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COMMENTS

Comments are short papers which criticize or correct papers of other authors previously published in **Physical Review B**. *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on "Relation between copper L x-ray fluorescence and $2p$ x-ray photoelectron spectroscopies"

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Kawai *et al.* [Phys. Rev. B **48**, 8560 (1993)] concluded that for Cu compounds and high-T_c superconductors, there is a strong correlation between the L_3 x-ray emission spectroscopy (XES) spectrum satellite intensity and the $2p_{3/2}$ x-ray photoelectron spectroscopy (XPS) spectrum satellite intensity. They interpreted the XES satellite to be mainly due to the transition from the initial core-hole charge-transfer (CT) shakeup state rather than due to the $L_2L_3M_{4,5}$ Coster-Kronig (CK) decay preceding the $L_3M_{4,5}$-$M_{4,5}M_{4,5}$ spectator x-ray emission transition. One of the available experimental data shows that, despite a significant initial core-hole CT shakeup satellite intensity increase from metal Cu to high-T_c superconductors, the relative L_3 XES satellite intensity does not change at all because of the relative CK satellite intensity decrease. The latter is due to the decrease of the CK decay energy from metal Cu to high-T_c superconductors.

A hump at the high-energy shoulder extending to about 5 eV above the main peak of the L_3 Cu x-ray emission spectroscopy (XES) spectra of Cu metal, divalent and monovalent Cu compounds, and high-T_c superconductors (HTSC's) is considered to be predominantly due to the Cu$L_2L_3M_{4,5}$ Coster-Kronig (CK) decay preceding the $L_3M_{4,5}$-$M_{4,5}M_{4,5}$ spectator x-ray emission transition rather than due to the transition from the initial core-hole charge-transfer (CT) shakeup state.[1,2] Recently Kawai *et al.*[3] argued that the high-energy hump is mainly due to the latter rather than the former. Assuming that the full width at one-third of the maximum of the main-line peak reflects the satellite intensity, they concluded that there is a strong correlation between the full width at $\frac{1}{3}$ maximum and L_3 x-ray photoelectron spectroscopy (XPS) satellite intensity. With an increase of the XPS satellite intensity, the XES satellite also increases. Thus the enhanced high-energy satellite originates from the initial core-hole shakeup satellite state. In the light of other experimental data, I would like to comment on their conclusion.

Wassdahl and co-workers[4-7] studied in detail the satellite structures of the $L_{2,3}$ x-ray emission spectra of Cu metal and $YBa_2Cu_3O_{7-\delta}$ (YBCO). They obtained the L_3/L_2 spectral intensity ratio of 7.5 and 5.5 for Cu metal and YBCO, respectively. They differ considerably from the ratios determined by Kawai *et al.* The L_3 spectrum excited at 935 eV reflects emission essentially free from the initial-state shakeup and shakeoff and the $L_2L_3M_{4,5}$ CK-preceded satellites, since the excitation has been made close to the L_3 binding energy. The final-state shakeup satellite is negligible.[4] By subtracting the shifted pure L_3 profile from the L_2 band, after normalizing to equal height, they found that the L_2 shake satellite contributes 16% (18%) of the L_2 spectral intensity of Cu (YBCO). Similarly Wassdahl *et al.* assigned 30% of the high-energy-excited L_3 spectrum to satellite for both Cu and YBCO. They obtained the L_3/L_2 main-line intensity ratio of 6.25 for Cu metal, which is close to the L_3-$M_{4,5}M_{4,5}(^1G_4)/L_2$-$M_{4,5}M_{4,5}(^1G_4)$ Auger main-line intensity ratio of 5.3.[8] Assuming statistical L_3/L_2 population, they could estimate the satellite intensity in the L_3 band associated with the $L_2L_3M_{4,5}$ CK process to be 24% (21%) of the total spectral intensity of Cu (YBCO). The ratio between the CK decay rate and Auger decay rate can be determined from the spectral intensities of the L_2 line and the part of the L_3 satellite which corresponds to CK-formed initial states.[5,8,9] Assuming that the Auger decay rates are the same for the L_2 and L_3 core holes and using the CK decay rate of 0.68 eV, previously determined from an analysis of the $L_{2,3}$ XPS spectra of Cu metal,[9] the Auger decay rate for metallic Cu was determined to be 0.32 eV.[6,7] The Auger decay rate determined from the Auger satellite is 0.34 eV,[8] and the theoretical prediction by a Green function calculation is 0.43 eV.[10] The estimate of the Auger decay rate from the $L_{2,3}$ x-ray emission spectrum is quite accurate. The Auger decay rate is not expected to differ much for

YBCO because the Auger decay energy is large enough so that the decay rate is insensitive to both the change of the Auger decay energy and the screening of the final-state two-hole potential. Hence, using the Auger decay width of 0.32 eV, one obtains 0.43 eV for the CK width of YBCO.[5-7] The observed CK decay rate difference between Cu metal and YBCO is related to the decay energy difference. The CK decay energy for YBCO is estimated to be 7.7 eV, while the one for Cu metal is about 10 eV.[11] The CK decay rate depends critically on the decay energy, particularly when the decay energy is small.[12] Near threshold the CK decay rate increases with an increase of the CK decay energy. This appears to be the case with the present observation. The variation of the CK decay rate has never been discussed in this context. As one goes from Cu metal to YBCO, the relative CK satellite intensity to the total spectral intensity decreases from 0.24 to 0.21, while the relative L_3 (L_2) shakeup/shakeoff satellite intensity increases from 0.06(0.16) to 0.09(0.18). As a result the relative L_3 satellite intensity does not change at all, despite a significant initial-state shakeup intensity increase in the XPS spectrum from Cu metal to YBCO. The dominant part of the satellite intensity is due to the CK decay not due to the core-hole CT shakeup.

It has been reported that the $L_{2,3}VV$ Auger satellite intensity increases as one progresses from metal Cu, Cu_2O, CuO, $La_2Sr_2Cu_3O_7$ (LSCO), to YBCO.[13] Auger-photoelectron coincidence spectroscopy (APECS) study of metal Cu demonstrated a direct link between the L_2 photoionization and the satellite in the L_3VV Auger spectrum, namely, the L_2-$L_3M_{4,5}$ CK-preceded Auger decay products part of the satellite besides the shakeoff process which will produce similar initial states for the decay.[14,15] It has been shown that these processes generate a satellite with a spectral intensity relative to the main line approximately equal to 0.75 in Cu metal, and similarly in Cu_2O and CuO.[14] Moreover, the $L_{2,3}VV$ Auger satellite intensity remains constant in the CuX_2 halides, while the XPS satellite intensity increases sharply as one progresses up the series Br, Cl, and F.[13,16,17]

Ramaker[13] concluded that all of the CT shakeup states must relax before the core-hole decay because the shakeup excitation energy is much larger than the core-level width. (Note that this does not seem to be the case with CT systems such as adsorbates. See Refs. 18 and 19 for the incomplete core relaxation in adsorbates.) In the case of the Auger decay, it appears that it is agreed that the initial-state shakeoff and the CK-decay-preceded Auger decay account for the greater share of the Auger satellite of Cu metal and Cu compounds except for the HTSC's where a significant satellite increase is claimed.[20]

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