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Many-electron effects in x-ray photoelectron spectroscopy as a diagnostic tool for metallic glasses

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We report on x-ray photoelectron spectroscopy observations on the valence bands of $(\mathrm{Ni}_{1-x}\mathrm{Fe}_x)_{77}\mathrm{Si}_{10}\mathrm{B}_{13}$ metallic glasses. The Ni $2p$ core-level spectra show peak asymmetry and satellite positions which are sensitive to changes in the metallic glass composition. We discuss the information content of these many-electron effects and show that addition of Fe causes a decrease in the local density of Ni states per Ni atom at E_F in these glasses.

Since the discoveries twenty years ago by Duwez,[1] concerning the possibilities of the preparation of metals in an amorphous state, there have been a great many publications on these new materials. They have been found to exhibit a great variety of physical properties[2–4] and have already shown potential for various applications. Full understanding of these physical properties is ultimately dependent on the knowledge and understanding of the electronic structure of metallic glasses. This latter presents an enormous challenge because a metallic glass is, by definition, an ensemble of atoms in a disordered state with no long-range periodicity. This absence of periodicity precludes the uses of most of the theoretical methods upon which our understanding of the electronic structure of ordered metals is based (see, e.g., Ref. 5). In this situation experimental studies of the electronic structure take on a doubled importance, and of the experimental methods for studies of the whole of the occupied valence bands the last two decades have shown photoelectron spectroscopy to be the most powerful.[6] In this paper we use x-ray photoelectron spectroscopy (XPS). There have been XPS studies of many metallic glasses[3,7,11] but these have concentrated to a large extent on the single-particle properties, such as chemical shifts of core levels and the shape of the valence band, although there are of course a few papers on core-level asymmetries.[12–14] In this short report we describe results indicating the presence of strong many-body effects on the core-level line shapes in a series of metallic glasses. We show that they may be correlated with ground-state properties, such as the local magnetic moments and can be indicative of the site-selected density of states at the Fermi level. We also show that in the particular case we consider that it is possible to deduce features of the local environment around Ni sites in a metallic glass.

Two forms of many-body effects on core-level line shapes are important here. The first is creation of electron-hole pairs in the valence band simultaneous to core-hole creation (see, e.g., Refs. 12–20). This leads to tailing to the high-binding-energy side of the core-level XPS lines, which is well understood in principle,[20] even if an exact mathematical description is not always possible. The strength of the asymmetry is chiefly determined by the density and symmetry (s, p, d, etc.) of the electronic states near E_F.[12–20] It is most important to note that in an alloy the strength of core line asymmetry predominantly relates to the density of states at E_F whose wave-function amplitude is strong on the site of the core hole created.[12,20] The asymmetry is thus, in principle, a probe of the local density of states.

The second many-body effect we consider is a discrete satellite commonly found in Ni and its compounds and alloys.[12,21–29] In a simplified scheme this satellite arises because the ground state of Ni in a metallic environment can be thought of as a linear combination of atomlike Ni d^9 and Ni d^{10} wave functions:

$$\psi = a\Phi(d^9) + b\Phi(d^{10}) \ . \tag{1}$$

The $\Phi(d^n)$ include the appropriate s electrons and are nearly degenerate in the ground state of a solid. A Ni core hole in the XPS final state results in a lowering of the energy of the d^{10}-like configuration with respect to the d^9-like configurations. This results in the emergence of core-level XPS satellites $\sim$6 eV below the main d^{10}-like XPS peaks due to transitions to d^9-like final states. The relative intensities and positions of the satellites are intimately related to the coefficients a and b in Eq. (1) and to the effective Ni bandwidth.[21–29] They are also sensitive to the chemical environment of Ni. The strongest reduction of the satellite intensities yet observed are for Ni silicides.[30] In Ni_3Si the satellite intensity is reduced by only $\sim 25\%$ (Ref. 31) but in Ni_2Si its intensity is reduced to $\sim 10\%$ (Ref. 30) and in NiSi to almost zero.[30] We have found no reports of the satellite intensity of Ni borides.

In this study we report studies of the series of metallic glasses $(Ni_{1-x}Fe_x)_{77}Si_{10}B_{13}$ with $x=0$, 0.3, 0.6, and 1.0. These were ribbons 20—30 μm thick and 2 mm wide prepared in an Ar atmosphere by melt-spinning techniques. The amorphous state was confirmed by x-ray diffraction.

The XPS spectra were measured using unmonochromated Al $K\alpha$ radiation in ultrahigh vacuum (10^{-10} torr). The samples were sputtered with Ar until the O 1*s* line could not be further reduced. At this stage the O 1*s*:Si 2*s* peak intensity ratios were typically 1:8 for all the metallic glasses which, according to Scofield's cross-section tables[32] is indicative of an O:Si atomic ratio of $\sim$1:4. Oxygen contamination of this order is common in XPS studies of metallic glasses[7–11] and must unfortunately be accepted (for an exception see, e.g., Ref. 33). XPS core-level studies indicated that the oxygen here was predominantly bound to the metalloid elements with some slight effect on the Fe levels in Fe metallic glasses.

XPS valence-band studies of Ni, Fe, and the metallic glasses are given in Fig. 1. The most noticeable characteristic of these spectra are the widths, which are not easily quantified because of the long tails to high binding energy. The full width at half maximum (FWHM) measured as constructed for Fe in the figure, increases when Fe is alloyed with Si and B to make a glass. It decreases quite regularly to the value for Ni as the Fe content is reduced. The spectra of the glasses $(Ni_{1-x}Fe_x)_{77}Si_{10}B_{13}$ with $x=0.3$, 0.6 (i.e., $\sim$23 and $\sim$46 at. % Fe), are not well reproduced by addition of appropriate weights of the $Ni_{77}Si_{10}B_{13}$ and $Fe_{77}Si_{10}B_{13}$ metallic-glass spectra. Of most interest to us is the region of the spectrum near the Fermi level, E_F. Ni has a high density of states (DOS) at E_F (Ref. 5) and this is reflected in a peak just below E_F, whose 0.75-eV separation from the 50% point at the high-energy cutoff in Ni is determined by the instrumental resolution. The Fe XPS spectrum peaks at 1.0 eV in our spectra and at up to 1.33 eV binding energy in the metallic glasses containing Fe. For Fe itself, DOS calculations ignoring spin give a peak at E_F (Ref. 5) but calculations with spin show an exchange splitting and a strong peak in the DOS due to majority states $\sim$1 eV below E_F.[34] Thus it is primarily the exchange splitting of the Fe *d* states which causes the peak in the Fe XPS valence-band (VB) spectrum to be at higher binding energy than that in Ni. In the metallic glasses containing Fe the peak in the XPS VB is deeper below E_F than in Fe itself. Similar trends have been observed in disordered crystalline Fe-Ni alloys.[35] Unambiguous interpretation of this shift is not possible at present, but it is suggestive of enhancement and not diminution of the exchange splitting at the Fe site in Fe metallic glasses. The final point concerning the XPS valence bands in Fig. 1 is that in the metallic glass containing Fe the intensity at E_F is less than 50% of the peak value (in the Fe-Ni metallic glasses the effect is more marked). In other earlier studies it was possible to correlate a decrease in XPS intensity at E_F for many Ni alloys with a decrease in the electronic specific heat and the DOS at E_F (see, e.g., Ref. 29). Our results indicating the decrease of the DOS at E_F with the increase of Ni concentration are in qualitative agreement with the recently published specific-heat data.[36]

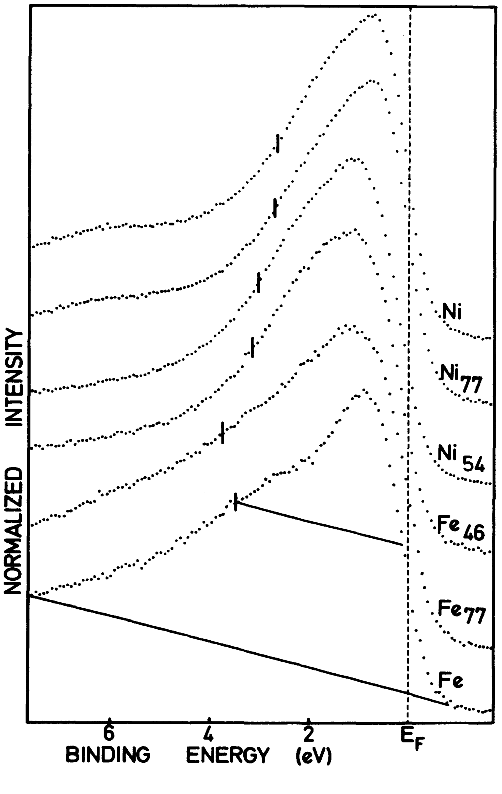

FIG. 1. XPS valence-band spectra of $(Ni_{1-x}Fe_x)_{77}Si_{10}B_{13}$ metallic glasses and Ni and Fe metals. The shorthand notation for alloy composition in the figure gives the concentration of atomic percent of Fe or Ni. For Ni_{77}, $x=0$ in the general formula $(Ni_{1-x}Fe_x)_{77}Si_{10}B_{13}$; for Ni_{54}, $x=0.3$; for Fe_{46}, $x=0.6$; for Fe_{77}, $x=1$.

The observation of a change in density of states at E_F in the $Ni_{0.4}Fe_6$ and $Ni_{0.7}Fe_{0.3}$ metallic glasses prompts the question of how the Fe and Ni state densities at E_F are individually affected. For information on this we turn to the core-level line shapes which are shown for the Ni 2*p* level in Fig. 2. These spectra show a sharp peak at $\sim$852.6 and 852.9 eV and a satellite at $\sim$859 eV. The spectra in Fig. 2 have been normalized to the peak maximum and shifted to superimpose the peaks. The low binding-energy sides of the main peak are identical in shape. However, the high binding-energy sides of the peaks change; there is a general decrease in the intensity of the tail and the Ni satellite moves to higher energy as the Fe content of the glass is increased (see Table I). Note that the satellite intensity, integrated as in Ref. 29, does not change significantly (see Table I).

The observations of the Ni satellite characteristics are not easy to interpret at present and no literature exists on many obvious "calibration" samples. The retention of the satellite intensity in the metallic glasses suggests that the

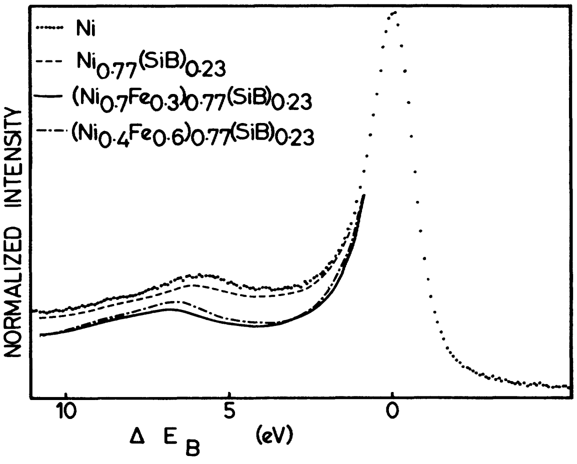

FIG. 2. XPS spectra of the Ni 2*p* levels in Ni and metallic glasses containing Fe. The spectra have been normalized and shifted to superimpose the main peaks. The recorded Ni 2*p* binding energies are Ni = 852.6; $(Ni_{0.77}SiB)_{0.23} = 852.6$; $(Ni_{0.7}Fe_{0.3})_{0.77}(SiB)_{0.23} = 852.8$; $(Ni_{0.4}Fe_{0.6})_{0.77}(SiB)_{0.23} = 852.9$ eV.

TABLE I. Some properties of the metallic glasses studied. *M* is the average magnetic moment per 3*d* element. *I* designates intensity and ΔE is the relative position of the satellite.

Sample	M $(\mu_B)^a$	I(sat)/I(total) Ni $2p_{3/2}$	ΔE(sat) (eV)
Ni	0.6	0.29	5.8±0.4
Ni_2Si^b	. . .	0.10	7.5±0.4
$Ni_{77}Si_{10}B_{13}$	0.0^c	0.31	6.1±0.4
$(Ni_{0.7}Fe_{0.3})_{77}Si_{10}B_{13}$	0.76	0.29	6.7±0.4
$(Ni_{0.4}Fe_{0.6})_{77}Si_{10}B_{13}$	1.34	0.30	6.8±0.4
$Fe_{77}Si_{10}B_{13}$	1.97	. . .	. . .
Fe	2.2	. . .	. . .

[a] References 37 and 38.
[b] Reference 27.
[c] Pauli paramagnet.

first coordination sphere of the Ni is not dominated by Si because in NiSi the satellite intensity drops to almost zero. Comparison with extended x-ray-absorption fine-structure results on this point would be interesting. The retention of intensity also indicates that no larger charge transfer to Ni takes place because this would also strongly decrease the satellite intensity.[29] The large shifts of the Ni 2*p* satellite position are very interesting and have potential use for diagnosis of the chemical environment of the Ni atoms, and for the electronic structure of the Ni alloy. However, first the shifts must be better understood and we will continue to investigate this point.

The overall decrease of intensity in the tail of the Ni 2*p* XPS peak can be taken to indicate a decrease with respect to Ni itself in the local density of Ni 3*d* states per Ni atom, at E_F in the Ni metallic glass. As Fe is substituted into the metallic glass this effect becomes more marked. Influence of oxygen contamination of the metallic glasses can be ruled out because this increases the intensity in the tail region. For the Fe levels, which become more asymmetric in some cases, this argument does not hold so we do not discuss the Fe core levels further here.

The implications of the decrease in the DOS, and particularly the Ni partial DOS at E_F in the glassy Fe-Ni alloys, are important for interpretation of the magnetism[37,38] known to exist in these materials. $Ni_{77}Si_{10}B_{13}$ is a Pauli paramagnet, so that the Ni has zero local moment in this glass. This has been confirmed recently with ^{61}Ni Mössbauer effect measurements.[39] In the glasses $(Ni_{1-x}Fe_x)_{77}Si_{10}B_{13}$ with $1.0 > x > 0.3$ the saturation magnetic moment can be fitted if each Fe atom provides a moment of $1.97\mu_B$ and each Ni provides $0.33\mu_B$.[37,38] As our results indicate a low density of Ni *d*-state character near E_F then one can best rationalize the Ni contribution as due to Ni *d* character in the unoccupied (minority) states of largely Fe *d* character. A Ni *d* band at E_F with a small exchange splitting to give $0.33\mu_B$/atom would probably not give rise to the strong diminution of the Ni 2*p* many-body tail as Fe is substituted for Ni in the $(Ni_{1-x}Fe_x)_{77}Si_{10}B_{13}$ metallic glasses.

In conclusion, we note that we have observed strong chemical sensitivity of many-electron effects in the Ni 2*p* core-level spectra of $(Ni_{1-x}Fe_x)_{77}Si_{10}B_{13}$ metallic glasses. These effects are a potential source of information on the local electronic structure at a particular site in complex materials. We shall ourselves continue with a more complete study of Ni-Fe, Ni-Co, and similar metallic glasses. We have published this article now because although such many-electron effects are not normally included in XPS studies of metallic glasses, our results indicate that they could be advantageously utilized.

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[5] See, e.g., V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

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