition-rate was the same as the one of the XFEL-beam. The pump power was reduced to about 200 $\mu\text{J}/\text{pulse}$ using a filter, and the delay between pump- and probe-pulses was adjusted using an optical delay stage in the range from -100 to $+200$ ps. The typical acquisition time of a Ti 1s HAXPES spectrum for the time-resolved measurement was about 15 min.

At BL19LXU, on the other hand, the apparatus was installed in the experimental hutch EH3. The experimental setup was almost the same as that of the SACLA experiment [5] except for the use of a pump-laser with a repetition-rate different from the synchrotron radiation (SR) probe-beam. The photon energy of the SR-beam was 7.925 keV. The pulse duration was 40 ps, and the beam size at the sample position was less than 0.5 mm. The 800 nm pump-laser-beam was guided to the target position at an angle of 45 degrees relative to the SR-beam. The repetition rate of the pump-laser was 1 kHz and the pulse duration was about 100 fs. The incident power was measured to be about 360 $\mu\text{J}/\text{pulse}$ at a beam diameter of about 3 mm. The SPring-8 storage ring was operated in an H-mode, *i.e.* 11/29-filling+1 bunch [6]. Although the pump-laser was synchronized to the storage ring, the repetition-rate of the pump-laser was different from that of the probe-pulses, *i.e.* 208 kHz. Thus we did not carry out an ideal pump-probe measurement in the preliminary experiments. The target material was a valence-fluctuating compound YbInCu_4 , which is well known as a typical material exhibiting the isostructural first-order valence-transition at $T_v \approx 42 \sim 52$ K [7,8]. The temperature of the target was maintained around 15 K, which is well below T_v , during measurements.

3. RESULTS AND DISCUSSION

3.1 TR-HAXPES experiments at SACLA

Our first step in realizing TR-HAXPES with XFEL-radiation is to establish the optimum conditions for both optical-pump and XFEL-probe pulses, since both pulses are typically intense and can lead to severe distortions of the photoelectron spectra due to space-charge effects [9]. As we showed in a previous paper [5], we needed to reduce the XFEL power to about 10 % of the double-crystal monochromator output, *i.e.* 0.3 $\mu\text{J}/\text{pulse}$, so as to reduce the XFEL-probe induced space-charge effects. Figure 1 shows the measured Ti 1s HAXPES spectrum (red solid curve) plotted together with that obtained at BL19LXU of SPring-8 (blue open circles) with much higher energy resolution, $\Delta E \sim 60$ meV. The energy scale of the Ti 1s HAXPES spectra measured at SACLA was adjusted to that of the well-calibrated spectrum recorded at BL19LXU. The most intense photoemission peak at a binding energy of 4,969 eV originates in the Ti 1s core-level.

Fig. 1 Ti 1s HAXPES spectra of STO measured at SACLA (red solid curve) and BL19LXU (blue open circles). The theoretical spectrum calculated by the cluster-model is also shown (black solid curve).

According to the cluster-model calculation, weak satellites at 4,983 and 4,975 eV can be explained as the charge-transfer satellites [10]. In the calculation, we used the $(\text{TiO}_6)^{8-}$ cluster model with O_h symmetry including the full-multiplet coupling effects in a Ti ion. In the Hamiltonian, we included the inter-atomic hybridization between Ti 3d and O 2p ligand states, and the intra-atomic multiplet coupling. We also mixed, as the ground state, three configurations, $3d^0$, $3d^1\bar{L}$ and $3d^2\bar{L}^2$, where $\bar{L}$ represents a hole in the ligand O 2p state. The Slater integrals and the spin-orbit coupling constants were calculated by Cowan's Hartree-Fock program [11] and then the Slater integrals were scaled down to 85 %. We used the following parameters : the Coulomb interaction between Ti 3d states $U_{dd} = 4.0$, the charge transfer energy $\Delta = 3.0$, the core-hole potential $U_{dc} = 6.0$, the hybridization $V(e_g) = 3.4$, the crystal field splitting $10Dq = 1.8$, all in units of eV. The ground state character was $3d^0 = 33.1\%$, $3d^1\bar{L} = 50.4\%$, and $3d^2\bar{L}^2 = 16.5\%$. The lifetime broadening of the Ti 1s core-hole was taken to be 0.6 eV. The calculated spectrum was convoluted with an experimental broadening function (Gaussian FWHM = 0.2 eV). As we see in Fig. 1, the observed spectra are well reproduced by the theoretical cluster-model calculation.

First we have confirmed the experimental conditions required for negligible space-charge effects on the Ti 1s

Fig. 2 Two dimensional correlation map of pump-laser induced space-charge effects on Ti 1s HAXPES spectra as a function of pump-probe delay and kinetic energy.

HAXPES spectrum due to the XFEL-probe and found that the XFEL-power of 0.3 $\mu\text{J}/\text{pulse}$ gives us an acceptable condition. In this condition, several tens of Ti 1s photoelectrons are emitted toward the electron analyzer, and we have carried out systematic measurements of pump-induced space-charge effects on Ti 1s core-level photoelectron spectra, as a function of delay between pump- and probe-pulses, with the pump-power set to 200 $\mu\text{J}/\text{pulse}$. In Fig. 2, we show the results of time-resolved Ti 1s HAXPES spectra of STO as a function of pump-probe delay. We can recognize the slight kinetic energy (KE) shift of Ti 1s photoelectrons around zero delay in Fig. 2. In order to quantify the energy shift due to the space-charge effects, we have carried out simple analyses for all the spectra shown in Fig. 2 after subtracting a Shirley type background [12] from each spectrum. The peak position of the Ti 1s core-level was determined by a least-squares fitting procedure.

The results are plotted in Fig. 3(b) together with simulation based on a mean-field model [13] originally used for ultrafast electron packet propagation. In Fig. 3(a), we also show a typical energy distribution curve of low-KE photoelectrons induced by the pump-pulses. These low-KE electrons are mostly emitted by the multi-

photon absorption due to the non-linear processes. This energy distribution curve was incorporated into the simulation using an extended 2D mean-field model [14]. In the simulation, we used the following parameters : $E_{\text{kin}}(\text{probe}) = 3035.9 \text{ eV}$, $E_{\text{kin}}(\text{pump}) = \text{measured spectra shown in Fig. 3(a)}$, and number of electrons emitted by pump-laser $N = 200,000 \pm 20,000$ (best fit). As is described in the previous paper [9], the pump-laser induced low-KE photoelectrons wafting above the sample surface will affect the probe-induced Ti 1s high-KE photoelectrons ($E_{\text{kin}} \sim 3,036 \text{ eV}$) in two different ways, depending on the sign of the pump-probe delay. In the case of negative delay, the probe-induced high-KE electron-cloud (HKEe-cloud) does not see the pump-induced low-KE electron-cloud (LKEe-cloud) or the associated mirror charges for an initial stage as the pump-pulse has not reached the sample surface. After the arrival of a pump-pulse, the HKEe-cloud is always boosted by the Coulomb field generated by the LKEe-cloud until it reaches the analyzer. Mirror charges generated in the target are efficiently screened by the LKEe-cloud. In the case of positive delay, on the other hand, the HKEe-cloud feels the attractive Coulomb field by the mirror charges produced in the target and also the repulsive Coulomb field generated by the preceding LKEe-cloud. These facts cause pushing back the HKEe-cloud to a lower kinetic energy. At a certain time, the HKEe-cloud overtakes the LKEe-cloud, and after overtaking, the HKEe-cloud is boosted by the Coulomb field generated by the expanding LKEe-cloud. At zero delay, the HKEe-cloud gets the maximum energy gain by the Coulomb field of the high-density LKEe-cloud, and it also gets the maximum energy broadening. As we can see in Fig.3(b), the general trend of the temporal evolution of the space-charge effect is well reproduced by the model calculation. Details of the simulation will be described elsewhere [14]. From the experimental and simulation results of the pump-laser induced space-charge dynamics, we have found that the temporal evolution gives us the precise definition of time zero for the pump-probe measurement as is discussed in the recent paper [15]. We have also noticed that it seems to be difficult to extract dynamical information on the photoinduced material properties from the core-level shift, as e.g. in studies of the surface photovoltage effect, by means of the pump-probe type TR-HAXPES using the intense XFEL-beam. This suggests that we rather focus on observing the changes in the spectral shape induced by pump-laser irradiation as is described in the next subsection.

Fig. 3 (a) Typical energy distribution curve for the pump-laser induced low-kinetic energy photoelectrons. (b) Temporal evolution of the pump-laser induced Ti 1s core-level shift in comparison to the results of the extended 2D mean-field model calculation.

3.2 Real-time observation of laser-assisted valence-transitions at BL19LXU

Before applying HAXPES to the real-time observation of a laser-assisted valence-transition in the valence-fluctuating compound YbInCu_4 , we have measured the temperature-dependent Yb 3d HAXPES spectra near the transition temperature T_v . Our results show the Yb 3d spectral feature of the high-temperature phase at 53 K and that of the low-temperature phase at 48.3 K, respectively. Thus we could conclude that the transition temperature for our sample is in between 48.3 and 53 K. Hence in the laser-assisted valence-transition measurements, we set the sample temperature to around 15 K,

Fig. 4 Kinetic energy versus time map showing the real-time changes of the spectral shape due to the pump-laser ON/OFF condition (lower-left panel). Upper panel : projected spectra for both pump-OFF (blue open circles) and pump-ON (red solid circles) conditions. Lower-right panel : temporal evolution of the intensity of the Yb^{2+} component showing drastic changes due to pump-ON/OFF conditions.

which is well below T_v . The pump-laser was introduced onto the sample surface with an incident power of 360 $\mu\text{J}/\text{pulse}$. We checked that the temperature rise near the sample due to the pump-laser irradiation was less than 1 K by using a Si-diode thermosensor. But in this preliminary experiment, we could not measure the actual local temperature of sample-surface when the optical pump-laser is ON.

For the real-time observation, we have operated the analyzer in “fixed” mode with a pass energy of 500 eV. We consecutively measured Yb $3d_{5/2}$ HAXPES spectra every 5 seconds. In total, 90 images of photoelectron spectra of the Yb $3d_{5/2}$ $2+$ and $3+$ components were accumulated in the “add dimension” mode. The results are summarized in Fig. 4. The pump-laser ON/OFF conditions were changed at 55 sec (OFF→ON) and 200 sec (ON→OFF), respectively. We can observe that a relatively fast transition to the high-temperature phase occurs at around 55-60 sec and that a relatively slow relaxation back to the low-temperature phase takes place at around 260-280 sec.

In the relaxation, there seems to be a time lag to change the phase. Although we do not know the actual time-scales for the transition and the relaxation at this moment, we can assume that the photoinduced target property gets to the stable equilibrium in the high-temperature phase due to the high repetition-rate of the strong pump-laser field. This fact seems to indicate the observed laser-assisted valence-transition can possibly

be due to a thermal effect. However, in analogy with previous work on photoexcited carrier relaxation dynamics in heavy fermion compounds [16], we expect that it is possible to observe ultrafast phenomena using TR-HAXPES if we can adjust the pump-laser power to the optimum condition. This implies the need of a pump-probe type TR-HAXPES experiment for studying the detailed time-dependence of the laser-assisted (or photoinduced) valence-transition. Such experiments are scheduled to be performed in the near future.

4. PERSPECTIVE OF TR-HAXPES

Using TR-HAXPES, the temporal evolution of the transient electronic structure of various materials induced by the pump-laser can and will be probed by (ultra)short high-brilliance X-ray pulses at the SACLA XFEL facility and the 27m-long undulator beamline BL19LXU of SPring-8.

In order to observe the ultrafast dynamics of materials properties, we definitely need the X-ray probe from the SACLA XFEL facility. As for the observation of relatively slow relaxation, we can use both the SACLA and the SPring-8 BL19LXU as the X-ray probe source. In the near future, we will advance the systematic studies of TR-HAXPES to investigate the photoinduced valence-transition in valence-fluctuating compounds, such as YbInCu_4 , at both X-ray sources.

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