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Spin-polarized Auger-electron diffraction study of the magnetic poisoning of Fe(001) by sulfur

B. Sinković
Department of Physics, New York University, New York, New York 10003

P. D. Johnson, N. B. Brookes,* and A. Clarke†
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

N. V. Smith
Advanced Light Source, Lawrence Berkeley Laboratory, Berkeley, California 94720
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Spin-polarized angle-resolved sulfur $L_{2,3}VV$ Auger-electron spectra have been recorded for the $c(2\times2)$S/Fe(001) system. The data show the modulation of the sulfur Auger spin polarization as a function of emission angle, which represents an observation of spin-polarized Auger-electron diffraction (SPAED), a potentially powerful tool for the study of local magnetic structure at surfaces, interfaces, and thin films. Theoretical modeling of the SPAED data indicates a large decrease in the magnetization of the top iron layer, suggesting a magnetic poisoning induced by the sulfur overlayer. These findings are independently supported by the observation of a large decrease of secondary electron spin polarization upon sulfur adsorption.

The magnetic properties of surfaces and thin films have been a topic of continuing research interest.[1] The paramount techniques in the study of near-surface properties have traditionally been the various electron spectroscopies. Conversion of these techniques into a spin-polarized mode[2,3] has opened up a broad front on the problem of surface and thin-film magnetism. As examples, spin-polarized low-energy electron diffraction[4] has been shown to be sensitive to long-range surface magnetic order, while spin-polarized Auger-electron spectroscopy[5,6] is capable of probing the local magnetic properties. This paper reports a successful attempt to detect spin-polarized Auger-electron diffraction. The angular dependence of Auger emission is recognized as an important tool in the study of surface geometries.[7–10] As such, it may be anticipated that the spin dependence of this phenomenon can be employed to probe the local magnetic order. Similar spin-dependent scattering is also implicit in earlier spin-polarized photoelectron-diffraction (SPPD) experiments.[11–13] The work reported here represents the direct measurement of spin-dependent (Auger) electron diffraction, which does not rely on an internal spin-polarized source. Combined with theoretical modeling of the observed spin polarization this represents a demonstration of a local near-surface magnetic structure determination. The results suggest a large decrease in the magnetization of the top iron layer upon sulfur adsorption, a magnetic poisoning effect, which is independently supported by a large decrease in the spin polarization of the secondary electrons.

The $c(2\times2)$S/Fe(001) is a well characterized adsorbate system. The surface geometry has been well established by low-energy electron diffraction (LEED),[14] the electronic structure has been studied with angle-resolved photoemission,[15] and a theoretical study of the structural, electronic, and magnetic properties of the system[16] has also been reported. The magnetic properties have been studied by spin-polarized angle-resolved photoemission[17,18] and spin-polarized Auger-electron spectroscopy.[6] The latter study concentrated on the magnetic properties of the adsorbate. In the present study we examine the angular dependence of Auger-electron spin polarization which reflects the magnetic structure around the emitter, i.e., the Fe substrate.

The Auger electrons are excited by a 2-keV-electron beam incident at an angle of 45° with respect to the surface normal. The angle, energy, and spin of the ejected electrons have been measured in an apparatus described in detail elsewhere.[19] Briefly the electrons are detected by an electron spectrometer backed by a compact low-energy spin detector of the type described by Unguris *et al.*[20] The energy resolution was of the order of 0.25 eV and the angular resolution $\pm1.5°$. The angle-resolved experiments were performed by keeping the sample fixed and rotating the electron analyzer so that the Auger-electron emission angle was scanned in the (100) plane of the crystal. The Fe(001) crystal was magnetized parallel to the surface and in the plane of electron emission. The sulfur $c(2\times2)$ structure was obtained by our segregating sulfur from the bulk.

Figures 1(a) and 1(b) show spin-resolved spectra taken at polar angles of $+10°$ and $+2.5°$, respectively. It will be noted that there is little change in the basic line shape of these spectra. Indeed all the spectra show a broad main peak (full width at half maximum ~4.0 eV) and a strong shoulder at ~5 eV higher energy. This line shape is well reproduced by the self-convolution of the calculated spin-resolved density of states on the sulfur site (see Ref. 6) and can be fitted by a simple two-Gaussian fit. The only difference between the spectra recorded at different angles is their relative intensity. These intensity modulations have been attributed to scattering of outgoing Auger electrons or Auger-electron diffraction (AED).

Auger-electron diffraction patterns have been successfully used in studies of both surface and interface geometries.[7–10] The majority of these studies have employed higher-energy Auger electrons ($\geqslant300$ eV). In the case of low-energy Auger-electron diffraction ($\leqslant100$ eV), it has been suggested

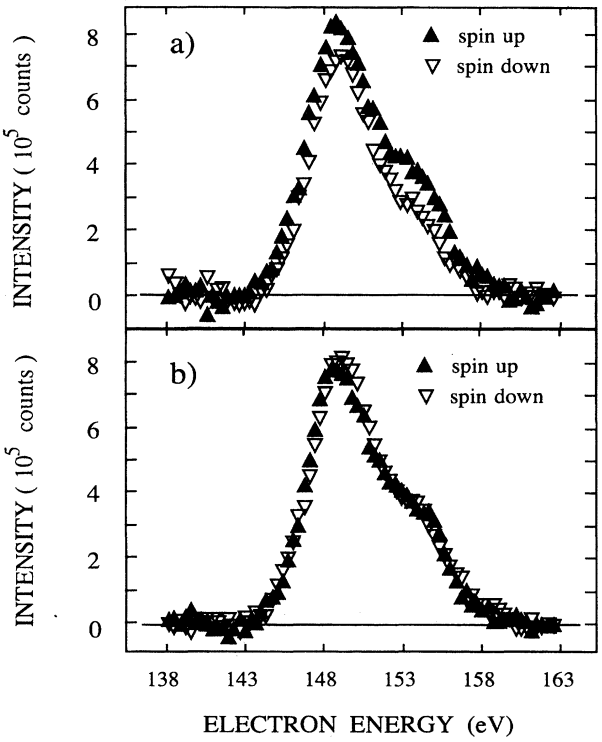

FIG. 1. Spin-resolved sulfur $L_{2,3}VV$ Auger-electron spectra from the $c(2\times2)$S/Fe(001) system [majority spin (▲) and minority spin (▽)]. Electron emission angles are (a) $\theta=+10°$, and (b) $\theta=+2.5°$.

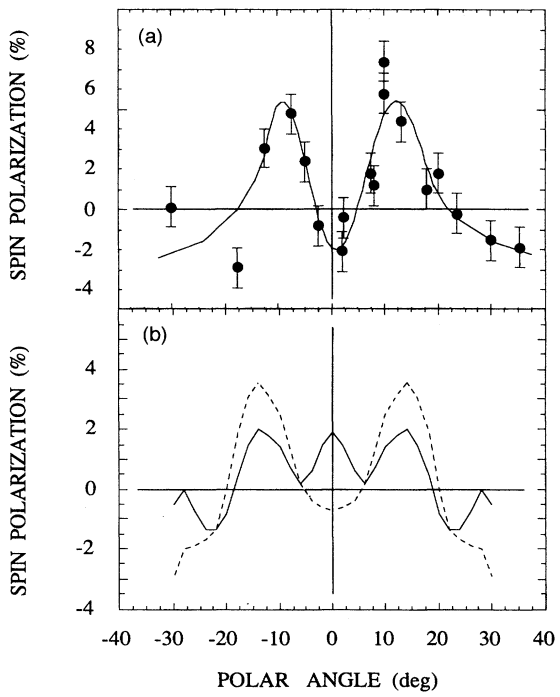

FIG. 2. (a) Measured spin polarization of the $L_{2,3}VV$ Auger-electron diffraction pattern (SPAED) for the main peak (the line is a guide to the eye). The polar angle scan is measured in the (100) plane. (b) Calculated sulfur $L_{2,3}VV$ SPAED pattern for two different surface Fe layer magnetizations: equal to the Fe bulk magnetization (full line) and magnetically dead (dashed line).

that both the electron scattering and angular anisotropy inherent in the Auger transition play an important role.[21–23] Interference among different Auger transition channels can in principle alone induce intensity modulations. The Auger matrix elements for the $L_{2,3}VV$ Auger transition have been reported by Feibelman, McGuire, and Pandey.[24] It can be shown from their analysis that the single Auger transition channel with an outgoing p wave has an angular matrix element an order of magnitude greater than any other possible transition channel. Therefore in the case of $L_{2,3}VV$ emission, the observed intensity modulations can be solely attributed to electron diffraction. The modeling of such spin-integrated AED patterns confirms the atomic structure of the $c(2\times2)$S/Fe(001) system established previously,[14] and will be discussed elsewhere.[25]

Figure 2(a) shows the spin polarization $[P=(I_\uparrow-I_\downarrow)/(I_\uparrow+I_\downarrow)]$ in the angular dependence of the sulfur $L_{2,3}VV$ Auger electron intensity. The spin-resolved intensities ($I_\uparrow$ and $I_\downarrow$) were obtained by measuring the peak heights. An identical spin polarization curve was obtained by fitting the Auger spectra with two Gaussians (representing the main peak and the shoulder) and using the Gaussian peak area. It will be recognized from Fig. 1 that this polarization, although detectable, is small ($\Delta P=\sim7\%$), and it contains a mirror symmetry along the surface normal, as expected. We offer it here as direct evidence of spin-polarized Auger-electron diffraction (SPAED).

The spin dependence in the electron-atom scattering can in principle result from spin-orbit and/or exchange processes.[26] Because the electron emission direction contains a mirror plane of the crystal and the spin polarization is measured within that plane, any spin dependence derived from the spin-orbit interaction will be canceled out and hence the SPAED data presented here will reflect the exchange interaction alone. Since the exchange scattering depends on the relative orientation of the spin of the electron being scattered and the magnetic moment of the scattering atom, the SPAED pattern contains information on the short-range magnetic order around the emitter atom. Comparison of observed SPAED patterns with model calculations should then allow determination of the local magnetic order at surfaces, interfaces, and thin films, just as AED experiments have provided structural information on these systems.

It is interesting to note that we observed a similar shape in the SPAED patterns of both the main sulfur Auger peak and of the shoulder (not shown).[25] The only difference between the two patterns is in the average spin polarization, being lower (close to zero) for the main peak. This point, discussed in our earlier paper,[6] reflects the fact that the shoulder in the sulfur Auger spectra results from hybridization with the Fe $3d$ orbital which will then result in an overall larger spin polarization for this part of the spectrum. These observations demonstrate that (i) effectively nonmagnetic atoms can be used for SPAED, and (ii) the SPAED pattern is insensitive to small changes in energy at ~150 eV.

It is useful to compare the SPAED experiment described

here with spin-polarized photoelectron diffraction (SPPD).[11–13] Both experiments probe the local magnetic order around the emitter, but they differ in the way the spin dependence is measured. The SPPD measurements have relied on the multiplet splitting of shallow core levels as the source of spin-polarized electrons. In the SPAED experiments reported here, the spin of the ejected electrons is measured directly. This has the advantage that (i) by definition, only spin-dependent scattering effects are measured, (ii) the emission from nonmagnetic emitters can be employed, and (iii) the experiment can be performed in the laboratory using an e gun. On the other hand, such measurements are limited to samples with a net macroscopic magnetization, as is the case for any spin-polarized electron technique involving either a spin-polarized analyzer or external spin-polarized electron source. We also note that SPAED is limited to low-energy Auger transitions as spin-dependent scattering is appreciable only in the low-energy region ≤ 200 eV. Finally, the geometry of our SPAED experiments indicates that appreciable spin asymmetries exist in backscattering, which are important in spin-dependent extended x-ray-absorption fine structure (EXAFS) measurements.[27,28]

We have attempted to simulate the SPAED data by performing model single-scattering cluster calculations[13] using the spherical wave approximation.[29,30] This method has worked well in the analysis of photoelectron and Auger-electron diffraction data.[7,10] The outgoing Auger-electron wave was chosen to have p symmetry (as discussed earlier). The cluster contained 150 atoms. All the structural parameters are taken from LEED analysis of the same system.[14] The exchange potential was evaluated from the standard form $\alpha\rho(r)^{1/3}$ but with an energy-dependent $\alpha(\epsilon)$ of Dirac-Hara form[31] as used previously in spin-polarized LEED calculations.[32] The results of calculations using double scattering did not differ appreciably from those obtained using single scattering.

The calculated spin asymmetries are shown in Fig. 2(b). It was assumed that sulfur has no magnetic moment (consistent with the experimental and theoretical findings of a very small moment of $\sim 0.1\mu_B$)[6,16] and the moment of the top Fe layer is equal to the bulk value (full line). The comparison with the measured spin asymmetries [Fig. 2(a)] indicates only fair agreement. The calculations predict a maximum excursion of about $+2\%$ at $\pm 14°$, which is in qualitative agreement with the experiment. The calculation, however, requires an additional positive maximum ($+2\%$) along the normal, whereas the corresponding experimental polarization shows a negative minimum. The agreement could not be improved by changing a number of nonmagnetic parameters such as the mean free path, the cluster size, the electron wavelength,[33] and the double-scattering contributions.

The calculated asymmetries were, however, found to be sensitive to the magnitude and direction of the magnetic moment of the top two Fe layers. We have performed a number of model calculations assuming different short-range magnetic order around the emitter (sulfur) atom. The most successful and physically reasonable of these models involves varying the magnetic moment (magnetization) of the top substrate (Fe) layer (M_s). It was found that reduction of M_s tends to improve the agreement with the experiment, especially in reproducing a negative spin-polarization minimum along the surface normal and increasing the overall size of the polarization variation to a value closer to the experiment [see Fig. 2(b); dashed line]. Using this limited SPAED data set, however, we cannot pinpoint the size of M_s, although the data do suggest an appreciable reduction of the magnetic moment of the surface Fe layer in agreement with the idea of magnetic poisoning of the surface layer as predicted by theory.[16] The SPAED data, however, suggest a much larger degree of magnetic reduction which is nevertheless consistent with the observation of a smaller than predicted sulfur exchange splitting.[18] The measurement of the $L_{2,3}VV$ sulfur Auger SPAED in two other channels of the spin detector (spin polarization perpendicular to the plane of electron emission) found only negligible spin asymmetries ($<1\%$) ruling out the possibility that the reduced in-plane component of the top Fe layer magnetization is due to a simple out-of-plane rotation of the moment. We also point out that our SPAED measurements are sensitive to the net layer magnetization and are not able to distinguish magnetically dead from antiferromagnetic order.

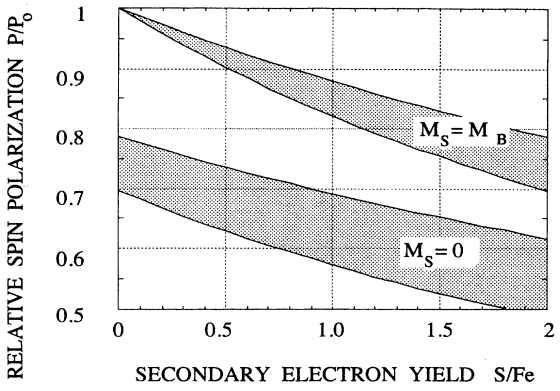

FIG. 3. Modeling of the decrease of secondary electron spin polarization upon sulfur adsorption as a function of electron mean free path (in the range of 4–6 Å), and sulfur secondary electron yield (per Fe-atom yield). The range of two assumed surface Fe layer magnetizations are shown as shaded areas: being equal to the Fe bulk magnetization (top area), and magnetically dead (bottom area).

The finding of magnetic poisoning in $c(2\times 2)$S/Fe(001) deduced from SPAED data is independently supported by the observation of a large change in the spin polarization of the secondary electrons. A decrease in the spin polarization of the secondary electrons is expected to occur due to the addition of an effectively nonmagnetic sulfur layer, but the level of reduction cannot be explained solely on these grounds.[34] We find the spin polarization of the secondary electrons at 160 eV (just above the $L_{2,3}VV$ sulfur Auger peak), to change from $P_0=18\%$ for clean Fe(001) to $P=13\%$ for $c(2\times 2)$S/Fe(001). Simple modeling (see Fig. 3) of the change of the secondary electron spin polarization shows it is not possible to explain the observed 28% decrease ($P/P_0=0.72$) for a range of reasonable electron mean free paths (4–6 Å) and including the contribution of the sulfur overlayer to the secondary electron yield (sulfur/iron ~ 1.0; per atom). However, this observation is consistent with a

decrease in polarization of the top iron layer. As shown in Fig. 3 reasonable agreement is achieved assuming a large reduction in magnetization of the top iron layer which is in agreement with the SPAED data.[35] However, we point out that because of large uncertainties in the modeling of secondary electron emission and in principle the much larger SPAED data set, SPAED is a more sensitive and quantitative tool for the study of local magnetic order near surfaces.

In summary our results represent a clear demonstration of how the measurement of the angular dependence of the spin polarization of Auger electrons (or photoelectrons) may be used to study the local, element specific, surface, and near surface short-range magnetic structure. Further refinements of both the experimental methods and the theoretical model are expected to lead to new insights into the magnetic structure of complex surfaces, overlayers, and interfaces.

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*Present address: ESRF, BP220, F38043 Grenoble Cedex, France.

†Present address: Kodak Ltd., Surf. Sci. W93, Healstone Drive, Harrow, Middlesex HA1 4OY, UK.

[1] L. M. Falicov, D. T. Pierce, S. D. Bader, R. Gronsky, K. B. Hathaway, H. J. Hopster, D. N. Lamberth, S. S. P. Parkin, G. Prinz, M. Salamon, I. K. Schuller, and R. H. Victora, J. Mater. Res. **5**, 1299 (1990).

[2] *Polarized Electrons in Surface Physics*, edited by R. Feder (World Scientific, Singapore, 1985).

[3] J. Kirschner, in *Polarized Electrons at Surfaces*, Springer Tracts in Modern Physics Vol. 106, edited by G. Höhler *et al.* (Springer-Verlag, Berlin, 1985).

[4] R. J. Celotta, D. T. Pierce, G. C. Wang, S. D. Bader, and G. P. Fletcher, Phys. Rev. Lett. **43**, 728 (1979); U. Gradmann in Ref. 2, Chap. 7.

[5] M. Landolt and D. Mauri, Phys. Rev. Lett. **49**, 1783 (1982); M. Landolt in Ref. 2, Chap. 9.

[6] B. Sinkovic, P. D. Johnson, N. B. Brookes, A. Clarke, and N. V. Smith, Phys. Rev. Lett. **62**, 2740 (1989).

[7] C. S. Fadley, Prog. Surf. Sci. **16**, 275 (1984); in *Synchrotron Radiation Research: Advances in Surface Science*, edited by R. Z. Bachrach (Plenum, New York, 1990), and references therein.

[8] W. F. Egelhoff, Phys. Rev. B **30**, 1052 (1984).

[9] S. A. Chambers, H. W. Chen, I. M. Vitomirov, S. B. Anderson, and J. H. Weaver, Phys. Rev. B **33**, 8810 (1986).

[10] Y. U. Idzerda and D. E. Ramaker, Phys. Rev. Lett. **69**, 1943 (1992).

[11] B. Sinkovic, B. Hermsmeier, and C. S. Fadley, Phys. Rev. Lett. **55**, 1227 (1985).

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

[13] B. Sinkovic, D. Friedman, and C. S. Fadley, J. Magn. Magn. Mater. **92**, 301 (1991).

[14] K. O. Legg, F. Jona, D. W. Jepsen, and P. M. Marcus, Surf. Sci. **66**, 25 (1977).

[15] R. A. Didio, E. W. Plummer, and W. R. Graham, Phys. Rev. Lett. **52**, 683 (1984).

[16] S. R. Chubb and W. E. Pickett, Phys. Rev. B **38**, 10 227 (1988); **38**, 12 700 (1988).

[17] P. D. Johnson, A. Clarke, N. B. Brookes, S. L. Hulbert, B. Sinkovic, and N. V. Smith, Phys. Rev. Lett. **61**, 2257 (1988).

[18] A. Clarke, N. B. Brookes, P. D. Johnson, M. Weinert, B. Sinkovic, and N. V. Smith, Phys. Rev. B **41**, 9659 (1990).

[19] P. D. Johnson, N. B. Brookes, S. L. Hulbert, R. Klaffky, A. Clarke, B. Sinkovic, N. V. Smith, R. Celotta, M. Kelly, D. T. Pierce, M. R. Scheinfein, B. J. Waclawski, and M. R. Howells, Rev. Sci. Instrum. **63**, 1902 (1992).

[20] J. Unguris, D. T. Pierce, and R. J. Celotta, Rev. Sci. Instrum. **57**, 1314 (1986).

[21] L. McDonnell, D. P. Woodruff, and B. W. Holland, Surf. Sci. **51**, 249 (1975).

[22] S. P. Weeks and A. Liebsch, Surf. Sci. **57**, 197 (1976).

[23] G. Allie, E. Blanc, and D. Dufayard, Surf. Sci. **57**, 293 (1976).

[24] P. J. Feibelman, E. J. McGuire, and K. C. Pandey, Phys. Rev. B **15**, 2202 (1977).

[25] B. Sinkovic (unpublished).

[26] *Polarized Electrons*, edited by J. Kessler (Springer-Verlag, Heidelberg, 1985).

[27] G. Schutz, W. Wagner, W. Wilhelm, P. Kienle, R. Zeller, R. Frahm, and G. Materlik, Phys. Rev. Lett. **58**, 737 (1987).

[28] G. Schutz, R. Frahm, P. Mautner, R. Wienke, W. Wagner, W. Wilhelm, and P. Kienle, Phys. Rev. Lett. **62**, 2620 (1989).

[29] J. J. Rehr, R. C. Albers, C. R. Natoli, and E. A. Stern, Phys. Rev. B **34**, 4350 (1986).

[30] M. Sagurton, E. L. Bullock, R. Saiki, A. Kaduwela, C. R. Brundle, C. S. Fadley, and J. J. Rehr, Phys. Rev. B **33**, 2207 (1986).

[31] S. Hara, J. Phys. Soc. Jpn. **22**, 710 (1967).

[32] R. Feder, S. F. Alvarado, E. Tamura, and E. Kisker, Surf. Sci. **127**, 83 (1983).

[33] This is consistent with our observation of similar SPAED patterns obtained from the main sulfur Auger peak and the shoulder at ~ 5 eV higher kinetic energy.

[34] Similar observations have suggested the creation of magnetically dead Ni layers for the system $c(2\times1)$O/Ni(110). In this case the Ni surface undergoes a reconstruction. D. L. Abraham and H. Hopster, Phys. Rev. Lett. **58**, 1352 (1987).

[35] If the surface layer of clean Fe(001) crystal before sulfur exposure is assumed to have 30% enhanced magnetization over the bulk (see A. J. Freeman *et al.* in Ref. 2, Chap. 1), the range of magnetically dead surface layer shown in Fig. 3 (bottom area) is shifted to lower P/P_0 values by -0.05.