PHYSICAL REVIEW B VOLUME 52, NUMBER 8 15 AUGUST 1995-II

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

Jun Kawai
Department of Materials Science and Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

Kuniko Maeda
The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako, Saitama 351-01, Japan

Katsumi Nakajima and Yohichi Gohshi
Department of Applied Chemistry, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

(Received 3 April 1995)

Ohno's preceding Comment [Phys. Rev. B **52**, 6127 (1995)] was based on experimental raw spectra of copper L x-ray emission. The Cu L x-ray emission spectra were, however, heavily smeared by the self-absorption effect, which was a source of contradiction. The electronic structure of divalent copper oxide was calculated placing one core hole and two $3d$ holes, with the result that the spectator $3d$ holes were delocalized in the adiabatic limit. This implies that the spectator $3d$ hole produced by the $L_{1,2}L_3M_{4,5}$ Coster-Kronig transition preceding the L_3-M x-ray emission will be mostly delocalized at the time of the L_3-M x-ray emission, and thus the spectator satellite will be weaker than is expected for the free atom. Ohno did not consider this delocalization, which was another source of contradiction.

Ohno,[1] based on the experimental x-ray emission spectra measured by Wassdahl and co-workers,[2-4] where the L_3/L_2 spectral intensity ratio was 7.5 for Cu metal, has commented on our previous work.[5] The ratio L_3/L_2 for the metal, however, ranges between 3.6 (100% Cu metal) and 9.5 (3% Cu–97% Sn dilute alloy) because of the self-absorption effect, shown in our previous work.[6] The self-absorption effect thus causes smearing of the profiles of L_3-V ($L\alpha$) and L_2-V ($L\beta$) x-ray emission spectra of transition-metal compounds. Though the threshold excitation experiments of Wassdahl and co-workers[2-4] were excellent, the spectra reported were raw data without a correction for the self-absorption effect. The absorption coefficient just above the threshold x-ray energy is remarkably different from that just below the threshold energy. The thresholds are on the high-energy shoulder of the L_3-V and L_2-V x-ray emission lines. What makes the matter difficult is that the x-ray absorption near-edge structure (NEXAFS) is different among monovalent copper [Cu(I)], divalent copper [Cu(II)], and metallic copper compounds. The profile of Cu(I) and metallic copper is edge shaped, but that of Cu(II) is a sharp peak. Thus the correction of this self-absorption effect is essentially required before extracting physical information from the measured spectra. Sugiura[7] reported a dip on the high-energy shoulder of the L_3-V x-ray emission line due to the presence of the absorption peak when comparing the x-ray emission and absorption spectra. We took into account the self-absorption effect in Ref. 5. Figure 1 shows Cu $L_{3,2}$-V x-ray emission spectra of 100% Cu metal and Cu(3%)-Sn(97%) dilute alloy, where the intensity ratio L_3/L_2 changes drastically in spite of the fact that these are metallic. Ohno[1] used raw data without the self-absorption correction, which was a source of contradiction with our work in Ref. 5.

The first motivation of our previous work[5] was to find the two components in L_3-V x-ray emission spectra, which are separated peaks in the Cu $2p$ x-ray photoelectron spectra (XPS) of CuO: the 943-eV satellite (poorly screened $|2p^{-1}3d^9\rangle$ final state) and the 934-eV main line (well-screened $|2p^{-1}3d^{10}L^{-1}\rangle$ final state). The answer to this question is that the main line of x-ray emission spec-

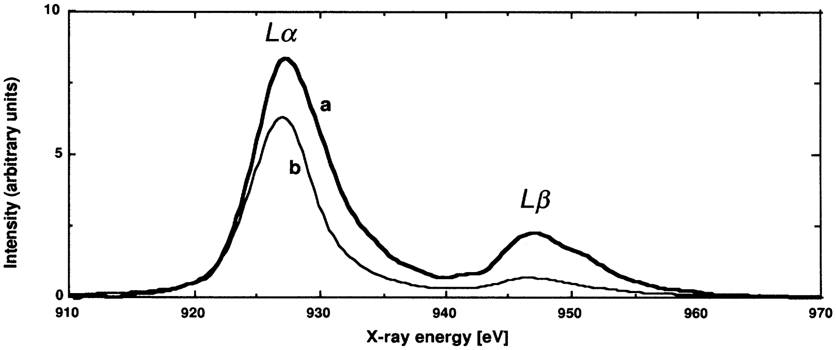

FIG. 1. Measured Cu $L_{3,2}$-V x-ray emission spectra of (curve a) Cu(3%)-Sn(97%) dilute alloy and (curve b) Cu(100%) metal. The spectrum a has been magnified so as to agree with the curve b at the low-energy tail of the L_3-V line.

0163-1829/95/52(8)/6129(3)/$06.00

tra is the $|2p^{-1}3d^{10}L^{-1}\rangle \rightarrow |3d^9L^{-1}\rangle$ transition (electron transition between well-screened states), and the so-called "Coster-Kronig satellites" in the x-ray emission spectra, which are the high-energy hump of the L_3-V line, are truly the $|2p^{-1}3d^9\rangle \rightarrow |3d^8\rangle$ transition (electron transition between poorly screened states). The contribution of the net Coster-Kronig satellite ($|2p^{-1}3d^8\rangle \rightarrow |3d^7M_{4,5}\rangle$) to the so-called "Coster-Kronig satellites" in the L_3-V x-ray emission spectra of divalent copper compounds is negligibly small. Here the so-called "Coster-Kronig satellites" are the high-energy humps on the $L_{3,2}$-V x-ray emission spectra.

This has been proved by the experimental work in Ref. 5. In this paper, we report a theoretical confirmation of our previous work[5] as follows.

We have calculated the electronic structure of a planar CuO_4 cluster (D_{4h} symmetry), which is the model cluster of oxide superconductor solids, but valid for other Cu(II) compounds. We have used the spin-unrestricted discrete-variational (DV) Hartree-Fock-Slater ($X\alpha$) method[8] for the electronic structure calculation. We have calculated the transient electron counts in atomic orbitals as follows.

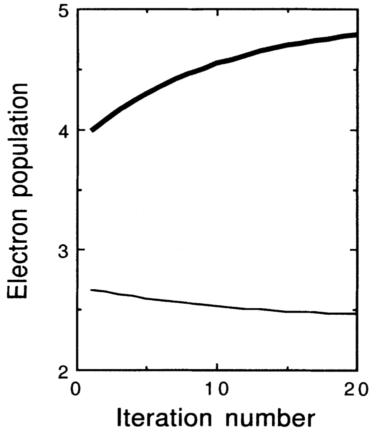

FIG. 2. Calculated $3d\downarrow$ (heavy solid line) and O $2p\downarrow$ (thin solid line) electron populations plotted against the SCF iteration times. The sum of $3d\downarrow$ population and four times the O $2p\downarrow$ population remains mostly constant.

First we obtained a self-consistent field (SCF) solution for the ground state; the ground-state electron configuration was $3d\uparrow^{4.96}3d\downarrow^{4.41}4s\uparrow^{0.17}4s\downarrow^{0.18}$ O $2p\uparrow^{2.96}$ O $2p\downarrow^{2.85}$. Then we calculated a SCF solution of the Cu $1s^{-1}$ core-hole state; the converged $1s\uparrow^{-1}$ hole-state electron configuration[9] was $1s\uparrow^{-1}3d\uparrow^{4.99}3d\downarrow^{4.99}4s\uparrow^{0.22}4s\downarrow^{0.23}$ O $2p\uparrow^{2.92}$ O $2p\downarrow^{2.67}$. Here the effective electron count is the Mulliken population.[10] The calculated population indicates that 0.58 electrons are effectively transferred from the O $2p\downarrow$ to the Cu $3d\downarrow$ orbital by the Coulomb attraction potential of the $1s\uparrow^{-1}$ core hole. This is the origin of the well-screened peak (i.e., the charge-transfer peak at 934 eV) in the $2p_{3/2}$ XPS spectra of Cu(II) oxides. We put an additional hole in the Cu $3d\downarrow$ orbital in the SCF solution of the $1s\uparrow^{-1}$ hole state, and SCF iterations were done (i.e., the initial condition of the SCF was $1s\uparrow^{-1}$ $3d\uparrow^{4.99}3d\downarrow^{3.99}4s\uparrow^{0.22}4s\downarrow^{0.23}$ O $2p\uparrow^{2.92}$ O $2p\downarrow^{2.67}$). The resulting transient electron populations are plotted against the iteration times in Fig. 2. The Cu $3d\downarrow$ electron population gradually increased and the O $2p\downarrow$ electron population decreased. The finally converged SCF solution of the additional $3d\downarrow^{-1}$ hole initial state was $1s\uparrow^{-1}3d\uparrow^{4.99}3d\downarrow^{4.91}4s\uparrow^{0.23}4s\downarrow^{0.27}$ O $2p\uparrow^{2.91}$ O $2p\downarrow^{2.42}$. 0.92 electrons were thus added to the $3d\downarrow$ orbital, which were transferred from surrounding oxygen atoms. The iteration time in Fig. 2 is physically the time after sudden annihilation of both $1s\uparrow$ and $3d\downarrow$ electrons. The valence-electron response to the sudden annihilation of the $1s\uparrow$ and $3d\downarrow$ electrons is similar to the final state of the $L_{1,2}L_3M_{4,5}$ Coster-Kronig transition.[11] The L_3-V x-ray emission preceded by the $L_{1,2}L_3M_{4,5}$ Coster-Kronig transition was believed to be the major origin of the double-hole satellite ($L_3M_{4,5}$-$M_{4,5}V$),[12] because of the existence of the spectator hole ($M_{4,5}$) during the x-ray emission process. This is possible for isolated atoms or isolated ions, but the spectator $M_{4,5}$ hole will be filled by an electron transferred from O $2p$ orbitals, if the relaxation time is infinitely long.

The SCF solution in the $1s^{-1}$ hole state is the adiabatic limit of photoionization, i.e., the photoionization process is infinitely long. The sudden approximation well reproduces the experimental results.[13] That is to say, the measured $2p$ photoelectron spectrum of CuO is composed of $|2p^{-1}3d^{10}L^{-1}\rangle$ and $|2p^{-1}3d^9\rangle$ with the relative intensity of 1.00 and 0.58, respectively.[14] Thus the adiabatic solution gives the major electron configuration $|2p^{-1}3d^{10}L^{-1}\rangle$ of the experimental result. This is also supported by the analysis of Ni $2p$ x-ray photoelectron spectra of Ni(II) compounds by Zaanen, Westra, and Sawatzky,[15] where the major configuration in the core-hole state is $|2p^{-1}3d^{10}L^{-2}\rangle$ or $|2p^{-1}3d^9L^{-1}\rangle$, though the major configuration in the ground state is $|3d^8\rangle$. One or two hole(s) in the $3d$ orbital will be filled by electron(s) transferred from the ligand. The final state of the Cu(II) $L_{1,2}L_3M_{4,5}$ Coster-Kronig transition is similar to Ni(II) $2p$ photoionization. Consequently, the spectator $M_{4,5}$ hole in Cu(II) compounds, which is created by the $L_{1,2}L_3M_{4,5}$ Coster-Kronig transition or shake process, is delocalized at the time of the L_3-V x-ray emission.

Ohno supposed in his Comment[1] that the satellites in the $L_{2,3}VV$ Auger spectra originated from (1) the Auger transition preceded by the $L_{1,2}L_3M_{4,5}$ Coster-Kronig transition or (2) the Auger transition preceded by the $3d$ electron shakeup or shakeoff at the $2p$ electron photoionization. Another origin of satellites is, however, possible in solids; the charge-transfer process. The $M_{4,5}$ hole, which is (1) intrinsically present because the solid is a Cu(II) compound, (2) produced by the $L_{1,2}L_3M_{4,5}$ Coster-Kronig transition, (3) produced by the $3d$ electron shakeup or shakeoff at the $2p$ electron photoionization, or (4) produced by the $L_{2,3}VV$ Auger transition, will tend to delocalize through hybridization with the ligands.[16] If this delocalization is not taken into account and considered within the isolated atomic picture then the Auger satellite behavior seems to break the sudden approximation.[17–19] Thus the $L_{2,3}VV$ Auger satellites, which were analyzed by Ohno within the isolated atomic picture in

Ref. 1, should be reanalyzed in the charge-transfer picture, i.e., the initial state of the Auger transition is a mixture of the two configurations of $|2p^{-1}3d^{10}L^{-1}\rangle$ and $|2p^{-1}3d^{9}\rangle$. The localization or delocalization of the additional $M_{4,5}$ spectator hole should be studied from the viewpoint of the competition between hybridization and Coulomb repulsion (Cini-Sawatzky theory[20,21]). This was not considered in Ref. 1, so it was another source of contradiction with our paper.[5]

Recently, a charge-transfer mechanism of the high-energy hump of the L_3-V x-ray emission spectra has been supported by Fomin and Murakhtanov[22] and Bernotas *et al.*[23]

In summary, our conclusion in Ref. 5—the main line of L x-ray emission spectra originates from transition between well-screened states, and the high-energy hump originates from transition between poorly screened states—is correct.

Thanks are due to Dr. N. Wassdahl for sending us his Ph.D. thesis and to C. Suzuki for performing the molecular-orbital calculations of the CuO_4 cluster.

---

[1] M. Ohno, preceding paper, Phys. Rev. B **52**, 6127 (1995).

[2] N. Wassdahl, J.-E. Rubensson, G. Bray, P. Glans, P. Bleckert, R. Nyholm, S. Cramm, N. Mårtensson, and J. Nordgren, Phys. Rev. Lett. **64**, 2807 (1990).

[3] N. Wassdahl, Ph.D. thesis, Uppsala University, Uppsala, Sweden, 1987.

[4] N. Wassdahl, P. Bleckert, G. Bray, P. Glans, N. Mårtensson, J. Nordgren, J.-E. Rubensson, R. Nyholm, and S. Cramm, in *X-ray and Inner-Shell Processes*, edited by T. A. Carlson, M. O. Krause, and S. T. Manson, AIP Conf. Proc. No. 215 (AIP, New York, 1990), pp. 451–464.

[5] J. Kawai, K. Maeda, K. Nakajima, and Y. Gohshi, Phys. Rev. B **48**, 8560 (1993).

[6] J. Kawai, K. Nakajima, and Y. Gohshi, Spectrochim. Acta **48B**, 1281 (1993).

[7] C. Sugiura, J. Phys. Soc. Jpn. **63**, 1835 (1994).

[8] H. Adachi, S. Shiokawa, M. Tsukada, C. Satoko, and S. Sugano, J. Phys. Soc. Jpn. **47**, 1528 (1979).

[9] The $2p_{xy}$ orbitals are degenerate in the ground state, but after the creation of a p_{xy}^{-1} hole they have different eigenvalues. Thus in this study we calculated the $1s\uparrow^{-1}$ core-hole state in place of the $2p^{-1}$ core hole for simplicity, because the effect of the $1s^{-1}$ hole in the CuO_4 cluster on the valence-electron population was similar to that of the $2p^{-1}$ core hole as was reported in a previous paper [J. Kawai, Y. Nihei, M. Fujinami, Y. Higashi, S. Fukushima, and Y. Gohshi, Solid State Commun. **70**, 567 (1989)]. Additionally, we have checked in a previous paper [J. Kawai, C. Suzuki, H. Adachi, T. Konishi, and Y. Gohshi, Phys. Rev. B **50**, 11 347 (1994)] that the effect of $1s\downarrow^{-1}$ was quite similar to that of $1s\uparrow^{-1}$ with respect to the valence-electron population.

[10] R. S. Mulliken, J. Chem. Phys. **23**, 1833 (1955); **23**, 1841 (1955); **23**, 2338 (1955); **23**, 2343 (1955).

[11] We have used the similarity of valence-electron response to the $1s^{-1}$ and $2p^{-1}$, here.

[12] The shake process at the photoionization of the $2p$ electron also produces the spectator hole, and x-ray emission following is also a satellite line which is identical to the Coster-Kronig-preceded satellite. The shake hole also delocalizes due to charge transfer.

[13] J. Ghijsen, L. H. Tjeng, J. van Elp, H. Eskes, J. Westerrink, G. A. Sawatzky, and M. T. Czyzyk, Phys. Rev. B **38**, 11 322 (1988).

[14] D. E. Ramaker, J. Photoelectron Spectrosc. Relat. Phenom. **52**, 341 (1990).

[15] J. Zaanen, C. Westra, and G. A. Sawatzky, Phys. Rev. B **33**, 8060 (1986).

[16] D. D. Sarma, S. R. Barman, R. Cimino, C. Carbone, P. Sen, A. Roy, A. Chainani, and W. Gudat, Phys. Rev. B **48**, 6822 (1993).

[17] D. D. Sarma, C. Carbone, P. Sen, R. Cimino, and W. Gudat, Phys. Rev. Lett. **63**, 656 (1989).

[18] J. C. Fuggle and G. A. Sawatzky, Phys. Rev. Lett. **66**, 966 (1991).

[19] D. D. Sarma, C. Carbone, P. Sen, R. Cimino, and W. Gudat, Phys. Rev. Lett. **66**, 967 (1991).

[20] M. Cini, Solid State Commun. **20**, 605 (1976).

[21] G. A. Sawatzky, Phys. Rev. Lett. **39**, 504 (1977).

[22] E. S. Fomin and V. V. Murakhtanov, Zh. Strukt. Khim. **34** (4), 3 (1993) [J. Struct. Chem. **34**, 491 (1993)].

[23] A. Bernotas, Ch. Froese Fischer, J. Kaniauskas, and V. Tutlys, J. Phys. Condens. Matter **6**, 8349 (1994).