Spin Polarization of the Metallic Fe 3s Photoemission Spectrum

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Spin-resolved photoemission data of the Fe-metal 3s core level show that the two structures known from spin-integrated photoemission are of minority- and majority-spin character, the minority-spin peak being located at lower binding energy. The line shapes and intensity ratio of the peaks differ considerably from previous results based on fits of conventional photoemission data. The observed intensity ratio (1.16 ± 0.1) is similar to the value expected for delocalized d states (1.0).

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Since the discovery in 1969 of so-called magnetic splittings in 3s and 2s core-level photoemissions spectra of magnetic 3d transition metals and their compounds (both metallic and nonmetallic), these splittings have been used as a microscopic probe of the local moment.[1-7] This is based on the interpretation that the splittings are caused by the exchange interaction, which leads to an energy difference between final states with the spin of the remaining s electron parallel or antiparallel to the 3d spin. In experimental investigations it has been observed that gross trends of the magnitude of the splitting or the intensity ratio seem to be explained by this hypothesis. Nevertheless, detailed investigations often revealed inconsistencies. An extensive collection of data on Fe 3s splittings by van Acker *et al.*[6] shows that the intensity ratio does not correlate with the magnetic moment. The most remarkable result reported by the same authors is the observation of 3s splittings in compounds which do not have a local magnetic moment.

These findings may be taken as evidence excluding the exchange interaction as the origin of the observed splittings. Nevertheless, inner shells, e.g., the 3s shell, do in fact "feel" the moment of the d electrons via exchange, as can be seen from the hyperfine splittings in Mössbauer spectroscopy. However, this reflects a ground-state property, and in photoemission the excitation energy is so large that other interactions may be important. Yet if the exchange interaction really is the main cause, then the photoelectrons should be spin polarized. Evidence in support of this comes from photoelectron diffraction experiments; here the diffraction patterns are different for the two components of the photoelectron spectrum, which is ascribed to a spin-dependent part in the form factors.[8,9] However, such experiments have been performed on ionic compounds, whose spectra are *qualitatively* different from those of metallic systems. In a recent spin-resolved photoemission experiment,[10] it was shown that the minority-spin peak dominates the Fe 3s spectrum. However, due to the comparatively low photon energy, the 3s signal was superimposed on a large sloping background. This caused problems in determining the line shapes, especially that of the majority-spin component. So, the presently available experimental evidence is insufficient for reaching a satisfactory understanding of the 3s line shapes of magnetic 3d metals.

The general difficulty in analyzing such photoemission spectra is that one has to separate a broad spectrum into two overlapping components, and there is no way of telling whether a given analysis is appropriate or not. This problem is particularly serious for Fe, one of the paradigmatic examples showing a split 3s line. The *only* way to establish experimentally the line shapes, relative weight, and polarization properties is by directly measuring the spin character of the photoelectrons. In the light of the extensive use which has been and still is being made of the elusive correlation between the 3s splittings and the magnetic moment, it is important that we obtain a detailed microscopic understanding of the underlying physics. This was the reason for us to investigate the 3s spectrum by spin-resolved photoemission, starting with Fe as the most important ferromagnet.

In general, core-level spectra of a magnetic solid may be influenced by exchange (J) and Coulomb interaction (U_{cd}) between core hole and valence electrons, Coulomb interaction among the valence electrons (U_{dd}), and the bandwidth (W) of the valence electrons.[11-13] For Fe, these quantities are all of comparable magnitude, and a theory which is supposed to come anywhere near the truth has to treat all these interactions on the same footing. From the theoretical side, the only attempt on the problem including these interactions has been carried out by Kakehashi and co-workers.[11-13] Their model calculations illustrate again the necessity of spin-resolved data as more decisive indicators of which interactions are the most important ones.

As the 3s line is one of the weakest ones in the photoemission spectrum of Fe, both a high photon flux at a suitable energy and a spin analysis improved over the widely used Mott or LEED techniques are desirable. For high photon flux, the experiment was performed at the Flipper I beam line at HASYLAB (DESY) in Hamburg, using synchrotron radiation from the vacuum-ultraviolet branch of the undulator beam line.[14] To obtain a low and flat background we used a photon energy $h\nu = 250$ eV, giving a ratio of Fe 3s signal to secondary background of about 1/2.3. Identical results were also

obtained at 300-eV photon energy. The photoelectron spectrometer was based on a commercial hemispherical analyzer with 50-mm mean radius. The combined resolution of monochromator and electron spectrometer was 0.8 eV. For spin analysis, we applied very-low-energy scattering from magnetic Fe(100),[15] whose figure of merit is about 2×10^{-3}. The energy-analyzed electrons were transferred by an electrostatic lens from the exit slit of the spectrometer towards the spin-analyzer crystal. The angle of incidence with respect to the surface normal of the spin analyzer was 10°. Specularly reflected electrons were counted by a channeltron. Both sample and spin-analyzer crystal were films of about 50-Å thickness of α-Fe(100) grown epitaxially on Ag(100). The substrates were cleaned by repeated sputtering with Ne^+ ions of 500 eV, followed by annealing, and showed a sharp 1×1 LEED pattern. While taking data, the pressure in the experimental chamber was 3×10^{-10} mbar, and stayed below 6×10^{-10} mbar during Fe evaporation. After deposition of Fe, a slightly more diffuse 1×1 LEED pattern with a smaller lattice constant, rotated by 45° with respect to the Ag LEED pattern, was observed, in accordance with the known growth properties of Fe on Ag(100). The Fe films were magnetized parallel to the surface by means of 1-ms current pulses through small coils located close to each of the films. Test runs with neither or only one of the Ag(100) substrates coated with Fe demonstrated the absence of apparatus asymmetries. Because of the high photon flux and the high efficiency of this spin detector, total count rates (including secondary background) exceeding 500 s^{-1} have been obtained in the Fe 3s peak while the DORIS II ring was operating in the high-energy-physics mode with 5.3-GeV ring energy and 35-mA injected beam currents. This count rate was about $\frac{1}{10}$ of the count rate without spin analysis. Effective acquisition time for the data shown below was less than 2 h.

Prior to taking spin-resolved energy distribution curves (EDCs), the spin sensitivity was determined individually for each freshly prepared analyzer surface. To find the optimum scattering energy, the spin-induced scattering asymmetry was measured as a function of the scattering energy by setting the spectrometer to various kinetic energies in the inelastic background away from the 3s line, where the spin polarization was known.[16] The spin sensitivity so determined was the same as determined by polarized electron scattering in numerous preparations of epitaxial α-Fe(100).[15] By comparison to previous data[16] we estimate the uncertainty of the spin polarization to be $\pm6\%$.[17] Because of the high count rate the polarization is recognizable after the first sweep, and neither the spin-integrated nor the spin-resolved data showed any change during the time used for data accumulation. The spin-resolved Fe 3p spectrum was in agreement with published data.[18]

Figure 1(a) shows the spin-integrated Fe 3s core-level spectrum. The spectrum shows the well-known doublet

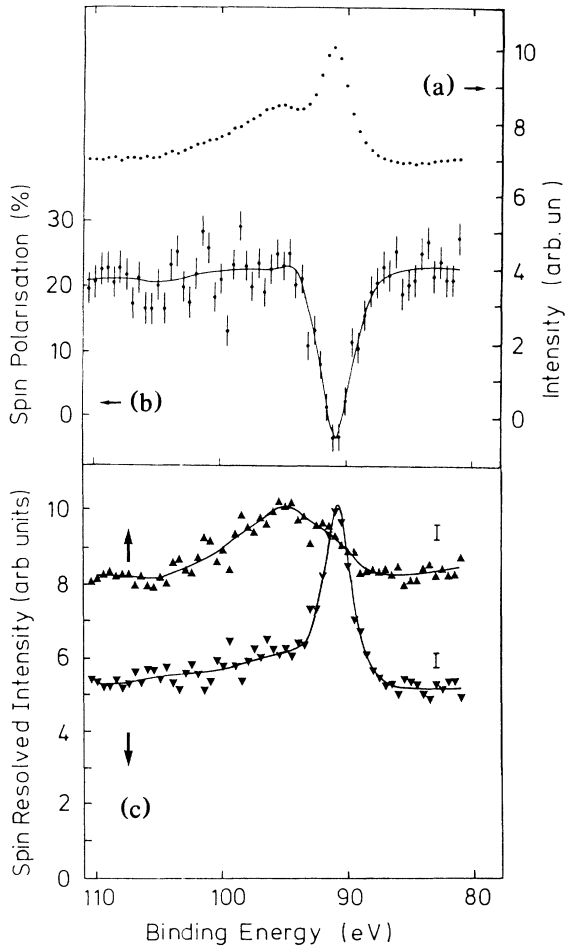

FIG. 1. Photoemission spectra of the Fe 3s core level taken with 250-eV photon energy at 0.9-eV total energy resolution. (a) Spin-integrated energy distribution curve. (b) Spin polarization with statistical error bars. (c) Spin-resolved energy distribution curves with statistical error bars.

structure with a splitting of 4.5 eV between the two main features. On the high-binding-energy side, the spectrum tails out 10 eV below the main line. Figure 1(b) shows the measured photoelectron spin polarization. The background away from the 3s spectrum shows a positive polarization of about +22%. At the main 3s peak, the polarization drops to −3%, showing that this peak has strong negative polarization. This is also borne out in the spin-resolved EDCs (SREDCs) shown in Fig. 1(c), which are obtained in the usual manner from the unpolarized EDC $I(E)$ and the spin polarization $P(E)$ by $I^{\uparrow,\downarrow}(E)=I(E)[1\pm P(E)]$. The arrows ↑ and ↓ refer to majority- and minority-spin electrons, respectively. The spin-resolved spectra show that the two structures known from conventional photoemission spectroscopy indeed represent a pair of exchange-split peaks. The minority peak appears to be a Lorentzian with an intrinsic full width at half maximum (FWHM) of 2.3 eV, while the majority peak is much wider ($\approx$ 10 eV FWHM).

To discuss the spectrum in more detail, we present in Fig. 2 the same results after subtracting flat backgrounds and averaging over the data points. The minority-spin peak has a high-binding-energy tail which spreads over the whole $3s$ spectrum. Apart from that, its shape and width appear to be similar to $3s$ lines observed for nonmagnetic materials, e.g., Cu.[7] It is unlikely that the wide tail is just an effect of electron-hole excitations across the Fermi level, which leads to a Doniach-Sunjic-type line shape, as the tail is wider than the valence band. The majority-spin distribution peaks at 4.5 eV higher binding energy than the minority one, and has a low-binding-energy shoulder in the region of the minority-spin peak. There is no way to explain its large width purely by lifetime. The different widths of the two spin channels show the presence of a spin-dependent broadening mechanism. The measured SREDCs differ considerably from previous results obtained by fitting conventional x-ray-photoemission data with two asymmetric Lorentzians. In those analyses the majority-spin contribution has been strongly underestimated, giving intensity ratios of minority- to majority-spin peaks in the range of 2 to 4.5.[1-6] In contrast to that, we obtain from our data after subtracting flat backgrounds a ratio of 1.16 ± 0.1. This value is much closer to the intensity ratio of 1 expected for the fully delocalized case[11,12] than to 1.9 obtained by interpreting the effective moment of Fe as a local moment.[1,6] All results derived from fits to spin-integrated data depend largely on the choice of parameters; width ratios between 1 and 1.8 have been given.

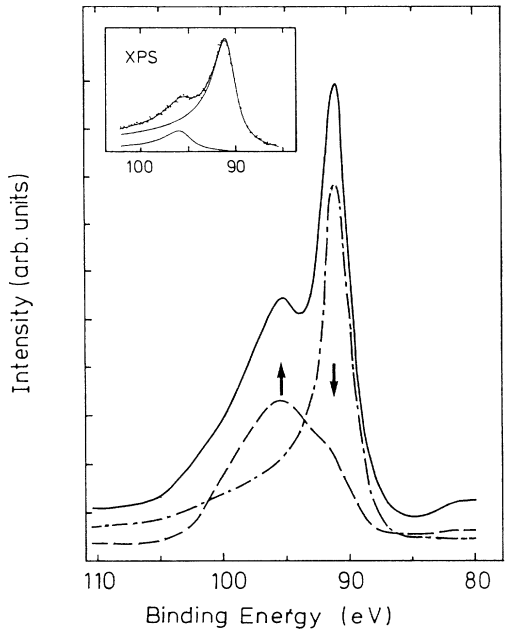

FIG. 2. Spin-integrated (solid line) and spin-resolved (dashed lines) Fe $3s$ photoemission spectra after subtraction of background and averaging over the data points. Inset: An Fe $3s$ spectrum measured with Al $K\alpha$ photons (1486.7 eV) taken from Ref. 6. The deconvolution into two asymmetric Lorentzians tends to underestimate the majority-spin intensity.

In a first approach at interpreting this spectrum, one might assume that the core-hole potential is strong enough to localize a d^8 state at the ionized site. The spectrum may then be governed by atomic splittings of the $3s^1 3d^8$ configuration. If one compares the energy difference between the minority and majority peaks with the exchange splitting expected in an atomic picture,[1,19] one finds that the experimental splitting is much smaller. A reduced exchange splitting has been observed in other cases,[1,20] and was satisfactorily explained by configuration interaction of the majority emission involving $3s^2 3p^4 3d^{n+1}$ configurations, where n is the ground-state d occupancy. This effect does not only lead to an apparently smaller exchange splitting, but also to a reduction of the majority weight, as intensity is shifted to the satellites. This shift in intensity is the cause for the intensity ratio deviating from the ratio expected without configuration interaction. For a d^8 final state we expect a ratio of $I_{\mathrm{min}}/I_{\mathrm{maj}} = 2$, and this effect would lead to an even larger ratio, in contrast to our experimental result.

Spin-polarized model calculations for core spectra of magnetic metals including atomic and solid-state effects (U_{cd}, U_{dd}, J, and W as given above) have been performed by Kakehashi and co-workers.[11-13] The calculated spectra show three peaks, corresponding to—in order of increasing energy—final states with two, one, or no d electrons present. Within the single-band Hubbard model used for these calculations the leading peak corresponds to a core hole in the presence of a filled band, and consequently it has nearly equal majority- and minority-spin weights. In reality, even though the core-hole potential will attract screening charge, the lowest-energy final state will not be one in which locally *all* the d states are filled, so this peak will not be observed in a real spectrum. For a good description of the experimental spectra the degeneracy of the d bands has to be taken into account. Experimentally, core-level photoemission spectra of Ni are known to exhibit a splitting arising from final states with different d occupancy. For Fe this splitting mechanism is thought to be not as important, because such a splitting should be observable for all core levels. As pointed out by Kakehashi and Kotani,[13] the treatment in Refs. 11 and 12 is more appropriate to the localized limit; this is also seen from the splitting caused by different d occupancies. The absence of such splittings in Fe hints to a more delocalized situation, and in fact a treatment more appropriate for this case[13] yields unpolarized spectra much more similar to the spin-integrated experimental data. It seems promising to perform such calculations for a magnetic ground state including spin polarization.

In conclusion, we have shown by spin-resolved photoemission that the Fe $3s$ spectrum is spin split into two lines of opposite spin. The exchange interaction may not

be the only factor, but it is certainly an important contributing factor leading to the observed line shape of the Fe 3*s* spectrum. The ratio of minority- to majority-spin intensities is 1.16 ± 0.1, showing that the majority-spin weight had been strongly underestimated in the past. A theoretical description of the Fe 3*s* photoemission spectrum accounting for the observed line shapes and intensity ratio, which now have been established experimentally, will provide new insights into the relative importance of competing interactions in magnetic materials.

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[1]C. S. Fadley, D. A. Shirley, A. J. Freeman, P. S. Bagus, and J. V. Mallow, Phys. Rev. Lett. **23**, 1397 (1969); C. S. Fadley and D. A. Shirley, Phys. Rev. A **2**, 1109 (1970).

[2]S. Hüfner and G. K. Wertheim, Phys. Rev. B **7**, 2333 (1973).

[3]F. R. McFeely, S. P. Kowalczyk, L. Ley, and D. A. Shirley, Solid State Commun. **15**, 1051 (1974).

[4]D. J. Joyner, O. Johnson, and D. M. Hercules, J. Phys. F **10**, 169 (1980).

[5]J. Azoulay and L. Ley, Solid State Commun. **31**, 131 (1979).

[6]J. F. van Acker, Z. M. Stadnik, J. C. Fuggle, H. J. W. M. Hoekstra, K. H. J. Buschow, and G. Stroink, Phys. Rev. B **37**, 6827 (1988).

[7]A. S. Arrott, B. Heinrich, C. Liu, and S. T. Purcell, J. Magn. Magn. Mater. **54–57**, 1025 (1986).

[8]B. Sinkovic and C. S. Fadley, Phys. Rev. B **31**, 4665 (1985).

[9]B. Hermsmeier, J. Osterwalder, D. J. Friedman, and C. S. Fadley, Phys. Rev. Lett. **62**, 478 (1989).

[10]C. Carbone, T. Kachel, R. Rochow, and W. Gudat, Z. Phys. B **79**, 325 (1990).

[11]Y. Kakehashi, K. Becker, and P. Fulde, Phys. Rev. B **29**, 16 (1984).

[12]Y. Kakehashi and P. Fulde, Phys. Rev. B **32**, 1595 (1985); Y. Kakehashi, Phys. Rev. B **32**, 1607 (1985).

[13]Y. Kakehashi and A. Kotani, Phys. Rev. B **29**, 4292 (1984).

[14]F. Senf, K. Berens v. Rautenfeld, S. Cramm, J. Lamp, J. Schmidt-May, J. Voss, C. Kunz, and V. Saile, Nucl. Instrum. Methods Phys. Res., Sect. A **246**, 314 (1986).

[15]D. Tillmann, R. Thiel, and E. Kisker, Z. Phys. B **77**, 1 (1989).

[16]E. Kisker, W. Gudat, and K. Schröder, Solid State Commun. **44**, 591 (1982).

[17]The calibration uncertainty induces a systematic error in the spin-resolved intensities. The spin-resolved EDCs will be slightly more (less) separated if the spin sensitivity is actually smaller (larger) than assumed. The line shapes and widths are no more affected by the systematic error than by the statistical spread of the data points.

[18]C. Carbone and E. Kisker, Solid State Commun. **65**, 1107 (1988).

[19]A. Bringer (private communication).

[20]P. S. Bagus, A. J. Freeman, and F. Sasaki, Phys. Rev. Lett. **30**, 850 (1973).