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Why are the band-like states suppressed in the M_3–$M_{4,5}M_{4,5}$ super Coster–Kronig electron spectrum of Cu metal compared to those in the L_3–$M_{4,5}M_{4,5}$ Auger electron spectrum?

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Abstract

The relative spectral intensity of the band-like two $M_{4,5}$-hole state to the atomic-like localized one is much suppressed in the coincidence M_3–$M_{4,5}M_{4,5}$ super Coster–Kronig (sCK) electron spectrum of Cu metal compared to the one in the coincidence L_3–$M_{4,5}M_{4,5}$ Auger electron spectroscopy (AES) spectrum. The M_3-hole lifetime width of Cu metal is calculated by an ab initio atomic many-body theory (the extended relaxed core random phase approximation with exchange). The calculated M_3-hole lifetime width of Cu metal agrees well with the experimental one. The M_3–$M_{4,5}M_{4,5}$ sCK decay width of Cu metal decreases much with delocalization of the two $M_{4,5}$ holes in the sCK final state, whereas the Auger decay width is fairly independent of localization and delocalization of the two $M_{4,5}$ holes in the Auger final state. Thus, the relative spectral intensity of the band-like state is much suppressed in the coincidence M_3–$M_{4,5}M_{4,5}$ sCK-electron spectrum of Cu metal compared to the one in the coincidence L_3–$M_{4,5}M_{4,5}$ AES spectrum.

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1. Introduction

The relative spectral intensity of the band-like two $N_{4,5}$-hole final state to the atomic-like localized one in the coincidence N_3–$N_{4,5}N_{4,5}$ super Coster–Kronig (sCK) electron spectrum of Ag metal is enhanced compared to the one in the coincidence M_5–$N_{4,5}N_{4,5}$ Auger electron spectroscopy (AES) spectrum [1], while the relative spectral intensity of the band-like two $M_{4,5}$-hole final state to the localized one in the coincidence M_3–$M_{4,5}M_{4,5}$ sCK-electron spectrum of Cu metal is suppressed compared to the one in the coincidence L_3–$M_{4,5}M_{4,5}$ AES spectrum [2]. Recently, the puzzling variation in the relative spectral intensity of the band-like final state to the localized one with the core–hole decay channel, is attributed by the author to the change in the sCK decay rate with localization and delocalization of two holes in the sCK final state [3]. So far it has been widely believed that the relative spectral intensity of the band-like final state to the localized one depends solely on the ratio ($U/2W$) of the multiplet dependent Coulomb hole–hole repulsion energy (U) to the valence band width (W) [4,5]. However, this is not true, unless the decay rate is independent of localization and delocalization of two holes in the final state.

The Auger decay does not involve electrons in atomic shells the principal quantum numbers of which are the same as that of the intermediate core hole. The Auger electron kinetic energy (KE) then becomes very high and the Auger transition matrix element becomes small. The Auger electron KE is so high that the Auger transition matrix element becomes fairly independent of a change in the Auger final-state potential by localization and delocalization of two holes in the Auger final state [6–8]. However, the sCK decay involves only the electrons in atomic shells the principal quantum numbers of which are the same as that of the intermediate core hole. The sCK-electron KE then becomes very small and the sCK transition matrix element becomes large. The sCK transition matrix element depends critically on a change in the sCK final-state potential by localization and delocalization of two holes in the sCK final state [6–8]. The two holes are delocalized in the band-like final state, whereas they are localized in the atomic-like final state. We then expect that the relative spectral intensity of the band-like final state to

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the atomic-like one depends not only on the ratio of ($U/2W$) but also on whether the two holes are created by the sCK decay or the Auger decay. In the present paper, we calculate the M_3-hole lifetime width of Cu atom and Cu metal by an ab initio atomic many-body theory. The present many-body theory gives good agreement with experiment. The sCK decay width depends critically on localization and delocalization of two $M_{4,5}$ holes in the sCK final state. There is a significant reduction in the sCK decay width with delocalization of two $M_{4,5}$ holes in the sCK final state. This explains why the relative spectral intensity of the band-like final state to the atomic one is much suppressed in the coincidence M_3–$M_{4,5}M_{4,5}$ AES spectrum of Cu metal compared to that in the coincidence L_3–$M_{4,5}M_{4,5}$ one.

2. Auger-photoelectron coincidence spectroscopy (APECS) spectrum

We start our discussion with Auger-photoelectron coincidence spectroscopy because the experimental data by Bartynski et al. [1,2] were collected by APECS. A many-body theory of APECS was already developed as early as in late 70s as a part of an unified many-body theory of photoionization and core–hole decay by which they are treated on the same footing [9]. The doubly differential photoionization cross section of a photoelectron and an Auger (or sCK) electrons, the KEs of which are ε and ε_A, respectively, is [9]

$$\frac{d^2\sigma}{d\varepsilon d\varepsilon_A}=\sum_{i,f}|P_\varepsilon|^2 A_i(\varepsilon-\omega)\frac{\pi|V^a_{if}(\varepsilon_A)|^2}{\mathrm{Im}\,\Sigma_i(\varepsilon-\omega)}D_f(\varepsilon-\omega+\varepsilon_A) \quad (1)$$

P is the dipole transition matrix element of photoemission, ω the incident photon energy fixed far above the ionization threshold, the energy distribution of which is neglected for the sake of simplicity. A_i the core–hole (i) spectral function (Appendix A.1), V^a_{if} the Auger (or sCK) transition matrix element, Im Σ_i the imaginary part of the core–hole self-energy (Appendix A.1), D_f the spectral function (or density) of Auger (or sCK) final states.

We measure the AES (or sCK) spectrum in coincidence with photoelectrons of a selected KE (ε^0). We introduce in Eq. (1) the spectral function (R) of the fixed energy electron analyzer which accepts photoelectrons of a selected KE.

$$\frac{d^2\sigma}{d\varepsilon^0 d\varepsilon_A}=\sum_f\int|P_\varepsilon|^2 R(\varepsilon,\varepsilon^0)A_i(\varepsilon-\omega)\times\frac{\pi|V^a_{if}(\varepsilon_A)|^2}{\mathrm{Im}\,\Sigma_i(\varepsilon-\omega)}D_f(\varepsilon-\omega+\varepsilon_A)d\varepsilon \quad (2)$$

The coincidence AES (or sCK) spectrum is then the product of D_f and the branching ratio of the unrenormalized partial Auger (or sCK) decay width, convoluted by the product of the singles (noncoincidence) photoelectron spectroscopy (PES) spectrum of a selected intermediate core–hole state and R. Thus, the coincidence AES (or sCK) spectral line width becomes narrower than the singles one. Here, the unrenormalized Auger (or sCK) decay width is the Auger (or sCK) decay width when D_f is approximated by a delta function. When the resolution width of R is much narrower than the singles PES line width of a selected intermediate core–hole state, we can get rid of the core–hole lifetime broadening of the coincidence AES (or sCK) spectrum.

The coincidence AES (or sCK) spectral peak intensity is

$$\frac{d\sigma}{d\varepsilon^0}=\int|P_\varepsilon|^2 R(\varepsilon,\varepsilon^0)A_i(\varepsilon-\omega)\frac{\Gamma_{if}(\varepsilon-\omega)/2}{\mathrm{Im}\,\Sigma_i(\varepsilon-\omega)}d\varepsilon \quad (3)$$

$$\Gamma_{if}(\varepsilon-\omega)=\int 2\pi|V^a_{if}(\varepsilon_A)|^2 D_f(\varepsilon-\omega+\varepsilon_A)d\varepsilon_A \quad (4)$$

The coincidence AES (or sCK) peak intensity is the product of the singles PES spectrum and the branching ratio of the renormalized partial Auger (or sCK) decay width, convoluted by R. Eq. (4) is the (renormalized) partial Auger (or sCK) decay width. When the resolution width of R is very narrow, the coincidence AES (or sCK) peak intensity as a function of photoelectron KE is the partial singles PES spectrum as a function of photoelectron KE. The partial singles PES spectrum is the product of the singles PES spectrum and the branching ratio of the partial Auger (or sCK) decay width. Unless the intermediate core–hole state involves strong configuration interactions such as shakeup/down excitations, the branching ratio is independent of photoelectron KE [10].

3. Localization and delocalization of two holes in the sCK (or Auger) final state and the sCK (or Auger) decay width

When the Auger (or sCK) final-state splits into the localized two-hole state and the delocalized one, their spectral intensity ratio depends solely on D_f, if V^a_{if} is independent of the final state. Fig. 1(A–C) show schematically how the sCK (or Auger) decay width, i.e., the imaginary part of the sCK (or Auger) self-energy, varies with the sCK (or Auger) electron KE according to localization and delocalization of the two holes in the sCK (or Auger) final state. The imaginary part of the sCK (or Auger) self-energy surges toward the double ionization threshold with an increase in the effective particle–hole interaction energy I_{ph}, between the sCK (or Auger) electron and the two holes in the sCK (or Auger) final state. The $M_{2,3}$–$M_{4,5}M_{4,5}$ sCK decay width of Cu metal decreases with delocalization of the two holes in the sCK final state (Fig. 1A), whereas the $N_{2,3}$–$N_{4,5}N_{4,5}$ sCK decay width of Ag metal increases (Fig. 1B), despite that the sCK-electron KE of the former sCK decay is similar to that of the latter sCK decay.

I_{ph}, between the sCK electron and the two holes in the sCK final state in Ag metal is much larger than that in Cu metal because of an increase in the locality of electron orbitals involved in the sCK transition in Ag metal compared to that in Cu metal. The imaginary part of the sCK self-energy not only increases but also surges much more toward the double ionization threshold in Ag metal than in Cu metal. The $N_{2,3}$–$N_{4,5}N_{4,5}$ sCK decay width of Ag metal is about 5–6 times larger than the $M_{2,3}$–$M_{4,5}M_{4,5}$ sCK decay width of Cu metal. The “max” hole energy (or the sCK-electron KE) at which the imaginary part of the sCK self-energy maximizes and the real part becomes (almost) zero, approaches the double ionization threshold in Ag

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