# Oxygen-Induced Magnetism of the Nonreconstructed Chromium (100) Surface

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With use of the technique of spin-polarized photoemission the magnetic properties of the chromium (100) surface have been investigated. Highly diluted oxygen incorporated into the lattice induces magnetic long-range order whereas oxygen adsorbed on top of the surface does not. No indication of ferromagnetism of the oxygen-free surface has been observed.

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Surfaces respond in a variety of ways even to slight variations of the external conditions or composition. Among the thoroughly studied phenomena are, e.g., the temperature-induced surface reconstruction of tungsten,[1] the rearrangement of surface atoms of silicon[2] caused by minute adsorbate coverage, the high sensitivity of electronic surface states with respect to the structure and chemistry of the surface,[3] and the change of the work function[4] upon exposure of the surface to foreign atoms. The experiments reported in this paper add a novel phenomenon to this list: the drastic influence of small amounts of oxygen on the surface magnetic properties of chromium.

Among the nonferromagnetic $3d$ metals, vanadium and chromium are supposed to be the most likely candidates to show surface magnetic anomalies.[5] In particular, for the nonreconstructed Cr(100) surface the Stoner criterium for ferromagnetism was found to be fulfilled essentially as a result of the strongly enhanced electronic density of states at the Fermi level in the topmost atomic layer. Experimentally, this result appeared to be corroborated by observation of excitation of surface magnetoplasma waves on polycrystalline chromium films.[6] As these films were not evaporated under ultrahigh-vacuum conditions their chemical composition was largely unspecified. A recent study by electron-capture spectroscopy confirmed the existence of ferromagnetic order in a nearly oxygen-free $c(2\times2)$ reconstructed chromium (100) surface.[7] This seems in contrast to the results presented here, where surface magnetic order was observed —for the nonreconstructed surface—only if oxygen is incorporated into the chromium lattice.

A macroscopically defect-free (100) surface of a cylindrical (6-mm long, 6-mm diam) chromium single crystal was prepared by mechanical polishing, using powder sizes down to 1 $\mu$m. After insertion into the ultrahigh-vacuum chamber the sample was cleaned for a few days by repeated cycles of argon sputtering (500 eV, 8$\mu$A) and subsequent annealing at increasingly higher temperatures up to 800 °C. As found in previous work[8] the Auger spectra showed—apart from chromium —signals of oxygen and nitrogen. Depending on the duration of the final flashing treatment of the crystal it is possible to vary the oxygen concentration $c_{\rm O}$ of the surface from $\ll 1\%$ to about 4%. The atomic concentration $c_{\rm O}$ of oxygen is obtained from the relation

$$c_{\rm O} = (I_{\rm O}/s_{\rm O})/(I_{\rm O}/s_{\rm O} + I_{\rm Cr}/s_{\rm Cr} + I_{\rm N}/s_{\rm N}),$$

where $I_{\rm O}$, $I_{\rm Cr}$, and $I_{\rm N}$ are the peak-to-peak amplitudes of the Auger signals of oxygen (510 eV), chromium (529 eV) and nitrogen (338 eV) taken for identical instrumental parameters. The sensitivity factors belonging to the Auger transitions examined are, for the respective elements,[9]

$$s_0 = 0.50, \quad s_{\rm Cr} = 0.33, \quad \text{and} \quad s_{\rm N} = 0.33.$$

Since the distribution of the oxygen in the sample is not necessarily homogeneous the actual concentration may vary as a function of the distance from the surface. However, the relative weight of the contribution of a given layer is nearly identical for the Auger and the spin-polarized photoemission experiments because the escape depths of the emitted electrons are almost equal according to the standard curve of inelastic mean free paths.[10] Therefore the concentration relevant in the spin-polarized photoemission experiment —namely the absolute concentration reduced by a factor determined by the finite escape depth of the photoelectrons—is approximately the one given by the Auger spectra.

Although there is no detailed knowledge of the distribution of the oxygen in the surface layer sampled by Auger spectroscopy it is possible to characterize its location more precisely. The necessary information is contained in the value of the photothreshold. After flashing of the sample to 800 °C the oxygen is incorporated into the chromium lattice as opposed to chemisorption on top of the surface. Incorporated oxygen has almost no effect on the work function, its value being $4.10 \pm 0.05$ eV for all such surfaces independent of the oxygen concentration ($< 4\%$). On the other hand oxygen adsorbed at room temperature from the gas phase stays on top of the surface giving rise to an electrostatic dipole layer by attracting negative charge. In this case the work function depends very sensitively on the amount of adsorbed oxygen causing an increase by as much as 1.5 eV for a monolayer coverage.[8] Accordingly, the two species of oxygen—incorporated or adsorbed on top of the surface—are easily distinguished by their influence on the work function. In the following it is shown that they affect the magnetic properties of the surface in a completely different manner. In contrast to the oxygen the distribution of the nitrogen is well known: Its easy removal by slight argon sputtering indicates that it segregated from the bulk on top of the surface. This observation is supported by the findings of Ref. 8. Therefore, the Auger peak-to-peak amplitude of nitrogen can be expressed in terms of monolayer coverage. Its value was nearly identical for all samples and amounted to less than 1 monolayer. It stabilizes the unreconstructed $p(1\times1)$ chromium surface which produced a very clear and sharp low-energy electron-diffraction pattern for all oxygen concentrations examined.[11]

The picture emerging for the flashed chromium surface is thus the following: The surface contains oxygen incorporated into the lattice with an atomic concentration of the order of 1%. In addition there is a coverage of $< 1$ monolayer of nitrogen on top of the surface, stabilizing the unreconstructed $p(1\times1)$ structure.

Surfaces of various oxygen concentrations have been investigated by spin-polarized photoemission. A detailed account of this technique can be found in Alvarado *et al.*[12] In the experiment described in this paper the full spectrum of a mercury-xenon lamp having a high-energy cutoff of $h\nu = 5.7$ eV was used for photoexictation. The thickness of the surface layer probed by the experiment is given by the escape depth of the photoelectrons which amounts to about 20 Å in the energy range considered.[10] This is in contrast to the surface region probed in the experiment described in Ref. 7 where only the outermost tail of the electron distribution decaying into the vacuum is studied. Furthermore, in Ref. 7 the measurements were done on a reconstructed nitrogen-free chromium surface. The measured quantity is the spin polarization of the photoelectrons $P = (N\uparrow - N\downarrow)/(N\uparrow + N\downarrow)$, where $N\uparrow$ ($N\downarrow$) is the number of photoelectrons with spin magnetic moment parallel (antiparallel) to the external magnetic field.

Figure 1 shows the spin polarization $P$ of the photoelectrons as a function of the applied field $H_{\rm ext}$ for a sample containing 3.3% incorporated oxygen. A saturation polarization of 9% is

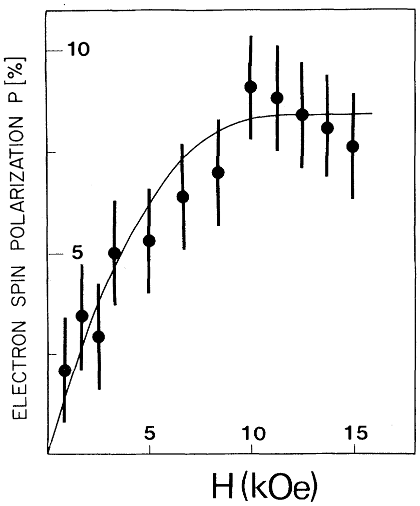

FIG. 1. Electron spin polarization $P$ vs applied magnetic field for a sample containing 3.3% incorporated oxygen.

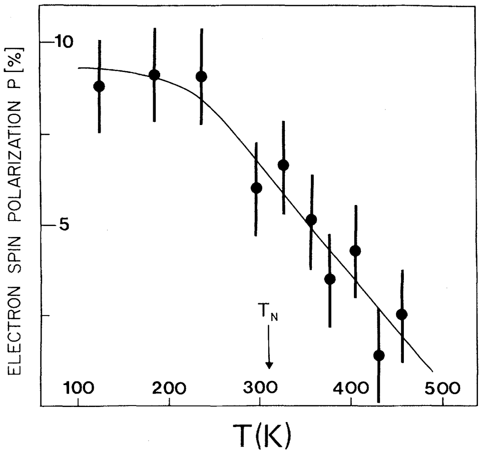

FIG. 2. Temperature dependence of the polarization in an external field of 10 kOe for the same sample as used for the measurement shown in Fig. 1. A vertical arrow shows the antiferromagnetic ordering temperature of Cr.

reached at fields $H_{\mathrm{ext}} \gtrsim 10$ kG. The existence of magnetic order in this surface is clearly established. The temperature of the sample was 230 K.

The temperature dependence of the polarization is displayed in Fig. 2. The measurements were made in an external field of 10 kG. The fact that the polarization vanishes only at $T \gtrsim 500$ K presents strong evidence that the bulk antiferromagnetism of chromium ($T_N = 312$ K) is not related to the observed surface magnetism. It should be noted that the linear dependence of the magnetization—or, in the present experiment, the spin polarization—as a function of temperature is typical for surface magnetic order near the transition temperature.[13]

The saturation polarization versus the amount of incorporated oxygen is shown in Fig. 3(a). All measurements were taken at 230 K which is sufficiently below the magnetic ordering temperature to make the effect of thermal disorder negligible. For completeness the Auger signals of chromium and oxygen of the samples denoted I to IV are presented in Fig. 3(b). It is evident that the saturation polarization depends strongly on the oxygen concentration. Most important, in the absence of oxygen the polarization of the nonreconstructed Cr(100) surface becomes zero within the resolution of the experiment.

The surprising feature of these measurements is that a small amount of incorporated oxygen produces an unexpectedly large polarization. To appreciate this better it is useful to imagine that all oxygen is present in the form of a patch of the ferromagnetic compound $\mathrm{CrO_2}$ carrying a magnetic moment of $2\mu_{\mathrm{B}}$ per formula unit. If we suppose that all the $\mathrm{Cr^{++}}$ moments are fully aligned along the direction of the external field, the resulting maximum polarization is almost an order of magnitude smaller than the one actually observed: For an oxygen concentration of 3% in the form of $\mathrm{CrO_2}$ there are only three polarized $d$ electrons among about 600 unpolarized conduction electrons of the unoxidized chromium. About half of the occupied chromium $d$ band is sampled with the photon energies used. Then $P = 3/300 = 1\%$ as compared to 8% observed. Therefore stoichiometric $\mathrm{CrO_2}$ is to be excluded as the origin of the polarization: The resulting magnetization is much larger than that produced by the amount of $\mathrm{CrO_2}$ corresponding to the measured oxygen concentration. The implication is that oxygen diluted in the chromium lattice acts as a nucleation center for magnetic order in the metal surface.

This appears to be the first observation of oxygen-induced magnetism in a surface.

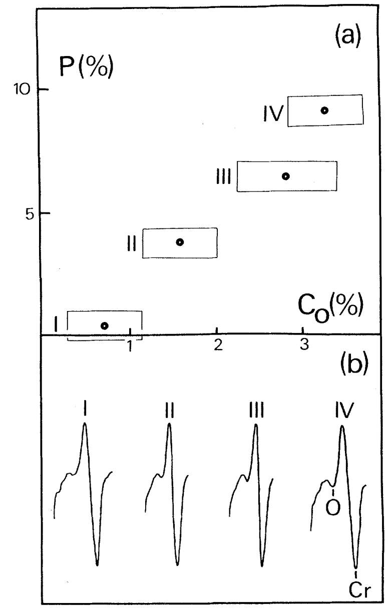

FIG. 3. (a) Saturation polarization as function of concentration of incorporated oxygen. (b) Auger spectra of samples I–IV of (a) showing the signals of chromium (529 eV) and oxygen (510 eV).

To investigate the effect of adsorbed oxygen on the magnetic properties of the nitrogen-stabilized chromium surface, an oxygen-free sample with $P = 0\%$ was exposed to oxygen gas at room temperature. The work function rose by 0.9 eV corresponding to a coverage of 0.6 monolayer (see Ref. 8, Fig. 4). The subsequent measurement of the polarization yields the same result as for the oxygen-free sample, namely 0%. Hence the charge transfer of adsorbed oxygen to the chromium surface has no influence on its magnetic properties. Apart from the findings of Ref. 8 there is therefore an additional distinction between the two binding states of oxygen: Adsorbed oxygen which affects the work function very strongly does not induce magnetism in the chromium surface, whereas incorporated oxygen which does not affect the work function drives the chromium surface into a magnetically ordered state.

In conclusion, the experiments described in this paper show that oxygen incorporated into the chromium surface causes magnetic long-range order even for concentrations as low as $\gtrsim 1\%$. No ferromagnetism was found for the oxygen-free surface. The measurements represent a hitherto unique example of magnetic order induced in the surface by trace amounts of a foreign atomic species.

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