Auger-Photoelectron Coincidence Measurements in Copper

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We demonstrate the feasibility of Auger-photoelectron coincidence spectroscopy (APECS) and use this technique to study the Cu $L_{23}M_{45}M_{45}$ Auger transitions. With APECS the Auger lines can be identified unambiguously and the Coster-Kronig–preceded Auger lines separated from the main $L_3M_{45}M_{45}$ lines. The background due to scattered electrons is strongly reduced relative to that in conventional Auger or photoelectron spectroscopy. Some other interesting experiments that can be done with this technique are discussed.

Auger and photoelectron spectroscopy are important sources of information on the electronic structure of atoms, molecules, and solids. In addition to the one-particle density of states obtained from photoelectron spectroscopy, Auger spectroscopy yields information about the two-particle density of states, from which one can obtain the hole-hole Coulomb interactions and, as recently shown, determine the influence of electron correlation effects.[1-6] In many cases, however, the desired information is obscured by the complexity of the spectra. For instance, in the mercury $N_{67}O_{45}O_{45}$ spectrum[7] there are eighteen lines, nine from each of the two initial states. Because the N_6 and N_7 groups strongly overlap, quantitative data analysis is difficult. In other cases the initial state of the Auger transition may not be a simple one-hole state but, because of shakeup or shakeoff in the photoionization or because of preceding Auger or Coster-Kronig transitions, may be a two-hole or multiple-hole state. The Auger transitions that deexcite the multiple-hole states are often at nearly the same energy as those deexciting the one-hole states, and, therefore, obscure the main features of the spectrum. Conversely, if the deexcitation of the multiple-hole states is the feature of interest, the spectrum corresponding to these transitions is obscured by that from the one-hole state.

If the initial hole state is produced by photoionization, then a measurement of the Auger spectrum in coincidence with a selected photoelectron avoids these difficulties. This technique will be referred to as Auger-photoelectron coincidence spectroscopy or APECS. To demonstrate the effectiveness of such a technique and the physics that can be illuminated by this approach, we have measured the $L_{23}M_{45}M_{45}$ Auger spectra of copper metal in coincidence with the $2p_{1/2}$ and $2p_{3/2}$ photoelectrons. This is to our knowledge the first report of such an experiment.

One of the reasons why copper is a good example for this measurement is that the $L_2M_{45}M_{45}$ Auger peak has abnormally low intensity compared to that of the $L_2L_{45}M_{45}$ peak. It is thought that the $2p_{1/2}$ hole decays partly by a normal Auger transition and partly by the Coster-Kronig transition, which leaves a vacancy in the $2p_{3/2}$ shell and one in the valence shell. The Auger transition following such a process has a kinetic energy slightly lower than that of a normal $L_3M_{45}M_{45}$ peak and appears as a low-energy shoulder on this peak.[8] Another explanation of the low-kinetic-energy structure on the $L_3M_{45}M_{45}$ line could be shakeup. Coincidence measurements can be used to shed further light on the origin of this structure since it should be coincident with the $2p_{1/2}$ photoelectrons if the Coster-Kronig explanation is correct and with the $2p_{3/2}$ if it is due to shakeup.

In these experiments the Auger spectrum has been measured in a conventional AEI ES200 spectrometer at a pass energy of 130 eV and with both the source and detector slits open as far as possible to maximize intensity. The photoelectrons were selected by means of a lens system and a 180° hemispherical analyzer, mounted on one of the available flanges of the AEI instrument. The resolution of the second system was about 4 eV, which is more than adequate for a clear separation of the L_2 and L_3 photoelectrons. The pulses from the channel multipliers were amplified in fast voltage-sensitive preamplifiers and in timing-filter amplifiers. The pulses from the amplifiers were sent to two constant-fraction discriminators, which provided the start and stop

pulses for a time-to-amplitude converter (TAC). The output of the TAC was analyzed in a pulse-height analyzer. The timing resolution of this system was about 16 ns, much longer than typical core-hole lifetimes which are of the order of 10^{-16} sec. In the most favorable case, the coincidence rate was 0.03 to 0.1 per second at a true-to-chance ratio of about 1 to 0.3. The true-plus-chance rate for each experiment was determined by integrating eight channels of the TAC spectrum and the chance rate by integrating 32.

The spectra were accumulated in two series of 24-h experiments. Each 24-h run began with cleaning the sample by argon-ion etching and heating, and each run covered eight points of the Auger spectrum. In the first series, 2–3 h was spent measuring the coincidence rate at each selected pair of Auger-photoelectron energies. Since the coincidence counting rate depends strongly on sample position and orientation, each set of points included a measurement of the coincidence rate between the $2p_{3/2}$ and $L_3M_{45}M_{45}$ electrons to which the others were normalized. Between sample cleaning the singles counting rate decreased slowly because of buildup of surface contamination. The coincidence rate falls off more rapidly than the singles rate, since the latter depends on the probability of two electrons escaping without energy loss through the contamination. To correct for this effect we have normalized the rates within each of these runs according to the product of the $2p_{3/2}$ and $L_3M_{45}M_{45}$ coincidence rates. This correction amounted to at most 20%. In the second series of runs the measurement of the Auger spectrum was under computer control. The photoelectron spectrometer was set on the $2p_{3/2}$ peak and the Auger spectrometer was cycled through eight points of the Auger spectrum, spending 15 min at each point and repeating the cycle about 12 times. In this case, no correction is necessary for change in sample contamination during the measurements, since all data were taken under nearly identical conditions. The results obtained by the two methods are in good agreement.

The results of our measurements are shown in Fig. 1. The curve marked A is the normal $L_{23}M_{45}M_{45}$ Auger spectrum without a coincidence requirement. Curves B and C are the Auger spectra in coincidence with the $2p_{3/2}$ and $2p_{1/2}$ photoelectrons, respectively. The coincidence data are normalized to the peak of the $L_{23}M_{45}M_{45}$ spectrum. Where duplicate measurements have been made, the weighted average is shown.

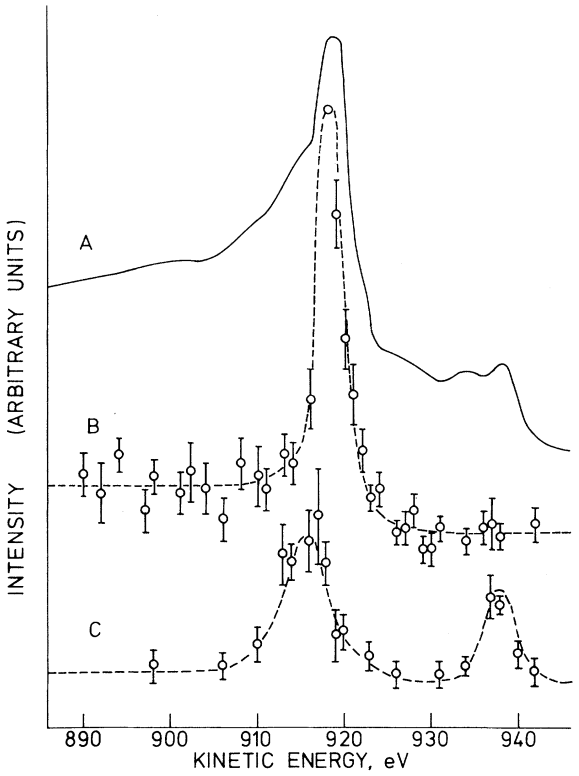

FIG. 1. Auger and Auger-photoelectron coincidence spectra of copper. The curve marked A is the normal Auger spectrum, B is the Auger spectrum in coincidence with the $2p_{3/2}$ photoelectrons, and C is the Auger spectrum in coincidence with the $2p_{1/2}$ photoelectrons.

Examination of the figure reveals several features. First, there are strong coincidences between the $2p_{3/2}$ photoelectrons and the $L_3M_{45}M_{45}$ Auger electrons and there are no coincidences between these photoelectrons and the $L_2M_{45}M_{45}$ Auger electrons. These results, which are expected, indicate that the experiment is working as designed and that there are no extraneous sources of coincidence.

Curve C in Fig. 1 shows that the Auger electrons in coincidence with the $2p_{1/2}$ photoelectrons come in two groups, one corresponding to the normal position of the $L_2M_{45}M_{45}$ electrons and one slightly lower than the position of the $L_3M_{45}M_{45}$ electrons. This lower peak arises from photoionization of the $2p_{1/2}$ shell followed by a Coster-Kronig transition and then an Auger transition. The coincidence spectrum confirms the hypothesis put forth to explain the low intensity of the $L_2M_{45}M_{45}$ Auger peak and the low-energy shoulder

seen on the $L_3M_{45}M_{45}$ peak in the normal Auger spectrum.[8] As pointed out in Ref. 8 the Coster-Kronig-preceded Auger transition is expected to be shifted to lower kinetic energy because of the Coulomb interaction with the extra $3d$ hole.

The integrated $2p_{1/2}$ coincidence intensity is approximately half the $2p_{3/2}$ intensity, as it should be. About $\frac{2}{5}$ of the $2p_{1/2}$ intensity is in the normal $L_2M_{45}M_{45}$ transition and about $\frac{3}{5}$ is in the Coster-Kronig-preceded $L_3M_{45}M_{45}$ region. These results are in excellent agreement with the values obtained by Antonides, Janse, and Sawatzky[8] from examination of the singles Auger spectrum of copper.

Another interesting aspect of the Cu Auger spectrum is the predicted[2] presence of a broad bandlike spectrum of the high-kinetic-energy side of the $L_3M_{45}M_{45}$ region. Although some structure is observed in this region[8] in the Auger spectrum it is not clear from the singles spectrum whether it is part of the L_2 or the L_3 spectrum. We should be able to identify this from the coincidence spectrum but with the present setup the signal-to-noise ratio is not good enough.

There is another quite different aspect of the coincidence spectra that is very interesting. In Fig. 1 we see that the intensity on the low-kinetic-energy side of the peaks is strongly reduced in comparison with that for the normal Auger spectrum. The large "background" in the normal Auger spectrum is usually attributed to inelastically scattered electrons. These, on the average, originate from somewhat deeper in the sample than the zero-loss electrons. In our experiment the one analyzer was set on the zero-loss photoelectron peak, thus selecting atoms close to the surface. The coincident Auger spectrum, which arises from the same atoms, has, therefore, a strongly reduced contribution from scattered electrons. It should be noted that in APECS all extrinsic-loss structure will be strongly decreased, thus providing a very interesting application of this technique to the study of the various contributions to the photoelectron line shape and satellites.

The counting rates in these experiments are more than 10^5 times a weak as those in a typical x-ray photoemission experiment. Part of this attenuation arises from poor alignment of the two analyzers, which must look at the same small spot on the sample, and part because the AEI analyzer is not for this kind of an experiment. A coincidence experiment requires the analyzers to look at a small spot with large transmission. We believe that redesign of the equipment and improvement of the coincidence timing will allow us to increase the effective rate by a factor of 10 to 1000. However, even at the low rates now available it is possible to illuminate the physics of the Auger process.

In conclusion we mention a few other interesting experiments which are planned with the improved instrument.

(1) Surface studies: The surface sensitivity is enhanced relative to photoelectron or Auger spectroscopy because both electrons must escape without loss.

(2) Intrinsic versus extrinsic contributions to the line shape and satellites: In APECS the extrinsic contributions will be strongly reduced, as discussed above for the scattered-electron contribution.

(3) Study of satellite structure: By APECS we should be able to resolve the Auger peaks originating from the main photoelectron excitation from those originating from the satellites.

(4) A detailed study of the various contributions to the x-ray photoemission spectroscopy and Auger line shapes: With APECS the contribution of the lifetime of the core hole can be removed and other broadening effects are modified.

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