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LETTER TO THE EDITOR

Photoemission measurements of nickel and nickel–iron alloys

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Abstract. We have studied the photoemission from the (110) faces of Ni and two disordered Ni–Fe alloys containing 25% and 50% Fe over the photon energy range 20–45 eV with the aim of investigating their electronic structure. We observe a number of features that disperse with photon energy and we discuss their possible origin.

Despite decades of intense experimental and theoretical activity many of the physical properties of Ni–Fe alloys—particularly those associated with the Invar phenomenon [1]—are still not fully understood. However, it is well known that properties such as strength, phase stability and magnetism depend on the underlying electronic structure. It is essential, therefore, that realistic and parameter-free models are developed which describe the electronic spectral density because one can then calculate the structurally dependent part of the total electronic energy and determine a range of ground-state properties such as the structure and lattice spacing, the bulk modulus and the magnetic moment. Significant progress has been achieved along these lines during the past four to five years with the development of an *ab initio* calculational scheme, the SCF-KKRCPA, which enables the electronic structure in random alloys to be determined self-consistently. On this basis, Johnson *et al* [2] and Staunton *et al* [3] showed that in Ni–Fe alloys the spin-up and spin-down electrons in the d channel experience considerably different degrees of disorder; the Ni and Fe potentials 'look' very similar to spin-up electrons and so the lifetimes of states in the majority-spin band are much longer than those in the minority-spin band. In addition, Johnson *et al* [4] showed that the calculated magnetic moments in (FCC) Ni–Fe alloys were in good agreement with the Slater–Pauling curve and that they were very sensitive to the lattice constant in the Invar region. Furthermore, Staunton *et al* [3] investigated the compositional order in Ni–25% Fe by calculating the pair correlation functions from the electronic structure. They concluded that the ordering is almost entirely of magnetic origin and is determined largely by the minority-spin electrons.

Since the electronic spectral density plays such a key role in understanding the physical properties of metallic alloys it is important that the results of electronic structure

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calculations are subject to experimental scrutiny. However, experimental work that probes the spin- and *k*-dependent details of the electronic structure in Ni–Fe alloys is rather limited; there are the spin-resolved threshold photoemission studies of Landolt *et al* [5] that provide information concerning the spin character of the density of states at the Fermi level, the photoemission measurements on a range of compositions at two photon energies carried out by Heimann *et al* [6] and Rogge *et al* [7], and a spin-resolved photoemission study of Ni–65% Fe(100) reported by Wassermann [1]. Given the paucity of data, we have embarked upon a study of the electronic structure in Ni–Fe alloys using angle-resolved UV photoelectron spectroscopy and in this letter we describe a series of measurements from the (110) faces of Ni and two disordered (FCC) Ni–Fe alloys containing 25% and 50% Fe. The measurements were made over the photon energy range $20\ \mathrm{eV} \leqslant h\nu \leqslant 45\ \mathrm{eV}$ using the VG ADES spectrometer at station 6.2 on the SRS, Daresbury Laboratory, with a total overall energy resolution of $\simeq 150$ meV. The specimens were cleaned *in situ* by a series of Ar^+ bombardment and annealing (at 600 °C for 30 min) cycles. Auger electron spectroscopy indicated that Ni is preferentially sputtered during Ar^+ bombardment but that after the anneal there was no evidence for any major segregation, in agreement with Rogge *et al* [7], although the possibility of a small enrichment of Fe at the surface cannot be ruled out entirely. (It should be noted that recent model calculations carried out by Modak and Khanra [8] suggest that segregation of Fe to the surface is expected in Ni-rich alloys.) 1 × 1 LEED patterns with sharp spots were obtained with no evidence of ordering. The ordering of Ni–25% Fe is known to be sluggish but we made additional careful checks by x-ray diffraction studies to ensure that the alloy specimens remained compositionally disordered after the anneal. The spectra we show here were all collected at normal emission using p-polarised light at an incidence angle, φ, of 30° in either the (001) or $(1\bar{1}0)$ plane, and they are normalised to maximum intensity.

For a number of reasons particular caution needs to be exercised when comparing photoemission spectra from Ni–Fe alloys with electronic structure calculations based on local density (LD) functional theory. Firstly, it must be borne in mind that photoemission probes the electronic structure of a bounded system rather than that of the infinite lattice. Secondly, one should consider the quasi-particle excitation spectrum rather than the one-electron LD eigenvalues; in view of the presence of an unfilled d band—and taking Ni as an example [9]—the many-body corrections to the LD electronic spectral density in Ni–Fe alloys are likely to be significant and dependent on spin, angular momentum and $\boldsymbol{k}$. Thirdly, according to the SCF-KKRCPA calculations [2, 3] the disorder broadening in Ni–Fe alloys, which has a direct influence on the width of peaks in photoemission spectra, is spin dependent and varies with energy and $\boldsymbol{k}$ in a complicated way. A calculational scheme has been developed for evaluating the photocurrent from a semi-infinite, disordered system on the same footing as the KKRCPA treatment for the electronic structure [10], but all the calculations carried out so far have involved the non-interacting, single-particle approximation [11]. In principle, photocurrent calculations may be extended by including an appropriate description of the various interactions in the formalism. To our knowledge little work has been attempted along these lines apart from that on Cu [12] and Ni [13–15]. In the absence of appropriate photocurrent calculations a detailed analysis of the experimental spectra on the basis of the recent electronic structure calculations is difficult to achieve.

In order to discuss our photoemission spectra we will refer to the band structure in Ni along the ΓKX direction shown in figure 1, which we calculated by the KKR method using potentials from spin-polarised SCF-LMTO calculations [16]. The bands and critical

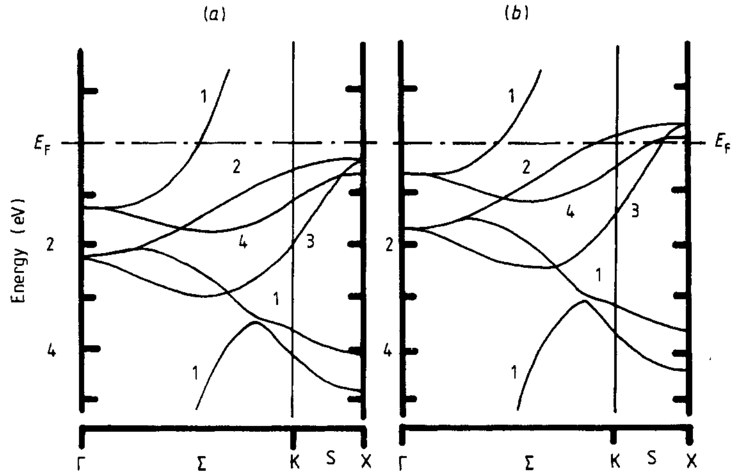

Figure 1. Band structure in pure Ni along the ΓKX direction for (*a*) spin-up and (*b*) spin-down electrons.

points are similar to those determined in previous one-electron calculations, e.g. by Moruzzi *et al* [17]. Since the electronic spectral density in the disordered alloys can be classified using the same symmetries as in pure Ni the same polarisation-dependent selection rules can be applied.

In figures 2(*a*)–(*c*) we show a set of normal emission spectra with the light incident in the $(1\bar{1}0)$ plane. At a given photon energy the spectra are all similar although the various features appear to broaden with increasing Fe content. The spectra are characterised by having considerable intensity between E_F and 0.5 eV, a peak (A) that disperses to increased binding energy with photon energy, and some weight (B) near 2.5 eV in spectra for $h\nu \leqslant 30$ eV. When $h\nu = 20$ eV the emission is from initial states near the X point [14, 18] and so the peak near E_F in figure 2(*a*) corresponds to emission from $X_5^{\uparrow}$ states. The corresponding peaks in the alloy spectra—of Σ_3 symmetry since no increase in intensity occurs when the incidence angle, φ, is increased—move to larger binding energies with increasing Fe content, which is consistent with the off-normal spectra published by Rogge *et al* [7]. They broaden considerably which, we suggest, is a consequence of the increases in spin splitting and disorder broadening with Fe concentration [1]. We identify peak A in figure 2(*a*) as emission from initial states along the S_3/Σ_3 band; see figure 1. At $h\nu = 40$ eV the emission is from states near $k = 0.65$, indicating a self-energy correction of $\simeq 0.7$ eV for the $\Sigma_3^{\uparrow}$ states at this value of k. The corresponding peaks in the alloy spectra seem to occur at smaller binding energies. Although the spin splitting increases with Fe content, the minority-spin states have shorter lifetimes than the majority-spin states and so it is likely that most of the intensity of peak A in the alloys arises from majority-spin initial states. When $h\nu \geqslant 35$ eV the features between E_F and 0.5 eV increase in intensity with φ, indicating that they originate from states of Σ_1 symmetry. Peak B is observed more strongly when φ is increased and has more weight as the Fe content increases. We identify it with emission from the Σ_1 bands near the K and X points, noting that the high density of states region of the lower Σ_1 band, at $k \simeq 0.65$, may well provide the major contribution; similar behaviour was observed by Sakisaka *et al* [19] in pure Ni. The binding energy of peak B shows little

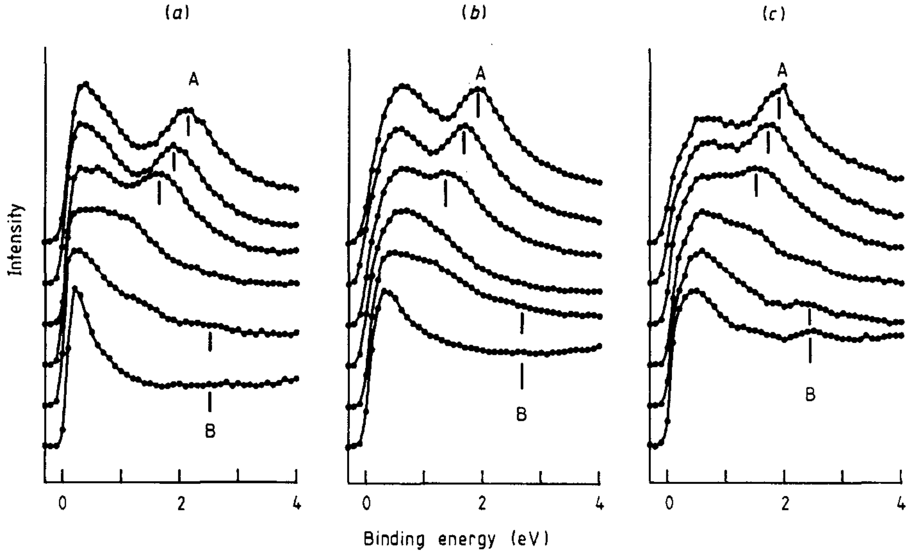

Figure 2. Photoemission spectra at normal emission from the (110) faces of (*a*) pure Ni, (*b*) Ni–25% Fe, and (*c*) Ni–50% Fe. The photon energy increases in 5 eV increments from 20 eV (bottom) to 45 eV (top). The incidence angle is 30° from the normal in the $(1\bar{1}0)$ plane.

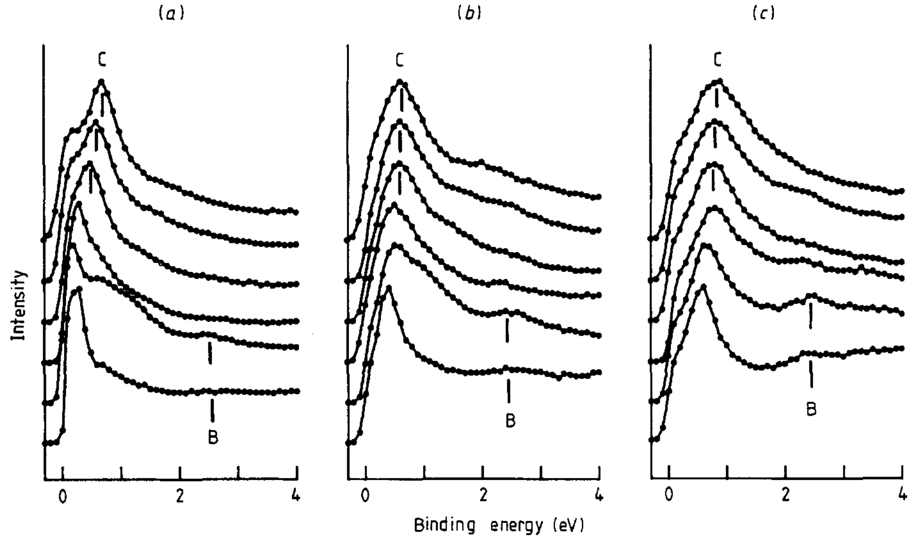

Figure 3. The conditions are the same as in figure 2 except that the light is incident in the (001) plane.

dependence on Fe concentration although there may be a small decrease ($\simeq$0.1 eV) between Ni and Ni–50% Fe.

In figures 3(*a*)–(*c*) we show a set of normal emission spectra with the light incident in the (001) plane. As before, at each photon energy there are features common to all spectra although they appear to broaden with increasing Fe concentration. When $h\nu$ =

20 eV, the peak near E_F in figure 3(*a*) corresponds to emission from $X_2^{\uparrow\downarrow}$ initial states, indicating substantial self-energy corrections to the eigenvalues shown in figure 1 [14]. The corresponding features in the alloy spectra occur at increased binding energies and shoulders are apparent on the leading edges. In all three cases, the peaks correspond to emission from initial states of Σ_4 symmetry since they do not increase in intensity as φ is increased. We suggest that the changes in shape that occur at $h\nu = 20$ eV in figures 3(*a*)–(*c*) are a consequence of the increase in spin splitting with Fe content [1]; the emission from spin-down states appears as a shoulder because their lifetimes are somewhat shorter than those of spin-up states. However, because of self-energy effects, the observed spin splittings—$\simeq 0.2$ eV in Ni [18] and 0.5 ± 0.2 eV in Ni–65% Fe [1]—are substantially smaller than the calculated values. Peak C in figure 3(*a*), which disperses quite strongly, corresponds to emission from initial states along the S_4/Σ_4 band. At $h\nu =$ 40 eV, the emission is from states near $k = 0.65$, suggesting a self-energy correction of $\simeq$ 0.6 eV ($\simeq 0.2$ eV) for the $\Sigma_4^{\uparrow}$ ($\Sigma_4^{\downarrow}$) states at this value of k. The corresponding peaks in the alloy spectra are broader and show less dispersion [7], for instance, at $h\nu = 40$ eV the binding energies are all very similar (i.e. within $\simeq 0.1$ eV). For the reasons stated previously we suppose that most of the intensity of peak C in the alloy spectra arises from spin-up initial states. When $h\nu \geqslant 35$ eV, the weight on the lower binding energy side of these peaks increases with φ indicating the presence of significant contributions from states with Σ_1 symmetry. When $h\nu \geqslant 25$ eV, additional weight appears at $\simeq 1$ eV in the spectra from Ni (and, to a lesser extent, from Ni–25% Fe) which we believe corresponds to emission from the regions of high densities of states at the bottom of the $\Sigma_4^{\uparrow\downarrow}$ bands. The latter are shifted (and broadened) considerably from the values given by one-electron band structure calculations, see figure 1, by self-energy effects [14]. Peaks (B) of Σ_1 symmetry at $\simeq 2.5$ eV binding energy also appear [19] whose origins we discussed above for the other azimuth.

Since the phase shifts in the d channel for the $\mathrm{Ni}^{\uparrow}$ and $\mathrm{Fe}^{\uparrow}$ sites are very similar [2, 3] it is tempting to conjecture that the alloying behaviour of the spin-up bands may be virtual-crystal-like. We might expect, therefore, that the gap between the top of the majority-spin d band and E_F, and the binding energies of peaks A and C, will decrease with increasing Fe concentration, as a result of the reduction in the d-electron count. A close inspection of the spectra in figures 2 and 3 would seem to indicate that this is not the case. However, the situation is complicated by the presence of self-energy effects that are composition dependent [20].

In summary, therefore, we have carried out a series of angle-resolved UV photoemission measurements on Ni and two disordered Ni–Fe alloys in an effort to elucidate their underlying electronic structure. Despite the presence of significant self-energy effects and disorder broadening, we have identified a number of features in the spectra that show dispersion and we have discussed their possible origin. In order to understand further the electronic structure in Ni–Fe alloys we believe that progress will be needed in two areas. Firstly, spin-resolved measurements are required so that the spin character of the various features can be uniquely defined [1]. Secondly, first-principles calculations of the photocurrent [10]—which include the effects of the surface, electron–photon matrix elements and self-energy corrections—are required, to provide a much more useful basis for comparing electronic structure calculations with experimental spectra.

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