PHYSICAL REVIEW B VOLUME 48, NUMBER 11 15 SEPTEMBER 1993-I

Many-body effects in the $M_{2,3}VV$ Auger line shape of copper

G. Chiarello, A. Amoddeo, R. G. Agostino, L. S. Caputi, and E. Colavita
Dipartimento di Fisica, Università della Calabria, 87036 Arcavacata di Rende, Cosenza, Italy

(Received 22 February 1993; revised manuscript received 2 June 1993)

We have observed atomiclike as well as multielectron relaxation effects in the $M_{2,3}VV$ Auger line shape of copper. From a comparison between the x-ray and the electron-excited Auger transitions, we have distinguished autoionizing features from multiplets and dynamical effects, all coupled to the $3p$ initial core-level excitation. Plasmon structures have been located and referred to each of the two Auger peaks split by spin-orbit coupling.

I. INTRODUCTION

Multielectron effects[1-4] occur very often in the electron spectra of solids and are responsible for changes from expected results based on one-electron theory. Sometimes the location and interpretation of the effects are less straightforward and more involved because the structures are usually weak. Particularly, multielectron effects influence the two-step one-electron Auger decay of the initial core hole and a wealth of papers show the presence of electron-electron interactions in metals leading to additional peaks.[5]

The importance of relaxation effects[4,6,7] depends on the core-hole lifetime and is expected to be negligible for the shallow core levels of Cu with which we are dealing. Nevertheless, we will show the presence of excitations created during the emission of the $3p$ core electron of Cu and the existence of a satellite structure accompanying each of the two main Auger transitions. Actually, many of them have already been foreseen theoretically.[8]

Since the dynamical response of bulk electrons to the external perturbation depends on the experimental probe, Mg $K\alpha$ x-ray excitation of the initial core hole, for example, is not expected to give rise to autoionizing decay channels.[9] On the other hand, features due to multiplets as well as to intrinsic plasmons are generally observed both by x-ray and electron-induced excitations.[10]

Recently, much attention has been paid to the origin of structures close to the L_2 and $L_3M_{4,5}M_{4,5}$ Auger lines of Cu and to their theoretical implications.[11-13] In comparison, less effort has been devoted to explain the features on the low and high kinetic-energy tail of the $M_{2,3}VV$ emission.

There exist several distinct structures on both sides of the main $M_{23}VV$ feature within about 10 eV from each Auger peak.[14] These structures may not belong to the main Auger decay and they still remain to be interpreted. No comprehensive explanation of the structures exists, to our knowledge, and, moreover, different experimental sources have not been used to discriminate among their possible origins. Fine structures on the high kinetic energy of the $M_{2,3}VV$ Auger peak were noticed by Jenkins and Chung[15] and attributed to a plasmon gain process of the escaping Auger electron. On the other hand, Salmeròn[16] assigned the same structures to the density of empty states. The broad bumps in the low kinetic-energy side of the main Auger peak, moreover, have not yet been throughly interpreted.

The aim of this work is to provide an understanding of the physical nature of the structures on the high as well as on the low kinetic-energy tail of the $M_{2,3}VV$ Auger line of copper. The electron-excited $M_{2,3}VV$ line has been compared with the Mg $K\alpha$ x-ray-excited Auger transition and, moreover, with the Cu electron energy-loss spectrum, in order to look for different contributions. Our measurements show that the Cu-$M_{2,3}VV$ line obtained by electron excitation contains a weak feature, absent in the x-ray-excited spectrum, whose origin has been clarified.

II. EXPERIMENT AND RESULTS

Measurements were carried out on a Cu(100) single crystal mounted in an ultrahigh-vacuum system held at a base pressure of 5×10^{-10} torr. The sample surface was cleaned by cycles of ion bombardment and annealing at 700 K until no detectable traces of impurities were observed by the Auger technique. Both Auger and electron-energy-loss spectra (EELS) were recorded in the $N(E)$ mode by a Perkin-Elmer cylindrical mirror analyzer with a coaxial electron gun. The energy resolution was $\Delta E/E=0.6\%$. The x-ray-induced Auger spectrum was taken in the same acquisition mode by a Leybold-Heraeus EA 10.100. The energy resolution was much better for almost an order of magnitude. In both cases, data were numerically differentiated to obtain the second derivative and give prominence to the structures located near to the main Auger lines.

Figure 1 shows the $M_{2,3}VV$ Auger lines of Cu and their negative second derivative. On the high as well as on the low kinetic-energy side of the two principal lines there are several weak structures that appear to be independent on the primary electron-beam energy, at least in the range from 400 to 3000 eV. In order to get a better insight into these features and, moreover, to exclude spurious effects due to the differentiation procedure, they have been extracted from a background which reproduces the tails of the Auger lines taken in the integral form. The structures obtained in this way coincide in energy position and in number with those obtained from the deriva-

0163-1829/93/48(11)/7779(4)/$06.00

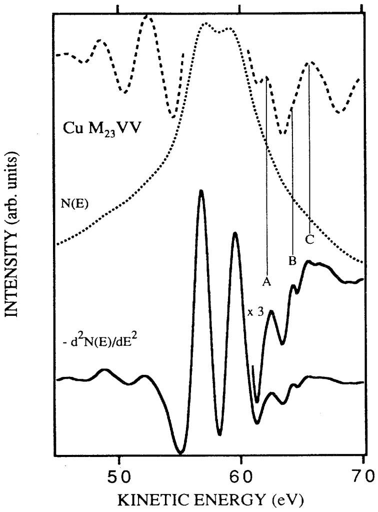

FIG. 1. Cu $M_{2,3}VV$ Auger spectrum taken in the $N(E)$ mode at 1500-eV primary beam energy. The weaker features have been extracted from the background and magnified (upper curve). The negative second derivative is also shown (lower curve).

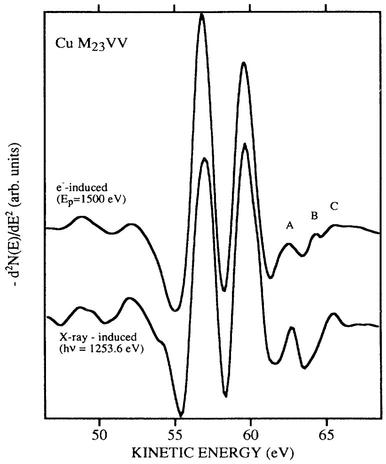

FIG. 2. Comparison between the negative second derivatives of the Cu $M_{2,3}VV$ Auger spectra excited by x-ray ($h\nu = 1253.6$ eV) and by electrons ($E_p = 1500$ eV).

tive of the acquired spectrum.

The interpretation of the two main lines of copper Auger emission is well known, being due to the M_2VV and the M_3VV transitions separated by the spin-orbit splitting of the $3p$ levels. Actually, the atomic interpretation in terms of multiplets[8,17] foresees several components (i.e., ^{1}G, ^{1}D, ^{1}S, ^{3}F, ^{3}P) for each transition and thus the $M_{2,3}VV$ Auger line shape is expected to be the superposition of multiple atomic lines; it is thus difficult to make an assignment for each contribution. Nevertheless, it is accepted that the major contribution to the M_3VV and M_2VV transitions comes from the ^{1}G components.[8,17,18]

The left side portion of the spectrum contains two broad bumps while, in contrast, sharper features are present in the right part of the spectrum. This observation leads us to conclude that the low and the high kinetic-energy portions of the spectrum do not have a common origin. Actually, peaks A and C were observed in a previous investigation[15] whereas the structure B is noticed for the first time in the present experiment. Interestingly, the energy difference between peak A and the main Auger peak of lower energy is the same as that between peak C and the main Auger peak at higher energy. In other words, peaks A and C are related to the $3p_{3/2}$ core hole and to the $3p_{1/2}$ core hole, respectively, and the same deexcitation mechanism thus gives rise to two similar spectra rigidly shifted by spin-orbit splitting. However, the physical origin of the A and C peaks is different from that of peak B.

A comparison between the electron- and the x-ray-excited Cu-$M_{2,3}VV$ spectra shown in Fig. 2 reveals peculiar differences in the region above the main Auger transition. The x-ray-excited spectrum shows only two structures on the high kinetic-energy side, both coinciding with features A and C of the electron-excited spectrum. No evidence for peak B exists in the photon-excited spectrum which, instead, has a pronounced depression in this region of the second derivative spectrum.

The above probe-dependent behavior for feature B suggests that it is due to a resonant recombination of the initially created $3p_{1/2}$ hole.[9,19] This mechanism is necessarily followed by the emission of electrons from the valence band into the continuum of states. Such a process can take place when the core hole is created by electrons or, eventually, by photons whose energy is closed to the core hole threshold energy, but not when energetic x-rays are used for the excitation of shallow core levels. In the latter case, in fact, the core electron is directly promoted to high energy levels of the continuum.

Recent theoretical work of Combet Farnoux[8] explains the several decay channels of the $3p-ns,d$ resonances in atomic copper. We interpret structure B at about 64-eV kinetic energy as due to the above resonances. One of the decay processes, $3p^63d^{10}4s^1 \rightarrow 3p^53d^{10}4s^2 \rightarrow 4p^63d^84s^2 + \varepsilon l$, provides the same multiplets of the Auger decay and also in this case the ^1G final state appears to be the most intense. This finding could explain the narrow shape of feature B which has an atomiclike character while its counterpart in $3d$ transition metals is quite broad.

The interpretation of the experimental results has been carried out so far in an atomiclike framework as usual for resonance processes. The assignment of structure A, instead, implies the consideration of dynamical multielectron effects related to the $3p$ initial core hole. For this picture, the solid is expected to experience multielectron excitations such as intrinsic plasmons and individual electron transitions, which can transfer energy[20] to the Auger electron. Thus, the latter will gain kinetic energy and will appear on the high energy side of the main Auger transition. The energy gain, the energy difference between structure A and the M_3VV peak, is about 6 eV and

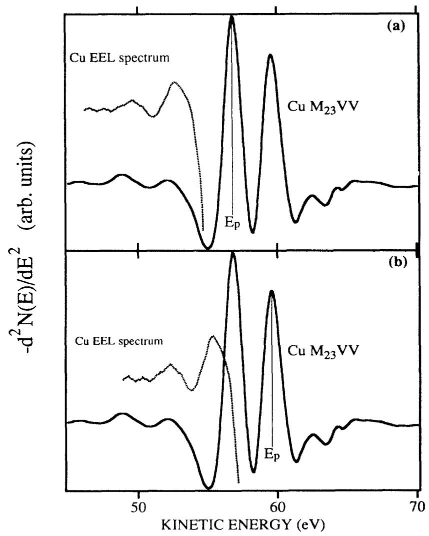

FIG. 3. Comparison between the negative second derivative of the Cu $M_{2,3}VV$ Auger and a portion of the EELS spectrum taken at a primary electron beam energy $E_p = 80$ eV. The elastic peak has been aligned, in turn, to the M_3VV (a) and to the M_2VV (b) Auger lines.

corresponds to the existence of strong absorption[21] in Cu at this energy for transitions from the valence band to *s*,p-like conduction bands. A component of the $3p^63d^84s^1$ Auger multiplet could also be present under structure *A*. Theoretical data of McGuire[17] locate the $M_3-M_{4,5}M_{4,5}$ ^1G multiplet in the low kinetic-energy Auger peak, and a superposition of $M_2-M_{4,5}M_{4,5}$ ^1G and $M_3M_{4,5}M_{4,5}$ ^3F multiplets in the high kinetic-energy Auger peak. Consequently, a simple calculation of energies indicates that the $M_2-M_{4,5}M_{4,5}$ ^3F multiplet could be located under structure *A*, but we could not then explain the *C* structure and, moreover, the $A-C$ energy difference which turns out to be equal to the spin-orbit splitting. We associate structure *A* with the M_3VV peak and structure *C* with the M_2VV peak and suggest that they are due to the same multielectron excitation in solid Cu.

Structure *B*, as already noted, is the result of a resonance deexcitation. Its counterpart would be close to structure *A* on its low-energy side. Actually, the x-ray-excited spectrum shows in correspondence a sharper feature as expected if the autoionization contribution vanishes.

The comparison of the electron-excited and the x-ray-excited spectra in the low-energy side shows the same structures only more resolved in the case of the x-ray-induced emission. This is also evident for the composite nature of each of those bumps. Their interpretation is carried out in terms of plasmons very likely with surface[23] contributions by a comparison (see Fig. 3) with the energy-loss spectrum taken at 80 eV (the EELS spectrum of copper is well known and interpreted; see, for example, Ref. 22). The elastic peak of the EELS spectrum has been aligned, in turn, to the M_3VV [Fig. 3 (a)] and M_2VV [Fig. 3 (b)] Auger lines. A good agreement with the experiment is obtained for the former case [Fig. 3 (a)], because the two losses of the EELS and of the Auger spectrum correspond with each other. Actually, the composite contribution to each loss structure is due to the overlap of the extrinsic plasmons[24] associated with the two pseudoelastic M_2VV and M_3VV peaks. In fact, the first loss of the M_3VV electron emission occurs under the much more intense M_2VV line, while the second one overlaps the first plasmon associated to the pseudoelastic M_2VV peak. The plasmons occur at $\Delta E_L = 4$ and 7 eV with respect to the M_2VV and M_3VV lines and are related to intense optical transitions at critical points from occupied valence states into the final bands $f = 6,7$ of its electronic structure.[25]

III. CONCLUSIONS

The $M_{2,3}VV$ Auger spectrum of copper contains atomiclike as well as broad bandlike effects. The former gives rise to the central doublet and to the autoionization satellite, the latter to the two side wings. The satellite of Cu was theoretically foreseen but never located as a distinct feature in the Auger spectrum. Thus, surrounding atoms and valence electrons do not wash out the atomic-like lines but contribute separate structures which are essentially related to the same excitation in metallic copper. On the high-energy side of the main Auger features we observe the result of a radiationless decay from excited $(sp)^*$ levels to $3d$ vacancies created together with the emission of the initial $3p$ core electron. The transition is optically allowed and corresponds to an absorption really observed in the optical spectrum of Cu. On the low-energy side of the main Auger features, instead, we have evidence of two plasmons related to the same electronic transitions involved in the structures of the higher-energy side.

ACKNOWLEDGMENTS

E. Li Preti and V. Fabio are gratefully acknowledged for their invaluable technical support.

---

[1] D. A. Shirley, in *Photoemission in Solids I,* edited by M. Cardona and L. Ley (Springer-Verlag, New York, 1978), p. 165 and references therein.

[2] T. Aberg, Phys. Scr. **T41**, 71 (1992).

[3] G. A. Sawatzky, in *Auger Spectroscopy and Electronic Structure,* edited by G. Cubiotti, G. Mondio, and K. Wandelt (Springer-Verlag, Heidelberg, 1989).

[4] D. E. Ramaker, in *Critical Reviews in Solid State and Materials Sciences,* edited by J. E. Greene (CRC, Boca Raton, FL, 1991), Vol. 17, Issue 3, p. 211 and references therein.

[5] J. W. Gadzuk, in *Photoemission and the Electronic Properties of Surfaces,* edited by B. Feuerbacher, B. Fitton, and R. F. Willis (Wiley, New York, 1978); W. Eberhardt, G. Kalkoffen, and C. Kunz, Phys. Rev. Lett. **41**, 156 (1978); B. Whitfield, G.

Bradley Armen, R. Carr, J. C. Levin, and B. Croseman, Phys. Rev. A **37**, 419 (1988), and references therein; M. Cini, J. Phys. Condens. Matter **1**, SB55 (1989).

[6] D. A. Shirley, R. L. Martin, S. P. Kowalczyk, F. R. McFeely, and L. Ley, Phys. Rev. B **15**, 544 (1977).

[7] O. Gunnarson and K. Schonhammer, Phys. Rev. B **22**, 3710 (1980).

[8] F. Combet Farnoux, Phys. Scr. **T41**, 28 (1992).

[9] S. D. Bader, G. Zajak, and J. Zac, Phys. Rev. Lett. **50**, 1211 (1983); G. Zajac, J. Zac, and S. D. Bader, Phys. Rev. B **27**, 6649 (1983).

[10] H. H. Madden, D. M. Zehner, and J. R. Noonan, Phys. Rev. B **17**, 3074 (1978).

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

[12] S. M. Thurgate and J. Neale, Surf. Sci. **252**, L605 (1991).

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

[14] They were not taken into account for the interpretation of the extended portion of the spectrum: R. G. Agostino, A. Amoddeo, L. S. Caputi, and E. Colavita, Phys. Scr. **T41**, 149 (1992).

[15] L. H. Jenkins and M. F. Chung, Surf. Sci. **26**, 151 (1971).

[16] M. Salmeròn, Surf. Sci. **41**, 584 (1974).

[17] E. G. McGuire, Phys. Rev. A **16**, 2365 (1977).

[18] E. Antonides, E. C. Janse, and G. A. Sawatzky, Phys. Rev. B **15**, 1669 (1977).

[19] G. Zajac, S. D. Bader, A. J. Arko, and J. Zak, Phys. Rev. B **15**, 5491 (1984).

[20] U. Beeker and R. Wehlitz, Phys. Scr. T **41**, 127 (1992).

[21] R. Lasser, N. V. Smith, and R. L. Benbow, Phys. Rev. B **24**, 1895 (1981).

[22] P. Aebi, M. Erbudak, F. Vanini, and D. D. Vvedensky, Surf. Sci. **264**, L181 (1992).

[23] H. Raether, *Excitations of Plasmons and Interband Transition by Electrons* (Springer, New York, 1980).

[24] C. N. Berglund and W. E. Spicer, Phys. Rev. **136**, A1030 (1964); **136**, A1044 (1964).

[25] G. Chiarello, E. Colavita, M. De Crescenzi, and S. Nannarone, Phys. Rev. B **29**, 4878 (1984).