The virtual bound states of Fe in AuFe studied by photoemission

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Abstract. By using synchrotron radiation photoemission with photon energies near to the Cooper minimum of Au we have detected virtual bound states (VBS) in $Au_{90}Fe_{10}$. A VBS peaking 0.7 eV below the Fermi energy is attributed to Fe minority states. Less intense features are observed at about 2.3 eV, 4–5.5 eV and 7.3 eV below the Fermi energy, close to the edges of the Au 5d bands, which we suggest are due to the Fe majority states broadened by strong hybridization with the Au valence band. These observations agree with the Friedel–Anderson model which predicts non-degenerate virtual levels with the majority spin population completely occupied and with the minority states spanning the Fermi level.

1. Introduction

The electronic structure of an alloy system with a small amount of 3d metal dissolved in a noble metal host has been studied extensively in recent years (Rizzuto 1974, Grüner 1974, Bosch *et al* 1984, Hüfner 1979, Grüner and Zawadowski 1974). In such 'zero-bandwidth' systems the 3d solutes can develop localized magnetic moments. Various theoretical models have been developed to explain the effect of a virtual bound state (VBS) resonance of the 3d impurity upon the host (see Grüner and Zawadowski 1974), of which the Friedel–Anderson model (Friedel 1958, Anderson 1961) is one of the most successful in terms of its physical simplicity, its assumptions and its agreements with experimental results.

For a non-magnetic impurity the impurity state is filled equally by spin-up and spin-down electrons. The existence of a magnetic moment on the impurity depends upon the VBS for the impurity spin-up and spin-down electrons being split about the Fermi level by the Coulomb exchange interaction. AuFe is a classic spin glass. Magnetic susceptibility measurements (Hurd 1967) show the $Au_{90}Fe_{10}$ alloy to be magnetic and so it is expected that there should exist Fe 3d minority spin states spanning the Fermi level. Support for this idea comes from optical reflectivity measurements (Beaglehole and Hendrickson 1969) showing a peak at 4–5 eV below the Fermi edge which was interpreted as experimental evidence of the impurity spin majority states.

If the electronic states of the impurity hybridize with those of the host metal valence band then band repulsion is expected, with the intensity of the majority spin VBS spread throughout the Au 5d bands and small peaks appearing near gaps in these bands. Weak mixing, on the other hand, is expected to lead to a sharply peaked majority VBS, with all the intensity within a narrow band not overlapping the Au 5d band. The impurity virtual bound states, and the difference between weak and strong mixing with the host valence bands, should be observable by photoelectron spectroscopy.

In fact photoemission studies of **AuFe** using He I and He II ultraviolet photons at $h\nu = 21.2$ eV and 40.8 eV (Reehal and Andrews 1980) show that there is a slight increase in intensity below the Fermi edge in the AuFe spectrum compared with a pure Au spectrum. Measurements using Al $K\alpha$ x-rays at $h\nu = 1486.6$ eV (Höchst *et al* 1980) show no clearly discernible feature attributable to the Fe. The problem in observing the VBS using conventional ultraviolet or x-ray photon sources is that at these energies the Fe 3d photoionization cross section is smaller than that of the Au 5d levels by a factor of between about 5 and 100 (Goldberg *et al* 1981, Yeh and Lindau 1985). Using synchrotron radiation it is possible to tune the energy of the photons to the Cooper minimum (Cooper 1962) of the Au 5d levels thus enhancing the relative intensity of the signal from the Fe 3d states. This technique has been used in several previous investigations of alloys (e.g. Wright *et al* 1987, Folkerts *et al* 1987, Greig *et al* 1989).

2. Experimental procedure

The AuFe alloy, with 10 atomic % Fe, was prepared by arc melting together the high purity components on a copper hearth in an atmosphere of argon. The specimen was homogeneous and was cold rolled prior to use to reduce the thickness of the ingot to a suitable value (about 1mm). A 99.99% pure Au specimen was rolled to a similar thickness and mounted on the manipulator with the $Au_{90}Fe_{10}$ sample so that a direct comparison of the two could be made.

The experiments were performed on beamline 6.1 at the Daresbury Synchrotron Radiation Source (SRS). The base pressure in the chamber was in the low 10^{-10} mbar range throughout the course of the experiments, and the sample was kept at room temperature. Photoelectron spectra were collected using a commercial (PHI) double pass cylindrical mirror analyser. The specimens were cleaned by mechanical scraping with a tungsten carbide blade. Photoemission from the O 2s level was monitored as a measure of surface cleanliness and a new surface created when an increase was seen in that region: using photon energies near to the O 2s threshold, this method is more sensitive than conventional Auger electron spectroscopy excited by high energy electrons.

For the experiments we used photons in the energy range 40–160 eV. The Cooper minimum of Au actually lies around $h\nu = 200$ eV (Folkerts *et al* 1987, Goldberg *et al* 1981, Yeh and Lindau 1985) but the flux from the monochromator (Howells *et al* 1978) is decreasing rapidly in this range, and the bandwidth $\Delta h\nu$ is increasing: $h\nu = 160$ eV is a compromise energy, adequate to show the effect. The overall resolution was estimated by fitting the Fermi edge of the pure gold specimen with a convolution of a step function and a Gaussian the width of which is equivalent to the resolution. This procedure was satisfactory only in the 40–130 eV energy range since at higher photon

energy the d contribution in the Au valence band was broadened up to the Fermi edge. In this range the resolution was found to depend linearly on the photon energy from 0.5 eV to 0.85 eV.

3. Results and analysis

Figure 1 shows the raw data, normalized to allow for the decay of the SRS beam current with time, for the valence band of $Au_{90}Fe_{10}$ at photon energies of 40 eV and 160 eV. Owing to the characteristics of the monochromator these two spectra were taken with resolutions of 0.5 eV and 1.6 eV respectively. The spectra also have different backgrounds due to scattered electrons.
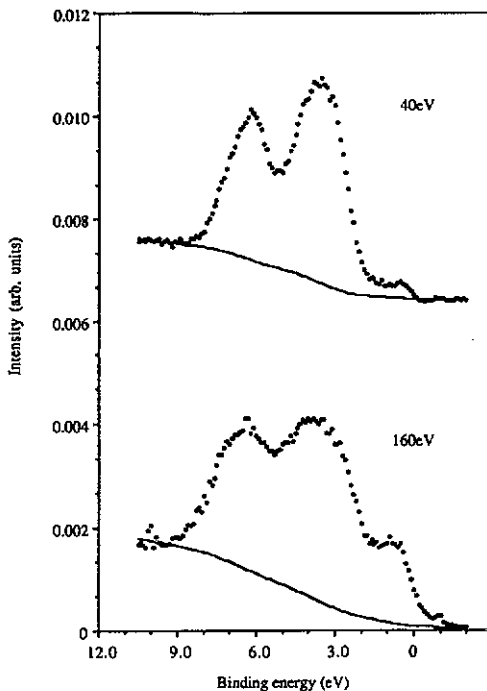

Figure 1. Photoemission spectra of $Au_{90}Fe_{10}$ valence band at photon energies of 40 eV and 160 eV. The computed backgrounds are shown as full curves.

So that the spectra taken at the two photon energies can be directly compared we correct for the variation in resolution with energy by convolving the spectrum excited with 40 eV photons with a Gaussian of 1.6 eV FWHM. We also subtract from each spectrum a background, the shape of which is proportional to the integral of that spectrum to higher kinetic energy (first described by Shirley (1972)). The constant of proportionality is chosen to bring the counts to zero in the region just above the Fermi energy and at the bottom of the d band on the high binding energy side; the background is shown as a full curve in figure 1. Figure 2 shows the spectra with this background subtracted and also the 40 eV spectrum broadened, along with a difference spectrum, the 40 eV spectrum being subtracted from that at 160 eV. Similar measurements for the pure Au specimen, analysed in the same way, are shown in figure 3.
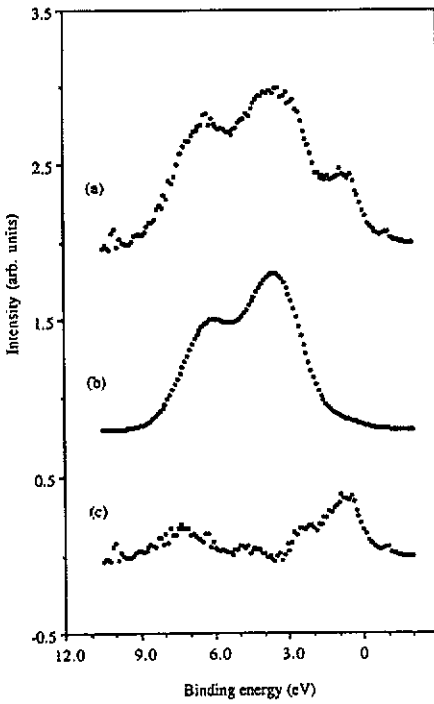
Figure 2. $Au_{90}Fe_{10}$ valence band spectra after background subtraction. (*a*) $h\nu = 160$ eV. (*b*) $h\nu = 40$ eV after broadening (see text). (*c*) Difference between (*a*) and (*b*).
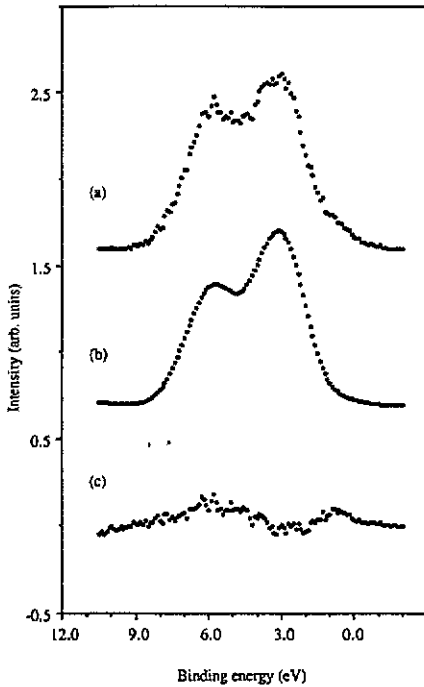

Figure 3. Au valence band spectra after background subtraction. (*a*) $h\nu = 160$ eV. (*b*) $h\nu = 40$ eV after broadening (see text). (*c*) Difference between (*a*) and (*b*).

The $Au_{90}Fe_{10}$ difference spectrum shows a peaked structure at 0.7 eV below the Fermi energy which we interpret as the iron virtual bound state for minority spin. For pure Au the difference spectrum does not show this peak; however it does have a contribution to the intensity in this region. This is due to the influence of the 6sp electrons on the difference between the spectra taken at 40 eV and 160 eV since the cross sections of the 6sp electrons are approximately constant over the photon energy range used while the 5d cross section approaches a minimum (Goldberg *et al* 1981, Yeh and Lindau 1985). The Au 6sp electrons might also be expected to contribute to the results for $Au_{90}Fe_{10}$. To allow for this we have subtracted the Au difference spectrum from the $Au_{90}Fe_{10}$ difference spectrum and plot this in figure 4(*c*).

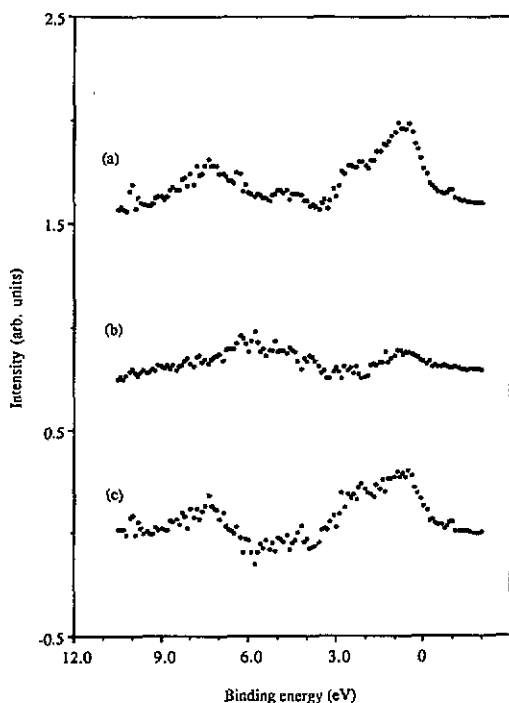**Figure 4.** Difference spectra of $Au_{90}Fe_{10}$ and Au valence bands. (*a*) $Au_{90}Fe_{10}$ difference between 160 eV and 40 eV photon energies, as in figure 2(*c*). (*b*) Au difference between 160 eV and 40 eV photon energies, as in figure 3(*c*). (*c*) Difference between (*a*) and (*b*), showing Fe virtual bound states.

The comparison of the two sets of $Au_{90}Fe_{10}$ spectra and the comparison of the difference of the $Au_{90}Fe_{10}$ data with the equivalent results for pure Au clearly show the Fe minority spin VBS peak in $Au_{90}Fe_{10}$. Further features are observed at binding energies of about 2.3 eV, not well resolved from the 0.7 eV state, and at about 7.3 eV. There is a hint of intensity at 4–5.5 eV below the Fermi level. It is clear that there is no strong peak at the top edge of the Au 5d band, as would be expected from weak mixing of Fe 3d and Au 5d states.

4. Discussion

For transition metal impurities in noble metal hosts, alloying can have two effects:

it may disturb the lattice and thus the host band structure and it may produce new localized states. Extracting the contribution from the impurity states then becomes complicated by the change in band structure. To correct for this the impurity systems can be compared to the pure host or to a different impurity system where the impurity has a similar ionic radius and similar charge difference but has fully occupied d states outside the valence band region (as used in varying degrees by Reehal and Andrews 1980, Höchst *et al* 1980 and Millar 1987). However the hybridization between the alloy and impurity d bands is not the same for different impurities so such a comparison is unlikely to be valid. Also a comparison of two such systems to establish the presence of a VBS due to one of the impurities is not a straightforward procedure and depends upon the way the spectra are normalized. Using synchrotron radiation, however, it is possible to compare spectra of the same sample at different energies and also to work near the Cooper minimum region of the noble metal increasing the relative spectral weight of the 3d transition metal. Thus the localized states of the impurity can be obtained and band structure alterations can be corrected by the comparison of spectra of the same specimen with different photon energies. That is the crux of this work.

In $Au_{90}Fe_{10}$ the Fe impurity atoms carry a local moment. Magnetic susceptibility measurements (Hurd 1967) give a magnetic moment of $3.68\mu_B$ corresponding to a spin of 3/2 which suggests a $3d^7 4s^1$ configuration of the Fe impurity, the $4s^1$ being itinerant in the solid. The Friedel–Anderson model gives rise to non-degenerate virtual levels with the majority spin population completely occupied and the minority one spanning the Fermi energy.

Our results demonstrate that there is a VBS for the occupied minority spin population 0.7 eV below the Fermi energy. This is in agreement with the previous data (Reehal and Andrews 1980) which showed an increase in intensity at about 0.7–0.9 eV below the Fermi energy, tentatively identified as a Fe impurity VBS. The low resolution does not allow a precise estimation of the width of this state. However the measured width of the VBS (FWHM about 1.3 eV) is comparable with the experimental bandwidth suggesting that the actual width is quite small.

The majority spin states are completely occupied so it is to be expected that this structure will be more intense than that due to the minority states. However, we suggest that the majority contribution is much broader than the minority contribution and hence although it is more intense, it is harder to discern. We do not see the sharp peak predicted by the non-self-consistent calculations of Weinberger and collaborators (Weinberger 1982, Weinberger *et al* 1990). We suggest that the weaker features observed at about 2.3 eV, 4–5.5 eV and 7.3 eV below the Fermi energy are due to the Fe majority states, considerably broadened by strong hybridization with the 5d electrons of the Au valence band. As expected under this model, our observed features appear close to the edges of the Au 5d bands. The idea of broadening is compatible with experimental and theoretical studies of Mn impurities in noble metals (van der Marel *et al* 1984, 1985, Jordan *et al* 1986) which concluded that whereas the impurity minority spin states are localized and span the Fermi level, the majority spin states hybridize with the host d band, to a greater extent than the minority d–s and d–d hybridizations, causing them to delocalize. We propose that such delocalization of the majority states is also happening in $Au_{90}Fe_{10}$.

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