Topic area: **CMMSP**

Electron Excited Auger Electron Spectroscopy of Copper

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Introduction

Recently hard X-ray induced photoemission spectroscopy (XPS) has become possible at synchrotron sources. This means that quantitative understanding of the KLL-Auger spectra with energies between 2 and 10 keV, which are a part of the complex photoemission spectra obtained, has become important. The investigation of the KLL-Auger spectra also provides vital information for testing the various theoretical models for Auger line position [1–3] and intensity [4–6] and could provide an energy standard for high energy spectrometers.

Of particular interest is the Auger spectra of Cu which has been comprehensively studied [6–9] but is still poorly understood. Recently [6, 8, 9] the presence of a satellite peak at small energy separation from the main $^1D_2$ line in copper have been observed and have been attributed to d-band spectator vacancy shake-up. In this paper we report the first high-resolution electron-induced KLL Auger spectra of Cu. The results presented are compared to available measurements and theoretical calculations. We also propose an alternate model for the observed structure.

Experimental considerations

The Auger measurements were done using the ANU (e,2e) spectrometer [10] and only details pertaining to these measurements will be discussed here. An electron gun produces a 25keV beam which impinges on a sample held at +6.5 kV. Thus 31.5 keV electrons strike the target. The Auger electrons, emitted from the sample, are decelerated and focused at the entrance of a hemispherical electron analyser with a pass energy of 400 eV (Figure 1). A two dimensional position sensitive detector mounted at the exit plane of the analyser measures a wide range of energies simultaneously. The energy resolution of the experiment is estimated to be 1 eV resulting from the natural resolution of the analyser 0.8 eV, a 0.1 eV high frequency ripple on the high voltage power supply and a typical 0.3 eV drift over a measurement period.

A thin (≈3 nm) amorphous carbon substrate covering an array of 0.3 mm holes in the target mount was further sputter thinned by argon ion etching until a number of the films broke. Thin (≈10 nm) polycrystalline Cu films were evaporated onto the remaining films in a preparation chamber. The thickness of the evaporated films was monitored by a crystal thickness monitor. The sample was then transferred under UHV conditions to the spectrometer. Most of the incoming beam is transmitted through the 13 nm thick C/Cu sandwich and dumped in a Faraday cup. In a thin free-standing film the incoming electrons are unlikely to lose most of their energy *and*

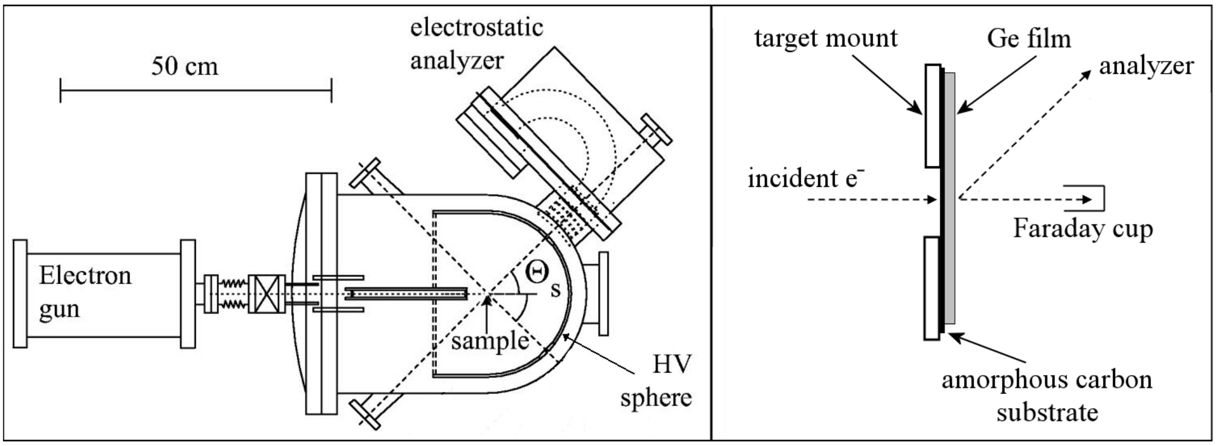

Figure 1: Overview of experimental setup (left) and schematic of sample mount (right).

be deflected over 45°. Thus using a thin free-standing target we can obtain electron-induced copper Auger spectra on a relatively low background. Measurements of the KLL Auger spectra were performed over 2-3 days with count rates of the order of 1.5 kHz and a signal to background ratio better than 1:3 for the main $^1D_2$ peak in Cu. As electrons are used to provide the initial core hole we are also able to measure the spectra without the additional photoemission lines which appear near the lines of interest in the published data [6].

Results and Discussion

The Cu KLL Auger spectra excited by electron impact are shown in Figure 2 (Left), both of the previously reported [6] satellites are resolved. Inelastic background is simulated using the Shirley model [11], while measurement of the peak structure is performed using a pseudo-Voigt type peak deconvolution with free fitting parameters for peak position, height and width. Excellent agreement is found for the relative energy of the spectral lines between these measurements

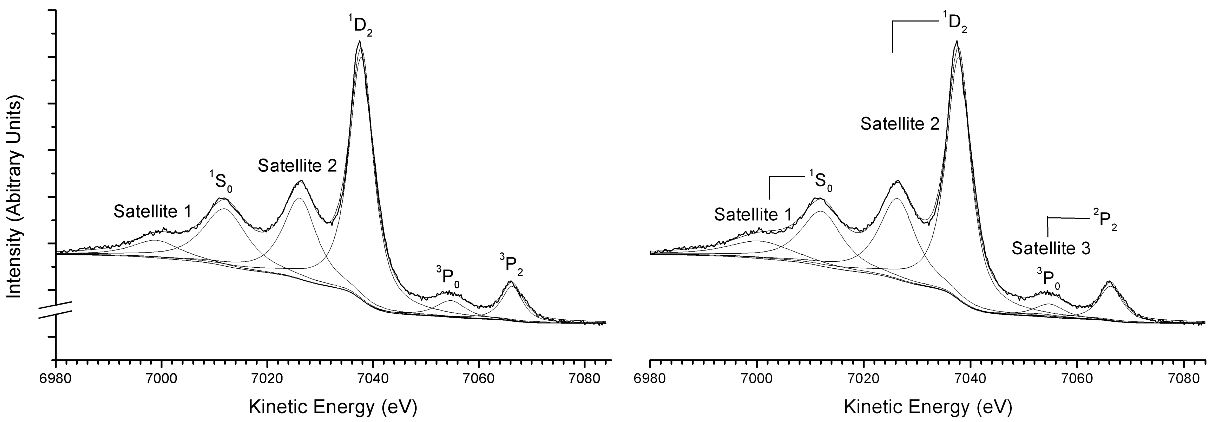

Figure 2: Electron excited Cu KLL spectra from thin self-supporting metallic samples of ≈10 nm thickness. Figure shows line shape deconvolution on top of a Shirley type background. The left panel shows a fit assuming four multiplets($^1S_0$, $^1D_2$, $^3P_0$ and $^3P_2$) and two satellites (Fit 1). The right panel shows the same spectra, but analysed assuming an identical satellite structure for each of the $^1S_0$, $^1D_2$ and $^3P_2$ peaks (Fit 2).

and those performed previously [6] (Table 1). Agreement with theory is reasonable for the relative energy of the multiplets. The calculated absolute energy of the $^1D_2$, as calculated by Larkins [2] is 7 eV lower than the observed energy. The most notable disagreement however is that some of the observed lines (marked satellite 1 and satellite 2 in Table 2) are not predicted by many of the current theoretical approaches implying that the models used are incomplete. The molecular orbital theory of Cserny *et al.* [1] is the only theory to predict the position of satellite 2. They found that the position of this satellite is dependent on the amount of screening of the core holes which varies from -15.8 eV for an unscreened hole, to -10.5 eV for a screened hole, suggesting the importance of screening in Cu [1].

Table 1: Cu KLL energies relative to the $^1D_2$ line and KL_2L_3 ($^1D_2$) transition energy (eV): (T)heory and (E)xperiment. Bracketed numbers represents the error in the last two significant figures.

Line	This work	Ref. [6](E)	Ref. [2](T)	Ref. [3](T)	Ref. [1](T)
Satellite 1	-38.8(1.0)	-39(1.5)	-	-	-
KL_2L_2 ($^1S_0$)	-25.8(0.5)	-26.0(1.0)	-24.2	-29	-
Satellite 2	-11.6(0.5)	-11.3(0.5)	-	-	-10.9
KL_3L_3 ($^3P_0$)	17.0(1.0)	15.9(1.0)	16.3	-	-
KL_3L_3 ($^3P_2$)	28.5(0.5)	28.7(0.5)	26.6	26	-
E($^1D_2$)	7037.8(1.0)	7038.2(0.5)	7031.1	-	-

Table 2: Cu KLL intensities relative to the KL_2L_3 ($^1D_2$) line (%)

Line	This work FWHM (eV) Fit 1	This Work Intensity Fit 1	This Work Intensity Fit 2	Ref. [6](E)	Ref. [4](T)	Ref. [5](T)	Ref. [6](T)
Satellite 1	11.1	15	19	6(1)	-	-	-
KL_2L_2 ($^1S_0$)	10.0	42	38	17(1)	9	9	-
Satellite 2	7.7	47	50	22(+7)	-	-	3.4
KL_2L_3 ($^1D_2$)	5.6	100	100	100	100	100	100
KL_3L_3 ($^3P_0$)	6.9	9	3	5(1)	4	3	-
Satellite 3	-	-	6.5	-	-	-	
KL_3L_3 ($^3P_2$)	4.8	12	13	14	15	16	-
I($^3P_2$)/I($^3P_0$)	-	1.4	5.0	3.3(0.4)	3.8	5.3	-

In Table 2 we also present the measurements of the FWHM for the peaks examined. While the other experimenters [6] do not list their measured values for peak widths a casual inspection of their results indicate that the FWHM is the same for each peak which is contrary to our analysis. The increase in width with decreasing kinetic energy indicates that the life-time of the final state of the Auger decay is a strong function of its energy. The large discrepancies between these measurements and those of Kövèr *et al.* [6] for the relative intensities (Table 2) are in part due to varying width in our analysis, and due to the differences between the modified Tougaard background correction model used by Kövèr *et al.* [6] and the simple Shirley model we implemented. This difference is particularly evident in the region between the $^1S_0$

line and satellite 2 where the modified Tougaard background correction, as used by Kövèr *et al.* [6], reduces the spectra to zero intensity. This is in contrast to what we see with our simple correction method and to a later paper by Kövèr *et al.* [7] who obtain a similar source function to ours over this region, with a non-zero intensity between the two peaks.

More interesting is the extremely large difference in the value of the intensity of satellite 2 predicted by theory (3.4%) [6] and measured here (47 %) or by Kövèr *et al.* (22%) [6]. This raises doubt about the theoretical interpretation.

Kövèr *et al.* [6] recently described the two satellites observed in the Cu KLL Auger spectra as being from the $^1D_2$ line via d-band spectator vacancy shake-up but gave no reason as to why satellites from other lines in the spectra are not visible. Based on the assumption that all of the peaks should produce satellites we fitted the data taking this into account. Figure 2 (Right) shows the Cu Auger spectra evaluated under the assumption that the $^1S_0$, $^1D_2$ and $^3P_2$ lines all have a shake-up satellite with half the intensity of the parent peaks (satellite 1, 2 and 3 respectively). The same energy separation of the satellite to the main line (11.44 eV) is used for all three components, but the width is left free. This model provides good agreement with measurements except in the region around satellite 1 and in the region between the $^1D_2$ and $^3P_2$ line. The latter of these problems is due to additional intensity from the $^3P_0$ line; Including this component in the model increases the ratio $I(^3P_2)/I(^3P_0)$ given in Table 2 to 5 which is more in line with the other observation and theoretical treatments.

Summary

We have demonstrated that Auger electron spectroscopy can be performed using electrons to produce deep core holes. The determined relative KLL transition energies for Cu show excellent agreement with previous experiments and reasonable agreement with various theoretical models. We have provided an alternate description of the Cu spectra. Basing this description on the presence of satellite structure from each of the three main peaks, this model adequately describes the observations but shows that this system is still poorly understood. Problems with the relative intensities are evident and depend on the background correction model, a problem that needs to be addressed before a more quantitative comparison of theoretical and experimental intensities can be made.

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