Spin-resolved x-ray-photoelectron-spectroscopy study of ferromagnetic iron

D. G. Van Campen,* R. J. Pouliot,* and L. E. Klebanoff†
Department of Chemistry and Zettlemoyer Center for Surface Studies, Lehigh University, Bethlehem, Pennsylvania 18015
(Received 29 June 1993)

A spin-resolved x-ray-photoelectron-spectroscopy study of the deep core levels of ferromagnetic Fe are reported. The $2p_{3/2}$, $2p_{1/2}$, and $2s$ core levels, as well as the more shallow $3p$ level, all display interesting spin-dependent structures. These findings indicate the importance of intra-atomic exchange in deep-core-level photoemission from Fe. The electronic response of the metal to core-hole creation is found to be dependent on the spin of the core hole.

Core-level x-ray-photoelectron spectroscopy (XPS) has provided a vast body of information concerning the electronic and structural properties of solids.[1] Since the core-level electron is excited far above the photoelectric threshold into a spectroscopically structureless continuum final state, a given core-level XPS spectrum of an N electron system is shaped primarily by the core-level electronic structure, with significant modification by the response of the $N-1$ electron system to the creation of the core hole.[2] The $N-1$ electron response can be quite rich and includes (1) the excitation of low-energy valence electron-hole (e-h) pairs,[3,4] leading to asymmetric core-level XPS line shapes;[5] (2) core-hole filling by Auger and Coster-Kronig radiationless transitions;[6] and (3) spin and orbital angular momentum coupling between the core hole and the valence shell, leading to final-state multiplet structure imposed on the core-level XPS line shape.[2] Clearly, the core-level electron-spin angular momentum is central to a quantitative theoretical understanding of these phenomena, and to the description of experimental techniques based on *deep* core-hole creation such as Auger-electron spectroscopy, x-ray-absorption, and x-ray-emission spectroscopy. Until now, however, the deep-core-level electron spin has been an unobserved quantity in previous XPS studies.

There have been spin-resolved ultraviolet photoelectron spectroscopy (SRUPS) studies of the rather shallow $3s$ and $3p$ core levels of Fe (Refs. 7–10) and the $3p$ core level of Co.[11] However, no *detailed* line-shape analyses of these data were performed, due in some cases to the very large and sloping spectral background present in the low photon energy SRUPS data. It is important to extend spin-resolved photoemission study to the deeper core levels, thereby making contact with the large body of XPS data concerning deep states, providing line-shape data that characterizes the $N-1$ electron response to core-hole spin, and providing spectroscopic information for experimental methods dependent on the creation of a deep core hole. We present here spin-resolved XPS (SRXPS) results for the deep-lying $2p_{3/2}$, $2p_{1/2}$, and $2s$ levels, as well as the $3p$ level, of ferromagnetic Fe. The results demonstrate the importance of intra-atomic exchange in deep-core-level photoemission from Fe, and reveal a dependence of the many-body response of the $N-1$ electron system to the spin polarization of core holes.

Our Fe sample was a film prepared by evaporating high-purity Fe in ultrahigh vacuum onto the surface of a sputter-cleaned cobalt-based ferromagnetic metallic glass of composition $Co_{66}Fe_4Ni_1B_{14}Si_{15}$.[12] The glass substrate consisted of a loop that could be easily magnetized to saturation by passing current through coils wrapped around the legs of the loop. This arrangement allowed the preparation of high-purity polycrystalline Fe films with thicknesses of 20–30 Å with very little oxygen contamination.[13] The ferromagnetic exchange coupling between Co and Fe conveniently leads to an in-plane magnetically saturated Fe film (with negligible stray magnetic field) that is required for SRXPS study. A fresh Fe film was prepared every 12–24 h as needed. The very-surface-sensitive 30-eV secondary-electron-spin polarization showed excellent reproducibility and stability throughout all measurements.

Our SRXPS spectrometer[14] combines a VG MkII XPS hemispherical electron-energy analyzer with an electron-spin detector based on the low-energy diffuse scattering method.[15] The photon source is an unmonochromatized Mg $K\alpha$ ($h\nu = 1253.6$ eV) x-ray source operating at 510 W power. The instrumental energy resolution was 1.6 eV full width at half maximum (FWHM). The spectrometer vacuum during measurement was 5×10^{-10} Torr.

The spin-resolved data were collected into four channels N_L^+, N_L^-, and N_R^+, N_R^-. Here, N_L^+ represents the number of electrons diffusely scattered to the left (L) from the Au target in the spin detector when the sample magnetization is positive (+). N_R^- is the number of electrons scattered to the right (R) from the Au target when the sample magnetization has been reversed to the negative (−) direction. The electron beam polarization P can then be expressed as[16]

$$P=\frac{1}{S}\left[\frac{\sqrt{N_L^+N_R^-}-\sqrt{N_L^-N_R^+}}{\sqrt{N_L^+N_R^-}+\sqrt{N_L^-N_R^+}}\right], \tag{1}$$

where S is the analyzing power of the spin detector, known as the Sherman function. The value of S for our measurements was 0.04.[17] SRXPS measurements using both (+) and (−) magnetizations [Eq. (1)] remove from the polarization-data apparatus asymmetry effects unrelated to the spin of the electron beam.[16] Hysteresis

0163-1829/93/48(23)/17533(5)/$06.00

curves acquired with x-ray-excited spin-polarized 30-eV secondary electrons were quite square, with a 30-eV spin polarization ($P=0.27$) consistent with the known Fe magnetic moment of 2.2 μ_B. Count rates (summed over both detectors) for the $2p_{3/2}$, $2p_{1/2}$, $2s$, and $3p$ levels were approximately 2700, 2290, 1560, and 220 s^{-1}, respectively.[18]

The polarization data can be separated into individual $N\uparrow$ and $N\downarrow$ SRXPS spectra for the majority-spin ($\uparrow$-spin) and minority-spin ($\downarrow$-spin) photoelectrons, respectively.[19] The $N\uparrow$ and $N\downarrow$ components for the Fe $2p_{3/2}$ level are shown in Fig. 1. The lines through the raw data are simplex fits to the individual $N\uparrow$ and $N\downarrow$ spectra using a single Doniach-Sunjic (DS) line shape[5] convoluted with a 1.6-eV FWHM Gaussian representing the instrumental response.

The $N\uparrow$ and $N\downarrow$ Fe $2p_{3/2}$ spectra are both fitted very well with a single DS line. The $N\uparrow$ DS component has a binding energy of 706.69±0.03 eV;[20] the $N\downarrow$ Fe $2p_{3/2}$ DS component has binding energy of 706.21±0.03 eV. Thus, an apparent "exchange splitting" of 0.48±0.05 eV is observed. Baumgarten and co-workers,[21] using the photoemission magnetic circular dichroism (MCD) technique to probe the Fe $2p_{3/2}$ level, estimated a splitting of 0.5±0.2 eV, with the majority-spin component possessing the higher binding energy. The two measurements are, therefore, in excellent agreement for the Fe $2p_{3/2}$ level. The $N\uparrow$ and $N\downarrow$ SRXPS DS line shapes have values for the singularity index α of 0.46±0.02 and 0.42±0.02, respectively. The $N\uparrow$ $2p_{3/2}$ component has a larger FWHM Lorentzian broadening (0.56±0.04 eV) than the $N\downarrow$ component (0.44±0.04 eV). The $N\uparrow/N\downarrow$ Fe $2p_{3/2}$ integrated intensity ratio is 0.81±0.05.[22]

The XPS line-shape asymmetry is intrinsic to the photoelectron spectrum. The asymmetric component exists at the moment of photoelectric excitation, and is not produced with significant intensity (over the energy range of the fits) by extrinsic inelastic scattering of the outgoing photoelectrons.[23] Therefore, no extrinsic inelastic background has been incorporated into the DS fits. Citrin, Wertheim, and Baer[23] have emphasized the inability to extract meaningful line-shape information when inelastic backgrounds are erroneously included in the analysis of XPS spectra.

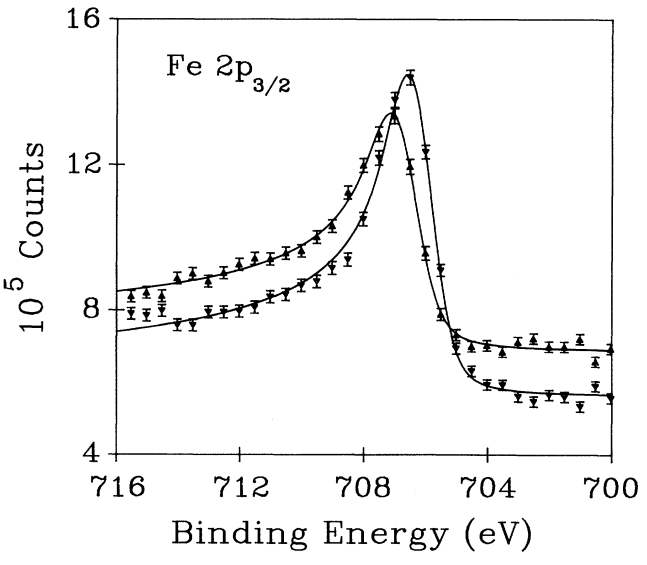

FIG. 1. Separate $N\uparrow$ and $N\downarrow$ SRXPS spectra for the Fe $2p_{3/2}$ majority-spin (▲) and minority-spin (▼) photoelectrons, respectively. The lines through the data are the result of a simplex fit to each spin component using a single Doniach-Sunjic line shape convoluted with a Gaussian of 1.6 eV FWHM.

Figure 2 presents $N\uparrow$ and $N\downarrow$ SRXPS spectra for the Fe $2p_{1/2}$ level. Neither the $N\uparrow$ $2p_{1/2}$ component nor the $N\downarrow$ $2p_{1/2}$ component can be reasonably fit with a single DS line. In particular, the $N\downarrow$ component seems to consist of a main peak accompanied by a broad shoulder on the high-binding-energy side. The spectral complexity of the $2p_{1/2}$ SRXPS spectra makes it difficult to view the Fe $2p_{1/2}$ level as simply an exchange-split doublet. The interpretation[21,24] of photoemission MCD measurements of the Fe $2p_{1/2}$ level suggests a $2p_{1/2}$ $N\uparrow$, $N\downarrow$ doublet split in heavy by 0.3±0.2 eV. Given the relatively large uncertainty associated with the photoemission MCD measurements, the photoemission MCD and SRXPS results for the Fe $2p_{1/2}$ level are in overall qualitative agreement. However, the SRXPS results for the $2p_{1/2}$ level suggest additional spectral complexity not resolvable in the photoemission MCD studies.

The Fe $2s$ SRXPS data are shown in Fig. 3. The Fe $2s$ data could not be adequately fit over the entire binding-energy range. We have, therefore, fit the $2s$ data over the energy range 856–825 eV. The Fe $2s$ $N\uparrow$ peak is located at 843.82±0.2 eV with a Lorentzian width of 9.2±0.5 eV and a singularity index of $\alpha=0.54\pm0.05$. The Fe $2s$ $N\downarrow$ component has a binding energy of 842.63±0.2 eV, with $\alpha=0.44\pm0.05$ and a Lorentzian width of 7.6±0.5 eV. Thus a $2s$ "exchange splitting" of 1.2±0.3 eV is observed. Although the $N\uparrow$ component has a larger singularity index and lifetime broadening than the $N\downarrow$ component, the two Fe $2s$ spin-resolved components have

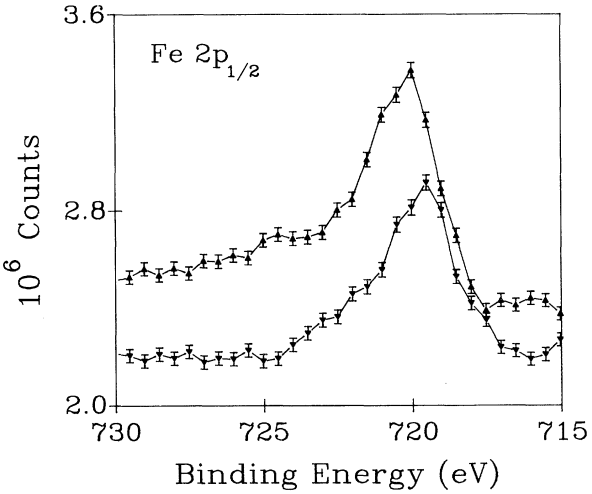

FIG. 2. Separate $N\uparrow$ and $N\downarrow$ SRXPS spectra for the Fe $2p_{1/2}$ majority-spin (▲) and minority-spin (▼) photoelectrons, respectively. The graph lines connect the experimental data points.

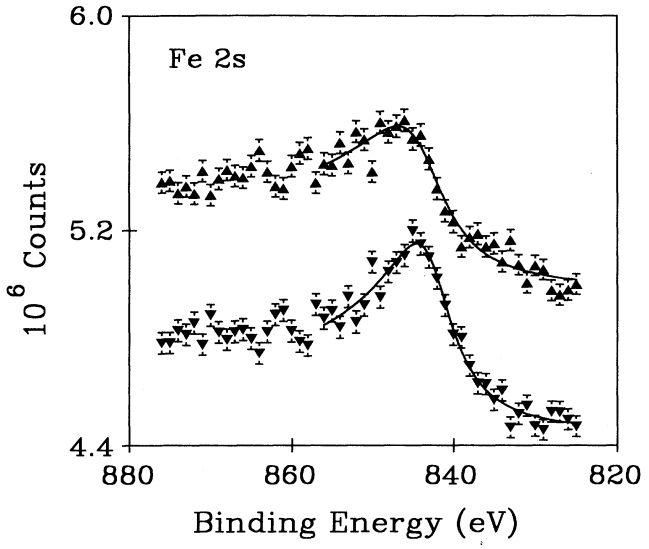

FIG. 3. $N\uparrow$ (▲) and $N\downarrow$ (▼) spectra for the Fe $2s$ peak. The lines through the data are the result of a simplex fit to each spin component using a single Doniach-Sunjic line shape convoluted with a Gaussian of 1.6 eV FWHM. The binding energy range for the fit was 856–825 eV.

similar overall line shapes. This is in contrast to the Fe $3s$ level, which displays drastically different line shapes for the $N\uparrow$ and $N\downarrow$ components.[7] It may be that a form of intrashell electron correlation[25] is responsible for the unusual Fe $3s$ line shapes. The Fe $2s$ $N\uparrow/N\downarrow$ intensity ratio is 0.9 ± 0.1 over the range of the fit.

Figure 4 displays SRXPS Fe $3p$ data. The $N\uparrow$ DS binding energy is 52.15 ± 0.03 eV; the $N\downarrow$ DS binding energy is 51.89 ± 0.03 eV. Thus, a splitting of 0.26 ± 0.05 eV is observed. The $N\uparrow$ $3p$ peak has a FWHM Lorentzian width of 1.43 ± 0.04 eV with $\alpha=0.39\pm0.02$. The $N\downarrow$ $3p$ peak has a width of 1.04 ± 0.04 eV with $\alpha=0.35\pm0.02$. The Fe $3p$ $N\uparrow/N\downarrow$ intensity ratio is 0.80 ± 0.02.

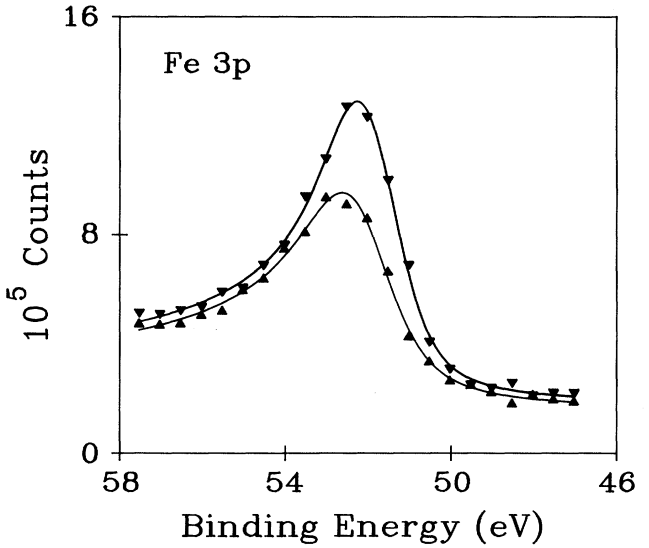

FIG. 4. Separate $N\uparrow$ and $N\downarrow$ SRXPS spectra for the Fe $3p$ majority-spin (▲) and minority-spin (▼) photoelectrons, respectively. The lines through the data points are the results of simplex fits to each spin component using a single Doniach-Sunjic line shape convoluted with a Gaussian of 1.6 eV FWHM. The statistical error is smaller than the symbol size.

The strong spin dependence observed for all the core levels in this study paper reveals the prominent role of intra-atomic exchange in core-level XPS from ferromagnetic Fe. The $N\uparrow$ peaks consistently possess a higher binding energy than the associated $N\downarrow$ down peaks, in qualitative agreement with theories incorporating intra-atomic exchange.[26] It is interesting that the core-valence exchange coupling is sizable for the deep core levels even though the exchange interaction between the $n=2$ and $3d$ orbitals is spatially limited by the very small (~0.15 Å) radial extent of the $2p_{3/2}$, $2p_{1/2}$, and $2s$ orbitals.[27] A fundamental result of this work is that intra-atomic exchange effects in XPS are important and observable even for the very tightly bound core levels.

This result requires that any quantitative description of physical processes involving deep core holes in ferromagnets, such as L_3XX Auger transitions, must explicitly include the spin-dependent splittings of these deep levels. For example, it has been shown by Kotani and Mizuta[28] that the theoretical spin polarization of the $L_3M_{2,3}M_{2,3}$ Auger spectrum of Fe depends sensitively on the $2p$-$3d$ exchange coupling adopted in the theory.

There is no evidence for structure caused by spin-independent phenomena such as crystal-field splitting (theoretically predicted to be negligible[29]), or extrinsic electron-energy-loss structure. There is also no evidence for discrete core-hole satellite structure, such as that observed for Ni core levels, attributable to valence electron correlation.[30] This lack of spectral structure suggests that the valence band of Fe is too delocalized to support strong atomiclike valence excitations.

Spin-integrated XPS studies of the Fe $3s$ core level have often adopted an atomic picture of the observed splittings, especially when comparing the metallic splitting with that of iron compounds.[31] The SRXPS data strongly suggest that an atomic view has little validity for core-level XPS from metallic Fe. The simple two-peak structure observed for the $2p_{3/2}$ level indicates that the complicated spectral structure expected[32] from an atomic view of $2p_{3/2}$ photoemission simply does not exist in the SRXPS data. Evidently, an atomiclike core-valence orbital angular momentum coupling is largely lost in metallic Fe, although the core-valence spin angular momentum coupling survives as demonstrated by measurable $N\uparrow$ and $N\downarrow$ spin-dependent splittings.

The $N\uparrow$ core-level components have larger Lorentzian broadenings than the associated $N\downarrow$ components, indicating that the transition rates for core-hole filling are dependent on the spin of the core hole. The spin-resolved $3p$ widths suggest that valence-electron filling of a $3p$ hole conserves spin, with the preponderance of majority-spin valence electrons being responsible for the higher rate of filling for the majority-spin $3p$ hole.[33] The $2p_{3/2}$-width data reveal a core-hole spin dependence to the integrated $L_3M_{2,3}V$ and L_3VV Auger decay rates. The width of the $2s$ level is thought to be largely determined by very rapid

$L_1L_{2,3}X$ Coster-Kronig transitions, in particular the $L_1L_{2,3}V$ transition.[6] The differences observed for the $N\uparrow$ and $N\downarrow$ $2s$ linewidths suggest a core-hole spin dependence to these $2s$-$2p$ filling processes.

The DS line-shape singularity index α is consistently larger for the $N\uparrow$ SRXPS components than the $N\downarrow$ components. The $N\uparrow$ SRXPS peaks are, therefore, more asymmetric than the $N\downarrow$ peaks. This indicates that the e-h-pair excitation spectrum accompanying core-hole creation is intrinsically spin-dependent and is stronger for the majority-spin core hole. This phenomenon differs physically from the excitation of e-h pairs by low-energy electron scattering that produces the secondary electron majority-spin polarization enhancement at low energies in Fe.[34] It may be that photoelectric emission of an $\uparrow$-spin core electron appears to the valence band as a sudden net increase in the $\downarrow$-spin electron density in the core level. Such an increase in $\downarrow$-spin core character could induce a spin-conserving transition of a $\downarrow$-spin valence electron into the unoccupied portion of the $\downarrow$-spin $3d$ valence band. This excitation would have a highly probability than the excitation of an $\uparrow$-spin valence electron (caused by $\downarrow$-spin core-level emission) because there are fewer unoccupied $\uparrow$-spin states in the Fe valence band. This speculative picture would cause the preferential emission of reduced-energy majority-spin electrons in the asymmetric tail of the $N\uparrow$ SRXPS peaks, leading to the larger values of α.

There is virtually no theoretical work concerning the dependence of the metallic $N-1$ electron response, in all of its forms, to the spin of a core hole. Previous calculations of the itinerant e-h-pair response to core-hole creation treat the core hole as spinless.[3,4,29] Kakehashi has performed calculations[26] treating the core-valence exchange with varying valence-band delocalization. However, large simplifications concerning the valence band preclude a meaningful comparison with experiment. It is our hope that the detailed SRXPS line-shape information and the qualitative theoretical considerations given here stimulate quantitative spin-dependent theories of both itinerant e-h-pair excitation, and core-hole filling.

SRXPS measurements of the deep core levels of the $3d$ transition metals have great potential for magnetic interface studies. Further experimental and theoretical work is required to reveal the extent to which quantitative information regarding the atomic magnetic moment can be extracted from the SRXPS spectra.

The authors thank Professor Michael Scheinfein for very valuable discussions of electron-spin-detector design. Thanks are also extended to Professor David Shirley and Dr. John Unguris for helpful discussions. This paper was based upon work supported by the National Science Foundation under Grant No. CHE-9117138. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of the research. Financial support also came from the Camille and Henry Dreyfus Foundation, The Charles A. Dana Foundation, and Lehigh University. R.J.P. acknowledges support from the USDE.

*Also with the Department of Physics.
†Author to whom correspondence should be addressed.

[1]See, for example, C. S. Fadley, Prog. Surf. Sci. **16**, 275 (1984).
[2]D. A. Shirley, in *Topics in Applied Physics, Photoemission in Solids I,* edited by M. Cardona and L. Ley (Springer-Verlag, Berlin, 1978), p. 165.
[3]P. Nozières and C. T. De Dominicis, Phys. Rev. **178**, 1084 (1969)
[4]G. D. Mahan, Phys. Rev. B **11**, 4814 (1975).
[5]S. Doniach and M. Sunjic, J. Phys. C **3**, 285 (1970). See also J. W. Gadzuk and M. Sunjic, Phys. Rev. B **12**, 524 (1975).
[6]E. J. McGuire, Phys. Rev. A **3**, 587 (1971).
[7]F. U. Hillebrecht, R. Jungblut, and E. Kisker, Phys. Rev. Lett. **65**, 2450 (1990).
[8]B. Sinkovic, P. D. Johnson, N. B. Brookes, A. Clarke, and N. V. Smith, Phys. Rev. Lett. **65**, 1647 (1990).
[9]C. Carbone, T. Kachel, R. Rochow, and W. Gudat, Solid State Commun. **77**, 619 (1991).
[10]C. Carbone and E. Kisker, Solid State Commun. **65**, 1107 (1988).
[11]W. Clemens, E. Vescovo, T. Kachel, C. Carbone, and W. Eberhardt, Phys. Rev. B **46**, 4198 (1992).
[12]Allied Signal MetGlas Alloy #2714A.
[13]XPS analysis indicated an O/Fe stoichiometric ratio of 0.09. Assuming oxygen contamination exists as Fe_2O_3 (Ref. 8), 6% of the Fe atoms exist as Fe^{3+}. This oxidation produces very small peaks chemically shifted by 4.5 eV to higher binding energy in the $N\uparrow$ Fe $2p_{3/2}$, Fe $2p_{1/2}$ spectra.
[14]L. E. Klebanoff, D. G. Van Campen, and R. J. Pouliot, Rev. Sci. Instrum. **64**, 2863 (1993).
[15]M. R. Scheinfein, D. T. Pierce, J. Unguris, J. J. McClelland, R. J. Celotta, and M. H. Kelly, Rev. Sci. Instrum. **60**, 1 (1989).
[16]J. Kessler, *Polarized Electron* (Springer-Verlag, Berlin, 1985), p. 234.
[17]The systematic uncertainty in S is estimated to be 10% ($S=0.04\pm0.004$). Reference 14 describes the method of spin detector calibration.
[18]Count rates reflect the total photoelectric signal (peak+background).
[19]The $N\uparrow$ and $N\downarrow$ spectra are calculated from the polarization P by the relations $N\uparrow=2N_{\rm TOT}(1+P)$; $N\downarrow=2N_{\rm TOT}(1-P)$, where $N_{\rm TOT}=(N_L^+ + N_L^- + N_L^+ + N_R^-)/4$. Statistical error bars ($\pm\delta N\uparrow\downarrow$) shown in the figures are calculated via the expression $\delta N\uparrow\downarrow = N\uparrow\downarrow(1/S\sqrt{4N_{\rm TOT}})$.
[20]The error indicates binding energy precision, not accuracy.
[21]L. Baumgarten, C. M. Schneider, H. Petersen, F. Schäfers, and J. Kirschner, Phys. Rev. Lett. **65**, 492 (1990).
[22]Intensities used for the ratios are the integrated area under the DS fit, over the energy range of the fit, with the intensity of the lowest binding energy spectral point set equal to zero.
[23]P. H. Citrin, G. K. Wertheim, and Y. Baer, Phys. Rev. B **16**, 4256 (1977).
[24]H. Ebert, L. Baumgarten, C. M. Schneider, and J. Kirschner, Phys. Rev. B **44**, 4406 (1991).
[25]P. S. Bagus, A. J. Freeman, and F. Sasaki, Phys. Rev. Lett. **30**, 850 (1973).
[26]Y. Kakehashi, Phys. Rev. B **32**, 1607 (1985), and references

therein.

[27]The expectation value $\langle r \rangle$ for the $n=2$ and orbitals of Fe are approximately 0.15 and 0.48 Å, respectively: R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981), p. 236.

[28]A. Kotani and H. Mizuta, Solid State Commun. **51**, 727 (1984).

[29]R. P. Gupta and S. K. Sen, Phys. Rev. B **10**, 71 (1974).

[30]L. A. Feldkamp and L. C. Davis, Phys. Rev. B **22**, 3644 (1980), and references therein.

[31]For example, J. Azonlay and L. Ley, Solid State Commun. **31**, 131 (1979).

[32]A jk coupling scheme (Ref. 27, p. 130) for an Fe atom in a ^{3}H ($2\ \mu_B$) ground state would predict 12 discrete states for $2p_{3/2}$ photoemission.

[33]This mechanism has been put forth in Fe $3p$ SRUPS studies (Ref. 10).

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