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A Cooper minimum photoemission study of the Au₉₅Pd₅ alloy

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Abstract. We present the results of a valence band (VB) photoemission study of a Au₉₅Pd₅ alloy in a photon energy range covering the Cooper minima of the Pd 4d and Au 5d photoionization cross sections, ($h\nu = 90\text{--}280$ eV). The spectra show the presence of the Pd 4d-derived virtual bound state (VBS) which we find to lie between the Au 5d band and the Fermi level with a binding energy of 1.45 eV. The intensity of this peak goes through a minimum at $h\nu = 140$ eV. The results are discussed in terms of the spatial distortion of the Pd 4d wavefunction in the alloy. Subtractions between the alloy and metallic Au spectra at different photon energies reveal marked differences in the Au 5d part of the valence band. These differences are ascribed to modifications in the density of states caused by the presence of the impurity and to the variation in the photon energy dependence of the cross section of different parts of the VB spectrum.

1. Introduction

The Cooper minimum (CM) effect [1] has been used to obtain information on the properties of the electronic structure of metals [2], interfaces [3] and alloys [3–8]. By performing photoemission with a tunable photon source it is possible to enhance or depress the contribution from different atom and angular momentum components of a joint valence band (VB) density of states (DOS) by exploiting the variation of the photoionization cross section of nd initial states, for $n > 3$, in the energy region around the CM. It is known that the intensity and energy of the CM are sensitive to the chemical environment of the photoemitting atoms. The environmental distortions of the radial part of the initial-state wavefunction give rise to changes in cancellation effects in the transition matrix element. The CM can be used in this way to monitor the degree of hybridization and of interaction between the valence wavefunctions of the atoms [2–8].

The surface and bulk electronic properties of dilute alloys of Pd with noble metals are an interesting subject of investigation due to the technological potential of these systems in catalysis and material science. They are also of fundamental interest as probes of electron scattering, localization and correlation. The random alloy system Au _{x} Pd _{$1-x$} forms a continuous series of face-centred-cubic solid solutions over the entire compositional range. A number of theoretical results of electronic structure calculations, obtained using different

methods and approximations, are reported in the literature, [9–14]. Experimental data on the electronic properties obtained from spectroscopies such as ultraviolet photoemission [9, 13, 15], x-ray photoelectron (XPS) [16, 17], x-ray emission [10] and Auger emission [17, 18] have also been reported. It was found [9, 16] that in the low-Pd-concentration limit the Pd 4d-derived states are well described by the presence of a virtual bound state (VBS) with a Clogston–Wolff Hamiltonian [19–21], although some interaction between the host and the impurity d states influences the characteristics of the VBS.

In order to investigate this interaction we performed a VB photoemission study of a Au₉₅Pd₅ alloy over a wide photon energy range ($h\nu = 90\text{--}280$ eV) covering the CM of the Pd 4d- and Au 5d-states cross sections. To our knowledge, this is the first study exploiting the CM of the photoemission cross section from d states of two different alloying species.

2. Experiment

The experiments were performed on beamline 5U.1 of the Synchrotron Radiation Source, Daresbury Laboratory (UK). The radiation emitted by the undulator 5U was monochromatized by a plane grating monochromator and focused by a spherical and an ellipsoidal mirror. The measurement station consisted of a ultrahigh-vacuum chamber with a base pressure less than 5×10^{-10} mbar. A polycrystalline specimen of Au₉₅Pd₅ was obtained from Metal Crystal Ltd. The specimen was cleaned by *in situ* mechanical scraping with a tungsten carbide blade and the surface cleanliness was monitored with XPS. The photoemission spectra were taken with a Vacuum Science Workshop HA100 hemispherical analyser with a multichannel detection system. The overall resolution of the VB photoemission spectra (obtained by measuring the Fermi edge width) varied between 0.2 and 0.3 eV. The pure Au VB spectra which were used in the difference curves of figure 3 (see later) were obtained on station 6.1 of the SRS in a previous experiment [7].

3. Results and discussion

Figure 1 shows the VB spectra obtained from Au₉₅Pd₅ for different photon energies. Their overall shapes are very similar to the spectra of pure Au with two components derived from the 5d spin–orbit splitting but with the clear presence of the Pd 4d VBS at a binding energy (BE) of 1.45 eV. The relative intensity of the latter feature goes through a minimum at $h\nu = 140$ eV, and is high at higher photon energies where the Au 5d CM is found. The wider Au-derived parts of the spectrum change in shape and relative intensity with $h\nu$. This photon dependence is a consequence of the varying photoemission cross section of the different electronic states derived from Au 5d and Pd 4d which contribute to the VB.

Measurements of the intensity of the VBS as a function of photon energy are difficult to make because the VBS lies on a steep background caused by the onset of the Au 5d-state emission and the impurity d states interact with the host states giving rise to an ill defined lineshape for the VBS [9]. We performed a least-squares fitting in a limited region of the spectra with BE between 3.5 and 1 eV, and representing the background with a third-order polynomial and the VBS peak with a Gaussian lineshape. We then subtracted the fitted background from the spectrum and measured the area of the remaining peak. The results were not affected critically by the choice of the lineshape or by the order of the polynomial. The results obtained for the ratio of the intensity of the Pd VBS to that of the Au d band are shown by the open circles in figure 2. Figure 2 also shows the ratios of the Pd and Au photoelectron cross sections obtained from the literature for the metals $((\sigma_{Pd}/\sigma_{Au})_{met})$,

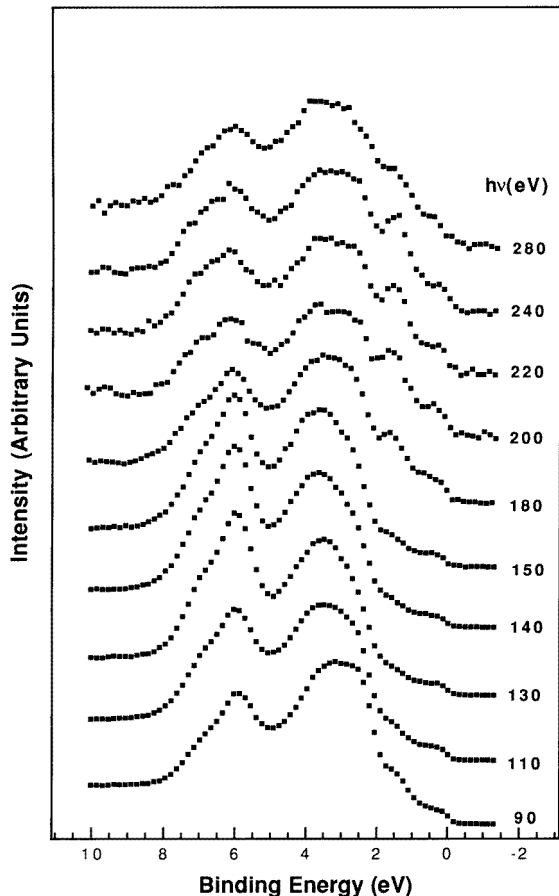


Figure 1. VB spectra of Au₉₅Pd₅ alloy taken at different photon energies. The spectra have been normalized to their areas.

experimental results) and atoms ($(\sigma_{Pd}/\sigma_{Au})_{at}$, theoretical results) [2, 22]. The results are plotted on a logarithmic scale in figure 2, with each curve normalized to its maximum and multiplied by 100, as in a similar analysis performed on the AgCd and AgAl systems [8].

We have chosen to represent the results in figure 2 in terms of the ratio of the Pd and Au intensities due to the closeness of the Pd and Au CM and in order to avoid the terms present in the expression for the photoelectron intensity of Rossi and co-workers [3], namely the photoelectron escape depth, the efficiency of the photoelectron detector, the photon flux and the experimental factor resulting from the analyser geometry (see also [7]). Since the VBS contributes only a small fraction of the total VB intensity we find that a representation of the results in which the VBS intensity is compared to the total VB after the subtraction of the VBS component yields results very similar to figure 2.

Although the three curves shown in figure 2 have a similar behaviour, each has its CM at a different energy. Also, the $(\sigma_{Pd}/\sigma_{Au})_{met}$ minimum is shallower than the $(\sigma_{Pd}/\sigma_{Au})_{at}$ one and is shifted to higher $h\nu$. The VBS intensity has the shallowest CM at the highest photon energy. In seeking an explanation for these results we note that it is well known that the behaviour of the CM of the Pd 4d state depends on the chemical environment of

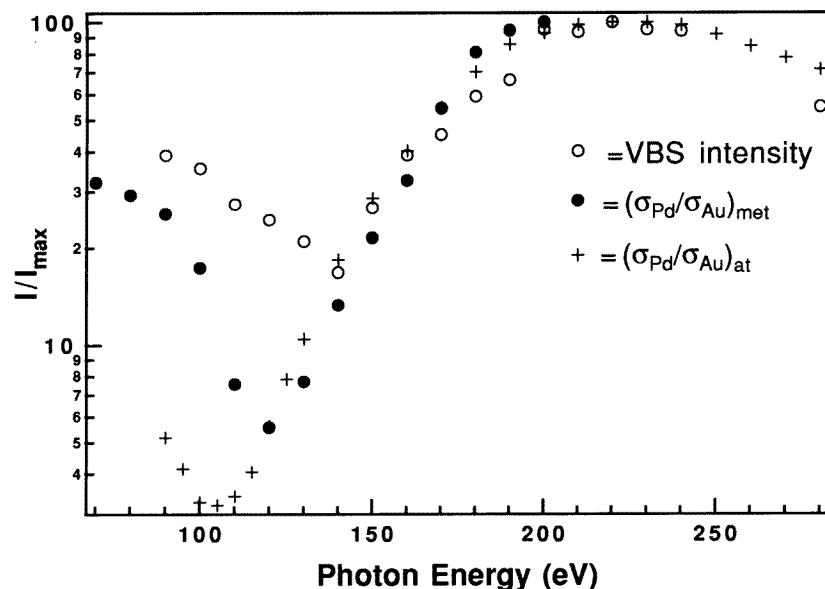


Figure 2. Open circles: the normalized VBS intensity versus $h\nu$. Full circles: the ratio of the metallic Pd 4d and Au 5d experimental photoionization cross sections, $(\sigma_{Pd}/\sigma_{Au})_{met}$ [2]. Crosses: the ratio of the atomic Pd 4d and Au 5d theoretical cross sections, $(\sigma_{Pd}/\sigma_{Au})_{at}$ [22]. The curves have been normalized to their maxima and are plotted on a logarithmic scale.

the photoemitting atom; in particular, the difference between the values of $(\sigma_{Pd}/\sigma_{Au})$ for free atoms and metals is caused by the spatial distortion of the d wavefunction in the metal environment [2], as the d states participate in the bonding. From figure 2, it is clear that this effect is even stronger in the $Au_{95}Pd_5$ case, indicating that there is a higher degree of distortion of the Pd 4d wavefunction in the Au host and a strong interaction between the Au 5d and Pd 4d states. This effect has been observed in other alloying systems [8].

In order to investigate the influence of the Pd impurity on the Au 5d band we obtained difference spectra for the difference between the VB photoemission of pure Au [7] and that of $Au_{95}Pd_5$ as a function of photon energy. As already described above, the photoemission cross sections of Pd 4d and Au 5d states vary significantly in this energy range. Therefore the difference spectra that we obtain can give selective information on the modification of the DOS due to the alloying process, with the enhancement of the differences in various parts of the VB due to the strong intensity variations of the matrix element.

The valence band spectra were smoothed and a background removed according to the procedure used in [23]. In addition, prior to the subtraction, the alloy spectra at each photon energy were convoluted with Gaussians to make them comparable to the lower-resolution spectra measured for pure Au [7] and each spectrum was normalized to unit area between binding energies of 0 and 10 eV. The results for the VB spectra of Au and $Au_{95}Pd_5$ at a selection of photon energies are shown in the upper panel of figure 3. The corresponding difference spectra are shown in the lower panel of figure 3.

The difference spectra (figure 3) change significantly when the exciting photon energy is increased from 100 eV to 130 eV. The Pd VBS has a maximum intensity at a BE of 1.45 eV, and it is associated with a deep minimum (labelled **a** in figure 3) at 2.5 eV which almost disappears at $h\nu = 130$ eV. The asymmetric shape of the VBS can be ascribed to the

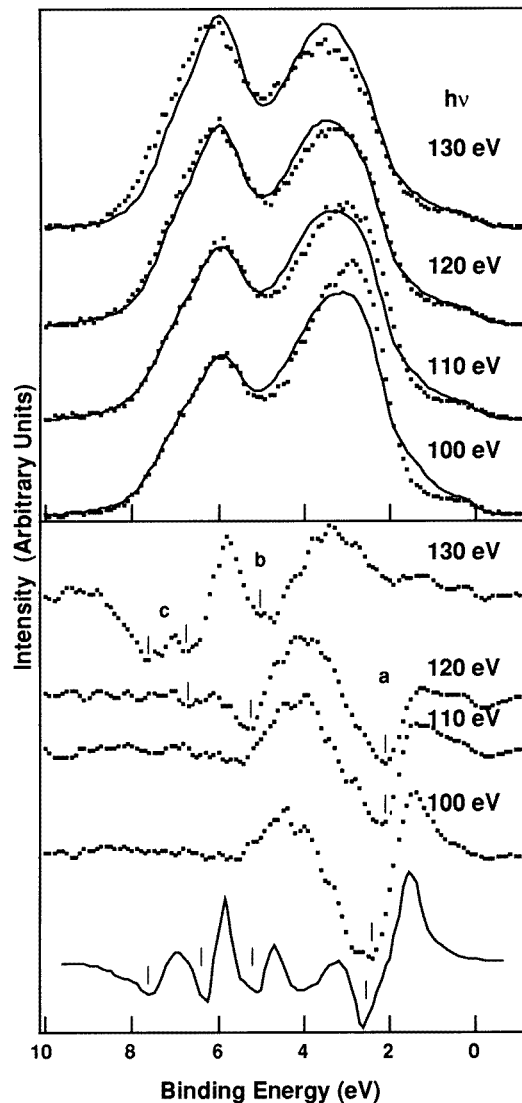


Figure 3. Upper panel: VB spectra of $\text{Au}_{95}\text{Pd}_5$ (continuous lines) and pure Au (dots) taken at different photon energies. Lower panel: relative difference spectra (dots), and the difference between the theoretical DOS of $\text{Au}_{95}\text{Pd}_5$ and that of pure Au (continuous line) [9].

interaction between the Pd 4d and Au 5d wavefunctions [3, 4]. At higher photon energies two features, labelled **b** and **c** in figure 3, appear in the difference spectra. The dip in the difference spectra **b** which occurs at a binding energy of 4.8 eV increases in depth as the photon energy increases from 110 eV to 130 eV while the double-dip feature at binding energies of 6.8 and 7.7 eV is only visible in the difference between spectra excited at a photon energy of 130 eV.

A theoretical study [9] calculated the expected DOS difference between the valence band of $\text{Au}_{95}\text{Pd}_5$ and that of metallic Au. Most of the features were obtained also using a calculated DOS of pure Au with random vacancies, instead of the $\text{Au}_{95}\text{Pd}_5$. By comparing our experimental results with the theoretical difference spectrum obtained from [9] and shown by the lower full curve in figure 3, we see that there is generally good agreement between theory and experiment for the positions of the maxima and minima observed in the

difference spectra. Variations in photon energy lead to differences in the experimental intensity of features predicted by theory but not in their binding energies. The only significant deviation from this observation occurs for the region at around 4 eV in binding energy where a deep minimum in the theoretical results is not present in our data. The difference between theory and experiment in this energy region is ascribed to the effect of the photoionization cross section matrix element, as was previously found by comparing the theoretical and He I UPS difference spectra [7]. The intensity behaviour of the minimum **a**, which goes through a minimum at $h\nu = 130$ eV (an energy value very close to the one where the VBS CM occurs), and the asymmetric shape of the VBS can instead be ascribed to an interaction between the Pd impurity 4d and the host 5d states.

It is well known that the intensity ratio of the two spin-orbit-derived features in the spectra of the 5d band of pure Au are very sensitive to the photon energy in this photon energy range. In particular the intensity ratio of the two features is observed to reverse between $h\nu = 120$ and 130 eV [24]. This sensitivity is also present in the spectra of the Au 5d band of the alloy studied here. The difference curves show that there is also an influence of the interaction between the Au 5d and Pd 4d states in the binding energy region between 5 and 8 eV, where the intensity of the structures **b** and **c** changes significantly with $h\nu$ varying between 100 and 140 eV, and revealing a different behaviour of the relative intensity of the spin-orbit-split Au 5d bands with respect to pure Au.

4. Conclusions

We have studied the photon energy dependence of the photoemission spectrum of the valence band of Au₉₅Pd₅ in the range where the Cooper minima effect for the Au 5d and Pd 4d states occurs. The Pd 4d-derived VBS shows an intensity behaviour which is ascribed to a high degree of distortion of the Pd 4d radial wavefunction caused by an interaction between the Au 5d and Pd 4d states. We have also derived difference spectra for the difference between Au₉₅Pd₅ and pure Au that reveal features occurring at the same binding energies as features found in the differences between theoretically calculated DOS. These features were also obtained theoretically using a DOS with vacancies instead of the one with the alloy. However, the relative intensities of these features vary with photon energy, a result that we attribute to the interaction of the Au 5d states with the Pd 4d VBS.

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