Simplification of the $N_{6,7}O_{4,5}O_{4,5}$ Auger spectrum of Au

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Abstract. The $N_7O_{4,5}O_{4,5}$ and $N_{6,7}O_{4,5}O_{4,5}$ Auger spectra of metallic Au have been measured separately by using synchrotron radiation to scan through the N_7 and N_6 electron levels. Subtracting the $N_7O_{4,5}O_{4,5}$ spectrum from the combined $N_{6,7}O_{4,5}O_{4,5}$ Auger profile yields the $N_6O_{4,5}O_{4,5}$ contribution.

1. Introduction

In metals with narrow d bands, the analysis of the spectra of CVV transitions which create two-hole final states (d^2) in the d band yields information on electron correlation energies and their dependence on the *LSJ* multiplet splitting $U(d^2: LSJ)$, the degree of localisation of the d^2 states and the local density of states of d character [1–5]. Since the Auger profiles are an envelope of overlapping contributions from the d^2 final state multiplet structure components, it is important to minimise the broadening arising from the lifetime of the initial core-hole states. For this reason, the most useful Auger spectra are those arising from the decay of the longest lived initial core-hole states which, since they do not experience decay by Coster–Kronig processes, belong to the least bound orbitals of filled shells. To minimise the lifetime broadening arising from other Auger processes it is also advisable to use initial states in the least bound orbital with principal quantum number one less than that of the valence d band.

For the noble metals Cu, Ag, and Au, the optimum transitions for probing the valence d bands are respectively the $L_{2,3}M_{4,5}M_{4,5}$, $M_{4,5}N_{4,5}N_{4,5}$, and $N_{6,7}O_{4,5}O_{4,5}$. The $L_{2,3}M_{4,5}M_{4,5}$ Auger spectrum of Cu and the $M_{4,5}N_{4,5}N_{4,5}$ Auger spectrum of Ag each consist of two well separated groups of transitions since the spin–orbit splitting in the initial states (19.6 eV for Cu and 6.7 eV for Ag) is large compared with the width of the final state *LSJ* multiplet splittings [6–8]. For this reason it has been possible to analyse these transitions within the Cini–Sawatzky theory [1–3] and obtain useful information about the local electronic structure of these elements and their alloys [6–13]. For the $N_{6,7}O_{4,5}O_{4,5}$ Auger spectrum of Au, however, the initial state $N_{6,7}$ spin–orbit splitting is small (3.7 eV [8, 14]) compared with the $5d^2$ multiplet structure splitting [15] and the

5d spin–orbit coupling constant is large, $\xi_{5d} \simeq 0.6\,\text{eV}$ [15], and makes a significant contribution to the width of the 5d band density of states, $W \simeq 6\,\text{eV}$ [16–18]. For these reasons the spectral envelopes of the $N_6O_{4,5}O_{4,5}$ and $N_7O_{4,5}O_{4,5}$ groups overlap and it is difficult to use these transitions to probe the local electronic structure of Au and its alloys.

In order to analyse the Au $N_{6,7}O_{4,5}O_{4,5}$ Auger transitions it is clearly useful to have some way of separately determining the profiles of the $N_6O_{4,5}O_{4,5}$ and $N_7O_{4,5}O_{4,5}$ transitions. We have achieved this in this work by using the tunable characteristics of synchrotron radiation to measure the joint $N_{6,7}O_{4,5}O_{4,5}$ profile and the $N_7O_{4,5}O_{4,5}$ profile of metallic Au separately and then subtracted the latter from the former to obtain the $N_6O_{4,5}O_{4,5}$ profile.

2. Experimental details

The experiments were carried out on station 6.1 of the Daresbury Synchrotron Radiation Source. The experimental chamber was pumped by a turbo-molecular pump, an ion pump and titanium sublimation pumps. A pressure in the low 10^{-10} Torr range was maintained throughout the experiment. The Au specimen was 99.99% pure and was cleaned by mechanically scraping with a tungsten carbide blade so that there was no trace of the O 2s photoemission line. The Auger profiles were measured over one-hour experimental periods at the end of which there was still no trace of the O 2s photoemission line. From the photoelectron cross-sections [19] and electron escape depths [20] it is clear that the level of oxygen on the solid surface never exceeded 0.1 monolayers.

The Auger and photoelectron spectra were collected by a cylindrical mirror analyser. Auger profiles were measured using photons of several energies; in particular 115 eV which excites both the $N_{6,7}$ levels and generates the full $N_{6,7}O_{4,5}O_{4,5}$ Auger spectrum and 86 eV which, since it falls between the binding energies of the N_6 (87.7 eV [14]) and N_7 (84.0 eV [14]) core levels excites only the $N_7O_{4,5}O_{4,5}$ transitions.

3. Results and discussion

The $N_{6,7}O_{4,5}O_{4,5}$ Auger spectrum excited by 115 eV photons is shown in figure 1(*a*). This spectrum consists of three features, two intense peaks at $\simeq 71$ eV and 73 eV and a weaker one at $\simeq 67$ eV. The low energy feature can be attributed to the $^1S_0$ component of the $N_7O_{4,5}O_{4,5}$ group since this component is expected to be well separated from the rest of the multiplet structure [15]. The $N_7O_{4,5}O_{4,5}$ Auger spectrum excited by 86 eV photons is shown in figure 1(*b*). Two features are observed in this spectrum, a main peak and the $^1S_0$ component to lower kinetic energy. The onset of the photoelectron spectrum of the Au 5d band can be observed at the high kinetic energy end of this spectrum.

The $N_{6,7}O_{4,5}O_{4,5}$ Auger spectrum of Au has also been measured by Nyholm *et al* [21] using photons of energy $h\nu = 110$ eV. To within statistical factors, the spectral profile we observed using 115 eV photons agrees with their results. As Nyholm *et al* [21] point out, the advantage of exciting these transitions with low energy photons is that only the 4f initial states are excited, so the spectra are not influenced by any Auger vacancy satellite processes that occur to low kinetic energy and arise from Coster–Kronig decay of deeper levels [4, 6, 7, 9]. It is also possible to minimise referencing errors by making
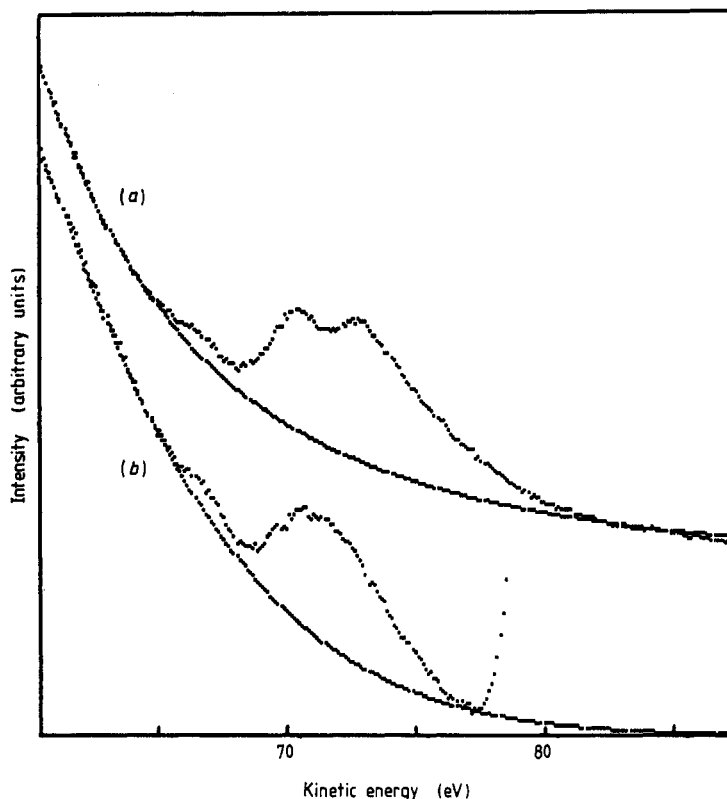
Figure 1. The spectra of the $N_{6,7}O_{4,5}O_{4,5}$ (a) and $N_7O_{4,5}O_{4,5}$ (b) Auger transitions of Au excited by photons of 115 eV and 86 eV respectively. The onset of the photoelectron spectrum of the Au 5d band can be seen on the right hand side of (b). Both spectra lie on a background of low energy scattered electrons which rises smoothly with decreasing kinetic energy. The lower curves in each figure are smooth fits to these backgrounds. The kinetic energy scales in figures 1 and 2 are referenced to the Fermi level.

accurate measurements of the energies of the Au 4f photoelectron spectra, the $N_{6,7}O_{4,5}O_{4,5}$ Auger spectra and the position of the Fermi level.

We are interested in comparing the shapes of the spectral profiles rather than their absolute intensities so the profiles of figure 1(a) and 1(b) are corrected for the decay of the beam current in the synchrotron between the two experiments by dividing the electron counts, I, in the spectra by I_0 which is a signal proportional to the synchrotron beam current. Due to their low kinetic energies, the Au $N_{6,7}O_{4,5}O_{4,5}$ Auger spectra lie on top of the rapidly rising background of scattered electrons which occurs to low energy in all electron spectra (figure 1). However, this background is quite smooth and can be removed by interpolating in the region of the Auger profiles using a parametrised expression that fits the background to low and high kinetic energy of the spectra of interest. The lower curves in figures 1(a) and 1(b) show backgrounds obtained in this way. The spectra obtained by subtracting these backgrounds are shown in figure 2. Of course there is no guarantee that the backgrounds subtracted from the spectra are an accurate representation of the spectrum of scattered electrons but our procedure does not introduce any structure into the Auger profiles of figure 2 that cannot be observed
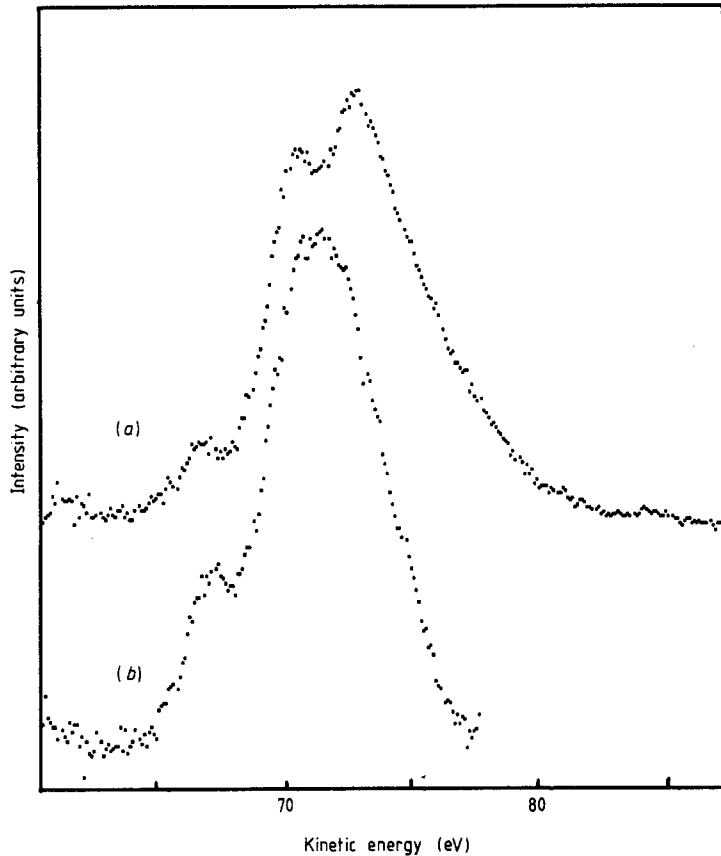
Figure 2. The spectra of the $N_{6,7}O_{4,5}O_{4,5}$ (*a*) and $N_7O_{4,5}O_{4,5}$ (*b*) Auger transitions of Au after the smooth backgrounds shown in the corresponding spectra of figure 1 have been removed.

in the original spectra. It is usually found that the relative intensity of the low energy regions of spectral profiles obtained by subtracting backgrounds in this way is sensitive to the details of the background subtraction procedure. This is true in this case, and the difference in the relative intensity of the low energy $^1S_0$ component in the spectra of figures 2(*a*) and 2(*b*) can be attributed to this effect.

The spectral shape of the $N_6O_{4,5}O_{4,5}$ transitions was obtained by subtracting the spectrum of figure 2(*b*) from that of figure 2(*a*). Since this procedure involves the subtraction of two difference spectra, the statistical noise makes a significant contribtion to the results for the spectral shape and to compensate for this the data points of the final spectrum were added in groups of four. The results obtained for the $N_6O_{4,5}O_{4,5}$ and $N_7O_{4,5}O_{4,5}$ spectral profiles are now shown in figure 3. In this figure the energy scale is the binding energy of the $5d^2 : LSJ$ two-hole final states obtained from

$$E_B(5d^2 : LSJ) = E_B(N_i) - \text{KE}(N_iO_{4,5}O_{4,5}) \tag{1}$$

where N_i refers to either the N_6 or N_7 level and all the energies are referenced to the Fermi energy.

The $N_{6,7}O_{4,5}O_{4,5}$ Auger transition has two initial states, N_6 and N_7, each of which decays into the $5d^2$ final states: ^1S, ^3P, ^1D, ^3F, and ^1G. The $^1S_0$ component has a high
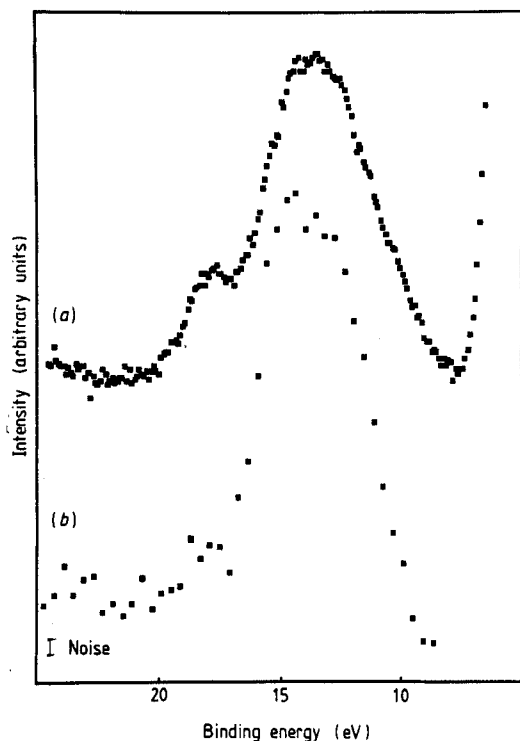
Figure 3. The spectra of the $N_7O_{4,5}O_{4,5}$ (a) and $N_6O_{4,5}O_{4,5}$ (b) Auger transitions of Au. The $N_6O_{4,5}O_{4,5}$ spectrum was obtained by subtracting the $N_7O_{4,5}O_{4,5}$ profile (figure 2(b)) from the $N_{6,7}O_{4,5}O_{4,5}$ profile (figure 2(a)). Both profiles are plotted on the binding energy scale obtained from equation (1).

binding energy and is separated from the other components which have much smaller separations and are expected to overlap. The two features in the $N_7O_{4,5}O_{4,5}$ spectrum (figure 3(a)) can be identified as the $^1S_0$ component at a binding energy relative to the Fermi energy, $E_B(5d^2 : {}^1S_0)$, of 17.6 ± 0.3 eV and an envelope made up of the remaining less strongly bound components of the multiplet structure. We can determine the correlation energy of the $^1S_0$ state from

$$U(5d^2 : {}^1S_0) = E_B(5d^2 : {}^1S_0) - 2E_B(5d) \qquad (2)$$

where $E_B(5d)$ is the binding energy at the centre of the Au 5d band. The results of Christensen's [17] calculations give $E_B(5d) \simeq 4.3$ eV so we find $U(5d^2 : {}^1S_0) \simeq 9.0$ eV. Christensen [17] also finds the Au 5d band width W to be $\simeq 5.5$ eV. So applying the Cini–Sawatzky [1–3] theory we obtain $U/W \simeq 1.6$ which indicates that the $^1S_0$ component of the multiplet structure will be localised. U/W will be lower for the other LSJ components of the $5d^2$ multiplet structure so the intense peak to lower binding energy in figure 3(a) will be an envelope of the distorted band-like profiles characteristic of delocalised states.

The $^1S_0$ component can just be discerned in the profile obtained for the $N_6O_{4,5}O_{4,5}$ transitions (figure 3(b)). This component is obscured by the $N_7O_{4,5}O_{4,5}$ transitions in the $N_{6,7}O_{4,5}O_{4,5}$ Auger profile and the fact that we observe it at the same binding energy in the $N_6O_{4,5}O_{4,5}$ spectrum demonstrates the success of our background subtraction and differencing procedures. The more intense component of the $N_6O_{4,5}O_{4,5}$ spectrum has a different shape to the corresponding feature in the $N_7O_{4,5}O_{4,5}$ spectrum. The two sets of transitions are not expected to have identical profiles since the difference in the angular momenta of the two initial states leads to differences in the transition rates to

the various *LSJ* components of the final state multiplet structure. A similar effect is observed in the $M_{4,5}N_{4,5}N_{4,5}$ Auger spectra of Ag where the $^3F_4$ component is weak in the $M_4N_{4,5}N_{4,5}$ spectrum and strong in the $M_5N_{4,5}N_{4,5}$ spectrum [7].

4. Summary

By using synchrotron radiation and varying the photon energy we have determined the profiles of the $N_7O_{4,5}O_{4,5}$ and $N_6O_{4,5}O_{4,5}$ Auger transitions of metallic Au. It is anticipated that the application of this technique to the $N_{6,7}O_{4,5}O_{4,5}$ transitions of elements near to Au in the periodic table and to Au alloys will yield comparable information on local electronic structure to that obtained for the alloys of Cu, Ag and related elements.

Acknowledgments

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