Threshold Behavior of Cu L_3,$M_{4,5}M_{4,5}$ Auger of Cu Metal at the L_3 Edge

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Introduction

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] In resonant Auger, the absorption and decay process is 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. High resolution is required for both the photon and the electron such that the overall experimental resolution is comparable or smaller than the lifetime broadening of the core hole (e.g., ~ 2.4 eV for Ag L_3, ~0.4 eV for Cu L_3).[7]

Since the discovery of the Auger resonant Raman effect in Xe,[3,4] there have been some systematic studies of the phenomenon using the $L_3M_{4,5}M_{4,5}$ resonant Auger of the 4d noble metals.[7-9] The resonant Auger characteristics are (a) a dispersion in the kinetic energy of the Auger electrons with excitation photon energy in the vicinity of the threshold,[7,8] (b) a narrowing of the Auger line,[7,8] (c) a photon-energy-dependent line shape and Auger satellite structures associated with the electronic structure and decay dynamics,[8] and (d) a sub-lifetime appearance of the x-ray abortion near-edge structure (XANES) spectrum using partial Auger yield.[8,10]

Cu is the prototype for $L_{3,2}M_{4,5}M_{4,5}$ Auger studies of 3d metals.[1,11,12] The challenges are that the metal d-bands are directly involved in the Auger process, complicating 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).[7] 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. In this work, we report the observation of Auger resonant Raman effect in Cu metal. We will focus on the Cu L_3-edge excitation and the associated $L_3M_{4,5}M_{4,5}$ Auger decay channels.

Results and Discussion

The measurements were carried out at the SRI-CAT 2-ID-C undulator line at the Advance Photon Source. It is equipped with a spherical grating monochromator that operates at a tunable range of 0.5 -3.0 keV with a resolving power up to 10,000.[9] A 600 l/mm grating was used. With entrance and exit slit of 10 µm, this grating delivers a photon flux of ~ 10^{12} photons/sec at a spot size of ~ 0. 5 mm with a photon energy resolution of 0.2 eV at the Cu L_3 edge (~ 933 eV). A pass energy of ~ 6 eV was used for the Auger measurements. The experiments were carried out by first measuring the Cu $L_{3,2}$-edge XANES of a clean Cu, then Auger spectra were recorded with the photon energy tuned 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.

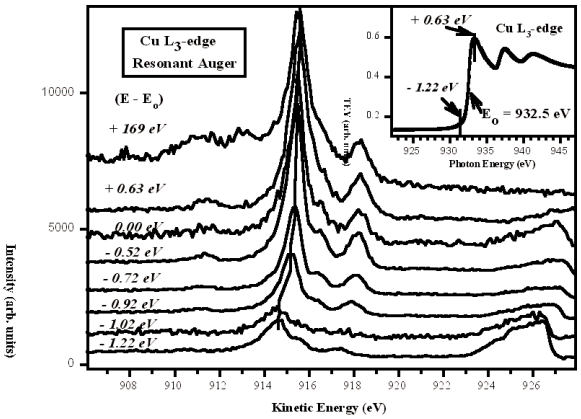

FIG. 1. Resonant Auger at the Cu L_3 edge.

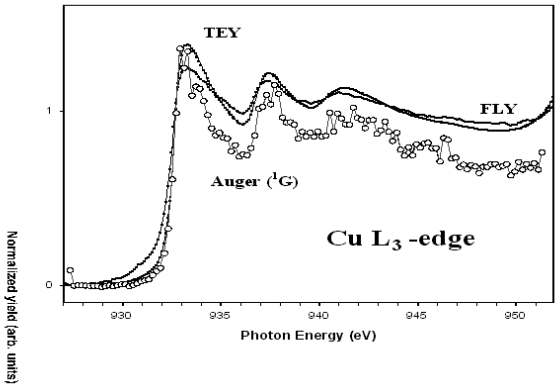

FIG. 2. Resonant Auger at the Cu L_3 edge.

The photon energy is referenced to the threshold energy, E_o, of 932.5 eV (the inflection point). The Cu L_3-edge XANES recorded in total electron yield (TEY) is shown in the inset. Several interesting features emerge from Fig. 1. First, the normal Auger exhibits the characteristic satellite structure in the region of 2 - 8 eV below the most intense ^{1}G peak. These features are absent in resonant Auger with threshold excitation.[11,12] Second, there is a noticeable dispersion of the Auger lines, which shift 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 ^{1}G peak. The intensity of the shoulder is photon-energy dependent and it skews the ^{1}G line as the photon energy moves slightly further below E_o.

We now turn to the dispersion behavior of the Auger multiplets. It is immediately apparent that the resonant Auger exhibits a Raman effect, similar to those observed in Ni[10] and 4d metals.[6,8] 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.[10] Dispersion is also seen in the ^{3}F and ^{1}S components. The skewing becomes more prominent as the photon energy decreases from the first resonance maximum to below the threshold. This behavior is summarized in Fig. 2.

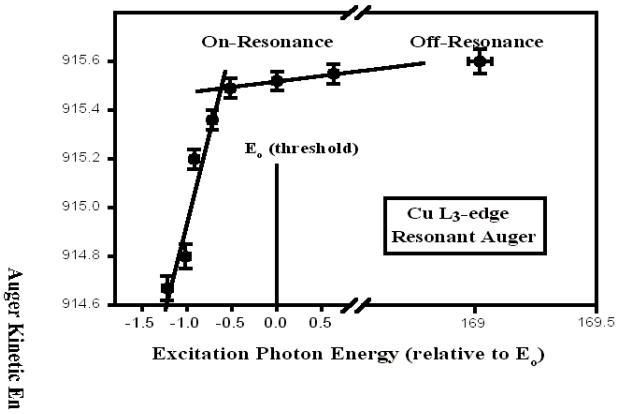

FIG. 3. Cu L_3 edge with TEY, FLY and Auger yield.

It is also interesting to note that in Fig. 3, the Cu L_3-edge XANES monitored with the peak high of the ^{1}G component exhibits a significant narrowing in the resonance. This observation is similar to the sub-lifetime spectra observed at the L_3 edge of 4d metals[6,9] and partial x-ray fluorescence yield (FLY) studies. Thus this techniques provides better sensitivity that can be used to investigate chemical systematic.[13, 14]

Acknowledgments

Argonne National Laboratory is supported by the U.S. Department of Energy, Basic Energy Sciences, under Contract No. W-31-109-Eng-38. Work at the University of Western Ontario is supported by NSERC of Canada.

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