Auger Photoelectron Coincidence Spectroscopy*

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Abstract

Auger photoelectron coincidence spectroscopy (APECS) involves measuring an Auger line in coincidence with the corresponding photoelectron line of an X ray excited spectrum. Such spectra are free of many of the complicating features of conventional data and display the correlations that exist between the lines. APECS has been used to study a number of fundamental aspects of Auger spectroscopy, such as the removal of complicating effects due to Coster–Kronig transitions in the $L_{2,3}VV$ spectra of Cu. We have been able to show similar behaviour in the Auger spectra of Co. In principle, APECS can also be used to make measurements of surface core level shifts, to examine the process of electron scattering in solids, and it holds some promise as a technique for the routine examination of materials. The coincidence technique discriminates against secondary electrons in the background, the Auger and photoelectron peaks appear on a flatter background, and this helps to make the interpretation of Auger data collected in coincidence more straightforward. A number of successful APECS experiments have been constructed, using either X ray tubes or synchrotrons as sources. When an X ray tube is used as a source, the principal problem has been with the length of time needed to acquire a sufficient number of counts. We have recently completed construction of a novel spectrometer that goes someway towards overcoming this problem, however the challenge still remains to produce an instrument that will permit routine measurement of these features.

1. Introduction

Auger photoelectron coincidence spectroscopy (APECS) measures Auger lineshapes in coincidence with the photoelectron emitted from the solid during the ionisation process. The net effect of making the measurement in this way is that it simplifies the data, making comparison with theory more straightforward. The simplifications that can be made involve the removal of some satellite contributions to the lines, the reduction of the secondary electron background from the data, the reduction of peak broadening due to secondary electron scattering, the improvement in energy resolution in some cases and the possibility of separating overlapping Auger lines in compound systems.

Clearly APECS can be used to help improve our knowledge of how to calculate Auger lineshapes from first principle. We hope that such efforts will result in

Auger spectroscopy from surfaces becoming more quantitative. The simplicity of the final data and the fact that some information can only be accessed via a coincidence experiment makes the experiment attractive as a routine surface science technique. What has prevented APECS from becoming more popular as such is the fact that the equipment is considerably more complex than conventional Auger apparatus and the data take a long time to acquire. We have gone some way towards simplifying the design and improving the performance of the apparatus.

2. Previous Work

Perhaps the most impressive illustration of the power of the APECS experiment was given by Haak *et al.* (1984) who looked at a number of transition metals and alloys. They were able to show that one could isolate the satellite contribution to the L_3VV component in Cu. With satellite contributions removed the L_3VV component was well fitted by a calculation of the atomic Auger lineshape. They went on to show that the loss of intensity of the L_2VV was fully accounted for by a Coster–Kronig redistribution of some of the L_2VV to the L_3VV energy.

As well as Cu, Haak (1983) examined Ni and CuNi alloy. Nickel shows some band-like as well as some atomic-like features and is on the boundary between those two types of transition metals (Ramaker 1988). As with Cu, there is a redistribution of part of the L_2VV to the L_3VV via the L_2L_3V Coster–Kronig process. Hence the coincidence Ni L_3VV spectra is somewhat changed in shape. It clearly shows part of its intensity as coming from atom-like states and part coming from its valence band. Nickel is also interesting as the $2P_{3/2}$ photoelectron spectra shows a shake satellite, the effect of which is generally to broaden the L_3VV Auger spectra. However, in coincidence it is possible to only measure those Auger electrons that were caused by a mainline $2P_{3/2}$ ionisation and not the shake component. The resultant Auger line is considerably sharper near the Fermi energy.

The work on the CuNi alloy (Haak 1983) illustrated the use of APECS in separating out contributions to particular Auger lines when the lines are from two different materials. In this alloy the Auger lines overlap, but the photoelectron lines do not. Hence Haak (1983) was able to show the Cu component of the CuNi Auger line from the alloy.

Jensen *et al.* (1989) have used a variation of the APECS experiment to determine the shape of the 3P photoelectron peak in Cu in coincidence with the MVV Auger line. They illustrated the fact that the photoelectron line energy changed as the energy of the Auger analyser was varied. As expected, they found that the sum of the Auger and photoelectron energy remained constant. They were able to show that the photoelectron peak was much narrower when measured in coincidence, due to the loss of scattered electrons in the peak and presented evidence showing that the photoelectron peak had been lifetime broadened to $1 \cdot 0$ eV.

3. Instrumentation

There are a number of factors that are important in the performance of an APECS spectrometer. These factors combine to produce two main measures

of the system performance. The first is the ratio of true events to random events (T:A ratio). True events are produced when both the photoelectron and the corresponding Auger electron are detected within the timing resolution of the system. Random events are those in which an electron which is not an Auger electron or a photoelectron, but has the energy of either, is detected in coincidence with another electron which also has the appropriate energy. Such random electrons are evenly spread in time, so one can discriminate against them by having very good timing resolution.

The second measure of the performance of an APECS spectrometer is the statistical reliability of the data collected. In order to get good statistics one must count for long enough to ensure that the number of true counts is meaningful. The ability of the instrument to get good statistics in a short time depends on the collection and detection efficiency of the spectrometers, as well as the intensity of the source and the cross section of the atom being investigated. The statistical reliability also depends on the ability of the experiment to determine the height of the random background, which may also depend on the T:A ratio, at least for the initial calibration of the system. Normally one has a 'window' into which the true counts go, plus any random counts that happen to fall in the same time window. One then uses the count rates outside the window to estimate the background that must be subtracted from the true signal. The statistical accuracy of the final estimate of the number of true counts is therefore dependent on the accuracy of the background determination.

Haak *et al.* (1984) used a pair of conventional electron spectrometers and a monochromatised Al Kα X ray tube to perform their experiments. As such, their equipment was limited by the inherent performance of both analysers. Their total timing resolution was about 16 ns, and the energy resolution about 0·2 eV. They used the conventional system of looking for coincidences by
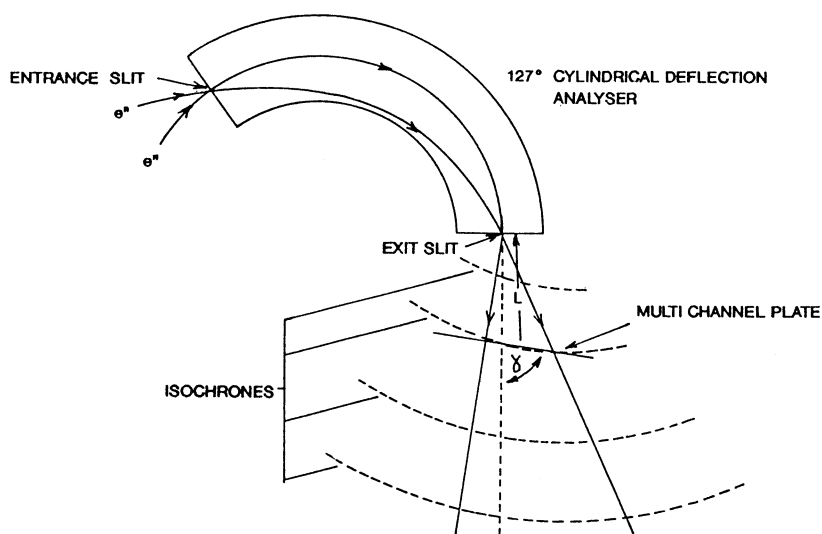
Fig. 1. Electron path through the analysers, showing the effect of tilting the multichannel plates.
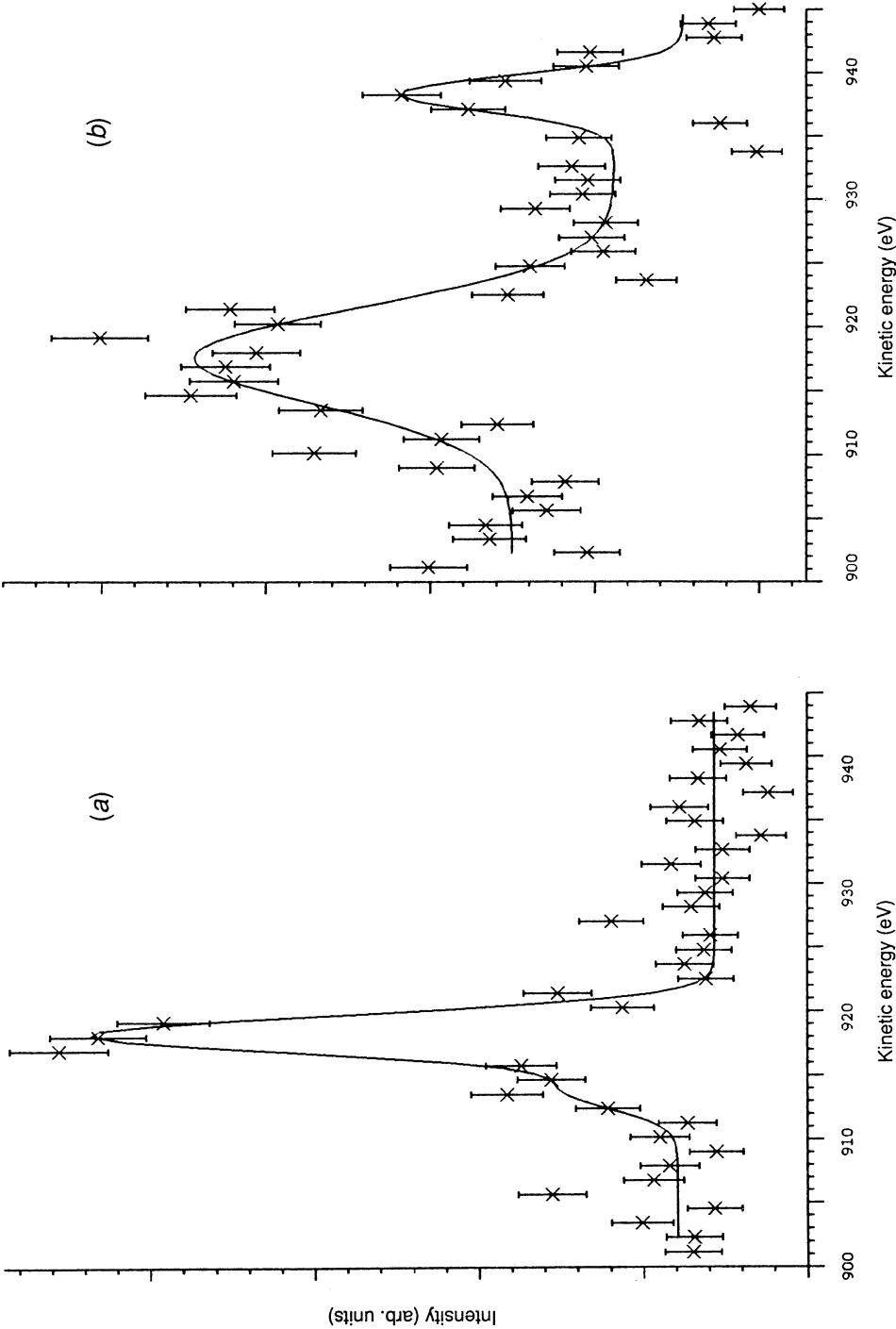
Fig. 2. Copper coincidence spectrum for (*a*) $L_3VV-2P_{3/2}$ and (*b*) $L_2VV-2P_{1/2}$.
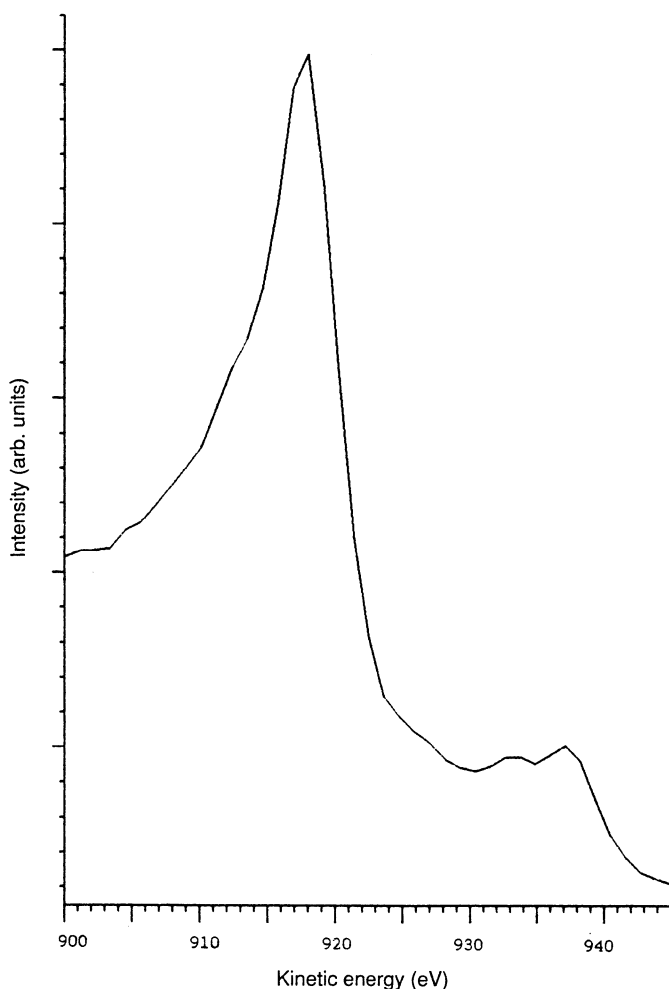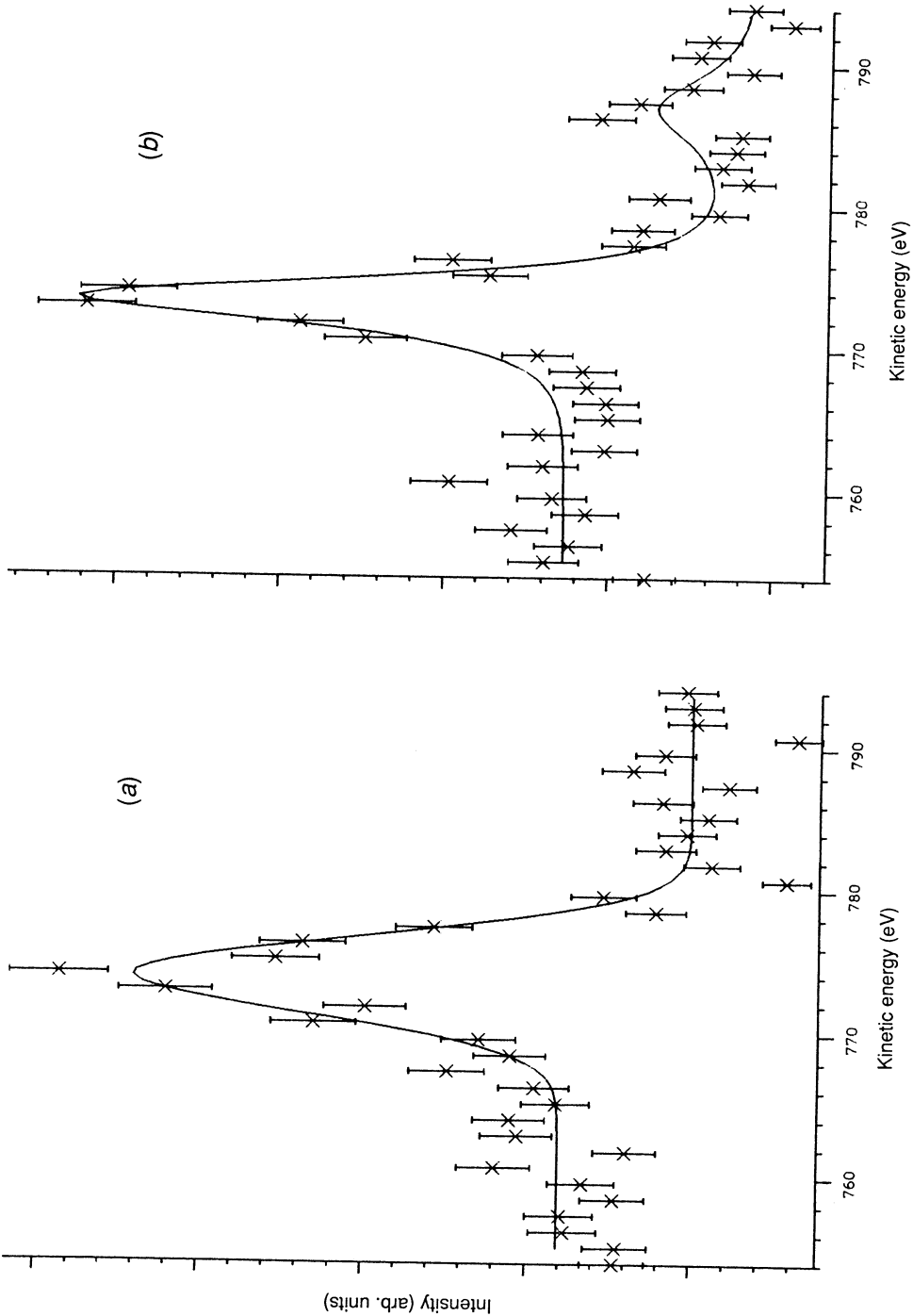
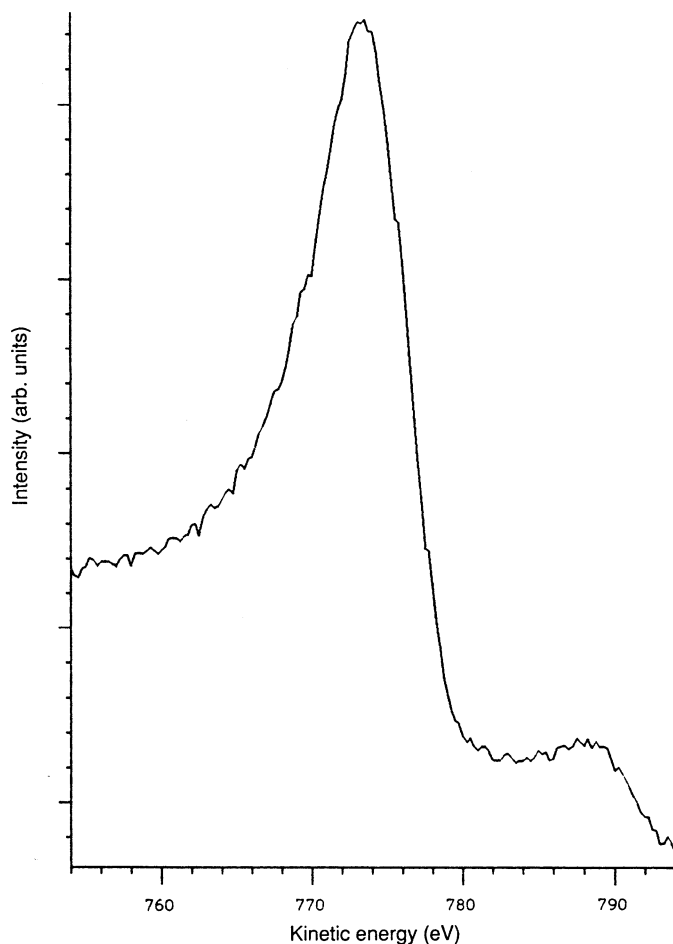**Fig. 3.** Copper $L_{2,3}VV$ conventional singles spectrum.

having a time-to-amplitude converter (TAC) which was started by a pulse in one channel and stopped by a pulse in the other. The output of the TAC was analysed with a multichannel analyser. Any correlated behaviour of the channels shows up as a peak in the time spectrum. The size of the background subtracted peak can be stored as a point corresponding to the settings of the two analysers.

Jensen *et al.* (1989) used a synchrotron as a source and used the time structure of the photon pulses to provide a convenient means of getting good timing resolution ($\approx$20 ns). They also used conventional double-pass cylindrical mirror analysers (CMA) to energy analyse the electrons in each channel. The pulse structure also provided a means of estimating the random background.

We have constructed an APECS spectrometer similar to that of Haak *et al.* (1984), except that it uses purpose built spectrometers. These differ from conventional analysers in that they use tilted multichannel plates (MCP) to correct for the time-of-flight spreading that is caused by the passage of

Fig. 4. Cobalt coincidence spectrum for (*a*) $L_3VV-2P_{3/2}$ and (*b*) $L_2VV-2P_{1/2}$.

Fig. 5. Cobalt $L_{2,3}$VV conventional singles spectrum.

the electrons through the analysers. This idea was based on the analysis of Volkel and Sandner (1983) who considered the time taken for electrons to travel through different paths in an analyser, and showed that the time difference could be compensated almost exactly by using a flat detector on an isochrone (surface of constant time). These surfaces lie at various angles to the mean circumference, depending on the particular analyser geometry. We used cylindrical deflecting analysers with a mean radius of 60 mm and sector separation of 3 mm, which gave a tilt angle of 26° for the MCPs, as shown in Fig. 1. The analysers had a total time spread of 1·6 ns when operated with a pass energy of 180 eV. This gave us an energy resolution of about 3·5 eV. The analysers had an acceptance angle of 4°, and were positioned at 90° to each other. The X ray tube used a Mg target and was run at 300 W. This gave coincidence rates of about 0·005 counts per second and a T:A ratio of 1:1 for the L_3VV peak of Cu. Other experimental details are given elsewhere (Thurgate *et al.* 1990).

4. Results for Cu and Co

The L_3VV and L_2VV coincidence spectra for Cu are shown together with the conventional singles spectra in Figs 2 and 3. The data are very similar to those collected by Haak *et al.* (1984). Fig. 2*a* shows the atom-like L_3VV Auger spectra of Cu. The main peak is attributed to a 1G term while the shoulder at 913 eV is due to a 1S term. The various peaks in the spectra correspond to different atomic terms, reflecting the possible transitions between the $M_{4,5}$ and $L_{2,3}$ levels. The most significant difference is that our data were collected with a resolution of $3 \cdot 5$ eV, while Haak *et al.* (1984) used a resolution of $0 \cdot 2$ eV.

Perhaps the most noticeable feature of the Cu data is the L_2L_3V Coster–Kronig process, where the initial L_2 hole is filled by an electron from the L_3 level, with consequent emission of an electron from the valence band. This can be followed by the Auger process L_3VV, but now in the presence of the additional valence band hole. This causes a shift of some $2 \cdot 5$ eV from the main L_3VV peak. This can be seen in Fig. 2*b* which shows the L_2VV spectrum taken in coincidence with the $2P_{1/2}$ electron. The L_2VV peak can be seen clearly at 939 eV. The peak at 918 eV is the Coster–Kronig shifted L_3VV that is still in coincidence with the $2P_{1/2}$ electron. This peak can be seen as a shoulder in the conventional singles spectra.

Figs 4 and 5 show the $L_{2,3}VV$ spectra of cobalt. Cobalt differs from copper in that it is clearly band-like. The Auger spectra show none of the sharp atom-like features found in Cu. In Fig. 4*a* the L_3VV spectra is shown in coincidence with the $2P_{3/2}$ photoelectron. When compared with the singles spectrum, the most noticeable difference is that the main peak has been narrowed on the low energy side. This is due to the removal from the peak of some of the electrons that were scattered as they left the solid. There is also a reduction in the height of the step beneath the peak when compared with the singles spectrum. This step is due to inelastically scattered electrons coming from the Auger electrons. Hence its reduction is due to the discrimination that the coincidence experiment has against electrons that have undergone some inelastic scattering in the solid. It should be noted however that some of the step is not removed so that some electrons are inelastically scattered and are still detected in coincidence.

Fig. 4*b* shows the Co L_2VV spectrum in coincidence with the $2P_{1/2}$ electron. As with the corresponding Cu spectrum, the L_2VV peak is clearly separated and there is a Coster–Kronig shifted component near the L_3VV energy. This component is $0 \cdot 5$ eV from the L_3VV peak, indicating that the valence band hole due to the L_2L_3V Coster–Kronig is better screened from the Auger transition than it is in Cu. However, the most noticeable difference is that the $L_2(M)–(M)L_3VV$ component is much narrower than the L_3VV measured in coincidence with the $2P_{3/2}$. Clearly, the initial state valence band hole affects the apparent densities of states during the Auger transition.

5. Conclusions

APECS is able to offer new data capable of simplifying Auger spectra. This makes comparison with theory somewhat more straightforward as the calculations can be simplified and the origin of the various peaks can, in many cases, be determined.

There is some potential for APECS to become a more routine technique. It can provide simpler data, free from background effects, and can sometimes give depth information. In the analysis of complex systems, APECS can determine the extent of individual contributions. APECS peaks are in general narrower than the corresponding conventional peaks. However, before APECS becomes more widespread, the instrumentation must give higher count rates so that data can be recorded in a more routine manner.

Acknowledgments

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