

Oxygen on Fe(100): An Initial-Oxidation Study by Spin-Polarized Auger Spectroscopy

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Spin-polarized Auger spectroscopy is applied to a study of initial oxidation of Fe(100). The O *KLL* lines are found to exhibit positive (i.e., parallel to the Fe magnetization) spin polarization for the singlet and near zero or negative spin polarization for the triplet final states. The finding is relevant for an experimental determination of orbital mixing coefficients. True secondary electrons reveal strongly spin-polarized O-induced structures at 3 and 12 eV above the vacuum level.

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The interplay between surface magnetism and chemisorption is of long-standing interest for both the surface-physics as well as the magnetism communities. Magnetism can be considered as a fine sensor for changing chemical properties, and chemisorption-induced magnetic properties, on the other hand, can serve as stringent tests for theoretical descriptions of surface magnetism. Applications reach from protective layers on magnetic information-storage media to monitoring of the kinetics of hydrogen storage in solids with magnetic components like FeTi or LaNi₅. Pioneering studies of the influence of chemisorption on surface magnetism were performed on finely dispersed Ni particles,¹ showing that one Ni atom becomes nonmagnetic per adsorbed H atom. Spin-polarized electron experiments^{2,3} later confirmed that observation. Two recent studies by spin-, energy-, and angle-resolved⁴ and by inverse⁵ photoemission went one step further and revealed changes of the electronic structure near the surface. In the case of Fe it was found⁴ that on an Fe-based amorphous ferromagnet oxygen chemisorption causes relatively minor effects without inducing magnetically dead layers. We were able to confirm the latter finding and progress another step. We study the influence of chemisorption on magnetism by spin-polarized Auger-electron spectroscopy (SPAES), which reveals qualitatively new and complementary experimental information. In particular, we show how the degree of mixing of adsorbate and substrate wave functions can be observed. Moreover, the spin polarization is able to detect adsorbate-induced changes in the unoccupied part of the electronic structure through the secondary-electron spectrum, which cannot be identified by intensity measurements alone.

Auger-electron spectroscopy (AES) is the universally used technique to determine the elemental surface composition. If we combine AES with a spin-polarization analysis of the emitted Auger electrons, we not only get chemical but magnetic information also. The power of SPAES relies on the fact that local magnetizations at specific atomic sites can be measured. This has already been demonstrated for a com-

posite system, the amorphous Fe₈₃B₁₇ glass,⁶ and the field is open now for various applications. A straightforward extension certainly is a chemisorption experiment which relates substrate and host magnetic moments. As a first step we chose an Fe(100) single crystal, exposed to different doses of oxygen at room temperature.

The experimental setup is the same as in previous secondary-electron-emission studies.⁶ The magnetized Fe(100) single crystal is irradiated with unpolarized electrons of a kinetic energy of 2500 eV at grazing incidence (70° off normal). The emitted secondary electrons are collected at normal emission, energy analyzed in a cylindrical-mirror analyzer, and their spin polarization measured with a Mott detector. According to usual convention, we define the spin polarization of the emitted electrons as $P = (n_{\uparrow} - n_{\downarrow}) / (n_{\uparrow} + n_{\downarrow})$, where n_{\uparrow} (n_{\downarrow}) is the number of electrons with magnetic moments parallel (antiparallel) to the magnetization of the sample. The Fe(100) surface was prepared by numerous cycles of mild Ne sputtering and subsequent heating to $T = 800$ K, and the expo-

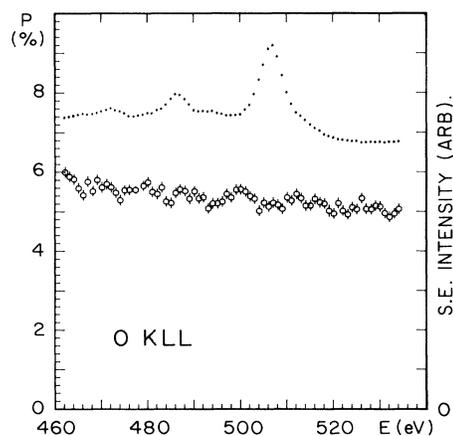


FIG. 1. Spin polarization P (dots) and intensity I (circles) vs kinetic energy of secondary electrons from Fe(100) covered with 250 L O₂.

sure to oxygen took place in the 10^{-7} -Torr range at $T=300$ K. Saturation was found to occur at ≈ 200 L O_2 [1 langmuir (L) = 10^{-6} Torr · sec], where no further increase in the O Auger intensity signal could be detected and no further changes occurred in the polarization spectrum.

The spectra of the emitted secondary-electron intensity $I(E)$ and spin polarization $P(E)$ in the vicinity of the O *KLL* Auger lines are shown in Fig. 1, for a saturation exposure of 250 L O_2 . The intensity shows distinct peaks, and the measured $P(E)$ spectrum exhibits a slight linear overall decrease near the O *KLL* Auger lines, and small structures corresponding in energy to the Auger intensity peaks. We eliminate the secondary electrons created by cascade processes and the inelastically rediffused primaries by subtracting linear backgrounds in intensity and polarization, and arrive at the effective O *KLL* Auger-electron signals I_{eff} and P_{eff} shown in Fig. 2. The effective spin polarization is obtained as $P_{\text{eff}} = P_0 + (P - P_0)I/(I - I_0)$, where P_0 and I_0 are the respective backgrounds.

The multiplets of all intensity structures of the O *KLL* Auger lines have been identified earlier. We note that the intensity spectrum has strong similarities to the *KLL* spectra of atoms such as Ne or Mg where the *2p* shell is filled.⁷⁻¹⁰ A direct conclusion from the intensity would be that Figs. 1 and 2 represent a closed-shell O_2 *KLL* Auger spectrum. Indeed, there are numerous different oxides all giving this type of Auger spectra. However, chemisorbed oxygen on W and Ru shows essentially no differences among the ox-

ides,¹⁰ neither in peak separation nor in intensity ratios. Hence we realize that even high-resolution non-differentiated Auger intensity measurements are of minor help in characterizing the chemisorption of O on Fe(100). Additional information is required for a description of the chemisorption state. The spin-polarization spectrum of the O *KLL* Auger lines gives some of this information and further elucidates the relation between magnetism and chemistry at surfaces.

The most remarkable fact is that the KL_2L_{23} line has a nonvanishing spin polarization: $P \approx 5\%$ with no spectral variation. Without any calculation we conclude from $P \neq 0$ that oxygen on Fe is not the closed-shell O_2^- ion, because (in the absence of resonant processes) a full shell has no preferential spin direction. We find that even screening of the created *1s* hole¹⁰ does not lead to a complete O *2p* shell. We further note that the KL_1L_{23} lines show a pronounced spectral variation. The singlet component 1P has $P \approx 4\%$, whereas the triplet 3P is essentially unpolarized or even slightly negative. Finally we see that $P \approx 0$ on the KL_1L_1 line, although the experimental uncertainty is large as a consequence of the low intensity.

A simple explanation for $P \neq 0$ on different O Auger lines would be based on resonant excitation of the initial *1s* hole to unoccupied states at the Fermi level, mostly Fe *3d* states. Since these states are spin polarized the resonance would lead to polarized *1s* holes, and the emitted Auger electrons consequently would be polarized, too. This process, however, must be excluded for several reasons. First, the KL_1L_1 Auger process should directly reveal this hole polarization, because it only involves inner shell *s* electrons. The polarization on this line, however, is close to zero. Second, the resonant *1s* excitation in energy-loss spectroscopy is too small by an order of magnitude to account for the observed $P \approx 5\%$.

Hence we conclude that nonresonant, single-site Auger processes are responsible for the nonvanishing spin polarization of the O Auger lines. In that case the *1s* hole is unpolarized, and $P \neq 0$ can only be achieved by spin-dependent admixture of Fe *3d* wave function to the O *2p* states. So the Auger polarization reflects the degree of mixing of Fe *3d* and O *2p* wave functions, and we can estimate the strength of the mixing as follows: The change of polarization of the background underlying the O Auger lines gives a rough value of the change of magnetization in the probed surface sheet upon O chemisorption. The decrease of $P \approx 7.5\%$ for clean Fe(100) to $\approx 5\%$ for Fe+O at $E=520$ eV indicates a reduction of magnetization to $\approx \frac{2}{3}$ of the Fe bulk value. In good agreement, the effective polarization of the Fe $L_3M_{45}M_{45}$ Auger line diminishes from $\approx 30\%$ ^{6,11} to $\approx 20\%$ on chemisorption of 250 L O_2 . Because this line involves two Fe *3d*

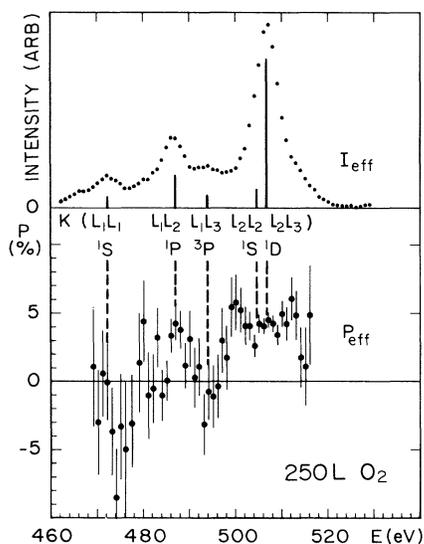


FIG. 2. Effective Auger-electron intensity I_{eff} and spin polarization P_{eff} vs kinetic energy for the *KLL* lines of O on Fe(100).

valence-band electrons, it seems to be reasonable to directly compare its polarization to the polarization of the O KL_2L_{23} line involving two O $2p$ electrons. The ratio of the effective polarizations, $P_{\text{eff}}(\text{O } KL_2L_{23})/P_{\text{eff}}(\text{Fe } L_3M_{45}M_{45}) \approx \frac{1}{5}$, qualitatively shows that mixing between O $2p$ and Fe $3d$ wave functions is quite strong. A quantitative evaluation of the mixing coefficients has not been available up to now. This first experiment clearly indicates, however, that studies of mixing between substrate and adsorbate wave functions are experimentally feasible by SPEAS, which opens new possibilities in chemisorption experiments. Current theories of molecular orbitals, after inclusion of the two-hole final states, will receive further input from the observed spin-polarization spectra.

Another conclusion to be drawn from the effective Auger polarization spectrum of Fig. 2 concerns earlier interpretations of the corresponding intensity spectrum. The high-energy shoulder of the KL_2L_{23} line in intensity spectra of oxides has been ascribed to cross Auger transitions (O K)(O L_{23})(Fe M_{45}).^{7,10} This interpretation is doubtful. The cross transition should have a polarization substantially higher than the O-only KL_2L_{23} transition, because in spite of the strong coupling between Fe and O wave functions the magnetic moment is still higher on the Fe site. The experiment shows, however, that not much spectral variation occurs along the O KL_2L_{23} line, which seems to exclude cross transitions as a cause for the weak-intensity shoulder.

Now we turn to the unoccupied part of the electronic structure. Spin-polarization spectra of true secondary electrons at low kinetic energy reveal pronounced features as a consequence of chemisorption of O on Fe(100). The spectrum of clean Fe(100) of Fig. 3 (top panel) shows a giant peak at ≈ 12 eV above the vacuum level in both intensity and spin polarization. At present we do not know its origin, although we note that the structure is absent in amorphous $\text{Fe}_{83}\text{B}_{17}$ and hence must be a crystalline effect. Similar structures in Ni single crystals even exhibit a face-dependent spin polarization.¹¹ Upon chemisorption of O, the overall polarization decreases and the peak fades away and finally is missing both in $P(E)$ and $I(E)$ for an exposure of 20 L O_2 , which corresponds to an O coverage of ≈ 1 monolayer¹² [see Fig. 3 (center panel)]. The remaining $P(E)$ behavior, i.e., its strong increase at $E \leq 10$ eV, is common to all transition-metal ferromagnets studied so far and is ascribed to exchange scattering of minority-spin hot electrons.^{13,14} Further exposure results in new structures in $P(E)$ and $I(E)$, which saturate at ≈ 200 L O_2 [see Fig. 3 (bottom panel)]. A comparison of the $P(E)$ shapes on the two lower panels of Fig. 3 indicates that two negatively polarized structures centered at ≈ 3 and ≈ 12 eV above the vacuum level are formed. Note

that the corresponding $I(E)$ structure cannot be seen at 3 eV because of the strongly varying secondary-electron background.

A clear interpretation of the peaks does not exist at present. O-induced peaks in the unoccupied band structure have been identified for various materials near the Fermi level.¹⁵ The huge spin polarization and the high energy above the Fermi level, however, are novel observations and will impose important confinements on forthcoming discussions. Extending the inverse-photoemission experiments of Ref. 5 to higher energies will provide complementary information, even k resolved, for the nature of these structures. We note that the O LLL or any other Auger process which could appear at very low kinetic energy can be excluded, since the 12-eV structure persists to a very low primary energy of 28 eV without dramatic change in intensity, whereas for an Auger process a typical threshold behavior would be expected.

At last we have to say a few words about the chemistry of the surface. Chemisorption of O on Fe is known to lead to different compositions depending on exposure rate, temperature, and crystal face. On Fe(100),

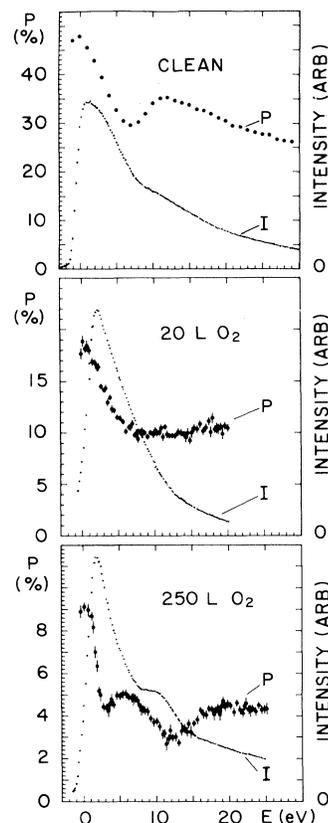


FIG. 3. Spin polarization P and intensity I vs kinetic energy of secondary electrons from Fe(100) covered with various doses of O_2 .

chemisorption at low exposure is followed by oxidation, which at $T=300$ K probably creates a γ - Fe_2O_3 -type oxide.¹² Our analysis of the Fe $M_{23}M_{45}M_{45}$ Auger line shape following Seo, Lumsden, and Staehle¹⁶ supports this interpretation, although α - Fe_2O_3 and FeOOH cannot be safely excluded. A comparison of the different Fe *LMM* Auger line intensities as proposed by Rao, Sarma, and Hegde,¹⁷ on the other hand, indicates oxide formation like Fe_3O_4 or Fe_2O_3 . So, the chemical composition near the surface is still unclear. It could even be that the oxide formation is depth dependent. Comparison of the two Fe Auger polarizations at 43 and 703 eV, respectively, seems to indicate that the magnetic properties of the oxide vary within the probing depth of ≈ 20 Å. Furthermore, the depolarization of the true secondary electrons at very low energies, presumably via exchange scattering, points to the fact that the oxygen atoms within the outermost surface layer form a paramagnetic sheet, whereas the oxide below is ferromagnetic or ferrimagnetic giving rise to nonvanishing Auger spin polarizations. Further experiments to elucidate these problems on well-defined Fe-oxide single crystals are planned.

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