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Magnetic moments and x-ray photoelectron spectroscopy splittings in Fe 3s core levels of materials containing Fe

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We present an attempt to establish an experimental basis for interpretation of so-called multiplet splittings in the Fe 3s core-level x-ray photoelectron spectroscopy (XPS) peaks. Fe 3s XPS splittings have been studied in various crystalline and amorphous alloys using x-ray photoelectron spectroscopy. It is found that there is poor correlation between the Fe 3s splitting and the magnetic moment on the Fe atoms in both alloys and inorganic compounds. We even find an Fe 3s splitting in some Pauli paramagnets. The ratio of the satellite to main peak intensity is always less than expected for either the atomic limit, or for itinerant magnetism. The implications of these observations are discussed. It is concluded that the Fe 3s splitting is not a reliable guide to local moments of Fe.

I. INTRODUCTION

It was first suggested about 15 years ago[1-4] that one could use the s core-level splitting as a monitor of the local moment or the hyperfine field because the splitting should vary linearly with the spin state of the unfilled inner shell, as proposed by van Vleck.[5] In the early and mid-1970s sample studies (see, e.g., Refs. 6–8) had shown that results from a number of x-ray photoelectron spectroscopy (XPS) measurements on nonmetallic transition metal compounds, and also on rare-earth metals and ionic compounds, were compatible with this scheme. On the basis of this evidence there have been various attempts to use multiplet splittings as a diagnostic of the local magnetic moment.[6,9-12] However, since the first measurements of multiplet splittings in XPS we have come to understand much more about screening of a core hole $\underline{c}$ by valence electrons (see, e.g., Refs. 13–16), and the original idea that the multiplet splitting gives a direct measure of the ground-state magnetic moment has been questioned (see, e.g., Refs. 17–20).

The basic idea here is that the ground state may be regarded as a mixture of basis states of similar energy but with different numbers of d or f electrons, so that the number of d or f electrons in the ground state is nonintegral. In the final state the energies of the corresponding $\underline{c}d^n$ and $\underline{c}d^{n+1}$ basis states are no longer similar, so that they mix less strongly, and separate peaks are observed in the XPS spectrum due to transitions to the different final states. There is often a strong transfer of weight to the lowest energy peak (see, e.g., Refs. 13, 17, 21, and 22). Examples are the observation of atomiclike $\underline{c}3d^9$ satellite structures in addition to the $\underline{c}3d^{10}$ main peak in the core XPS of Ni (Ref. 13) and the observation of peaks in the spectra of Ce compounds due to transitions to final states with 0, 1, and 2 $4f$ electrons, each with its own atomic multiplet structure.[21] Note, however, that the effects of multiplets and the charge fluctuations on the spectra are only separable if the Coulomb interactions between the valence electrons are very large by comparison with the matrix elements (i.e., hybridization or electron hopping integrals) mixing the different final-state configurations.[18,20] If this is not the case then the spectra can no longer be regarded as a superposition of two atomiclike multiplets. Examples of the breakdown of the separation have been identified in some Ni halides,[17] for Ce in Pd,[23] and for CeO_2.[24]

As pointed out by Kakehashi,[18,20] whilst the intensity ratio of the 3s multiplet peaks should be $S:(S+1)$ for Fe compounds with localized magnetic moments, one would naively expect a ratio of 1:1 for itinerant magnets. In fact, even in ionic compounds the ratio is often observed to be even lower than the atomic ratio of $S:(S+1)$ expected in simple atomic theory. Furthermore, the splitting is often smaller than that calculated in the Hartree-Fock approximation and extra peaks were observed at higher binding energy (BE). In some cases this can be attributed to configuration interaction between the $3s^13p^63d^n$ and the $3s^23p^43d^{n+1}$ configurations,[25,26] but this cannot explain all our observations.

The complications introduced by the factors discussed above are potentially severe and quantitative theoretical treatments of these effects are in their infancy, at best. This gives an added justification to studies, such as ours, to establish a more complete experimental data base and to establish empirical rules.

II. MAGNETIC MOMENTS IN Fe COMPOUNDS

The magnetic moment of Fe arises from the partially filled 3*d* shell. Many inorganic Fe compounds are considered to be ionic so that the magnetic moment on each Fe atom can be derived from the formal charge and number of 3*d* electrons on each Fe site. The orbital angular momentum of the 3*d* electrons is considered to be quenched,[27] so that the moment on each atom should be approximately 2*S*. There have been long discussions in the past about whether magnetism in Fe should be considered on the basis of localized or itinerant electrons (see, e.g., Ref. 28). Itinerant or band magnetism implies that the electrons are to a large extent delocalized and although we may still speak of an effective moment per atom the number of unpaired electrons per atom is by no means constrained to integral values.

The basis of the idea of a moment of an atom or site is that vector addition of moments gives the total magnetization of a sample. In certain circumstances the magnetic moments may be derived from the saturation magnetic moment, e.g., for ferromagnetic or simple paramagnets with only one magnetic element. But these cases are a minority. The major alternatives to this procedure involve the use of magnetic moments estimated from neutron scattering and Mössbauer hyperfine splittings. The former, which are generally regarded as a standard for research on magnetism, involve interpretation of the neutron scattered beam intensities using a form factor derived from the wave function for the "whole" atoms.[29,30] By contrast, Mössbauer spectroscopic estimates of magnetic moments rely on the hyperfine field at the nucleus and are dependent on the subtle distortions of the *s*-electron wave functions by the exchange interaction with unpaired spins in the unfilled valence states.[31–33] The correlation between effective atomic moments derived from Mössbauer and neutron scattering moments is far from perfect.[34] One might have thought that Mössbauer data would give the best correlation to core-level splittings found in XPS because the splitting is also determined by the distribution of electrons in the core of the atom. We will show that this is not the case. We will compare our XPS data separately with saturation moments, neutron scattering, and with Mössbauer data because of the difference in the physics involved in the techniques.

To end this section we note the special case of the Pauli paramagnets whose electrons are considered delocalized and nonmagnetic in the ground state. The moment on the atoms in these systems is unambiguously zero. Because of this, Pauli paramagnets will take on special significance in this work.

III. EXPERIMENTAL PROCEDURE

The alloys investigated in the experimental part of this study were prepared by melting together the requisite quantities of the component elements using rf heating. X-ray diffraction was used to check that the samples consisted of a single phase. The samples were scraped *in situ* before each experiment. Since the base pressure was in the 10^{-11}-torr range the buildup of surface contamination, as judged from the intensity of the O 1*s* XPS peak and the shape of the Fe $2p_{3/2}$ peak, was small. If prolonged measurement proved necessary, the sample was rescraped, typically every three hours. In some intermetallic compounds variations can occur within several monolayers of the surface (the region probed by XPS) depending on sample and surface preparation. In previous studies we have found that such effects are common and strong when inert gas sputtering is used to clean the surface, or when adsorbate of gases enhances surface segregation. In general, segregation is probably stronger in disordered alloys than in ordered intermetallic compounds because surface segregation runs counter to the thermodynamic tendency to order. In previous studies we have found that scraped intermetallic alloy surfaces show the least surface segregation[35] and thus we do not believe that surface segregation significantly influences the results described here.

The XPS spectra were measured in a modified Leybold spectrometer using monochromatized Al $K\alpha$ radiation as the exciting source. The large solid angle (0.1 sr) commercial x-ray monochromator was built by Vacuum Science Workshop,[36] according to our specifications, and had a band pass of 400 meV. The resolution of the total system was approximately 800 meV in the mode used.

Where the statistics permitted, the observed Fe 3*s* peaks were fitted to a Doniach-Šunjić line shape[37] with two peak contributions representing the main peak and the satellite. The fits were carried out to 10 eV below the main Fe 3*s* peak and no background corrections were made, in accord with standard practice. The asymmetry parameter was chosen to be the same for both peaks.

Of course, there are questions about the application of a Doniach-Šunjić (DS) line shape to transition metal XPS peaks because the 3*d* bands have strong structure and the DS line shape is for free-electron bands.[37] However, complete neglect of the asymmetry would not be acceptable, and as shown below, the quality of the fits is quite good, suggesting that the DS model line shape is reasonable here. In any case, use of fits based on the DS model gives us the best basis for discussion at the present time.

IV. RESULTS AND DISCUSSION

A. Preliminary survey

We have recorded XPS data for a number of iron alloys and compounds especially those alloys with low Fe

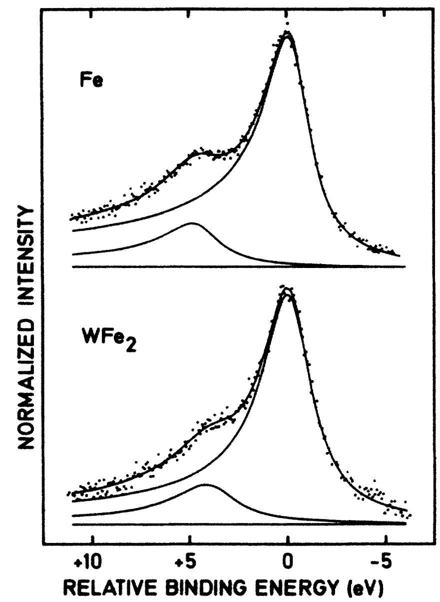

FIG. 1. Fe $3s$ core-level XPS data from Fe and WFe_2.

magnetic moments, because there is a wide selection of published data on inorganic compounds but less on Fe alloys. Some representative data are shown for Fe and WFe_2 in Fig. 1. Note that the higher BE shoulder is never completely resolved, but that for all the materials studied except $CeFe_2$ and $TiFe_2$ the fits to the data made with the DS line form were of the same quality as for Fe and WFe_2. This is perhaps surprising because the DS line shape was derived for free-electron-like materials and does not take into account structure in the density of states. For Pd, serious discrepancies related to the sharp cutoff of d states just above E_F are found.[38] Our results indicate that these effects are much weaker for the Fe $3s$ XPS peaks of Fe and its alloys.

The results of the computer fits to the $3s$ line shapes are given in Table I. The lifetime broadening of the main $3s$ peak (2γ) is comparable to that given elsewhere;[39] the second components of the lines are usually $\sim$20–60% broader. The ratio of the main peak to the satellite was the least reliable parameter of the fit and could be changed by 20% and in some cases by up to 40% without serious changes in the quality of the fit, if constraints were set on other parameters. However, it is still significant that the higher-energy component of the $3s$ peak of all magnetic Fe systems has an intensity which is less than either the 1:1 ratio predicted for itinerant magnetism, or even the $S:(S+1)$ ratio predicted for the atomic limit when we substitute the Fe moment μ for $2S$. A similar result has been found for $3s$ multiplets in ionic compounds,[25,26] and even gaseous Mn.[40] There it can be attributed to configuration interaction with the $3s^1 3p^6 3d^n$ and $3s^2 3p^4 3d^{n+1}$ states, which reduces the multiplet splitting and transfers weight away from the main satellite. Such effects may contribute here, but note that for some materials (e.g., WFe_2, and $NbFe_2$) a satellite is found where none is expected.

The observed $3s$ XPS peak splittings clearly do not correlate with the Fe magnetic moments in the materials we have studied (see Table I). For instance, the Fe $3s$ peaks of WFe_2 and $NbFe_2$ both exhibit splittings of 4.3–4.7 eV, whilst our own measurements of magnetic susceptibility show that the compounds are Pauli paramagnets, and hence have no significant local moment on the Fe site. This lack of correlation will be further discussed below with the aid of results from the literature. We may dispose here of arguments that the XPS technique merely probes the magnetic moment of a final state in which the ionized Z (Fe) atom behaves like a $Z+1$ (Co) impurity as a result of screening: $NbCo_2$ is also a Pauli paramagnet. We ourselves measured the temperature dependence of the magnetic susceptibility for $NbFe_{1.7}Co_{0.3}$ to simulate the $Z+1$ impurity more

TABLE I. Fe $3s$ XPS peak splittings (Δ, in eV) and other XPS peak parameters for Fe intermetallic compounds. 2γ is the Lorentzian broadening of the main Fe $3s$ peak; α is a dimensionless parameter defining the asymmetry of a Doniach-Šunjić line shape; I_b/I_a is the ratio of the satellite to main peak intensity. μ is the Fe magnetic moment in Bohr magnetons and $\mu/(\mu+2)$ is the XPS peak intensity ratio $S:(S+1)$ expected in simple van Vleck theory.

Compound	$\Delta E(3s)$ (eV)	μ	2γ (eV)	α	I_b/I_a	$\mu/(\mu+2)$
Fe	4.9	2.2	2.2	0.27	0.22	0.52
FeNi	4.7	2.6	2.5	0.14	0.38	0.57
Fe_6Ni_4	4.6	2.4	2.5	0.16	0.4–0.5	0.55
$GdFe_2$	4.7	2.1	2.7	0.14	0.21	0.51
Fe_3P	4.4	1.8	2.3	0.21	0.36	0.48
YFe_2	4.8	1.45	2.3	0.29	0.14	0.42
FeSi		0.0	2.2	0.26	0.0	0.0
$FeSi_2$		0.0	1.9	0.24	0.0	0.0
$NbFe_2$	4.7	0.0	2.0	0.28	0.16	0.0
WFe_2	4.3	0.0	2.6	0.16	0.21	0
$CeFe_2$[a]		1.25			<0.1	0.38
$TiFe_2$[b]	4.7	0.6				0.24

[a] Fit not possible because of Ce $4d$ peaks.

[b] Fit not possible.

closely and found this to be a Pauli paramagnet also. Thus the Co impurities do not have a magnetic moment, and whilst Fe^+ may resemble a Co impurity in the $NbFe_2$ matrix, it should still not have a magnetic moment to cause a core-level splitting.

We may also rule out the possibility that the structure in the Fe 3*s* peaks is only due to transitions to final states with different numbers of *d* electrons. If this were true, then one would expect similar structure in the other Fe core-level XPS peaks, as found for Ni. In fact, as shown for some Fe $2p_{3/2}$ XPS peaks in Fig. 2, we find only asymmetry of the 2*p* peaks consistent with a DS many-body tail and a small multiplet splitting of the 2*p* XPS peak. The Fe 3*s* XPS splitting of the Pauli paramagnets remains a serious problem.

B. Correlations between XPS data and other measures of the Fe magnetic moments

Much of the saturation moment data for Fe compounds relates to complicated systems with more than one magnetic ion and cannot be used to derive an unambiguous value for the moment on Fe atoms. Thus the data in Fig. 3 rely heavily on neutron scattering data (see the Appendix for more details on individual data points and sources). Sometimes more than one literature value of the XPS splittings is plotted in order to give a measure of the reliability of the data. The scatter of points is sometimes large, but usually insignificant by comparison with the scatter of points as a whole. For some substances with inequivalent magnetic sites, e.g., Fe_3P, neutron scattering gives several values for the magnetic moment. We note that the highest XPS splittings are observed for the inorganic materials where other methods indicate a high Fe moment, but there are many materials with a low Fe moment and a significant Fe 3*s* splitting. Prominent examples are the splittings of 4.3–4.7 eV for FeB, $NbFe_2$, and WFe_2. The data clearly indicate that Fe 3*s* XPS splittings are not a reliable guide to local moments. Materials with zero local Fe moment have been observed to have 3*s* splittings between ~0 and 5 eV. Conversely, an Fe 3*s* splitting of ~4 eV can be recorded for substances with a local Fe magnetic moment of between 0 and $\sim 5\mu_B$.

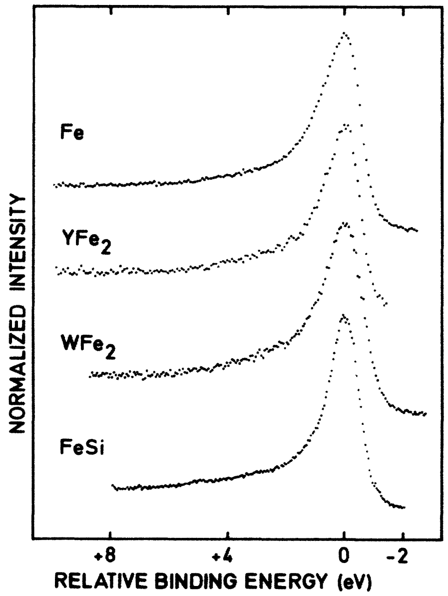

FIG. 2. Fe $2p_{3/2}$ core-level XPS data from Fe, YFe_2, WFe_2, and FeSi. Note that while the peaks show distinct asymmetry as a result of many-body effects, there is no shoulder which can be attributed to either oxide or multiplet splitting.

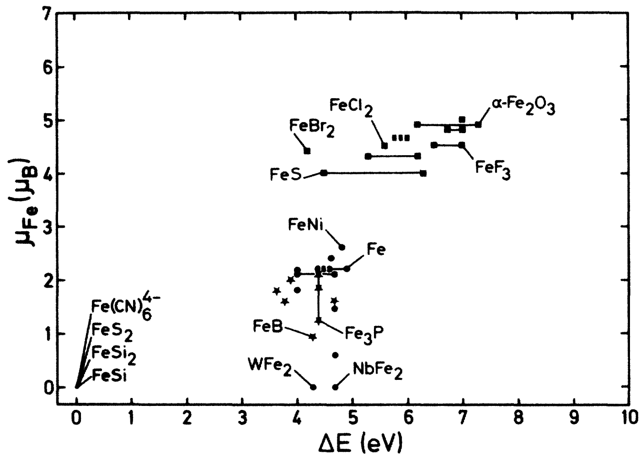

FIG. 3. Plot of the Fe local moment, derived from neutron scattering, as a function of the observed splitting of the Fe 3*s* XPS peak. Also included are data from saturation moments for the Pauli paramagnets ($NbFe_2$, WFe_2, etc.) and for a few systems where we consider saturation moment data a reliable guide to the local Fe moments. Certain data points discussed in the text are identified in the figure; others may be identified from data in Table II of the Appendix. ●, Fe compounds with metals; ★, with metalloids; ■, with nonmetals.

As mentioned above, Mössbauer hyperfine splittings,

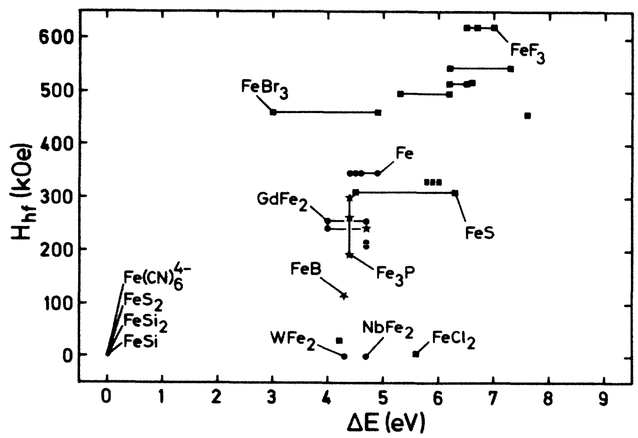

FIG. 4. Plot of hyperfine field at the Fe nucleus, derived from Mössbauer spectroscopy, as a function of the Fe 3*s* XPS splitting. The literature relating to this data is given in Table II of the Appendix. Symbols, as for Fig. 3.

like XPS core-level multiplet splittings, are dependent on subtle modifications of the wave functions in the core of an atom by exchange effects. There is some hope that they may give a better correlation with the magnetic moment of the Fe site. We plot in Fig. 4 the measured Fe 3*s* XPS splitting against the literature values for the hyperfine field H_{hf} at the Fe nucleus as measured by Mössbauer spectroscopy. Whilst the largest XPS splittings are found for systems with a large hyperfine field at the nucleus, we also sometimes observe large multiplet splittings when the hyperfine field is small. This latter situation was not restricted to any one class of compounds but is found for Fe compounds with metals ($\mathrm{NbFe_2}$, $\mathrm{WFe_2}$), metalloids (FeB), and nonmetals ($\mathrm{FeBr_2}$, $\mathrm{FeCl_2}$).

V. CONCLUDING REMARKS

Data from Mössbauer spectroscopy, neutron scattering, and magnetization measurements do indicate some scatter in the estimates of Fe magnetic moments by various techniques.[32,34] However, the experimental data we have collected indicate very poor correlation between XPS core-level splittings and moments measured by other methods, and it is clear that such XPS splittings are not a reliable guide to such moments. It is equally clear that the observed Fe 3*s* XPS splitting is not due to the (exchange) interaction between the core hole and the (unpaired) valence electrons alone. An explanation taking into account only the differences in the number of Fe valence electrons in the final states is also not sufficient because the core-level splitting is found only on the Fe 3*s* levels, not the Fe 2*p* levels. It is clear that the perturbation of the valence electrons by the core-hole potential is important, but we have obtained results which are not consistent with a description of the observed 3*s* splitting as a result of an exchange interaction between a core hole and the unpaired valence electrons on the "screened" final state. This was particularly clear for the results on $\mathrm{NbFe_2}$ (Sec. IV A).

In our opinion a proper description of the core-level XPS splittings will need to take into account the atomic

TABLE II. Summary of literature data and present work used to investigate the relationship between Fe 3*s* XPS splittings and the Fe magnetic moment.

Material	3*s* splitting (eV)	Ref.	Type of magnet	Fe moment (Bohr mag.)	Method	Ref.	Hyperfine field (kOe)	Ref.
Fe	4.9	this work	ferro-	2.21	sat. mag.	41	345	32
	4.5	42						
	4.4	2						
	4.6	43						
$\mathrm{YFe_2}$	4.8	this work	ferro-	1.45	sat. mag.	44	208,215	45
$\mathrm{GdFe_2}$	4.7	this work	ferri-	2.10	sat. mag.	46	255,240	45
	4.0	43						
				1.6	sat. mag.	47		
$\mathrm{GdFe_3}$	4.0	43	ferri-	1.83	sat. mag.	47		
$\mathrm{Gd_2F_{17}}$	4.0	43	ferri-	2.16	sat. mag.			
$\mathrm{NbFe_2}$	4.7	this work	Pauli para-	0.0	magnetization	this work	0	44
$\mathrm{WFe_2}$	4.3	this work	Pauli para-	0.0	magnetization	this work	0	44
$\mathrm{TiFe_2}$	4.7	this work	ferro-	0.6	sat. mag.	44		
$\mathrm{CeFe_2}$	0.0	this work	ferro-				165	45
				1.30	sat. mag.	48		
FeNi	4.8	this work	ferro-	2.6	neutron diffraction	49		
$\mathrm{Fe_6Ni_4}$	4.6	this work	ferro-	2.4	neutron diffraction	50		
FeB	4.3	42	ferro-	0.95	neutron diffraction	51	118	32
$\mathrm{Fe_2}$	4.7	42	ferro-	1.62	neutron diffraction	51	242	32
FeSi	0.0	this work	anomalous para-	0.0	neutron diffraction	52,53		
	0.0	54						
$\mathrm{FeSi_2}$	0.0	this work					0	55
$\mathrm{FeF_2}$	5.8	42	antiferro-	4.64	neutron diffraction	57	329	58
	5.9	4						
	5.85	8						
	6.0	56						

TABLE II. (*Continued*).

Material	3*s* splitting (eV)	Ref.	Type of magnet	Fe moment (Bohr mag.)	Method	Ref.	Hyperfine field (kOe)	Ref.
$FeCl_2$	5.6	7	antiferro-	4.5	neutron diffraction	59	4	60
$FeBr_2$	4.2	7	antiferro-	4.4	neutron diffraction	59	28.4	60
FeF_3	6.5	56	antiferro-	4.53	neutron diffraction	61	622	62
	6.7	42						
	7.0	2						
$FeCl_3$	5.3	56	antiferro-	4.3	neutron diffraction	63	495	64
	6.2	7						
$FeBr_3$	3.0	56					460	64
	4.9	7						
αFe_2O_3	7.3	7	antiferro-	4.9	neutron diffraction	66	544	67
	6.2	65						
γFe_2O_3	6.5	4	antiferro-				515	4
	6.2	65						
FeS	6.3	7	antiferro-	4.0	neutron diffraction	69	309	70
	4.5	68						
FeS_2	~0.0	71		0.0	susceptibility	72		
Fe_3P	4.4	this work	ferri-	1.84	neutron diffraction	32	190,262,304	32
$K_4Fe(CN)_6$	0.0	2,7	diamag-	0.0			0	33
$Na_4Fe(CN)_6$	0.0	2	diamag-	0.0			0	33
K_3FeF_6	6.7	56		4.8	susceptibility	73		
	7.0	7						
Na_3FeF_6	7.0	7		5.0	susceptibility	73		
		56						
K_2NaFeF_6	7.0	68					620	68
$NiFe_2O_4$	6.6	74	ferri-				498	75
$NiFeCrO_4$	7.6	74	ferri-				457	76
$a\text{-}Fe_{77}Si_{10}B_{13}$	3.9	77	ferro-	1.97	sat. mag.	77		
$a\text{-}(Fe_{0.6}Ni_{0.4})_{77}Si_{10}B_{13}$	3.6	77	ferro-	1.79	sat. mag. + Mössbauer	77		
$a\text{-}(Fe_{0.3}Ni_{0.7})_{77}Si_{10}B_{13}$	3.8	77	ferro-	1.61	sat. mag. + Mössbauer	77		

multiplet structure and exchange interactions between core and valence electrons, the Coulomb interactions between core and valence electrons with screening effects and charge variations in the different final states, effective electron (Mott-Hubbard) correlation between the valence electrons, and the strength of hybridization between the valence electrons, as well as the local moment on the Fe atoms in the ground state. This will be difficult. Our XPS results for Fe and its alloys and compounds show that our understanding of core-level splittings in the XPS spectra of Fe is poor and hopefully give a sound experimental basis for further theoretical studies. Similar studies of other 3*d* transition metals are desirable because it is probable that our understanding of these is also poorer than has been widely recognized until now. Clearly, recent literature using Fe 3*s* splittings as a measure of the magnetic moment on Fe, or even as a diagnostic for a local moment, is unjustified.

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APPENDIX

We present Table II, which is a summary of literature data and present work used to investigate the relationship between Fe 3*s* XPS splittings and the Fe magnetic moment.

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