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A Study of the Cascade Auger Process Using a Cluster Calculation

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The Auger process on shallow levels, caused by the Auger process in deeper levels, called "cascade Auger process", were studied. From the measurement result, the cascade Auger process can be clearly observed by the excitation of X-ray tubes instead of a synchrotron radiation source. Applying a theoretical investigation with a cluster calculation to the spectral change of the Ag $M_{VI,V}VV$ peak, it was theoretically shown that the cascade Auger process should be correct for explaining the observed spectral change. In addition, it pointed out the existence of a cascade Auger process caused by holes left by the Coster–Kronig process on deeper levels. For the first time the measurement of this process was successful using X-ray tube excitation.

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Introduction

Recently, Auger electron spectroscopy has become one of the popular surface analysis methods. And a widely used technique is a scanning Auger micro-analyzer (SAM) incorporating electron beam excitation. The generation process of an Auger electron is associated with at least two holes and one electron (this being the Auger electron). Thus, the interaction of these holes and the Auger electron dictates the fundamental shape of the Auger electron spectrum. In addition, shake-up, shake-off and other kinds of many-body effects, are dependent on the condition of excitation related to the fine structure of the Auger spectrum. This spectral change, observed as an energy shift and profile change, has been adapted as a practical analysis of the chemical state in a material.

In contrast, a theoretical investigation of changes in the Auger electron spectrum that corresponds to chemical state changes, especially concerned with the generation process of the fine structure, has not been performed extensively. Nevertheless, in the case of the 2nd period of elements, examples of calculation results of the fundamental shape of the spectrum were reported.[1] It seems that it is difficult to perform a rigorous theoretical analysis of the process of cascade electron transitions, including plural holes and electrons.

Recently, the measurement of an Auger spectrum with a tunable X-ray excitation source, such as synchrotron radiation, has been widely carried out. Using such an excitation source allows the user to set the excitation energy precisely so as to suppress the multiple-ionization process.[2] The investigation of the fine structure caused by the multiple ionization process has rapidly developed experimentally since a wide-spread use of synchrotron radiation. Such measurements are performed by scanning the excitation energy in the vicinity of a specific core level. In contrast, there is the case where changes in the Auger spectrum are observed when there are large changes in the excitation energy. For example, Von Busch *et al*. reported observing this phenomenon in an investigation using Dirac–Fock calculations.[3] Other investigations that employed a synchrotron-radiation source have recently reported observations of phenomena linked to the photoelectron-Auger electron coincidence process.[4] The cause of this spectral change was presumed to be the Auger process at the shallow energy levels, generated following the Auger process between deep levels. This process was named the "cascade Auger process". This phenomenon was independently confirmed by a group in Japan; the group performed experiments using SPring-8 BL15XU.[5] They measured the Ag $M_{VI,V}VV$ Auger spectrum, and compared the spectra of energies slightly smaller than the Ag L_{III} edge, and sufficiently lager than the Ag L_I edge. They concluded that this spectral change in Ag $M_{VI,V}VV$ was caused by the cascade Auger process of the $M_{VI,V}VV$ process, which in turn generated the LMM process.

In this paper, we report on an investigation of the cascade Auger process. This work was experimentally performed using X-ray tubes. Parallel simulations were performed using a cluster calculation. The first observation of the cascade Coster–Kronig–Auger process, using X-ray tubes, is presented in this paper.

Experimental

The measurement of a spectrum was carried out using an X-ray photoelectron spectrometer; a remodeling of the ULVAC-PHI Model 5500, which had two types of dual-target X-ray tubes, Mg (Mg K_α: 1253.6 eV)/Zr (Zr L_α: 2042.6 eV) and Ag (Ag L_α:

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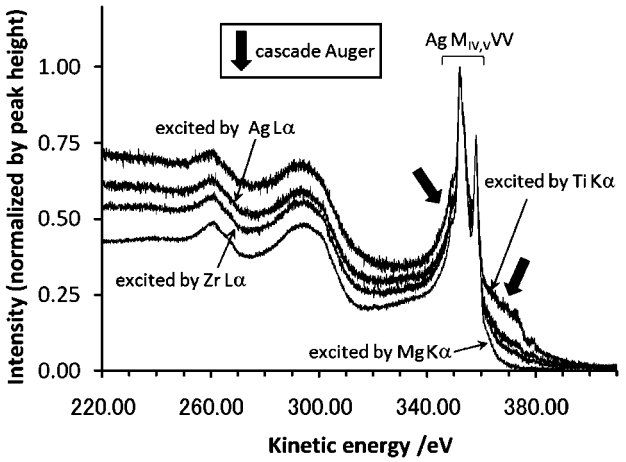

Fig. 1 Profile change of Ag $M_{VI,V}VV$ of metallic Ag depending on the difference of the characteristic X-ray for excitation.

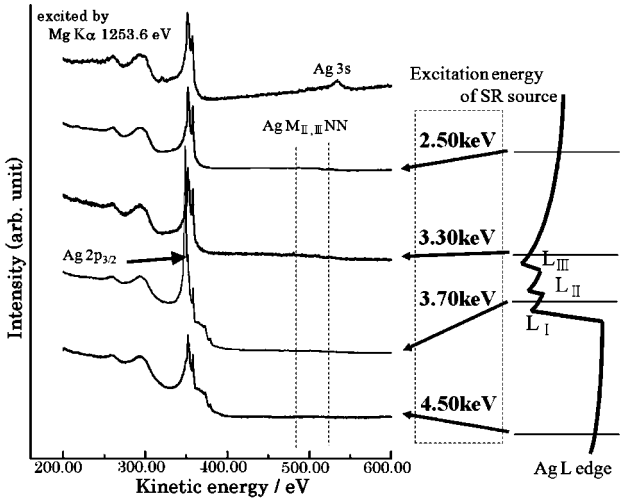

Fig. 2 Profile change of Ag $M_{VI,V}VV$ of metallic Ag corresponding to the excitation energy with the synchrotron-radiation source.[5]

2984.7 eV)/Ti (Ti K_α: 4510.2 eV), as excitation sources (all energy values are from Ref. 6). The vacuum pressure was about 1×10^{-7} Pa, while measurements were performed.

The samples were high-purity metallic plates (1 cm × 1 cm × 0.3 mm) of Ag, Mo, Zr and Au. All of the samples were cleaned by Ar^+ ion bombardment to remove carbon and oxygen from the sample surface.

All of the measured Auger spectra were shown as plots of the kinetic energy, because the excitation energy is not a consistent parameter. All spectrum data were corrected so that the peak positions of the Ag $M_{VI,V}VV$ of all spectra agreed with the peak position excited in Mg K_α, 1253.59 eV.[7]

Results and Discussion

The profile change of Ag $M_{VI,V}VV$

In Fig. 1, Ag $M_{VI,V}VV$ Auger spectra of metallic Ag, excited using 4 kinds of characteristic X-rays, are shown. Clearly, the data show that the slopes of both sides of the Auger $M_{VI,V}VV$ peak, excited by Ti K_α, are significantly different than those of

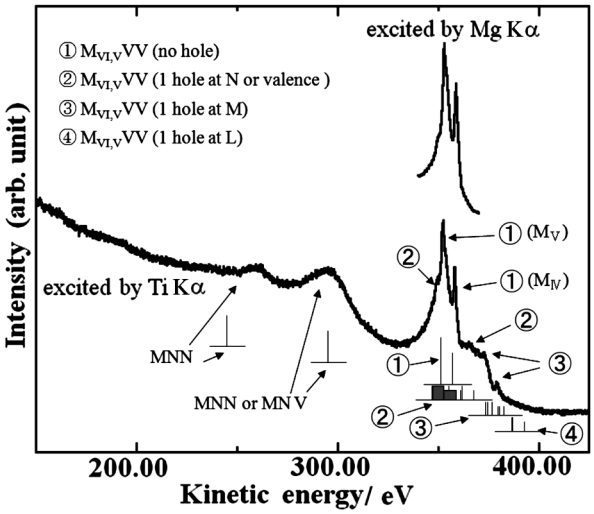

Fig. 3 Result of the DV-Xα cluster calculation for estimating the effect of the spectator hole at several levels.

the other peaks. Figure 2 shows a measurement of the changes of Ag $M_{VI,V}VV$ with respect to the change in the excitation energy around the Ag L edge using a synchrotron-radiation source (SPring-8).[5] The schematic drawing that shows the relationship between the excitation energy and the Ag L edge is also shown in this figure. From this figure, it can be found that the same spectral change, as shown in Fig. 1, results when the excitation energy is larger than the amount required to excite the of L_{II} edge. The difference in the spectrum between the excited Ti K_α (4510.2 eV) and Mg K_α (1253.6 eV) states is in good agreement with the spectral change shown in Fig. 2. From this figure, it is reasonable to conclude that the threshold value of the excitation of this structure exists between the L_{II} and L_I edge, at about 3.70 keV. In addition, from Fig. 2, it is found that this spectral change was only caused at the change of the excitation energy between 3.30 and 3.70 keV, and that no change was caused when the excitation energy was higher than 3.70 keV or lower than 3.30 keV. Thus, the cause of the spectral changes corresponding to the Ag L_α and Zr L_α excitation, shown in Fig. 1, may be due to excitation by higher energy components of the bremsstrahlung from the X-ray tube.

In general, multiple hole excitation, especially generating spectator holes at the initial state, should be considered to be the cause of this kind of spectral change. In an experiment using X-ray tubes, it can be said that the intensity (photon flux) of excitation X-rays was not very high (extremely less than 10^{15} photons/s as the total photon flux), and not enough to cause the "multi photon"–"multi hole" excitation process at any inner shell. Thus, the "one photon"–"multi hole" excitation process should only be considered in this case.

Assignment of the position of spectator hole using the cluster calculation

In the case of a "one photon"–"multi hole" model, two cases should be considered at the initial state. One is a shake-up/off process, and the other is the existence of spectator hole(s). In the case of this experiment, the threshold excitation energy of this spectral change takes around 3.30 to 3.70 keV. If the shake-up/off model should be considered, the multiple ionization on an Ag M shell must be considered in the $M_{VI,V}VV$ Auger process. Thus, the threshold energy of this spectral change

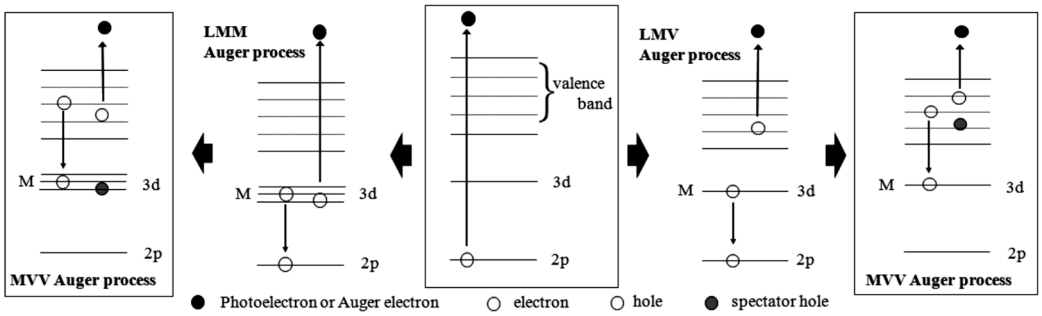

Fig. 4 Schematic figure of the LMM/LMV–MVV cascade Auger process.

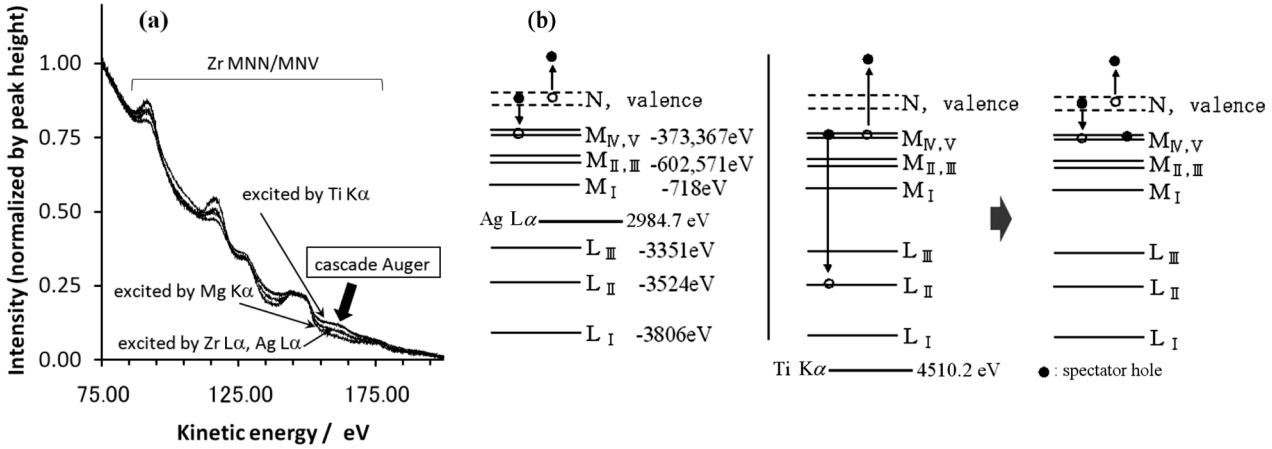

Fig. 5 Profile change of Zr MNN/MNV of metallic Zr due to the cascade Auger process. (a) Measured spectra, (b) schematic figure of cascade process.

should take a value around the Ag M edge. That value might be sufficiently smaller than 3.30 or 3.70 keV, obtained from the experiment. Thus, it can be concluded that the shake-up/off process should not be considered in this spectral change.

In terms of adopting the spectator model for this spectral change, it is necessary to examine on which level the spectator hole should exist. To investigate this model, a cluster calculation, using the DV-Xα method[8] was performed by one of the authors.[5] In that calculation, the metallic Ag takes the structure of the face-centered cubic type (lattice constant is 0.486 nm). Thus, the $AgAg_{12}^{0}$ cluster model (Oh symmetry) was proposed for the calculation model. Slater's transition method[9] was employed in order to include the relaxation of the valence electron structure in the Auger process.

The calculated energy positions of the Auger peaks from the cluster calculation ($AgAg_{12}^{0}$) are shown in Fig. 3.[5] Each calculated position was plotted relative to the reference, since the measured value of the Ag $M_{VI,V}VV$ peak agreed with the measured value. The calculated intensity of each component was estimated from the amount of local DOS at the center of the Ag atom of the cluster model (mainly 4d, and almost consisted of one peak). The transition probability between 3d and valence was neglected. From the calculation result, it can be concluded that the structure was caused by only one spectator hole at the M shell or valence band.

The important result is that the threshold energy of this change exists near the L absorption edge in spite of the position of the spectator hole; M shell or valence, not L shell. Thus, it is necessary to consider that the process of the excitation of the L shell generates one spectator hole on the M shell or valence band. The only possible model to explain of this result is shown in Fig. 4. This model consists of two Auger process steps. First, the LMM or LMV Auger process is caused by excitation of the L shell. In the final state of this first Auger process, two holes are left; one at M, and the other at M or V. The latter hole played the role of a spectator hole in the MVV Auger process. The complete process, shown in Fig. 4, is the cascade Auger process.

Observation of another cascade Auger process by X-ray tube excitation

The cascade Auger process was observed using two kinds of characteristic X-rays at two distinct energy levels, instead of using synchrotron radiation. In this work, since four kinds of excitation energies were available, the Auger transition between the valence and near-valence levels (excited by Mg K_α) and the Auger process at the deeper levels was employed in the investigation.

In Figs. 5 and 6, the measurement results of Zr MNN/MNV of metallic Zr and Mo MNN/MNV of metallic Mo are shown. A schematic figure of the levels of each case is shown.

The changes that appear on the spectrum are shown by arrow marks. Compared with the case of Mg K_α excitation and Ti K_α excitation, it can be seen that the new peak or band was

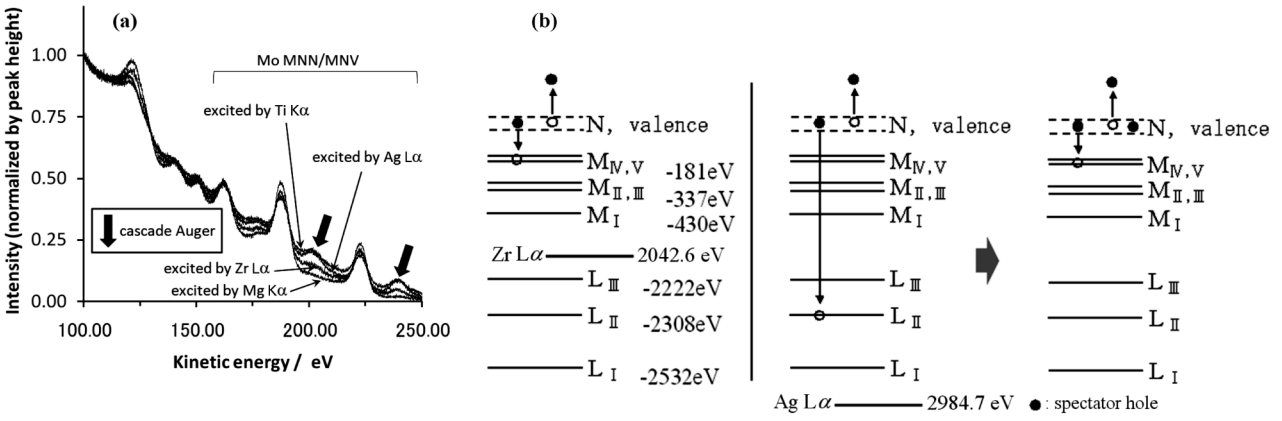

Fig. 6 Profile change of Mo MNN/MNV of metallic Mo due to the cascade Auger process. (a) Measured spectra, (b) schematic figure of cascade process.

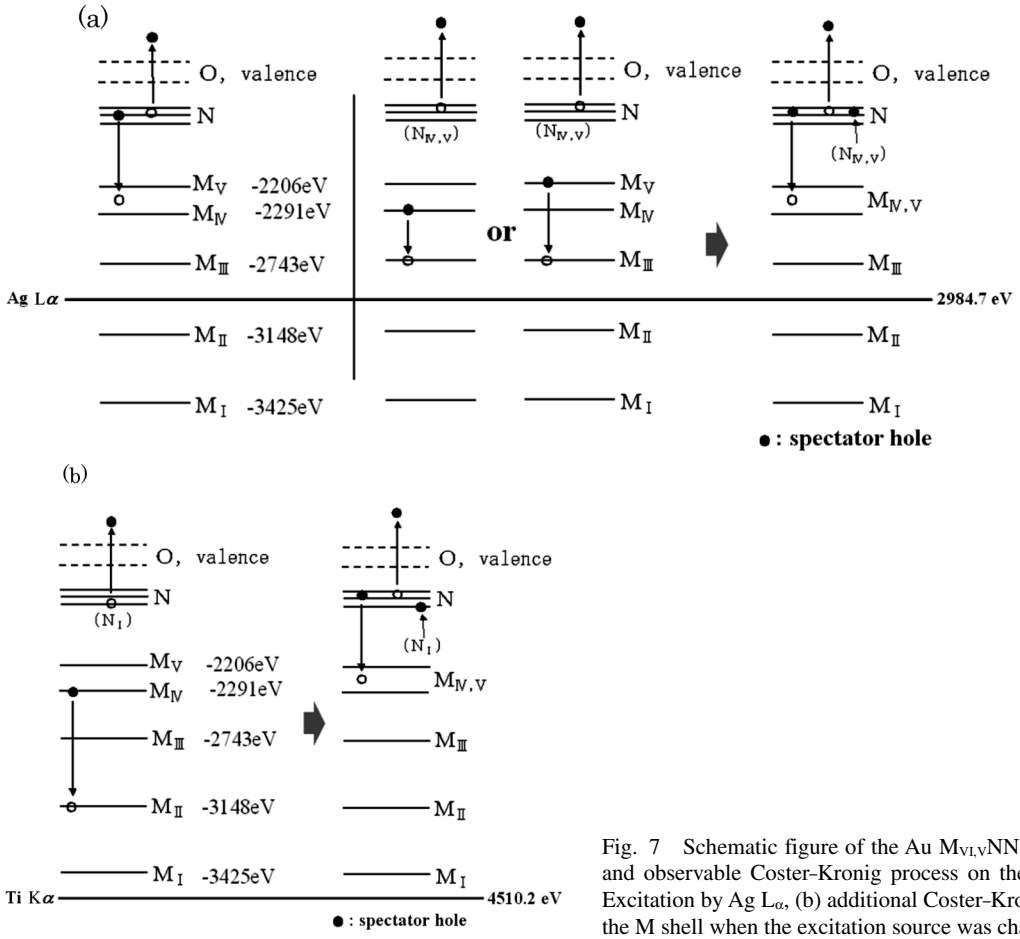

Fig. 7 Schematic figure of the Au $M_{VI,V}NN$ Auger process and observable Coster–Kronig process on the M shell. (a) Excitation by Ag L_α, (b) additional Coster–Kronig process on the M shell when the excitation source was changed to Ti K_α.

generated by excitation of the Auger process. Both cases of the cascade Auger process were simply activated using X-ray tube excitation.

Observation of the cascade Coster–Kronig–Auger process

The first part of the cascade Auger process may have left two holes in the final state; this part is not indicative of the Auger process. The Coster–Kronig process, similar to the Auger process, also exhibits a cascade process.

In Fig. 7(a), schematic diagrams of the $M_{VI,V}NN$ Auger process and the observable Coster–Kronig $M_{III}M_{IV,V}N_{IV,V}$ process[10] of Au, which can be excited by Ag L_α, are shown. In the case of excitation by Ti K_α, the whole M shell is excited. However, the additional observable Coster–Kronig process is only the $M_{II}M_{IV}N_I$ process[8] shown in Fig. 7(b).

The measurement of Au $M_{VI,V}NN$ excited by Ag L_α and Ti K_α is shown in Fig. 8. In this figure, the spectra shown in Fig. 8(a) are as measured, and the spectra of which the background removed using the iterative-Shirley method[11] are shown in Fig. 8(b). The difference of the profile of Ag L_α excitation and

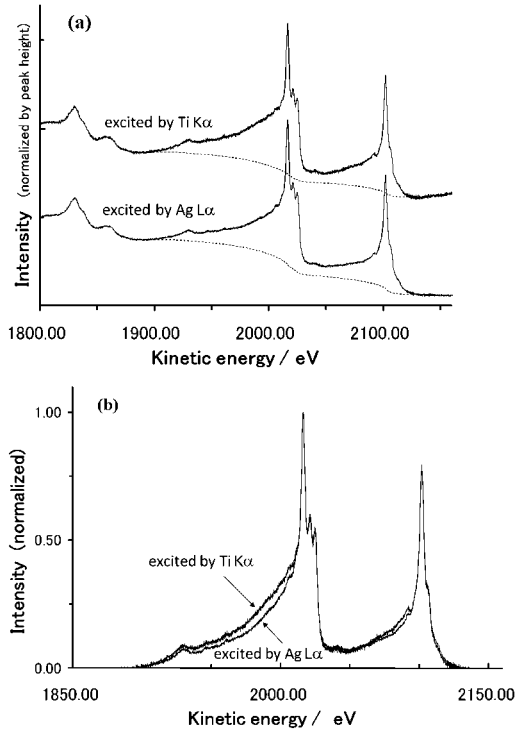

Fig. 8 Comparison of the profile of Au $M_{VI,V}NN$ between excitation by Ag L_α and by Ti K_α. (a) As measured, (b) after background subtraction by the iterative-Shirley method.[11]

Ti K_α excitation can be clearly seen in Fig. 8(b); the part excited by Ti K_α could be caused by the additional Coster–Kronig $M_{II}M_{IV}N_I$ process.

To the best of the author's knowledge, this is the first observation of the cascade Coster–Kronig–Auger process, obtained using X-ray tube excitation. From this measurement, it can be concluded that two types of cascade processes exist, Auger–Auger type and Coster–Kronig–Auger type.

Conclusion

In this report, the Auger process at the shallow levels, caused by the Auger process at the deeper levels, called the "cascade Auger" process, was studied. From the measurements, the cascade Auger process was clearly observed using the excitation of X-ray tubes instead of a synchrotron radiation source. A theoretical investigation was performed using the cluster calculation of the spectral change of the Ag $M_{VI,V}VV$ peak. It was shown that the cascade Auger process should be the correct explanation of the observed spectral changes. Some examples of the effect of the cascade Auger process excited using X-ray tubes were also shown.

In addition, it was pointed out that there are two kinds of cascade Auger processes. One is the Auger process, which is caused by holes left by the Auger process at the deeper levels. The other is caused by holes left by the Coster–Kronig process at the deeper levels. Using measurements of the spectral change of Au $M_{VI,V}NN$ excited by Ag L_α and Ti K_α, the existence of the cascade Coster–Kronig–Auger process was presented for the first time. A more detailed discussion with theoretical calculations will be a part of future work.

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