Threshold behavior of the Cu $L_3M_{4,5}M_{4,5}$ Auger effect of Cu metal at the L_3 edge

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The Cu $L_3M_{4,5}M_{4,5}$ Auger effect from Cu metal resulting from photoexcitation across the Cu L_3 edge has been investigated. We observe that (a) the resonant Auger features (lack of satellites below the ^1G line and narrower linewidths) are noticeably different from those of normal Auger excited with photon energy far above the threshold, (b) the Auger patterns exhibit a dispersion associated with varying excitation photon energy slightly below the threshold, in accordance with the resonant Raman effect, and (c) on the lower kinetic-energy side of the ^1G line there exists a shoulder not predicted by atomic theory; this feature skews the ^1G line and is attributed to density-of-state effects. This threshold behavior and its implications are discussed in terms of multielectron processes, resonant x-ray Raman scattering, and sublifetime x-ray-absorption near-edge structure measurements using a partial Auger yield.

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The creation and decay of a core hole of an atom at threshold excitation energies presents a very interesting problem both theoretically and experimentally.[1–10] In resonant Auger, the excited electron remains in the vicinity of the excited atom and will have an effect on the competing Auger and fluorescence deexcitation channels. More importantly, the conventional notion of a two-step process (creation of a core hole followed by Auger and fluorescence decay) is no longer valid. This area of research has received considerable attention lately partly because of the advancement in synchrotron light-source techniques and partly because of the advancement in theory.

The Auger resonant Raman effect refers to a phenomenon parallel to the resonant x-ray Raman scattering of the competing fluorescence channel induced by threshold excitation.[1–6] Resonant Auger is distinct from normal Auger in that the absorption and decay process has to be viewed as a single-step event. This situation arises when the excited core hole decays before its relaxation is completed and can be understood in terms of the Kramer-Heisenberg equation.[1] Experimentally, however, the required conditions to observe the above situation are stringent.[7,8] High resolution is required for both the incoming photon and the analyzed Auger electron such that the overall experimental resolution is comparable to or smaller than the lifetime broadening of the core hole (e.g., ~2.4 eV for Ag L_3 and ~0.4 eV for Cu L_3).[11] Thus experiments have to be conducted using synchrotron light sources with sufficient brightness and high-resolution monochromators to provide the essential flux and resolution.[6–10]

Since the discovery of the Auger resonant Raman effect in Xe,[3,4] there have been considerable systematic studies of the phenomenon using the $L_3M_{4,5}M_{4,5}$ resonant Auger emission of the $4d$ noble metals Rh, Pd, and Ag and their compounds.[7,8,12] The resonant Auger characteristics observed in these systems are (a) a dispersion in the kinetic energy of the Auger electrons excited with photon energy in the vicinity of the threshold,[7,8] (b) a linewidth narrowing of the Auger resonance,[7,8] (c) a photon-energy-dependent line shape and Auger satellite structures associated with the electronic structure and decay dynamics,[12] and (d) a sublifetime appearance of the x-ray-absorption near-edge spectrum using a partial Auger yield.[12]

Relative to $4d$ metals, studies concerning the above-mentioned threshold characteristics for the $3d$ metals are scarce. Weinelt *et al.* recently reported a detailed study of resonant photoemission of Ni using Ni $2p$ ($L_{3,2}$-edge) excitation.[13] They observed Raman behavior at threshold resonance. In Ni, the kinetic energy of the *d*-band photoemission electrons and the $L_{3,2}M_{4,5}M_{4,5}$ resonant Auger electrons at an Ni $2p$ threshold excitation overlap somewhat. In Cu, however, there is enough separation between them. In addition, Cu is the prototype for $L_{3,2}M_{4,5}M_{4,5}$ Auger studies[14,15] and there have been several synchrotron studies of Cu $L_{3,2}M_{4,5}M_{4,5}$ Auger of Cu and its oxides.[16–18] However, the emphasis of these studies was placed on the satellite structures, Coster-Kronig transitions, and chemical sensitivity of the delocalized two-hole final state in terms of the Cini-Sawatzky model.[19,20] The challenges in studying the Auger resonant Raman effect in $3d$ metals such as Ni and Cu are that the metal *d* bands are directly involved in the Auger process (this is not the case in $4d$ metals), which complicates the interpretation, and that the $2p_{3/2}$ and $2p_{1/2}$ core holes already have narrow widths (0.4 and 0.62 eV, respectively).[11] The latter means that high photon resolution has to be used and at the same time there must be sufficient photon flux to allow for good statistics. Undulator sources from third-generation storage rings now provide sufficiently high reso-

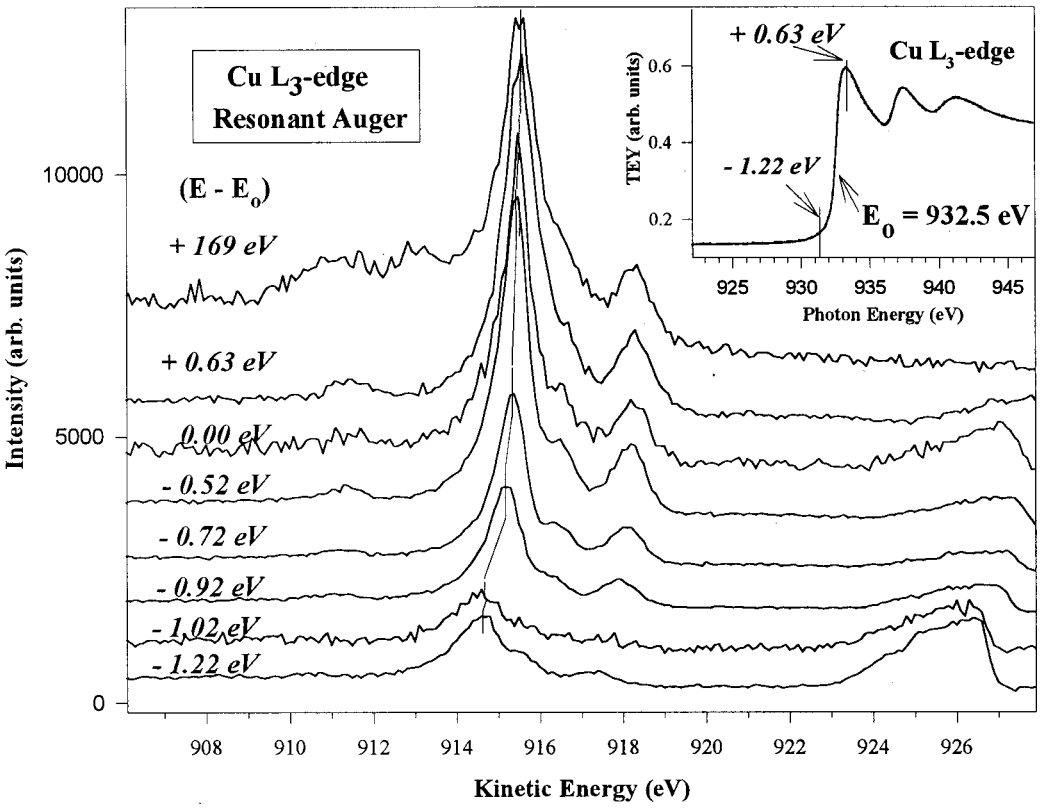

FIG. 1. Cu $L_3M_{4,5}M_{4,5}$ Auger effects of Cu metal at and far above the Cu L_3 edge. The excitation energy relative to the threshold is denoted E-E_0 with E_0=932.50 eV (inflection point). The Cu L_3-edge XANES recorded in TEY is shown in the inset.

lution and high flux for this type of experiment to be feasible. In this work, we report the observation of the Auger resonant Raman effect in Cu metal and related phenomena in the spirit of previous studies on 4*d* metals (the characteristics noted above).[7,8,12] We will focus on the Cu L_3 edge and the associated $L_3M_{4,5}M_{4,5}$ Auger decay channels.

The measurements were carried out using the SRI-CAT 2-ID-C soft x-ray undulator beamline at the Advanced Photon Source. The beamline is equipped with a spherical grating monochromator (SGM) which operates at a tunable range of 0.5–3.0 keV with a resolving power up to 10 000.[21] A 600-l/mm grating was used for the measurements. With entrance and exit slits of 10 μm, this grating delivers a photon flux of $\sim 10^{12}$ photons/sec at a spot size of $\sim$0.5 mm with a photon-energy resolution of 0.2 eV at the Cu L_3 edge ($\sim$933 eV). The monochromatic photons were focused onto the specimen inside an ultrahigh vacuum chamber, which is equipped with a Physical Electronics 10–365 Å hemispherical electron-energy analyzer with 16-channeltron detection and up to $\sim$25-meV resolution. Both 16- and single-channel detection were used to observe linewidth narrowing in resonant Auger. A pass energy of $\sim$6 eV was used for all the resonant Auger measurements reported here. The experiments were carried out by first measuring the Cu $L_{3,2}$-edge x-ray-absorption near-edge structure (XANES) of a clean Cu (prepared by Ar ion sputtering). Then high-resolution Auger spectra were recorded with the photon energy tuned across the edge in small steps, one step at a time. Caution was exercised to ensure that all the energies (photon and electron) were calibrated properly. Thus photon energy was recalibrated after each fill with reference to the Cu L_3-edge threshold energy, E_0 (inflection point of the edge jump), at 932.50 eV using both absorption and photoemission (Fermi edge). A high-accuracy encoder controls the accuracy of the SGM scanning mechanism. The uncertainty in the difference in photon energy is estimated at $\pm$0.02 eV. Incident-photon flux was monitored using a high-transmission gold mesh. Normal absorption was obtained in the total electron yield (TEY), using drained current, and total fluorescence yield (FLY), using a silicon photodiode. The partial Auger yield was obtained by monitoring the intensity of the ^1G peak in a constant final-state mode as the photon energy was scanned across the edge.

Figure 1 shows the Cu $L_{3,2}M_{4,5}M_{4,5}$ Auger spectra of Cu metal excited with photon energies riding on the rising edge and far above the edge. The photon energy is referenced to the threshold energy E_0 of 932.5 eV (the inflection point). The Cu L_3-edge XANES recorded in TEY is shown in the inset. The three-peak resonance is characteristic of clean Cu metal.[22] It should be noted that except for the normal Auger excited at 1100-eV photon energy, the rest of the series was recorded with a small difference (as small as 0.1 eV) within a span of $\sim$2 eV. Several interesting features emerge from Fig. 1. First, it can be seen that the normal Auger exhibits the characteristic satellite structure in the region of 2–8 eV below the most intense ^1G peak. These features are absent in

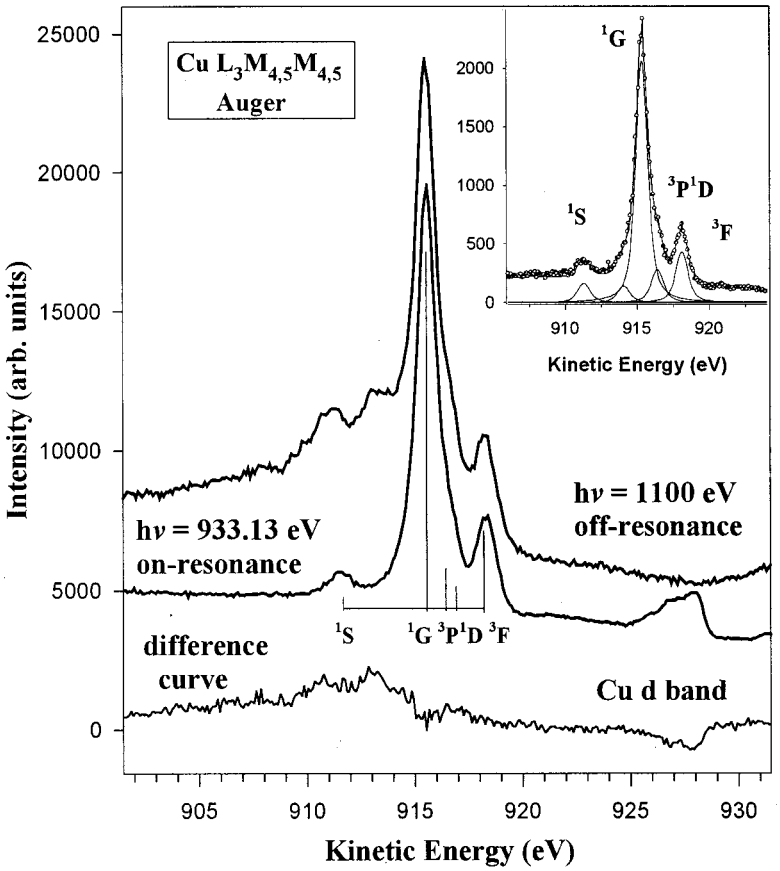

FIG. 2. Comparison of the normal and resonant Cu $L_3M_{4,5}M_{4,5}$ Auger effects of Cu metal. The difference curve corresponds to the shake-up satellites of the normal Auger. The inset shows a fit of the resonant Auger spectrum. Some unexpected intensity based on the atomic theory was seen in the region of ~914.0 eV (see text).

resonant Auger with threshold excitation. This finding is in good accord with a previous report.[17] The satellite in the normal Auger spectrum is attributed to multielectron (shake) processes associated with the creation of the core hole. When the core electron is excited with photon energy at the threshold E_0, the energy is not sufficient for the shake-up and shake-off processes to take place. In fact they are absent at all photon energies below the Cu L_2 edge. This result may indicate that the Coster-Kronig processes could also be responsible for the satellites. Second, there is a clearly noticeable dispersion of the Auger lines, which shifts to lower kinetic energy as the photon energy decreases below the threshold. Finally, there appears to be a noticeable skewing on the lower kinetic-energy side of the most intense ^1G peak. The intensity of the shoulder is photon-energy dependent and it skews the ^1G line as the photon energy moves slightly further below E_0.

Let us leave the dispersion behavior for the moment and compare in Fig. 2 the normal and resonant Auger excited with photon energy far above the edge (+169 eV) and at the first resonance (+0.63 eV), respectively. The atomic multiplets characteristic of Cu are also shown for comparison.[14] The spectrum below the resonant Auger in Fig. 2 is the difference between the normal and the resonant Auger after normalization. These features are the shake-up satellites of the normal Auger spectrum.[14,16,17] They arise from multielectron excitation, $L_3M_{4,5}$ shake-up. These processes require photon energy significantly exceeding the threshold energy, in good accord with previous results.[16,17] The resonant Auger was fitted with several components (inset). The fitting was performed with a Voight function using the lifetime broadening as the Lorenztian component. We see that the fit produces all the atomic multiplet features (^1S: −4.05 eV, $^3P^1D$: 1.07 eV, and ^3F: 2.76 eV, relative to ^1G at 915.52 eV) except a small shoulder (−1.29 eV) of the ^1G peak. This shoulder was needed to improve significantly the quality of the fit. It reflects the skewed line shape that modifies considerably as the photon energy moves below the threshold. This behavior is of considerable interest and it is likely of similar origin (densities-of-states effects at the Fermi level) as observed in Ag metal.[8] We return to this later. In addition, there are two barely visible features between 920 and 928 eV that may be associated with delocalized two-hole states in terms of the Cini-Sawatzky theory.[17,19,20] Still higher-resolution work is necessary to confirm these observations and their interpretation. Close examination of the ^1G peak reveals that the resonant Auger peak is slightly but noticeably narrower than the normal Auger (by 0.1 eV out of a width of ~0.9 eV). The feature around 928 eV in the resonant Auger spectrum is the Cu *d*-band photoemission, which appears in the vicinity of the Auger multiplets. Fortunately, this band is close enough to provide a calibration for the photon energy (position of the *d* band and relative intensity) but far enough from interfering with the major Auger features. The Cu *d* band exhibits enhanced intensity at resonance. This is connected to resonant photoemission in which

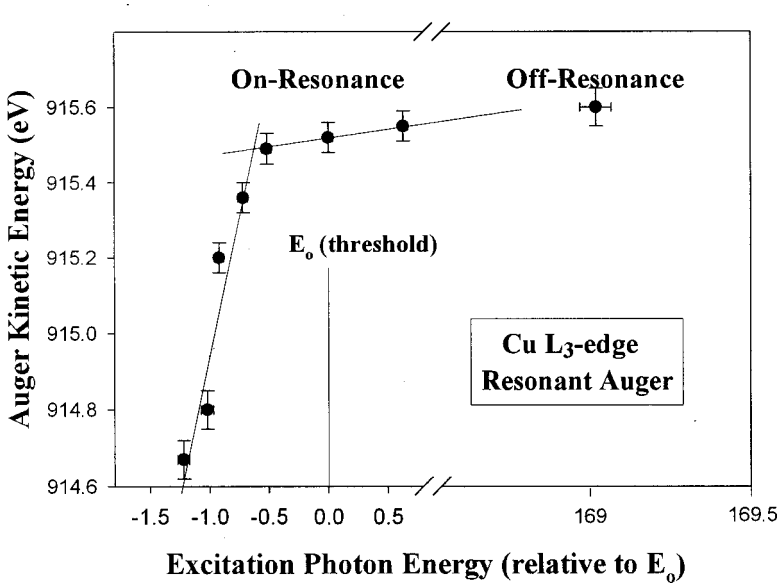

FIG. 3. A plot of the kinetic energy of the ^1G peak vs excitation photon energy on and off resonance $E_0 = 932.50$ eV. Two straight lines are drawn to guide the eye for the normal and resonant Auger region.

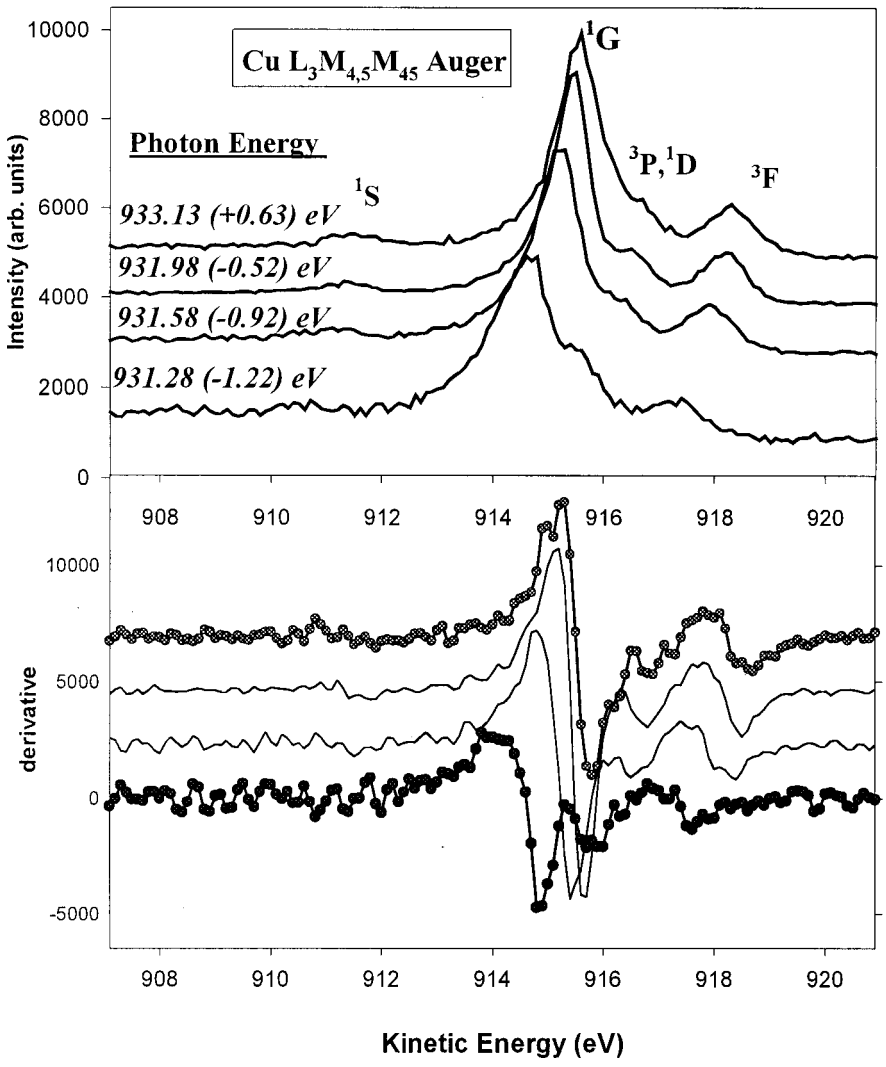

FIG. 4. Resonant Cu $L_3M_{4,5}M_{4,5}$ Auger effects of Cu metal at several photon energies above and below the threshold (932.50 eV) and corresponding derivatives. Notice the skewing of the ^1G peak shoulder at lower kinetic energy as the photon energy decreases below the threshold. This is accompanied by a reduction in peak height and a dispersion as noted above.

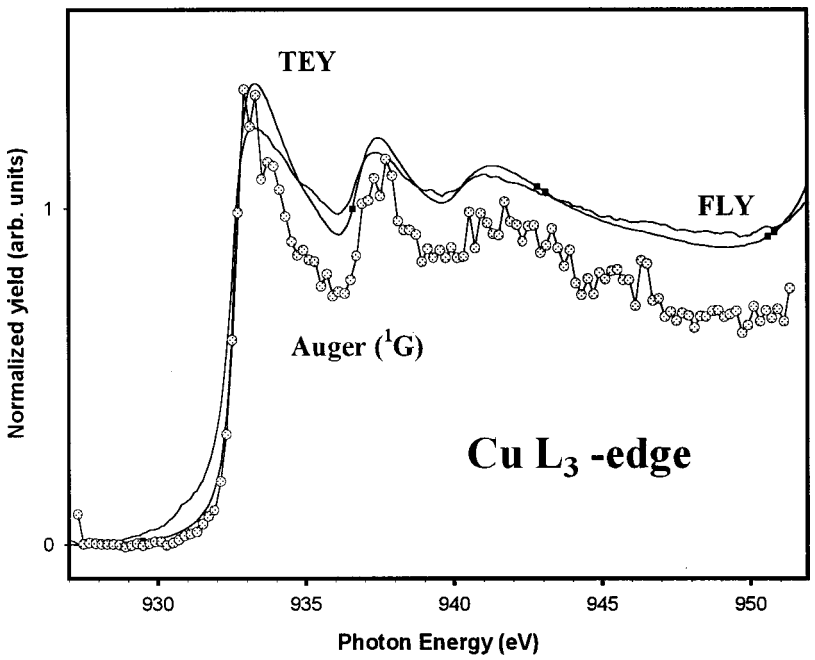

FIG. 5. Cu L_3-edge XANES of Cu metal recorded in TEY, FLY, and partial Auger yield (^1G, peak height, and a constant final-state mode). The spectra have been normalized to unity edge jump and the white line in the partial Auger yield is scaled to that of TEY.

the $2p$-$3d$-transition final state and the d-band-continuum final state become degenerated. These issues will be dealt with elsewhere.

We now return to the dispersion behavior of the Auger multiplets in Fig. 1. The correlation of excitation photon energy with the ^1G peak position is plotted in Fig. 3. It is immediately apparent that the resonant Auger exhibits a Raman effect, similar to those observed in Ni (Ref. 13) and $4d$ metals.[7,8] The slope of the dispersion starting at ~0.5 eV below the threshold is reasonably linear with a slope of ~1.1, similar to the Ni results.[13] Dispersion is also seen in the ^3F and ^1S components. It should be noted that the variation in both photon and electron energy in the region just below the threshold is within a span of ~1 eV, therefore high-energy resolution and precise photon energy are critical. We recall the extra shoulder in the inset of Fig. 2 to reflect the skewing of the line, which is not part of the atomic multiplets.[14,17] The skewing becomes more prominent as the photon energy decreases from the first resonance maximum to below the threshold. Figure 4 shows the progressive skewing of the line shape at the expense of the ^1G intensity as the photon energy moves slightly below the threshold. This behavior is similar to that observed in Ag and could be attributed to densities-of-states effects in the vicinity of the Fermi level.[8,22]

It is also interesting to investigate the appearance of the absorption spectrum monitored by a high-resolution partial Auger yield. It has been shown that when the resonant Auger/fluorescence were used to monitor the absorption, XANES with sublifetime resolution can be obtained.[7,12,23] Thus a high-resolution Auger yield is potentially a new method to obtain a high-resolution XANES and has been used to obtain high-resolution results with some success,[1] although its universality has not yet been fully established and requires more rigorous testing. Figure 5 shows the Cu L_3-edge XANES monitored with the peak height of the ^1G component together with XANES spectra recorded in TEY and FLY. The broadening seen in FLY is due to the thickness effect (self-absorption). The most interesting feature is the comparison between the TEY and the partial Auger yield. There is clearly a significant narrowing in the resonance seen in the XANES recorded with partial Auger yield. This observation is similar to the sublifetime spectra observed at the L_3 edge of $4d$ metals[7,12] and partial x-ray fluorescence yield studies.[23] Thus this techniques provides better sensitivity that can be used to investigate chemical systematic[12] as well as interface and buried layers in thin films as was recently reported.[24] In addition, this technique should also be applicable to the investigation of non-Fermi behavior of low-dimensional materials such as Luttinger liquids.[25]

We have reported a study of the threshold behavior of Cu $L_3M_{4,5}M_{4,5}$ Auger effects at the Cu L_3 edge. The study reveals the observation of resonant Auger Raman effects in Cu. It is also revealed that the general characteristics of resonant Auger in Cu such as linewidth narrowing, dispersion, and high-resolution partial yield, bear great resemblance to those of $4d$ metals, indicating universality of the behavior, although they differ in details. Finally, we want to reemphasize that the high-brightness synchrotron light source was an indispensable and necessary tool for these type of experiments.

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