

Photoemission studies of the Fe 3s spin splitting in Fe-V alloys

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The concentration dependency of the Fe 3s spin splitting in Fe-V alloys has been investigated using x-ray photoelectron spectroscopy and synchrotron radiation photoemission. Based on line-shape fits, we demonstrate that the spin splitting decreases with increasing V concentration in the same fashion as the local moment, indicating that there is a correspondence between them. It is found that the magnitude of the spin splitting, the line shape, and the intensity ratio of the two spin components are photon-energy dependent.

The correlation between the 3s spin splitting and local moment of the magnetic 3d transition metals has attracted the attention of physicists since the first measurements of such splitting by Fadley *et al.*¹ A number of experimental investigations have shown that the multiplet splitting of the Fe 3s core level can be used diagnostically to identify the presence of a local magnetic moment on the Fe site in different Fe-based compounds.¹⁻⁶ Theoretical calculations by Kakehashi⁷ have predicted that it is possible to measure the temperature and the concentration dependencies of the moment by use of 3s inner-core photoelectron spectra. Recently, however, van Acker *et al.*⁸ and Oh, Gweon, and Park⁹ suggested that the correspondence between Fe 3s splitting and the local moment was not as straightforward as suggested. For example, in Ref. 8 it was shown that alloys that were Pauli paramagnets also exhibited a spin splitting. The latter observations therefore may lead to the conclusion that the exchange interactions between core and valence electrons is not the basis of the observed splittings. However, the spin-resolved photoemission measurements of the Fe 3s core level reported by Hillebrecht, Jungblut, and Kisker¹⁰ and Carbone *et al.*¹¹ showed that the two features in the Fe 3s core-level spectrum are characterized by opposite spins, indicating that the exchange interaction was indeed a main cause of the multiplet splittings. Thus a puzzling question still remains as to whether the 3s splitting reflects the local moment of the ground state in Fe-based alloys and compounds. Clearly, what has been lacking is a study of the 3s spin splitting in an Fe-based alloy system in which the local moment on the Fe site varies in a known fashion. Accordingly, in this work we have chosen a series of Fe-V alloys for study including pure Fe, Fe-20% V, and Fe-70% V (both disordered bcc, α -phase alloys), as well as α' -FeV (CsCl structure). There are experimental^{12,13} and theoretical¹⁴ studies that indicate that the local moment on the Fe site decreases with increasing V concentration, and disappears at $\sim 77\%$ V concentration,¹⁵ making this an ideal system for study. It is worth noting also that the magnitude of the Fe 3s spin splitting and intensity ratio of the two spin components

in pure Fe measured from spin-resolved photoemission spectra¹⁰ differ considerably from results based on fits of x-ray photoelectron spectroscopy (XPS) data.^{1,8} The photon energies used in these two different kinds of measurements are 250 and 1486 eV, respectively, and an additional question arises as to whether the photon energy plays a role in determining those parameters. To shed light on this question, in the present work we used both synchrotron radiation and conventional x-ray sources; it is an extension of work reported earlier.¹⁶

Synchrotron-radiation-based photoemission measurements were conducted on the U7B beamline at the Brookhaven National Synchrotron Light Source. The photon energy used was 200 eV. A hemispherical electron-energy analyzer was used to collect and energy analyze the photoelectrons. The combined resolution of monochromator and spectrometer was 0.7 eV at a pass energy of 25 eV. All the data presented here were collected at normal emission. The base pressure in the

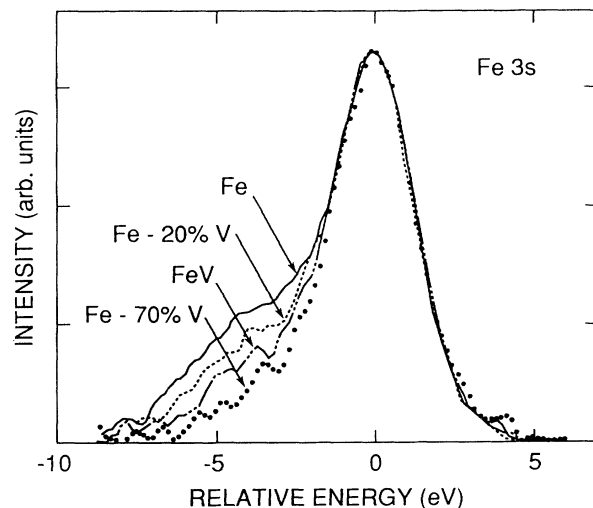


FIG. 1. Fe 3s photoemission spectra from Fe and Fe-V alloys using synchrotron radiation at 200-eV photon energy.

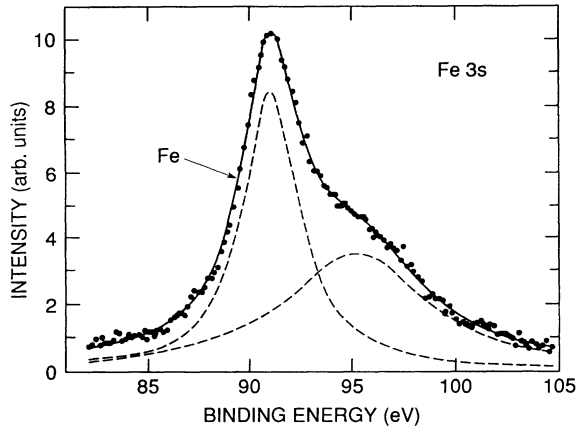


FIG. 2. Fe 3s photoemission spectrum taken from pure Fe at 200-eV photon energy fitted with two DS line shapes.

chamber was 1×10^{-10} torr. The XPS measurements, which have been reported previously,¹⁶ were performed using unmonochromatized Mg $K\alpha$ radiation (1253 eV) and an identical hemispherical electron-energy analyzer. The cleaning and annealing procedures were described in Ref. 16.

Figure 1 shows the photoemission spectra of the Fe 3s core level in pure Fe and the three alloys taken with 200 eV photons. In order to make comparisons easier, a linear background was removed from each raw spectrum and the main peaks were lined up and normalized to a constant peak height. The spectra show the well-known doublet structure, but a monotonically decreasing shoulder on the high-binding (low-kinetic) energy side of the main peak with increasing V concentration is obvious. According to the spin-resolved photoemission measurements,^{10,11} this doublet is made up from a pair of exchange-split peaks. The main peak has the minority-spin character and the shoulder the majority spin. (Similar line profiles were observed in the XPS spectra, which were presented in our previous report.¹⁶) In general, it is difficult to separate this broad spectrum into two overlapping components without *a priori* knowledge regarding the appropriate line shape of each component.^{17,18} However, in order to compare our data with earlier work we started our analysis by fitting two Doniach-Sunjić (DS) line shapes¹⁹ to the pure Fe 3s spectrum. Figure 2 shows

the deconvolution into two DS components of the Fe 3s photoemission spectrum taken for pure Fe at 200-eV photon energy. The circles are the raw data, the solid and dashed curves are the fitted line shapes. In Table I we list our fitting results along with those reported in Refs. 8,10. No constraints were imposed during our fitting procedure. The errors in our results arise from our use of several different sets of data and different background subtraction procedures.

It is apparent from our results that the spectra taken at 200-eV photon energy are in good agreement with those from the spin-resolved measurements performed at a photon energy of 250 eV (Ref. 10), while the resulting parameters of our XPS spectra are in fair agreement with earlier XPS work.⁸ The difference between the XPS and synchrotron-radiation photoemission results could be related to the photon energy, and therefore, the kinetic energy of the photoelectrons. It should be noted at this point that the probing depth of the photoelectrons varied with photoelectron kinetic energy. It is well established that the electronic and magnetic properties on the surface must differ, to some extent, from those of the bulk. The spectra taken at 200 (or 250) eV photon energy would contain more information from the surface than the bulk. The fact that the intensity ratio deduced from the synchrotron-radiation photoemission spectra is closer to the ratio of 1:1 predicted for itinerant magnetism may indicate that the surface properties of Fe are closer to the delocalized limit. One would expect a variation in the intensity ratio and line shapes in going from surface sensitive spectra to less surface sensitive XPS spectra, since the bulk transition metals are intermediate between the localized (atomic) limit and delocalized (itinerant) limit.²⁰ However, it is still significant that the intensity ratio obtained from XPS spectra is even less than $S:(S+1) \sim 0.5$ expected for the atomic limit,^{1,8,21} where S is the magnitude in the total spin of localized d electrons. This indicates that the two spin components in the XPS spectra may not have the DS line shapes. We attempted to fit the XPS spectra with a Lorentzian line shape for the minority spin and a DS line shape for the majority spin, as suggested by the shapes of the synchrotron-radiation spectra, but with no success because the minority spin has a large asymmetry index. Nevertheless, the good agreement between our results and the earlier work supports the validity of our fitting procedure. We have applied this pro-

TABLE I. Summary of data on 3s spin splitting in pure Fe from this and earlier work. Arrows \uparrow and \downarrow denote the spin-up and spin-down features, respectively. α is the singularity index defining the asymmetry of a DS line shape, and when $\alpha=0$ a Lorentzian is obtained.

Reference	Photon energy (eV)	Spin splitting (eV)	Intensity ratio ($I_{\uparrow}/I_{\downarrow}$)	Line shape	
				\downarrow	\uparrow
9	250	4.5	0.86	Lorentzian	
This work ^a	200	4.2	0.89	$\alpha=0.00$	$\alpha=0.03$
This work ^a	1253	4.8	0.33	$\alpha=0.19$	$\alpha=0.08$
8	1486	4.9	0.22	$\alpha=0.27$	$\alpha^b=0.27$

^aIn this work the error is ~ 0.2 eV for the spin splitting, $\sim 20\%$ for the intensity ratio. The singularity index $\alpha \equiv 0$ for the minority-spin component in the spectra taken at 200-eV energy. An error of ~ 0.02 for the rest of α .

^bIn Ref. 8 α was chosen to be the same for both components.

TABLE II. Parameters obtained from fitting two DS line shapes to each photoemission spectrum of Fe-V alloys. The error is ~ 0.2 eV for spin splitting, $\sim 20\%$ for the intensity ratio. The singularity index $\alpha \equiv 0$ for the minority-spin component in the spectra taken at 200-eV energy. An error of ~ 0.02 for the other α 's.

Photon energy (eV)	Sample	Spin splitting (eV)	Intensity ratio ($I_{\uparrow}/I_{\downarrow}$)	Index α	
				\downarrow	\uparrow
200	Fe	4.2	0.89	0.00	0.03
	Fe-20% V	3.8	0.79	0.00	0.21
	Fe-50% V	2.8	0.43	0.00	0.06
	Fe-70% V	1.2	0.33	0.00	0.30
1253	Fe	4.8	0.33	0.19	0.08
	Fe-20% V	4.5	0.35	0.18	0.15
	Fe-50% V	3.6	0.35	0.17	0.02
	Fe-70% V	1.0	0.39	0.16	0.23

cedure to each spectrum from the Fe-V alloys. (In the present work we have used an improved version of the fitting routine compared with that used in Ref. 16 and obtained good fits for all spectra including the XPS spectra, which were not fitted very well previously.) The results are listed in Table II.

The parameters in Table II show that the minority-spin component has a pure Lorentzian line shape in the spectra taken at 200-eV photon energy, whereas the asymmetry index α is roughly constant in all XPS spectra. The value of α for the majority spin-spin component varies in an irregular fashion, which is mostly likely due to the scatter on the data in this region. The intensity ratios between the two spin components obtained from the XPS data do not vary much with V concentration, whereas those deduced from the synchrotron-radiation photoemission spectra do.

In order to demonstrate the correspondence between the Fe 3s spin splitting and the local moment on the Fe site we plot them together as a function of V concentration in Fig. 3. The solid curve is from the calculations of the local moments for alloys with the disordered bcc structure reported by Johnson, Pinski, and Staunton.¹⁴ These calculated values are in good agreement with the neutron-diffraction data (crosses in Fig. 3) reported by Mirebeau, Parette, and Cable.¹³ The open and solid triangles are from our spin-polarized calculations for pure Fe and α' -FeV alloy, respectively, using the self-consistent-field-linear muffin-tin orbital-ASA method including the spin-orbit interaction, as described in our previous paper.¹⁶ The open square is the calculated local moment of ordered FeV alloy by Moruzzi and Marcus²² and the solid square is from the neutron-diffraction measurement for the ordered Fe-53.3% V alloy reported by Chandross and Shoemaker.²³ The spin splittings obtained from the XPS spectra are shown by open circles and those from the synchrotron-radiation photoemission spectra by solid circles. Figure 3 shows unambiguously that both the spin splitting and the local moment vary in the same fashion against the V concentration, indicating that there is a definite correlation between them. Based on fits of the synchrotron-radiation photoemission data it appears that the change in the profiles with increasing V concentration is a consequence of both reduction in the

spin splitting and decrease in intensity of the majority-spin component. However, the fitting results from the XPS data show a constant intensity ratio in all the spectra. This in turn shows that there is little prospect of making a definite statement of the correlation between the intensity ratio and the local moment. It was suggested by Kakehashi⁷ that systematic measurements of inner-core photoelectron spectra as a function of temperature and concentration would be of considerable importance for a quantitative estimation of the local moment. To do so, it seems that attention should be paid to the photon energy dependency of the photoelectron spectra, which may make quantitative estimations difficult.

In summary, the observed Fe 3s spin splitting is indeed a direct indicator of the local moment on the Fe site in the case of Fe-V alloys. The reduction in the spin splitting is apparently an important cause of the change in the profile with increasing V concentration. However, it is still ambiguous whether the intensity ratio plays a role because of the photon-energy dependency of the Fe 3s photoemission spectra. The latter would certainly affect

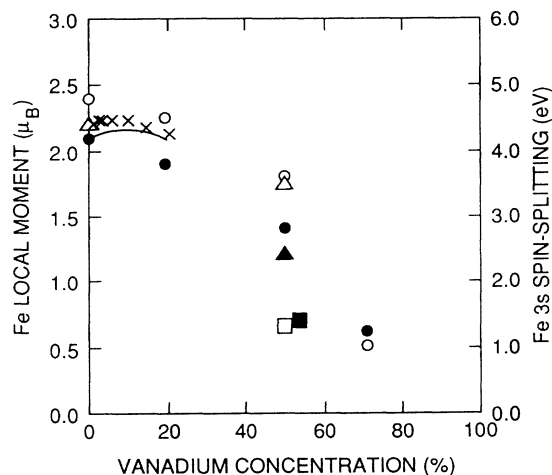


FIG. 3. Correspondence between the Fe 3s spin splitting (shown by open and solid circles) and the local moment on the Fe site in Fe-V alloys (shown by the other symbols). See text for details. The scale for the spin splitting is on the right-hand side.

the quantitative estimation of the local moment by use of inner-core photoelectron spectroscopy.

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