

# An Auger photoelectron coincidence spectrometer

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The feasibility of photoelectron Auger electron coincidence spectroscopy from solid surfaces has been demonstrated by Haak *et al.* [Ph. D. thesis, University of Groningen, The Netherlands, 1983; Phys. Rev. Lett. **41**, 1825 (1978); Rev. Sci. Instrum. **55**, 696 (1984)]. They were able to show the considerable power of the technique in deconvoluting the  $L_{23}M_{45}M_{45}$  line of Cu by finding those parts of the line that were due to a  $2p_{3/2}$  hole and those which were due to a  $2p_{1/2}$  hole. However, the technique is a difficult one, requiring two analyzers rather than one and complex coincidence electronics. Even then a single spectrum can take weeks to acquire. This initial work was followed up by Jensen *et al.* [Phys. Rev. Lett. **62**, 71 (1989); Physical Electronics Conference abstract A-5, July, 1988] using a synchrotron to provide the radiation and a means of getting very good timing resolution. They were able to acquire Cu spectra in 2–3 days using this system. We have constructed a set of electron analyzers specifically for this experiment. We used the ideas of Völkel and Sandner [J. Phys. E **16**, 456 (1983)] to produce analyzers that have good angular acceptance, good energy resolution, and very good timing resolution. With this system we are able to measure coincidence line shapes, for elements with large enough cross section, within a few days using a standard laboratory dc x-ray source.

## I. INTRODUCTION

There are many reasons why coincidence spectroscopies from surfaces are thought to be desirable. These are mainly centered around the idea that as an electron leaves the surface, it is likely that it will undergo further, complicating processes, resulting in complex, difficult to interpret spectra. To first order, coincidence spectroscopy frees one from these effects. The resulting spectra are on a flatter background, and many of the individual processes can often be separated out. Indeed, it has been shown that at least in principal, the reduction in the background should improve minimum detectable levels.<sup>1</sup> It is also of great use in systems where there is more than one element and the Auger and x-ray photoemission spectroscopy (XPS) features overlap.<sup>2</sup>

However, coincidence spectroscopy on surfaces is difficult. There have been a number of successful experiments, but also a number of fruitless attempts. Perhaps the best known experiment to date was that of Haak, Sawatzky, and Thomas.<sup>2</sup> They were able to show that the  $L_{23}M_{45}M_{45}$  Auger line of Cu could be simplified by looking at the line in coincidence with the XPS Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  lines.

A similar experiment has been performed by Jensen *et al.*,<sup>3</sup> also on Cu, but this time they examined the coincidence line shape of the  $3p$  photopeak. They used a synchrotron as their x-ray source and, in a novel way, made use of the time structure of the synchrotron's output to provide good timing resolution. This freed them of the need to have good intrinsic timing resolution in their spectrometers. Hence they could use spectrometers with large acceptance angles and high collection efficiencies.

We have designed and built a pair of analyzers specif-

ically for the coincidence experiment, using the ideas of Völkel and Sandner<sup>4</sup> to optimize the compromise between acceptance angle, energy resolution, and timing resolution. The resulting instrument has a performance that reduces the data acquisition times to the point where such experiments can be conducted routinely with a dc x-ray source.

## II. DESIGN

The key to performing coincidence spectroscopy from surfaces is in the timing resolution of the instrument. The large inelastic background generated as electrons leave the surface causes a high probability of an "accidental" coincidence. These are randomly distributed in time and so can be discriminated against by having very good timing resolution. However, in order to achieve good timing resolution, one must limit the angular acceptance of the device and the energy resolution. The principal reason for degradation of timing resolution is the possibility that electrons may take different paths through the analyzer and that these paths may not be of equal length, resulting in a spread of times. The larger the analyzer, the better the energy resolution, but the greater the difference in possible path lengths. Hence there are conflicting requirements for good energy analysis and good timing resolution.

The acceptance angle of the spectrometers must also be optimized as an analyzer with a large acceptance angle has a multitude of paths through it, giving poor timing resolution, but such an analyzer will also have the desirable property of having a high probability of detecting an emitted electron. It is essential that the efficiencies of the analyzers be as large as possible.

A solution to these problems has been suggested by

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Völkel and Sandner.<sup>4</sup> They proposed using an angled microchannel plate at the exit slit of the analyzer to compensate for the differences in flight times of electrons that took the "short path" and those that used the "long path" through. This compensation means that one can go to an analyzer with large mean radius and reasonable acceptance angle, while still retaining good timing resolution.

We decided upon 127° cylindrical deflecting analyzers (CDA) as being the most suitable for this application. The reason why they were preferred to the 180° spherical analyzer was that their property of not focusing in one plane allows one to open up the analyzer in that direction to achieve a larger acceptance angle. The timing correction works very well for the 127° analyzer, so the radius of the analyzer can be made large without corresponding degradations in the timing resolution, and hence the analyzer can be made to have both good energy and timing resolution. The other advantage the 127° analyzer has is that two of them can be placed together reasonably closely. We chose a mean radius of 65 mm with a sector separation of 5 mm, giving an acceptance angle of 4° in the focus plane and an energy resolution of  $\frac{1}{60}$  of the pass energy with 1-mm slits. These were the largest radius spectrometers that could be accommodated in the vacuum chamber and they had to be installed through the Wheeler flange of the system.

The time-of-flight correction was achieved by applying the expression of Völkel and Sandner<sup>4</sup> which suggested an angle of 26.6° to the mean radius would produce a residual time spread of 0.8 nS with a pass energy of 145 eV. This result was checked by modelling the analyzer with a simple computer program that used the known field to find the possible paths through the analyzer. The model confirmed the predictions of Völkel and Sandner.

The entrance and exit slits used guard electrodes to reduce fringing fields near them. These were based on the design of Jost.<sup>5</sup> The entrance lenses were simple three-element diaphragm lenses, built to meet the specifications as set out by Harting and Read.<sup>6</sup> The analyzers were run in the constant pass energy mode, so the lenses acted as so-called zoom lenses. Two programmable power supplies were used to control them, one to select the energy and the other to focus the electrons. The lenses were designed to have a magnification of one and an acceptance angle that would fill the analyzer in the energy dispersing plane. The aperture of the diaphragm was circular with a diameter of 5 mm. A drift tube was placed on the input end of each lens to shield them from electrons coming from sources other than the sample. The CDA sectors were made from OFHC copper as were the lens diaphragms. All surfaces seen by the electron beam were gold plated. The layout of the spectrometers is shown in Fig. 1.

### III. ELECTRONICS

The coincidence circuitry employed is typical of such experiments. It used a time to amplitude converter to measure the time between an electron arriving in the start channel and one arriving in the stop channel. Constant fraction discriminators were used to reduce the uncertainty

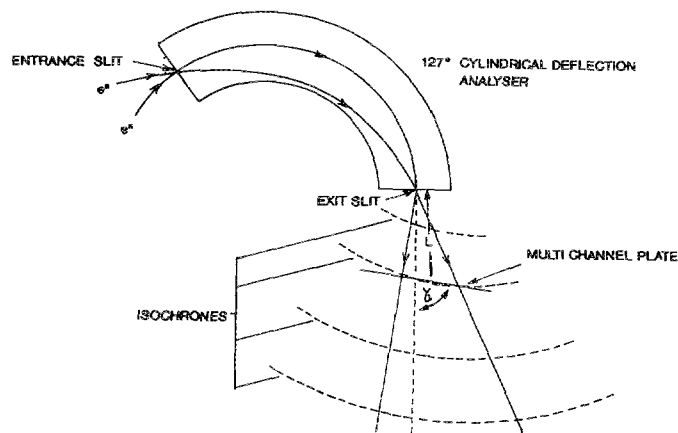


FIG. 1. Electron spectrometers.

in when the pulse was detected. The output of the TAC was analyzed with a multichannel analyzer, running in an IBM PC. The computer set the analyzer lens potentials and acquired the appropriate spectra through a MCA board. The computer stored each spectrum at each energy. We followed the ideas of Haak *et al.*<sup>2</sup> and swept through the range of energies, making three complete passes in 18 h. The sample was then cleaned again with Ar<sup>+</sup>-ion bombardment. The layout of the components used is shown in Fig. 2.

The decoupling capacitor and biasing resistors for the microchannel plates (MCP) were installed in vacuum as specified by the supplier (Comstock). The plates were arranged in pairs in a chevron configuration with a flat collecting plate behind them. The plates were biased with 1 kV across each plate. An accelerating potential of 300 V was applied to the electrons before they struck the front of the MCP. This was achieved by placing a high-transparency grid 3 mm from the front of the first plate. This preacceleration increased the detection efficiency of the plates. In this configuration, the plates produced pulses with a rise time of around 1.0 ns and a height of some 20 mV.

A preamplifier based on a high-frequency, three-transistor array was constructed and used. This had very good characteristics and the desirable quality that the transistor array could be replaced in about 2 min in the event that an arc over in the MCPs caused it to be destroyed. A noise gate was used to detect any electrical noise from the surrounding environment and to gate out the TAC.

Initially, there was a certain amount of cross talk between the signal coming from each analyzer. The slight ringing in the cable transmitting the pulse to the preamplifier caused the cross talk to produce a wavy background. We established that this was a reproducible effect in the background. We measured the shape of the background by counting at rates similar to those of a genuine coincidence measurement, but with the analyzers adjusted so that there was no chance of detecting any coincidences. We subtracted this background, after suitable scaling, from the genuine coincidence measurements. Once the background was subtracted, we counted the number of events occurring

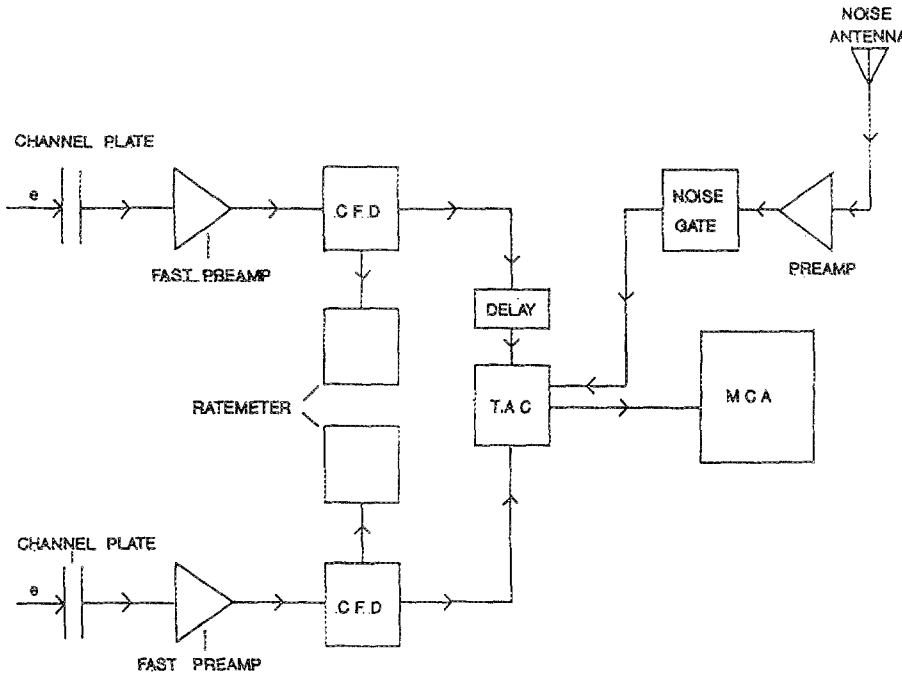


FIG. 2. Coincidence electronics.

in the coincidence window compared with the average background level. Subsequently, we found the source of the cross talk and eliminated it from the system. The data collected after this time used a cubic least-squares fit of the data either side of the coincidence window to estimate the background. Once a set of data had been produced, we fitted the entire spectrum using a simplex fitting program that minimized the average deviation of the points to the fitting functions.

#### IV. COINCIDENCE RATES

The important quantities in any coincidence experiment are the ratio of true to accidental counts and the time taken to achieve a reasonable ratio with good statistics. The important dependencies in this coincidence experiment can be illustrated in the following way. Consider the number of true and accidental counts made in a coincidence experiment in the time  $\delta t$ , the resolution time of the experiment. The number of true events will be

$$\begin{aligned}
 N_{\text{true}} = & (\text{Prob. that an Auger event will occur}) \\
 & \times (\text{Prob. that the Auger analyzer will see it}) \\
 & \times (\text{Prob. that the photoelectron analyzer will see it}) \\
 = & k_1 i_0 \delta t \epsilon_a \epsilon_p,
 \end{aligned} \tag{1}$$

where  $i_0$  is the incident flux,  $\epsilon_a$  and  $\epsilon_p$  are the efficiencies of the Auger and photoelectron analyzers, including the solid-angle collection efficiency, and  $k_1$  is a constant that includes the ionization cross section, the chance of decay from the ionized state by emission of an Auger electron, the size of the sample, its atomic density, and the escape depths of the outgoing electrons. Similarly, for the number of accidental counts, one can write

$$\begin{aligned}
 N_{\text{acc}} = & (\text{Prob. of detecting Auger}) \\
 & \times (\text{Prob. of detecting uncorrelated photoelectron}) \\
 & + (\text{Prob. of detecting Auger}) \\
 & \times (\text{Prob. of detecting background at PE energy}) \\
 & + (\text{Prob. of detecting PE}) \\
 & \times (\text{Prob. of detecting background at Auger energy}) \\
 & + (\text{Prob. of detecting background at Auger energy}) \\
 & \times (\text{Prob. of detecting background at PE energy}) \\
 = & i_0^2 \delta t^2 \epsilon_a \epsilon_p k_2,
 \end{aligned} \tag{2}$$

where  $k_2$  takes the sums of the products of the appropriate cross-section terms and the other factors similar to those included in  $k_1$ . Hence it is possible to find the ratio of true to accidental counts in a given time channel:

$$N_{\text{true}}/N_{\text{acc}} = k_1 / (k_2 \delta t i_0), \tag{3}$$

which is independent of the efficiencies of both the analyzers, but varies inversely as the incident flux and the timing resolution. The dependence on the efficiency of the analyzers can be readily seen from these relationships as well. In any practical experiment, the total number of counts in the true channel is as important as the ratio of trues to accidentals. The total number of true counts is proportional to the product of the efficiencies of both analyzers. Hence if the efficiency of both analyzers were to fall by say a factor  $f$ , then the number of trues would fall by a factor of  $f^2$ . This could be accommodated by increasing the incident flux, but that would reduce the ratio of trues to accidentals. Hence it is necessary to attempt to maximize the efficiencies of both analyzers.

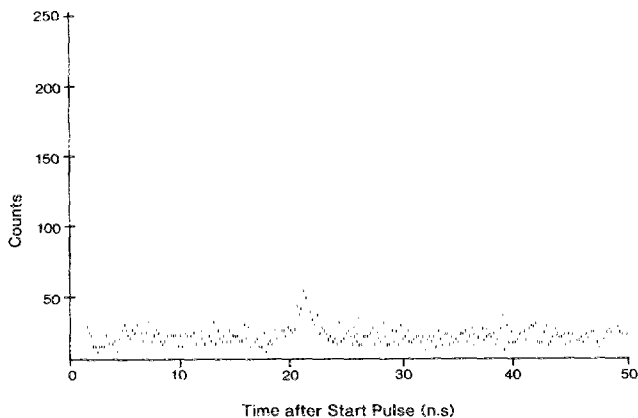


FIG. 3. Coincidence counts vs time spectrum showing a coincidence peak from the  $L_3M_{45}M_{45}$  and  $2p_{3/2}$  peaks in Cu.

## V. SPECTROMETER PERFORMANCE

A typical TAC spectrum is shown in Fig. 3. This shows the half width of the complete system is 1.5 ns. Considering that the rise time of the channel plates is 1.0 ns, this appears to be approaching what can reasonably be expected as an upper limit to the performance of such systems. However, this is a clear improvement of ten in timing resolution compared to the experiment of Haak *et al.*<sup>2</sup> Given that the acceptance angle of their spectrometer was approximately  $7^\circ$ , while our angular acceptance was  $4^\circ$ , then we can expect that our system should have an improvement in performance of about a factor of 6.

With the pass energy adjusted to give a resolution of 3.7 eV and using 300 W of incident power onto the x-ray anode (the tube produced  $MgK\alpha$  radiation) to give count rates of  $5 \times 10^4$  counts/s in the Auger channel on peak, we were able to achieve a background subtracted true coincident rate of 0.08 counts/s on the peak with a  $T/A$  ratio of  $\frac{1}{3}$ . This is comparable with the rates achieved by Haak *et al.*<sup>2</sup> and points to our collection efficiency being close to theirs. However, the good timing resolution of our system gives higher  $T/A$  ratios at high count rates and so improves the statistical reliability of the data.<sup>2</sup>

## VI. RESULTS

Figure 4 shows the Cu  $L_3M_{45}M_{45}$  Auger line measured in coincidence with the Cu  $2p_{3/2}$  XPS line. We collected this data in 5 days with  $1.7 \times 10^4$  counts/s in the photoelectron channel.

All the features in the spectrum are also seen in the results of Haak *et al.* However, they used monochromatized  $AlK\alpha$  radiation and had an energy resolution of around 0.5 eV, while our resolution was around 3.5 eV, so we were unable to see some of the fine splitting of the main peak. The 1S term can be seen at 4.5 eV below the 1G term. This is very similar to the 5-eV splitting found by Haak *et al.*

Figure 5 shows the Cu  $L_2M_{45}M_{45}$  Auger electron peak, collected in coincidence with the  $2p_{1/2}$  photoelectron line. Figure 6 shows a conventional  $L_{23}VV$  spectrum for com-

## Copper $L_3$ W Coincidence Spectrum

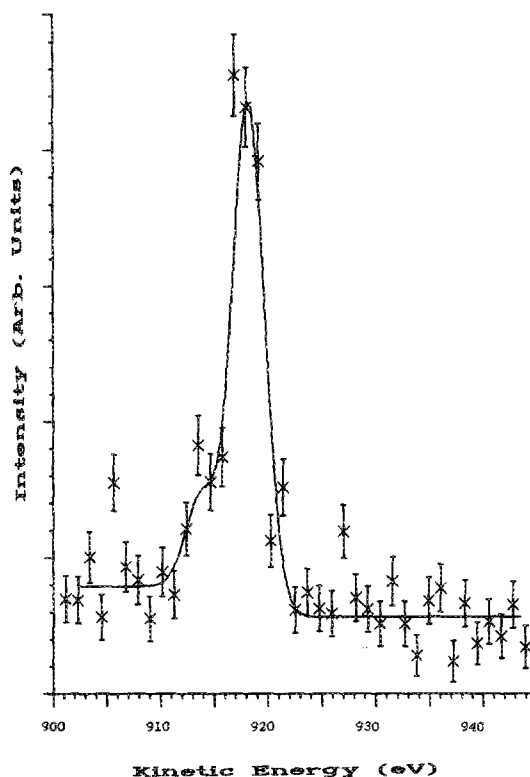


FIG. 4. Cu  $L_3M_{45}M_{45}$  Auger line in coincidence with the  $2p_{3/2}$  photoelectron line. The line through the data shows the best fit to a two-peak model, with a step on the low-energy side.

parison. The energy positions of the peaks are very comparable to those reported by Haak *et al.* The peak at lower energies is due to the presence of holes in the  $L_3$  and  $M_{45}$  levels, remaining from a Coster-Kronig transition ( $L_2L_3M_{45}$ ), causing a shifting of the  $L_2M_{45}M_{45}$  line to lower energies. The shifted peak, called the  $L_2(M)-(M)M_{45}M_{45}$  in the notation of Haak *et al.*,<sup>2</sup> is some 2.5 eV below the main  $L_3M_{45}M_{45}$ , again in agreement with their measurements. The  $L_2M_{45}M_{45}$  coincidence spectrum does not have the feature at 932 eV which is apparent in the singles spectrum. This feature has been attributed to a Coster-Kronig ( $L_1L_2M_{45}$ ) preceded  $L_2M_{45}M_{45}$ , causing a shift of the peak.<sup>2</sup> The fact that it is not seen in the  $L_2$  coincidence spectrum supports this view.

## VII. DISCUSSION

We have been able to construct a spectrometer that has very good timing resolution and is suitable for making APECS measurements. The good timing resolution gives excellent  $T/A$  ratios at high count rates. We were, however, limited in our ability to take full advantage of our increased timing resolution because of the limited intensity of our x-ray source. We can improve the performance of the system by replacing the input lenses with slit lenses that

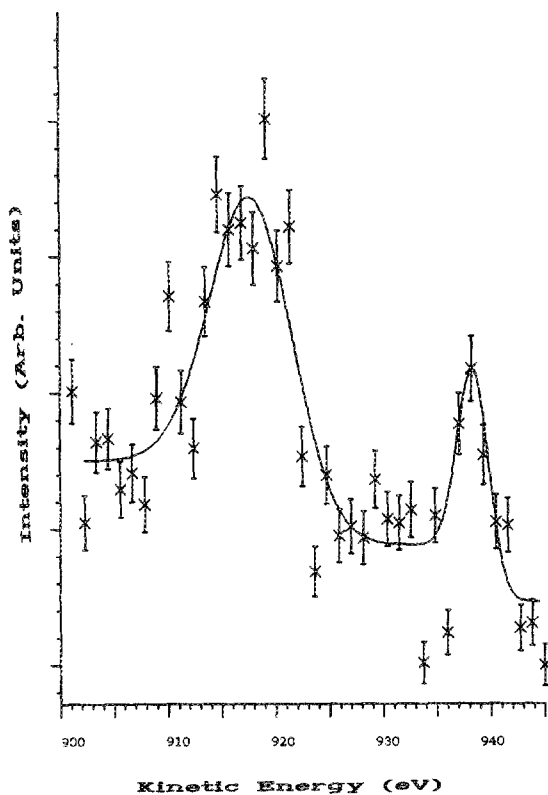
Copper  $L_2$  W Coincidence Spectrum

FIG. 5. Cu  $L_2M_{45}M_{45}$  Auger line in coincidence with the  $2p_{1/2}$  photoelectron line.

would fill the analyzers in the nondispersive plane. This would increase the angular acceptance by a factor of at least 2. The current lenses are not optimal as the retardation ratio when the spectrometer is set up for maximum resolution exceeds 10. A more appropriate lens (say a five-element lens) would improve the performance at higher-energy resolution.

The design of this instrument was heavily dependent on the analysis of Völkel and Sandner and the resulting spectrometer matches closely the predictions of their analysis. The data collected so far agrees well with that collected by Haak *et al.*<sup>2</sup>

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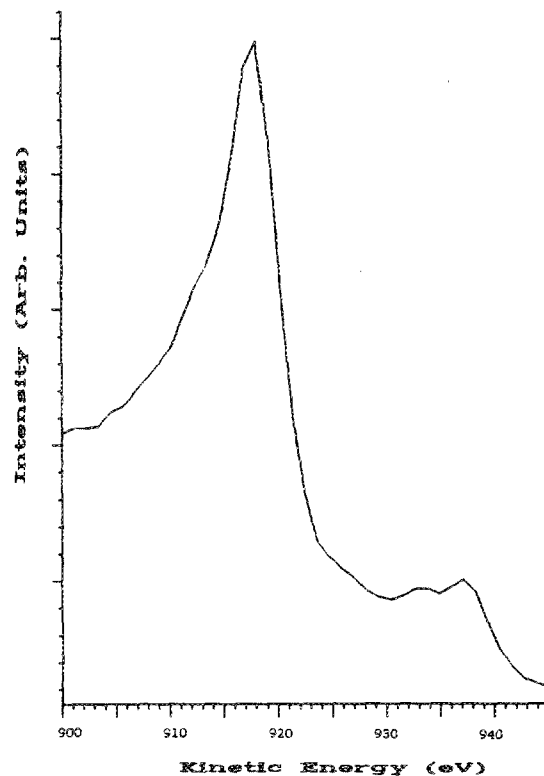
Copper  $L_{2,3}$  VV Singles Spectrum

FIG. 6. Cu  $L_{2,3}M_{45}M_{45}$  Auger line recorded in the conventional way with a single analyzer. The data were acquired at the same time as the spectra of Figs. 4 and 5.

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