Line Narrowing in Photoemission by Coincidence Spectroscopy

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We present photoemission spectra from the $3p$ level of Cu(100) obtained in coincidence with the M_3VV Auger line. The $3p$ level is narrowed from its 2.2-eV core-lifetime-broadened width to 1.0 eV, representing the intrinsic width of the ^1G Auger final state. The core line changes its energy within the 2.2-eV envelope as the Auger coincidence energy is changed, conserving the sum of Auger-electron and photoelectron kinetic energies.

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Auger-photoelectron coincidence spectra were first reported by Haak and co-workers.[1] Many potential enhancements of ordinary photoelectron and Auger-electron spectroscopies are described in the original papers.[1] Most are based on the extra discrimination provided by knowing which subpeak in the Auger spectrum is associated with which subpeak in the photoelectron spectrum. Also suggested was the possibility that core-hole lifetime broadening could sometimes be eliminated from the photoelectron spectrum. This is an especially exciting possibility, because the short Auger decay lifetime of core holes in solids can lead to broadening of more than an eV, obscuring interesting structure associated with chemical shifts, surface shifts, many-body structure, line shape, etc.[2] Poor instrumental energy resolution has previously prevented an experimental verification of this suggestion. In this paper we present data from the Cu(100) $3p$ core line in coincidence with the M_3VV ($3p\,3d\,3d$) Auger line illustrating this effect. The $3p$ linewidth is narrowed from 2.2 to 1.0 ± 0.2 eV. We believe that this 1.0 eV is the lifetime width of the ^1G Auger final state.

In this technique two electron energy analyzers are focused on one x-ray or uv illuminated sample. One analyzer is tuned to the energy of a core photoelectron and the other is tuned to an appropriate Auger decay energy. An event is recorded only when electrons are received in each analyzer simultaneously. This is interpreted to mean that both electrons are associated with the same photoexcitation event. Experimental details will be provided in another paper.[3] Briefly, commercial double-pass cylindrical-mirror analyzers[4] were set to 60-eV pass energy with 1-mm (small) apertures. One was fixed at a characteristic Auger energy, and the other was swept through the photoelectron spectrum. The 150-eV light from the National Synchrotron Light Source vacuum ultraviolet ring, was monochromatized by the U14 plane-grating monochromator.[5] The energy resolution, electron plus photon, in each system was <0.5 eV. The Auger (photoelectron) analyzer pulses provided starts (stops) for a time to amplitude converter. The output from the converter was analyzed by a multichannel analyzer. This provided output pulses for zero time delay (coincidence) and 180-ns time delay, each ± 10 ns. The 180-ns delay pulses (one revolution time in the storage ring) were used to subtract accidental coincidences from the spectra. The sample was sputtered and annealed once per day. No contamination was visible in electron stimulated Auger spectra. Each coincidence spectrum required approximately two calendar days of counting (about 2000 sweeps of 32 channels at 1 second per channel dwell). The peak count rate was 0.05 Hz, with 1 to 1 true coincidence to accidental ratio. Accidental coincidences have been subtracted from all reported spectra.

The Cu $3p$ linewidths ($p_{1/2}$, $p_{3/2}$) have been reported to be (2.0 ± 0.3, 1.6 ± 0.3 ev) from an evaporated film,[6] and (2.14, 1.93 eV) from a scraped polycrystalline sample.[7] We observed a $3p$ width of 2.2 ± 0.3 eV in our ordinary photoemission, or singles spectra. No widths from the $3p$ level of annealed single crystals are reported in the literature. These large widths are due to the large overlap between the $3p$ and $3d$ levels, which results in very rapid Auger decay and wide lifetime broadened peaks.

The Cu MVV Auger spectra are an example of the anomalously narrow CVV Auger spectra first explained by Cini[8] and by Sawatzky and Lenselink.[9,10] Briefly, the large $3d$-$3d$ Coulomb repulsion splits atomiclike states off from the band continuum. The Auger process then preferentially selects the atomiclike final states for core-hole decay. Because of the large $3p$ core-lifetime broadening and the small spin-orbit splitting, studies of the MVV spectra have not yielded much detailed information about the two d-hole atomic configurations involved.[11] Most detailed information about these states has come from the LVV spectra ($2p$ excitation).[12] McGuire predicts that the LVV and MVV spectra should have similar relative intensities of the multiplet structure.[13] The spectra are dominated by a large ^1G peak.

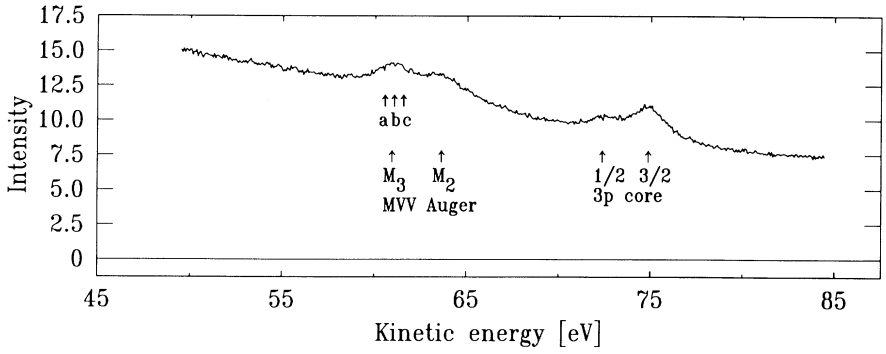

FIG. 1. Singles (ordinary photoemission) spectrum showing the Cu(100) $3p$ core lines and $M_{2,3}VV$ Auger lines at 150-eV photon energy. a, b, and c refer to the Auger analyzer settings for the coincidence spectra in Fig. 2.

The only other structure of any significance is predicted to be a ^3F peak of much smaller intensity at about 3-eV higher kinetic energy.

Figure 1 shows an ordinary photoemission scan through the Cu $3p$ core lines and the $M_{2,3}VV$ Auger lines. For the coincidence measurements, the Auger analyzer was fixed at each of the positions indicated by vertical arrows, a (60.6 eV), b (61.1 eV), and c (61.6 eV). At each position of the Auger analyzer, the photoelectron analyzer was scanned over the range 71.5 to 77.5 eV, and coincidence data were recorded. These are presented in Fig. 2. Also presented in Fig. 2 are background-subtracted singles spectra for comparison. In all spectra, the sample Fermi level is used as the zero kinetic energy.

Three interesting effects are immediately evident in the Auger-photoelectron coincidence spectra. First, the large background under the singles spectra, artificially removed for presentation in Fig. 2, is not present in the coincidence spectra. This effect, observed by Haak and co-workers,[1] has the simple explanation that the background, due mostly to inelastically scattered $3d$ photoelectrons, is not correlated with the Auger electrons, and thus does not appear in the coincidence spectra.

Second, the $3p_{1/2}$ component of the spectrum is nearly eliminated. The small remainder, observed about 2.5 eV below the main peak in Figs. 2(a) and 2(b), is due to Coster-Kronig decay of the $3p_{1/2}$ core hole into the $3p_{3/2}$ core hole, with subsequent M_3VV Auger decay.

Finally, the core lines in the coincidence spectra are significantly narrower than in the singles. The lines in the coincidence spectra move within the singles envelope in such a way as to conserve the sum of Auger-electron and photoelectron energies. These effects were predicted in Ref. 1, and in subsequent theoretical papers.[14] The argument is simple. If a system has a single long-lived Auger final state that is reached by decay of a short-lived core hole, then the principle of energy conservation demands that the sum of the kinetic energies of the

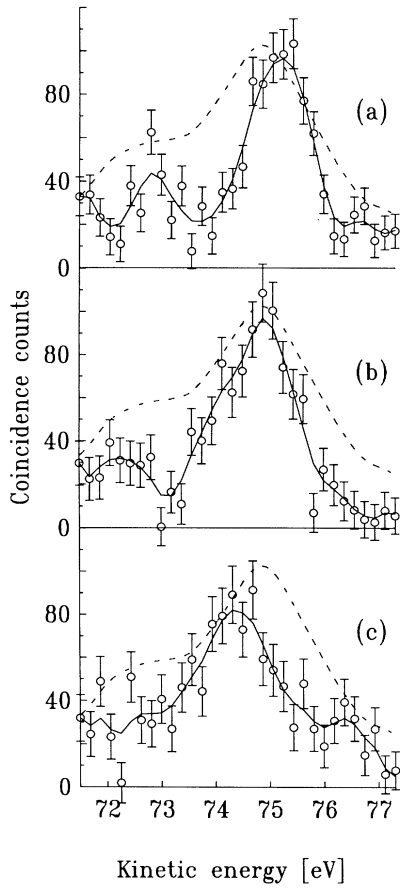

FIG. 2. Photoemission spectra of the Cu(100) $3p$ core lines in coincidence with the M_3VV Auger line taken at 150-eV photon energy. The data are open circles with error bars, the solid lines are digital smooths to the data (FWHM = 0.5 eV), and the dashed lines are background-subtracted singles spectra. (a) An Auger analyzer setting of 60.6 eV (arrow a in Fig. 1), (b) an Auger energy of 61.1 eV (arrow b), and (c) an Auger energy of 61.6 eV (arrow c).

Auger electrons and photoelectrons must be fixed, and equal to the photon energy minus the energy of the Auger final state. The sum is fixed, even though the energies of the photoelectron and Auger electron are each independently uncertain by the core-lifetime broadening. Thus any event that produces a photoelectron with greater than average kinetic energy must subsequently yield an Auger electron with correspondingly smaller than average kinetic energy. What makes this effect surprising and interesting is that it forces us to abandon the common "two step" picture of Auger decay in which the photoelectron and the Auger electron can be considered to be independent. The photoemission and subsequent Auger decay must be treated as a single coherent event if the observed line narrowing and peak motion are to be understood.

The observed width in Fig. 2(a) is 1.2 eV. After correction for instrumental contributions, we have determined that the intrinsic width is 1.0 ± 0.2 eV. The width due to dispersion of the two-hole state has been calculated to be 0.2 eV.[15] We interpret our much larger 1-eV width as dominated by the lifetime for cascade Auger decay of the ^1G Auger final state.

We believe that the extra structure observed at 76.5 eV, when the Auger analyzer is moved to position *c*, is due to transitions to other Auger final states, primarily the ^3F state. We plan a comprehensive study of the $M_{2,3}VV$ Auger spectrum to determine the transition strengths and intrinsic two-hole widths directly by holding the photoelectron analyzer fixed and scanning through the Auger spectrum.

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[1]H. W. Haak, G. A. Sawatzky, and T. D. Thomas, Phys. Rev. Lett. **41**, 1825 (1978); H. W. Haak, G. A. Sawatzky, L. Ungier, J. K. Gimzewski, and T. D. Thomas, Rev. Sci. Instrum. **55**, 696 (1984).

[2]Recent reviews of photoemission spectroscopy from solids including discussions of these effects include: N. V. Smith and F. J. Himpsel, in *Handbook on Synchrotron Radiation,* edited by E. E. Koch (North Holland, Amsterdam, 1983), Vol. 1; F. J. Himpsel, Adv. Phys. **32**, 1 (1983); E. W. Plummer and W. E. Eberhardt, Adv. Chem. Phys. **49**, 533 (1982).

[3]E. Jensen, R. Bartynski, S. Hulbert, and E. Johnson, to be published.

[4]Physical Electronics, Eden Prairie, MN, model 255G.

[5]Gwyn P. Willians, Malcolm R. Howells, Norene Lucas, and Peter Z. Takacs, Nucl. Instrum. Methods Phys. Res., Sect. A **222**, 99 (1984).

[6]Lo I. Yin, Isidore Adler, Tung Tsang, Mau Hsiung Chen, Douglas A. Ringers, and Bernd Crasemann, Phys. Rev. A **9**, 1070 (1974).

[7]G. K. Wertheim, M. Campagna, and S. Hufner, Phys. Condens. Matter **18**, 133 (1974).

[8]M. Cini, Solid State Commun. **24**, 681 (1977) and Phys. Rev. B **17**, 2788 (1978).

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

[10]G. A. Sawatzky and A. Lenselink, Phys. Rev. B **21**, 1790 (1980).

[11]A. M. Baro, M. Salmeron, and J. M. Rojo, J. Phys. F **5**, 826 (1975); H. H. Madden, D. M. Zehner, and J. R. Noonan, Phys. Rev. B **17**, 3074 (1978).

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

[13]E. J. McGuire, Phys. Rev. A **16**, 2365 (1977).

[14]M. Ohno, and G. Wendin, J. Phys. B **12**, 1305 (1979); O. Gunnarsson, and K. Schonhammer, Phys. Rev. B **22**, 3710 (1980); C.-O Almbladh, L. Hedin, in *Handbook on Synchrotron Radiation,* edited by E. E. Koch (North-Holland, Amsterdam, 1983), Vol. 1.

[15]Parameters of $U=8$ eV and $W=3$ eV were taken from Fig. 5 of Ref. 11, and used in Fig. 7 of Ref. 9 to determine this value.