

The use of Cooper minima effects and resonant photoemission in the study of the electronic structure of dilute alloys

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Abstract. It is shown that photon energy dependent photoemission, using a synchrotron radiation source, is a useful tool in studying the electronic structure of alloys. In AuNi a satellite structure at 1.9 eV is identified using a combination of cross-section effects and resonant photoemission. A model calculation is used to show that our observations are consistent with the magnitude of parameters describing the electronic behaviour in terms of correlation and hybridisation, obtained from other techniques.

Recently various studies of dilute alloys of 3d metals in noble metal hosts using electron spectroscopy techniques have been reported (Reehal and Andrews 1980, Andrews and Brown 1981, Bosch *et al* 1982, 1984, van der Marel *et al* 1984, 1985b). The reason for this interest is that these alloys represent 'zero-bandwidth' 3d systems, making them suitable for the study of electron correlation in solids.

It is well established that Ni impurities in Au have a 3d occupation of 9.3–9.5 electrons (Bosch *et al* 1982, 1984, Julianus *et al* 1981). This partial d occupation gives rise to satellite structure in the Ni2p XPS spectrum, which can be understood as reflecting $2p^5d^9$ local final-state configurations. The many-body behaviour of Ni3d electrons leads one to expect satellite structure also in the UPS spectrum of AuNi. However, a crude calculation shows that this part of the Ni local density of final states is likely to fall inside the Au5d band, which extends from 2 to 8 eV below the Fermi level ϵ_F .

In this paper we present photon energy dependent photoemission data on Au, AuCu and AuNi. Utilising the strongly different energy-dependent Au and Ni d cross section (Goldberg *et al* 1981), we determine the local Ni3d partial density of states. Using resonant photoemission (Guillot *et al* 1977, Kakizaki *et al* 1983), we demonstrate the presence of a Ni d⁸-like satellite, which occurs primarily inside the Au5d band. Recently published Auger theory (Vos *et al* 1984a, b) is used to establish the energetics of the d⁸ structure and the d–d Coulomb interaction.

Valence band photoelectron spectra of samples of Au, AuCu (5.0 at.% Cu) and AuNi (4.8 at.% Ni) were taken at the synchrotron radiation centre at Daresbury. The photon energy $h\nu$ ranged from 40 eV to 200 eV. The resolution is limited by the linewidth of the

incident radiation, which is 0.5 eV at $h\nu = 40$ eV and 1.1 eV at $h\nu = 160$ eV. The alloys were prepared from the melt under argon atmosphere. The samples were cleaned by sandpapering, polishing and argon bombarding. We did not anneal, to avoid surface enrichment of one of the components.

In figure 1(a) AuCu spectra are shown at different photon energies, clearly exhibiting strong energy-dependent cross-section effects. For comparison we show the corresponding spectra of pure Au in figure 1(b). In figure 1(c) difference spectra are given calculated from figures 1(a) and 1(b). To obtain the difference spectra, we first corrected the spectra for background and scaled them to the Au peak at 6 eV, as in this region little impurity density of states is expected. Also the effect of dilution on the Au5d density of states is small at this energy, as will be demonstrated later (figure 6). The relative Cu contribution to the spectra is largest at photon energies near the Cooper minimum (Cooper 1962) of Au (180 eV; Goldberg *et al* 1981). The maximum in the Cu local density of states is at 2.6 eV. These are in principle interesting results for a more detailed analysis to determine the local impurity partial density of states and the effects of Cu3d–Au5d hybridisation and lattice relaxation (van der Marel *et al* 1985a). The resolution of the present data, however, is not sufficient for such a detailed analysis. We present these data here primarily to demonstrate

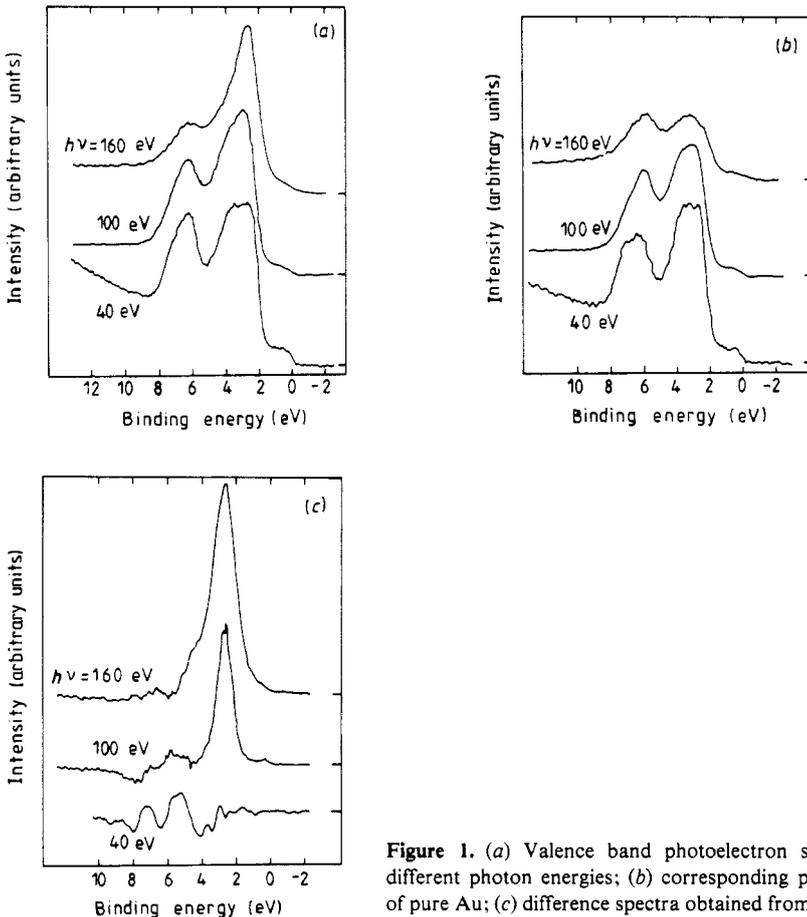


Figure 1. (a) Valence band photoelectron spectra of AuCu at different photon energies; (b) corresponding photoelectron spectra of pure Au; (c) difference spectra obtained from (a) and (b).

the usefulness of photon energy dependent studies in determining the electronic structure of impurities in metals.

In figures 2(a) and (b) the photoelectron spectra and the difference spectra of AuNi are shown at several photon energies. Clearly an impurity peak is shown near the Fermi level. Position E_d and width Δ of this peak were determined by Bosch *et al* (1984) by means of high-resolution UPS: $E_d = 0.5$ eV; $\Delta = 0.25$ eV. However, in these experiments a photon energy of $h\nu = 21$ eV was used, giving a very unfavourable Ni3d/Au5d cross-section ratio. To illustrate the cross-section effect the ratio of this Ni peak to the Au peak at 6 eV is shown in figure 3, and compared with the atomic Ni3d/Au5d cross-section ratio as calculated by Goldberg *et al* (1981). The scales differ by a constant factor which is caused by the ratio of constituent elements in the alloy, which accounts for a factor of 20, and by the differences in broadening and occupation of the Ni3d and Au5d states.

As the ground state of AuNi is of mixed Ni3d⁹-d¹⁰ character, ionisation from a Ni impurity state will result in d⁸-, d⁹- and d¹⁰-like final states, mixed with host conduction band states. From Auger studies (Antonides *et al* 1977) the average d⁸ energy is known to be about 3–3.5 eV higher than twice the 3d⁹ energy because of the Coulomb repulsion U between two holes in the d⁸ state. If U is much larger than the one-hole bandwidth the d⁸ final states can be treated separately. In the simplest model the peak at 0.5 eV is associated with mixed d⁹-d¹⁰ final states. Its width is determined by the hybridisation Δ_h with the Au conduction band and by the spin-orbit coupling and crystal field splitting on the Ni atom. From this it is concluded that $\Delta_h \approx 0.1$ eV, which is indeed much smaller than U (Bosch *et al* 1984).

As the photon energy exceeds the threshold of the Ni3p→3d optical absorption, a second process involving a Ni3p→3d optical transition followed by Auger decay of the 3p hole interferes coherently with the direct photoemission process. The cross section of

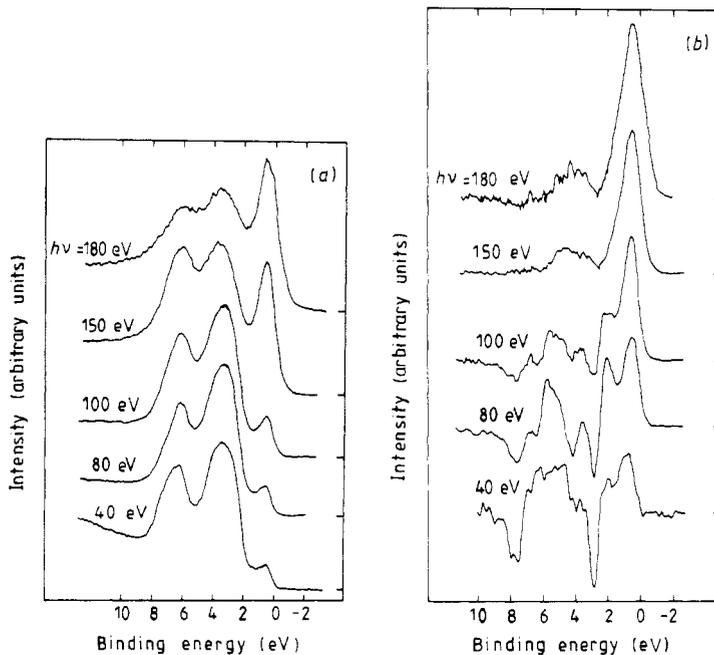


Figure 2. (a) Valence band photoelectron spectra of AuNi at various photon energies; (b) difference spectra obtained from (a).

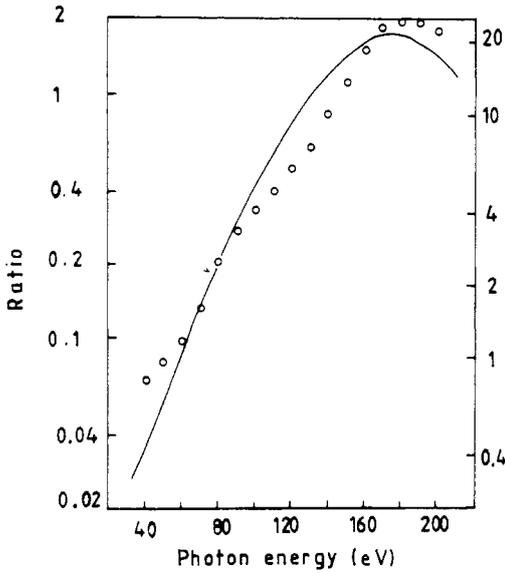


Figure 3. Calculated Ni3d/Au5d cross-section ratio obtained by Goldberg *et al* (1981) (drawn curve, right scale) as compared with the ratio of experimental peak heights (circles, left scale).

ionisation into d^8 -like final states is enhanced in this photon energy region, as only these states can be reached by the interfering two-step process. This means that at $h\nu \simeq 68$ eV we expect a strongly resonant enhanced satellite, while the main line will show a weak antiresonance (Davis and Feldkamp 1981). Photoemission spectra of AuNi for $h\nu$ around 68 eV are shown in figure 4(a). In the spectra at $h\nu = 68$ and 69 eV a weak shoulder is visible on the low-energy side of the Au5d band at ~ 2 eV below ε_F . The corresponding difference spectra are shown in figure 4(b). From these we deduce the satellite energy $\varepsilon_s = 1.9 \pm 0.2$ eV. In figure 5 we plot the height of main line and satellite as a function of photon energy. The behaviour is in qualitative agreement with the calculations of Davis and Feldkamp (1981) for Ni metal.

In order to describe the d^8 portion of the photoelectron spectrum we resort to the theory used to describe the d-d Auger spectra of impurities in metals (Vos *et al* 1984a). Because U is large compared to Δ_h , the d^{9-10} and d^8 -like final states hardly mix and therefore can be treated independently. The problem is that the d^8 spectral weight is situated inside the Au5d band and therefore these Ni states will strongly hybridise with the Au5d band states. This mixing and the hybridisation with the Au sp conduction band can be described by a combined Anderson-Clogston-Wolff Hamiltonian as discussed by Vos *et al* (1984a) and van der Marel (1985b). In general this Hamiltonian is

$$\mathcal{H} = \sum_{\sigma} \left[\sum_{nk} \varepsilon_{nk} C_{nk\sigma}^{\dagger} C_{nk\sigma} + \sum_m \left(\sum_l \eta_l d_{lmo}^{\dagger} d_{lmo} + (\varepsilon_{dm} - \langle \eta_l \rangle) d_{0mo}^{\dagger} d_{0mo} \right. \right. \\ \left. \left. + \sum_{nk} V_{nkm} (C_{nk\sigma}^{\dagger} d_{0mo} + d_{0mo}^{\dagger} C_{nk\sigma}) \right) \right] + \mathcal{H}_c.$$

Here ε_{nk} describes the dispersion of the Au sp band and η_l that of the d band. The indices n and m label the four sp bands and the d orbital degeneracy. It must be noted that by taking

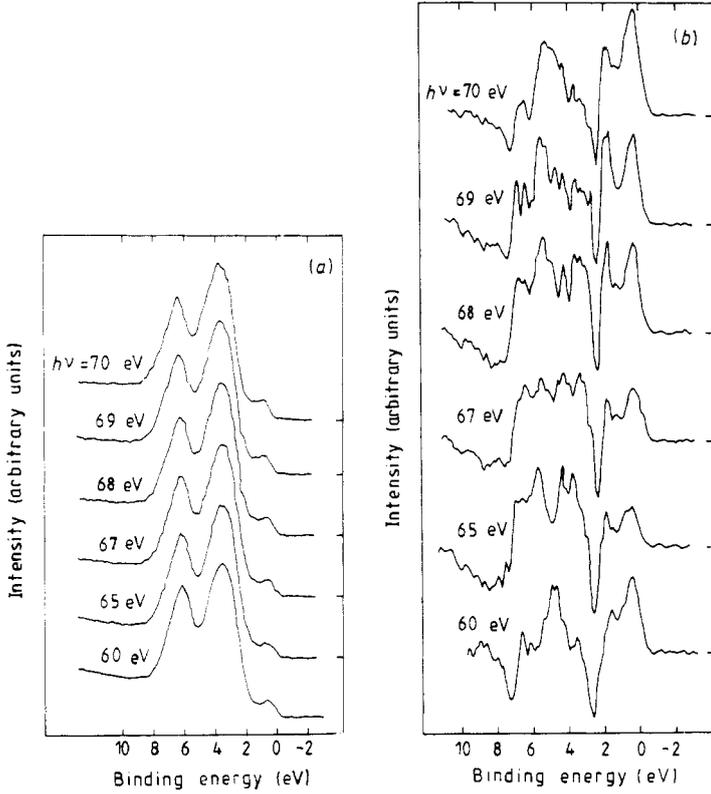


Figure 4. (a) Valence band photoelectron spectra of AuNi at photon energies around the Ni3p core hole energy; (b) difference spectra obtained from (a).

η_l independent of m it is assumed that all 5d orbitals give the same contribution to the Au5d density of states. This means that crystal-field and spin-orbit effects are neglected. $\epsilon_{dm} - \langle \eta_l \rangle$ is the average impurity energy relative to the Au5d band centroid; $d_{0m\sigma}^\dagger$

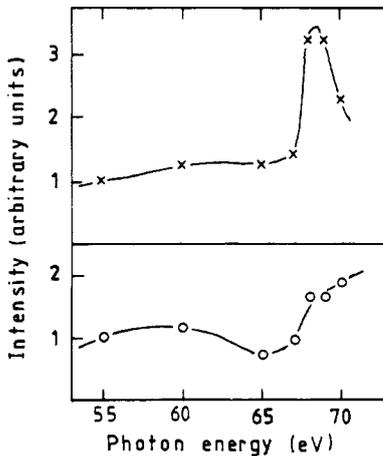


Figure 5. Intensities of main line (O) and satellite (x) as a function of photon energy.

creates a d electron at site 'zero' and is given by

$$d_{0m\sigma}^{\dagger} = N^{-1/2} \sum_l d_{lm\sigma}^{\dagger}.$$

V_{nkm} is the hybridisation of the impurity state with the Au sp band. \mathcal{H}_c represents the correlation between d electrons on the same impurity atom. This two-particle part of the Hamiltonian can in general be written

$$\mathcal{H}_c = \sum_{ijpq} U_{ijpq} d_{0i}^{\dagger} d_{0j} d_{0p}^{\dagger} d_{0q}$$

in which i, j, p, q combine the indices m and σ .

In working with difference spectra, one has to take into account the effect of dilution of the gold. In replacing Au atoms by Ni atoms, the hybridisation of Au5d functions is decreased, so the Au5d band is narrowed. This gives rise to wiggled structures in the difference spectrum in the energy range of the Au5d band. These can be estimated by considering the limit for $\varepsilon_{dm} \rightarrow \infty$, representing a vacancy in the gold lattice (van der Marel 1985b). It is found that there is a dilution contribution to the difference spectrum:

$$\Delta\rho \propto \pi^{-1} \text{Im} [(\delta/\delta\omega)\Gamma_{\text{exp}}/\Gamma_0^0]$$

where

$$\Gamma_0^0 = \sum_l (\omega - \eta_l)^{-1}$$

is the theoretical Au5d Green function, neglecting the host d-sp hybridisation, and Γ_{exp} is obtained from the pure host UPS spectrum:

$$I_d(\omega) = \pi^{-1} \text{Im} \Gamma_{\text{exp}}.$$

In figure 6 we show the curve of $\Delta\rho$, calculated from the pure host spectrum for $h\nu = 100$ eV (figure 1(b)) and using the interpolation calculation of the Au5d density of states from Smith *et al* (1974). The result is compared with the observed difference spectrum for AuNi at $h\nu = 100$ eV (figure 2(b)). From this comparison it may be concluded that the feature at 2 eV in the difference spectra is indeed due to Ni.

Since we are interested in the local two-hole density of states, we consider matrix elements of \mathcal{H}_c between d^8 states. Neglecting the crystal field, we can use LS basis states. The local two-hole Green function corresponding to a Ni d^8 -like satellite is then given by the relation (Sawatzky 1977)

$$G_{LS}^{LS} = \frac{g_0^0 \otimes g_0^0}{1 - U_{LS} g_0^0 \otimes g_0^0}$$

where \otimes refers to a convolution, g_0^0 is the one-hole impurity Green function and U_{LS} depends on the state in LS coupling.

If we approximate the environment of the impurity as spherically symmetric, the one-electron part of the Hamiltonian can be split into ten independent similar parts:

$$\mathcal{H}_1 = \sum_{k'} \varepsilon_{k'} C_{k'}^{\dagger} C_{k'} + \sum_l \eta_l d_l^{\dagger} d_l + (\varepsilon_d - \langle \eta_l \rangle) d_0^{\dagger} d_0 + \sum_{k'} V_{k'} (C_{k'}^{\dagger} d_0 + d_0^{\dagger} C_{k'})$$

where k' labels the appropriate part of the Au sp states. If we consider a constant Au sp

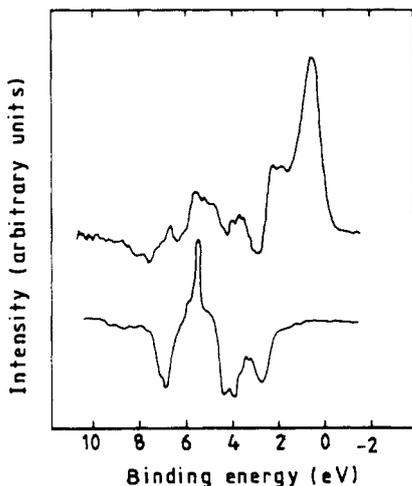


Figure 6. Calculated dilution contribution to the difference spectrum at $h\nu = 100$ eV (lower curve), as compared to the experimental difference spectrum of AuNi at $h\nu = 100$ eV (upper curve).

band density of states ρ and constant $V = V_{k'}$, we obtain from the above Hamiltonian for the impurity one-hole Green function g_0^0 :

$$g_0^0 = \frac{\Gamma_0^0}{1 - (\varepsilon_d - \langle \eta_l \rangle + i\pi V^2 \rho) \Gamma_0^0}$$

This consists of a lorentzian peak near ε_F plus a contribution in the region of the Au5d band. In figure 7(a) we show the result of a calculation in which we chose for Γ_0^0 a band consisting of two semicircles, resembling the Au5d band. The parameters $\varepsilon_d = 1.1$ eV and $V^2 \rho = 0.25$ eV are chosen in order to have g_0^0 resemble the part of the measured spectrum near ε_F .

In order to determine the satellite structure we require values of U_{LS} for the various possible d^8 -like final states. These states are 3F , 3P , 1D , 1G , 1S and the U values are determined by combinations of the Slater integrals F^0 , F^2 and F^4 (Slater 1960). From Auger spectroscopy, which is dominated by the 1G final state, $U(^1G)$ values for a large number of Ni alloys have been found and they are all in the range 3.0–4.5 eV (Bennett *et al* 1983). From Auger studies it has also been shown that the F^2 and F^4 integrals which determine the multiplet splittings are nearly independent of the environment and retain their atomic values in the solid (Antonides *et al* 1977). We take values of $F^2 = 9.6$ eV and $F^4 = 6.4$ eV as found for Ni metal and La_3Ni (Fuggle *et al* 1982).

The relative intensities of the various multiplets in photoemission are given by the coefficients of fractional parentage f_{LS} , which in this case are very close to the multiplicities:

$$I_{\text{sat}}(\omega) = \pi^{-1} \sum_{LS} f_{LS} \text{Im } G_{LS}^{LS}$$

The largest intensity is therefore expected for the 3F state which is also the lowest-energy d^8 state. Without hybridisation with the Au5d band, the $\text{Ni}3d^8$ 3F state is expected to be at $U(^3F) + 2\varepsilon_d \simeq 2.7$ – 4.2 eV. In figure 7(b) we show calculated satellite spectra for $U(^3F)$ values ranging from 0.5 to 2.0 eV. In these cases a 'bound state' of 3F character is pushed

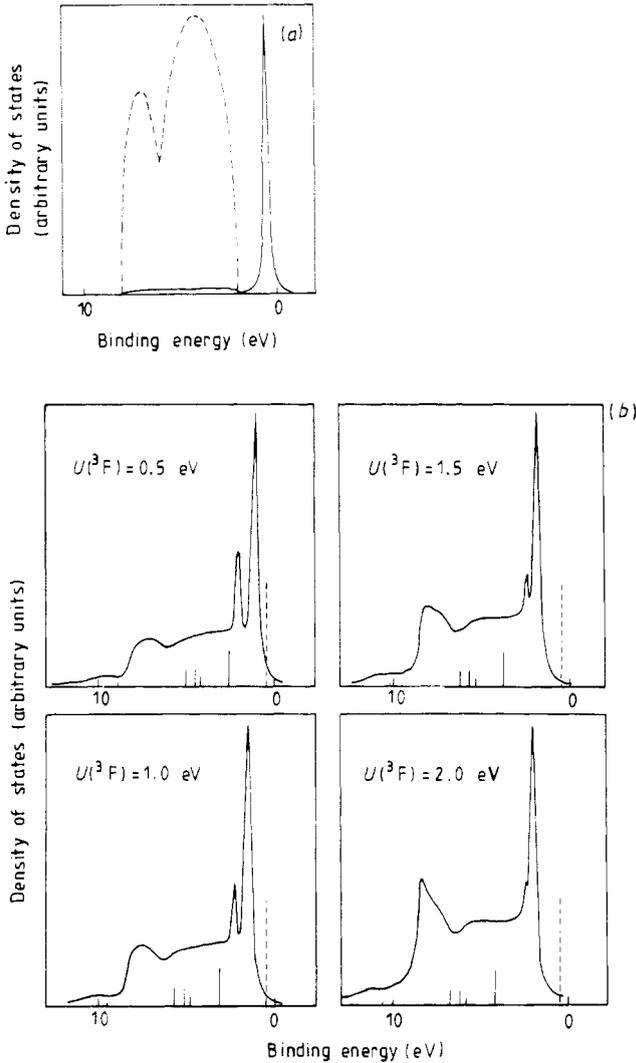


Figure 7. (a) Model density of states as used in our calculations. The dotted curve is the host d band and the full curve is the impurity one-hole density of states. (b) Calculated two-hole densities of states for various values of the Coulomb interaction. The bars show the positions of the unhybridised 1S , 1G , 3P , 1D and 3F states for a $3d^8$ configuration respectively. The dotted line shows the position of the hybridised Ni d^{9-10} peak.

out of the top of the Au5d band, resulting in a sharp feature as observed experimentally (figure 4(b)). The 1D , 3P , 1G and 1S states contribute to a total broad intensity distribution inside the Au5d band, making these difficult to identify experimentally. In our model the position of the observed satellite is reproduced best for $U(^3F) = 1.5\text{--}2.0$ eV. Taking into account the uncertainty in the position of the top of the Au5d band, this corresponds to a value of the Slater integral $F^0 = 3.5 \pm 0.5$ eV.

It must be noted that in our calculation we neglected the Au5d spin-orbit splitting, treating the 5d bandwidth as arising from Au d-d overlap only. Including it in the manner discussed by van der Marel *et al* (1985a) gives some minor changes in the calculated

satellite spectrum, which are not relevant in view of the poor resolution of our measurements.

From the reasoning so far it is clear that the peak at 2 eV, visible in the resonant spectra at $h\nu = 68$ and 69 eV and in most of the difference spectra, is attributed to a 3F -like Ni two-hole final state. For $h\nu > 100$ eV the peak diminishes in intensity. This is due to the inferior resolution at higher photon energies. Furthermore the peak contains appreciable Au5d character and the Au5d cross section is decreasing. This also accounts for the diminishing 'vacancy effect' at higher photon energies, leaving a broad Ni satellite contribution in the region 2–6 eV at $h\nu = 180$ eV (figure 2(b)).

From our measurements we could only derive an approximate value for U , but this value is consistent with results from other data (Antonides *et al* 1977, Bennet *et al* 1983). In summary, it is demonstrated that photon energy dependent photoemission, utilising cross-section effects, Cooper minima and resonant effects, is an extremely useful tool in the study of the electronic structure of dilute transition metal alloys.

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