The $N_{6,7}$ soft x-ray emission spectra of platinum–gold alloys

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Abstract. The $N_{6,7}$ soft x-ray spectra of platinum and gold from a series of platinum–gold alloys have been measured and their energies adjusted to compensate for the N_6 and N_7 core level shifts which were measured by XPS. The results are compared with the theoretical spectra published by Weinberger *et al*. The overall agreement in band shapes, peak positions and band widths is good and possible causes of minor discrepancies are discussed.

1. Introduction

Theoretical studies of the electronic structure of Pt–Au alloys have been published by Weinberger *et al* (1982a, b). In the first work a fully relativistic Korringa–Kohn–Rostoker coherent potential approximation (R–KKR–CPA) was used to treat the random substitution and Au_cPt_{1-c} alloys. The principle conclusion was that Au_cPt_{1-c} did not conform to a rigid-band model. In the second paper the $N_{6,7}$ soft x-ray emission spectra (SXES) of both Pt and Au from the Au_cPt_{1-c} alloys were calculated. This present work is in response to the second paper, seeking experimental verification or otherwise of the theoretical spectra and hence a check on the potential functions used in the calculations.

2. Experimental procedure

The alloys were prepared from metals of 99.99% purity by melting in an alumina crucible inside a graphite susceptor in an induction furnace. After cold rolling the alloys were given an homogenising anneal at 1280 °C for one day in an electric furnace. The samples were subjected to differential thermal analysis (DTA) to check for metastable phases. The $N_{6,7}$ emission spectra were measured using a grating soft x-ray spectrometer described in detail by Watson *et al* (1967) and the core level binding energies were measured using a Vacuum Generators ESCA3 x-ray photoelectron spectrometer.

3. Results

As heavy metals the $N_{6,7}$ emission bands of pure gold and pure platinum as well as their alloys, are superimposed on a pronounced high background. The exact form of the

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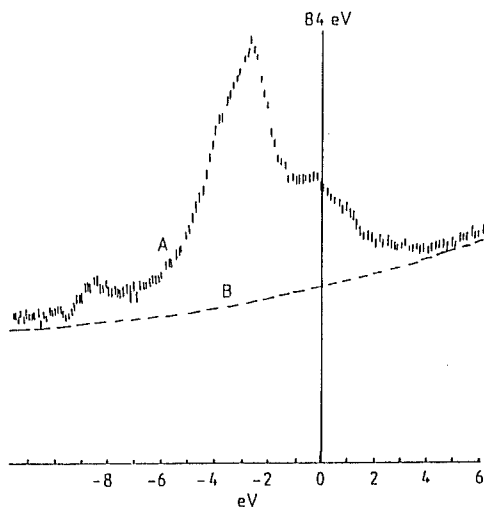‖ On leave of absence from Eotvos University, Budapest, Hungary.

Figure 1. Au $N_{6,7}$ emission spectrum (A) with extrapolated background (B).
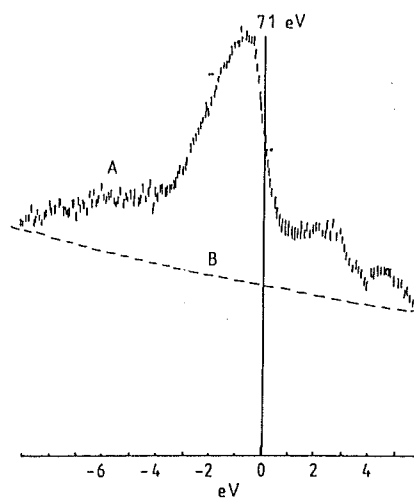
Figure 2. Pt $N_{6,7}$ emission spectrum (A) with extrapolated background (B).

background is not known; efforts were made to estimate the background using the spectrum of lead but unfortunately part of the second-order $N_{6,7}$ emission band of lead shares the Pt $N_{6,7}$ emission band range. Therefore background estimated in this way was unsatisfactory. A common background for each valence band also does not seem to be appropriate. Hence a smooth background for each individual spectrum was estimated by eye from well in front and well beyond the $N_{6,7}$ band and then subtracted. The zero of energy is taken to be the Fermi level of the N_7 spectrum of the pure metal as measured by Fomichev *et al* (1973). The corresponding N_6 spectra are shifted to higher energy by the appropriate difference in the $4f^{7/2}$ and $4f^{5/2}$ core level energies. Hence the region of the spectra at negative energies is due to the overlap of the low energy region of the N_6 spectrum with the N_7 spectrum while that at positive energies is due to the high energy region of the N_6 spectrum only.

The gold valence band emission spectrum in its processed form and the estimated background are shown in figure 1. Comparison with previously published spectra (Kapoor *et al* 1972, Fomichev *et al* 1973, McAlister *et al* 1971) shows that agreement in the overall shape is good. The spectrum at negative energies consists of a small peak at −0.5 eV and

Table 1. The Au and Pt N_6 and N_7 core binding energies from the pure metals and the alloys measured by XPS.

	Au (eV)		Pt (eV)	
	N_7	N_6	N_7	N_6
Au	83.9 ± 0.02	87.8 ± 0.02		
Pt			70.9 ± 0.02	74.32 ± 0.02
$Pt_{75}Au_{25}$	83.75 ± 0.02	87.43 ± 0.02	70.76 ± 0.02	74.08 ± 0.02
$Pt_{50}Au_{50}$	83.82 ± 0.02	87.72 ± 0.02	70.61 ± 0.02	74.04 ± 0.02
$Pt_{25}Au_{75}$	83.87 ± 0.02	87.74 ± 0.02	70.47 ± 0.02	73.70 ± 0.02

Table 2. The soft x-ray Fermi energy differences between Pt and Au in the alloys calculated from equation (2).

Alloy	${}^{(Au)}E_F^{(SXES)} - {}^{(Pt)}E_F^{(SXES)}$ (eV)
$Pt_{75}Au_{25}$	13.01 ± 0.05
$Pt_{50}Au_{50}$	13.21 ± 0.05
$Pt_{25}Au_{75}$	13.40 ± 0.05

a large prominent peak at -2.8 eV. A further low energy hump is apparent at -4 eV. The region of the N_6 spectrum at positive energies shows a steady decrease in intensity as energy increases. The peak at -8.5 eV is due to barium N_5O_3 and N_4O_2 emission lines from the $BaCo_3$ coating of the filament of the electron gun.
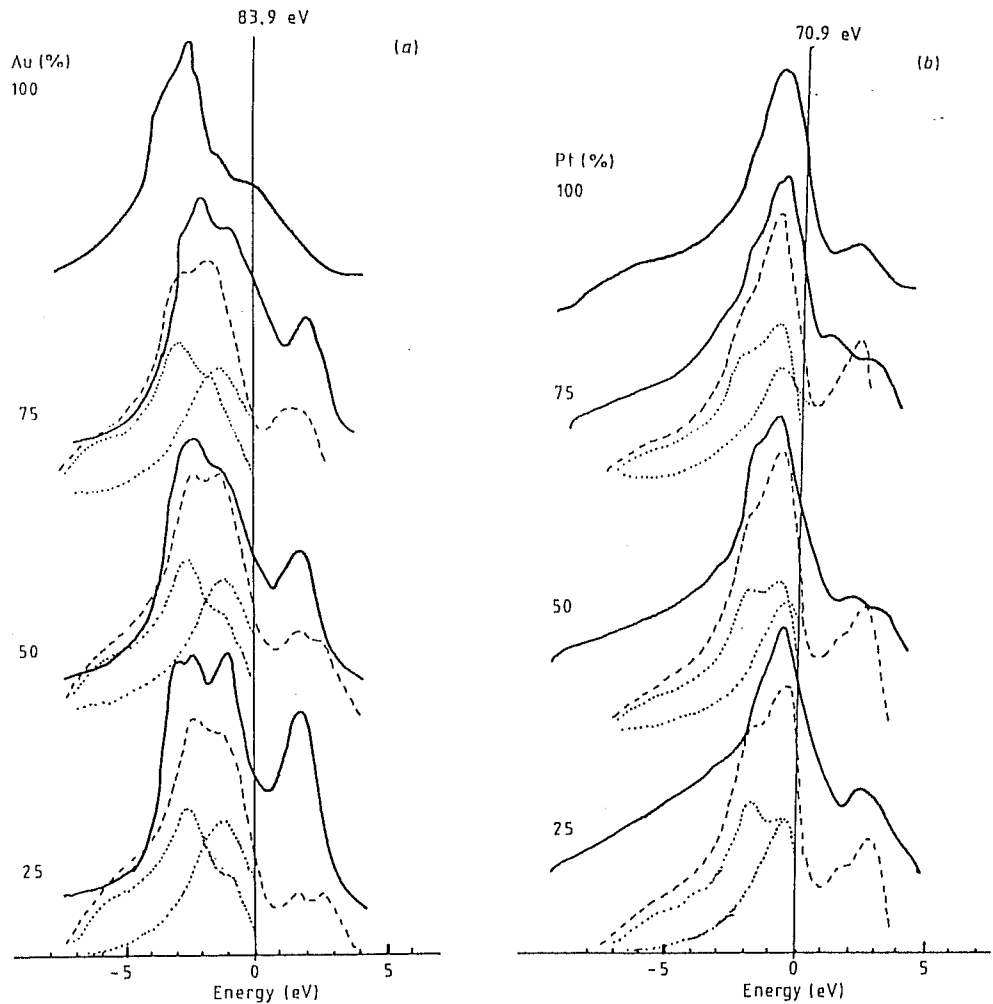

Figure 3. (*a*) Au $N_{6,7}$ spectra and (*b*) Pt $N_{6,7}$ spectra from the pure metals and the alloys with the zero of energy adjusted in each case to account for the core level shifts. The broken curves are the theoretical spectra of Weinberger *et al* (1982b). The dotted curves in the negative energy region show the contributions from the N_7 and the N_6 spectra.

The $N_{6,7}$ spectrum of pure platinum with the estimated background is shown in figure 2. Good agreement has been found with previous work (Fomichev *et al* 1973, Dobbyn *et al* 1974). The spectrum at negative energy consists of a prominent peak at −1.0 eV and in the region of the N_6 spectrum a small peak is located at 2.5 eV. The peak at 4.5 eV is again due to the Ba N_5O_3 and N_4O_2 emission lines.

To align the Fermi levels of the pure metal and alloy spectra account must be taken of the N_6 and N_7 core level shifts due to alloying. To do this the binding energies of the N_6 and N_7 core levels of the alloy components were measured by XPS and are listed in table 1. To relate the core level energy shifts to the position of the N_7 Fermi level in the SXES we use the following expression

$$E_F^{(SXES)} + W = E_{XPS}^{(N7)} \tag{1}$$

where $E_F^{(SXES)}$ is the N_7 Fermi energy measured by soft x-ray spectroscopy, W is the work function and $E_{XPS}^{(N7)}$ is the N_7 core level binding energy measured by XPS. Since the work function is unique for each alloy we can write

$$^{(Au)}E_{XPS}^{(N7)} - {}^{(Pt)}E_{XPS}^{(N7)} = {}^{(Au)}E_F^{(SXES)} - {}^{(Pt)}E_F^{(SXES)} \tag{2}$$

where the left-hand superscripts denote the elements in the alloy. This gives Fermi edge differences as listed in table 2. The Au $N_{6,7}$ and Pt $N_{6,7}$ spectra from the pure metal and the alloys with the energy scales adjusted according to the above and with $E_F^{(N7)} = 0$ are shown in figures 3(*a*) and 3(*b*). For ease of comparison the theoretical curves of Weinberger *et al* (1982b) are also shown. To separate the N_6 and N_7 spectra the shape of that part of the N_6 spectrum which overlaps the N_7 region would have to be taken from the calculated spectrum. Since the main objective of this paper is the comparison of the experimental and theoretical spectra, this has not been attempted.

4. Discussion

The main prediction of the theory is that if the Au and Pt $N_{6,7}$ spectra related to the same alloy Fermi energy are superimposed they will not coincide but their maxima will be separated by 1.5 eV, proving that these alloys cannot be described by a rigid-band model. This is adequately supported by the experimental spectra of figures 3(*a*) and 3(*b*) and differ from the behaviour of the Cu_cNi_{1-c} system studied by Clift *et al* (1963), who measured the $M_{2,3}$ emission bands and found the shape of the spectra broadly consistent with the rigid-band model. However, in this system deviations from rigid-band behaviour are not so readily observable since the spectra from the alloy components are so similar in shape to those of the pure metals.

Nevertheless, studies of random solid solutions are producing an increasing amount of evidence that KKR−CPA theory is accurate in predicting the electronic structure of such alloys. Hufner *et al* (1973) measured the conduction band for the Cu_cNi_{1-c} system using XPS and found that E_F does not change with respect to the Cu d bands but that the d bands are reduced in height with increasing Ni content and a completely new Ni-related peak appears between the upper edge of the Cu d band and E_F. A similar observation for the Pd_cAg_{1-c} system was made by McLachlan *et al* (1975), where a Pd-related peak appears between the upper edge of the Ag d band and E_F. This is good support for the coherent potential approximation (CPA) of Soven (1967).

It is difficult to detect clearly the breakdown of the rigid-band model in SXS as the Ni

L_3 and Cu L_3 in Ni_cCu_{1-c} alloys each consists of one peak and there are no dramatic changes accompanying the change in concentration. Durham et al (1979) solved the problem by measuring the L_3 binding energy of Cu and Ni for each alloy studied using xps and then shifting their measured $L\alpha$ emission spectra accordingly. With this treatment it became obvious that a $2P_{3/2}$ hole at a Cu site 'sees' a different conduction band than it would from a Ni site. They verified that the KKR–CPA description of the local densities of states in Cu–Ni alloys is substantially correct, also the quantitative agreement between theory and experiment shows that the potential functions used in the KKR–CPA calculations are reasonably accurate. Also analogous to the Pt_cAu_{1-c} alloys is the Pd_cAg_{1-c} system. Durham et al (1981) showed that the KKR–CPA theory adequately describes the observed split-band behaviour and, again, the potential function used gives a roughly correct account of the charge rearrangement on alloying.

Careful comparison of the experimental and the theoretical spectra shown in figure 3 shows general agreement but also some discrepancies which should be discussed further. While the experimental Pt N_6 spectrum for $Pt_{25}Au_{75}$ shows one peak only in the positive region, theory predicts a double peak for this alloy and where theory predicts a single peak in the $Pt_{50}Au_{50}$ and $Pt_{75}Au_{25}$ alloys, double peaks are observed. In the negative region the peak positions are in good agreement with each other, but the intensity ratios differ. The Pt N_6 emission intensity relative to that of the N_7 is much lower than the theoretical predictions. N_6N_7V Auger transitions provide a competing process for filling an N_6 vacancy and, since this was not considered in the theoretical calculations, could account for the discrepancy in the $N_6:N_7$ intensity ratio. Further, the contribution of the N_6 intensity in the N_7 spectrum region will be correspondingly reduced in the experimental spectra and could contribute to the discrepancies in the relative peak heights in the N_7 region.

In the case of gold there is general agreement in the N_7 region between the theoretical and experimental curves. The most obvious differences are that where theory predicts a double-peaked spectrum, three peaks are observed in the 25 and 75% Au spectra. Also, the relative intensity ratios of the peaks differ. The theoretically predicted peaks agree more or less with the positions of the experimental peaks; the third peak occurs at lower energies. For the positive energy N_6 region theory predicts a double-peaked structure in the alloys which is not observed experimentally. However, this could be due to the effect of the third order Pt N_4N_6 line which occurs in the same energy region as the Au N_6 band and accounts for the decrease in intensity in the N_6 region with increasing gold content of the alloys.

The band widths (Γ) of the Pt and Au N_7 emission bands were measured by taking the full width at half maximum intensity and are recorded in table 3, the band widths of the

Table 3. The theoretical and experimental full widths at half maximum intensity of the Au and Pt $N_{6,7}$ emission bands (in eV).

Au (%)	Γ (Au)		Γ (Pt)	
	Theory	sxs	Theory	sxs
25	3.93	3.9	2.77	2.93
50	3.84	3.95	2.56	2.93
75	3.67	4.03	2.8	2.7
Pure metal		3.1		2.68

theoretical Pt and Au N_7 emission bands are also included. The experimental and theoretical values generally are in good agreement but again the direction of increasing or decreasing band widths with element concentration do not agree. The width of the Au N_7 emission band increases with increasing gold content in contradiction to the theoretical predictions. The Pt N_7 emission band widths indicate an increase with increasing Pt content while the theoretical curves show that Pt_{25} and Pt_{75} have almost the same band width whereas the Pt_{50} curve has a lower width.

The reasons for the observed discrepancies could be significant but also due to experimental effects. Weinberger *et al* (1982a) predicted for these alloys a broad d-band complex with substantial intermingling of the Au and Pt bands as the splitting between the Pt $d_{3/2}$ and Au $d_{3/2}$ resonances is about the same as that between the Au $d_{5/2}$ and the Pt $d_{5/2}$ and is smaller than the spin–orbit splitting on either site; hence, in the valence bands the mixing of Au and Pt d resonances is expected. A greater overlap of the Au and Pt d peaks than theoretically predicted could be one reason for the discrepancies in the intensities in both the N_6 and N_7 regions, but the overlap of the third order Pt $N_4 N_6$ line with the Au N_6 band must contribute largely to the discrepancy in that case.

The critical reflectivity of platinum, which is used as a coating for the diffraction grating, could affect the Pt N_6 emission intensity. However, the N_7/N_6 intensity ratio of the pure Pt spectrum as measured by Fomichev *et al* (1973) using a gold-coated grating has a value of 3.68 which compares with the value of 3.65 in the present investigation.

Self-absorption within the anode could be another contributing factor to the discrepancies in the intensities. This would affect the gold spectrum more than the platinum since the x-ray photons emitted by the gold atoms have energies a few electron volts higher than the energy difference between the Pt $N_{6,7}$ core levels and the Fermi level; thus, the Pt atoms may absorb the x-rays emitted by the Au atoms, resulting in a distortion of the Au emission spectrum.

5. Conclusion

Comparison of the theoretical and experimental spectra shows reasonable agreement in terms of the position and widths of major features. In the Au spectra only the N_6 contribution shows above 84 eV (the Fermi level of the N_7 spectrum). This contribution is principally from valence-band $d_{3/2}$ states. According to Weinberger *et al* (1982b) the high energy structure below 84 eV is due to a combination of the N_6 and N_7 spectra and the lower energy structure is due mainly to valence-band $d_{5/2}$-state transitions to the N_7 level.

For platinum the high energy region below 71 eV is due to a combination of the N_6 and N_7 spectra, the lower energy structure due to valence-band $d_{5/2}$-state transitions to the N_7 level. Only the N_6 contribution shows above 71 eV (the Fermi level of the N_7 spectrum); this contribution is principally from valence band $d_{3/2}$ states. The relative intensities of the Pt peaks above and below 71 eV do not agree well with the theoretical spectra. This may be because the overlap of the Au and Pt d bands is greater than theoretically predicted but more likely it is due to the reduction in the N_6 emission intensity because of the $N_6 N_7 V$ Auger transitions. Furthermore, the discrepancy may be due in part to absorption in the Pt coating of the grating but the good agreement of the pure Pt spectrum with that reported by Fomichev *et al* (1973), measured using a gold grating, argues against this.

In Au the relative intensities of the peaks above and below 84 eV (the Au N_7 Fermi level) also do not agree with the theoretical spectra. This could be for the same reason as given for the Pt spectra but complicated also by the interference from the third order of the

Pt N_4N_6 transitions in the energy range of the Au N_6 band. Self-absorption by Pt of Au emission intensity may also distort the low energy range of the Au $N_{6,7}$ band.

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