

Ferromagnetic Order at Surfaces of Ultrathin Epitaxial fcc γ -Fe(111) $p(1 \times 1)$ Films on Cu(111)

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Electron-capture spectroscopy has been used to investigate long-ranged and short-ranged two-dimensional magnetic order at *free* (uncoated) surfaces of *homogeneous* (island-free), ultrathin fcc γ -Fe(111)(1×1) films pseudomorphically deposited on Cu(111) substrate crystals. At 298 K, the electron-spin polarization at the surface of a four-monolayer thin fcc Fe film amounts to +16%, directly revealing the existence of *long-ranged ferromagnetic* order. There is evidence that *short-ranged ferromagnetic* order still exists at 400 K at free surfaces of two- and one-monolayer thin fcc Fe films.

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Magnetic phenomena at surfaces and in ultrathin films are presently of great experimental and theoretical interest. Apart from their pivotal technological importance in many fields (catalysis, metallurgy, etc.), they contribute to our understanding of magnetic ordering in two dimensions and provide new insights into the effects of reduced symmetry on the properties of matter.

At a surface, the coordination number (number of nearest neighbors) z , which is known to influence magnetic ordering *strongly*, is intermediate ($z=4$ for a fcc lattice and $z=8$ for a bcc lattice; $z=4$ for a monolayer film) between the atomic ($z=1$) and the bulk limits ($z=12$ for fcc and $z=8$ for bcc). It is this intermediate situation which makes surfaces ideal for the search of changes in magnetic ordering: In going from the bulk to the surface, it is well known that a transition from paramagnetic to ferromagnetic or from antiferromagnetic to ferromagnetic ordering might occur. In addition, at surfaces the coordination number for a specific element can also be varied by depositing ultrathin films of the material and selecting, by use of the appropriate techniques, an *artificial* fcc ($z=4$) or bcc ($z=8$) lattice structure.

Recently, precise theoretical calculations of the magnetic properties of ultrathin films consisting of transition-metals atoms deposited on metallic substrates have been performed, and unusual and striking magnetic properties have been predicted for free (uncoated) surfaces.¹⁻⁴ In particular, the magnetic behavior of Fe was studied for various well-defined configurations (bulk Fe, surface of bulk Fe, ultrathin films of pseudomorphic Fe on Ag or Cu, unsupported Fe monolayer with Ag or Cu lattice spacing), and Fe surfaces were found to exhibit strongly enhanced magnetism compared to that of bulk Fe.

A fruitful interplay between theory and experiment requires that the investigated epitaxial films are deposited *pseudomorphically* and *island free* (i.e., free of inhomogeneities) on surfaces of *well defined* substrate crystals. This requirement is very difficult to fulfill, and contradictory results have been obtained for coated surfaces.⁵⁻⁸

No results have been reported for free surfaces.

In this Letter, we report the first measurements of the long-ranged (macroscopic) and short-ranged (microscopic) two-dimensional magnetic order at the *free* surface of ultrathin (one to four atomic layers) fcc γ -Fe(111) $p(1 \times 1)$ films pseudomorphically deposited on atomically clean and flat surfaces of Cu(111) substrate crystals.

While it is now well established, both theoretically and experimentally, that the surfaces of *bcc* α -Fe are ferromagnetic, the surface magnetic properties of *thin-film fcc* γ -Fe are still a matter of controversy. In a series of experimental investigations (magnetometric measurements,^{5,6} Mössbauer spectroscopy^{7,8}), the magnetic properties of surface-coated fcc γ -Fe films were studied, but contradictory experimental results were obtained. Magnetic measurements at free surfaces of fcc Fe films, however, were not available. The coated films studied so far were found to be either ferromagnetic at room temperature^{5,6} or paramagnetic at 300 K, exhibiting a transition to antiferromagnetism at lower temperatures.^{7,8}

It was still questioned whether these results pertained to the intrinsic magnetic properties of fcc γ -Fe films, or whether they were due either to the island structure of the films,⁷ to oxidation of the films (when the measurements were performed at atmospheric pressures on samples where the Cu-Fe-Cu sandwich layers were defective⁸), or to the use of different probes.

The major aim of the experiments described in this Letter is to investigate the long-ranged *and* the short-ranged electron-spin polarization (ESP) at the surface of well-prepared and characterized fcc γ -Fe films deposited on Cu substrate crystals, and to settle the key issue of *ferromagnetic versus antiferromagnetic* ordering in fcc γ -Fe films.

Using the electron-capture spectroscopy method, we find unambiguously that long-ranged ferromagnetic order exists at room temperature for uncoated surfaces of four atomic layers of fcc γ -Fe(111) $p(1 \times 1)$ films on Cu(111) substrates. Short-ranged ferromagnetic order is still detected at the surface of *one* atomic layer of fcc

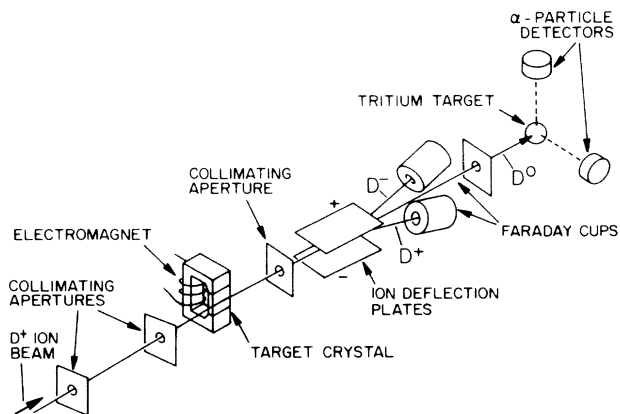


FIG. 1. Schematic diagram of the apparatus used in electron-capture spectroscopy experiments.

γ -Fe(111) $p(1 \times 1)$ on Cu(111).

The method of electron-capture spectroscopy shall now be briefly described. The fundamental process in this technique is the capture of one or two spin-polarized electrons during grazing-angle surface reflection of fast deuterons D^+ .⁹ In specular reflection (incidence angle 0.2°), the distance of closest approach of the deuterons is about 2 \AA , showing that the ions probe only the *topmost* surface layer of the sample. The experimental arrangement is schematically illustrated in Fig. 1. A well-collimated deuteron beam (half-angle of divergence $<0.02^\circ$) is reflected at grazing angle off the target surface, which is magnetized parallel to the surface plane. The beam then passes through a transverse electric field in order to separate spatially residual D^+ from D^0 and D^- atoms formed by one- and two-electron capture, respectively. Therefore, only D^0 atoms impinge on a tritium target and provide ${}^4\text{He}$ particles via the reaction $T(d,n){}^4\text{He}$. The ${}^4\text{He}$ particles are counted by two ${}^4\text{He}$ -particle detectors. The intensity of the deflected D^- and D^+ ion currents can be also monitored by means of two Faraday cups.

For the detection of *long-ranged* surface magnetic order, we investigate *one-electron* capture processes which result in the formation of D^0 atoms polarized in the electron shell. During an adiabatic transition taking place between the magnetic sample and the T target, part of the electron-spin polarization is converted to a D^0 nuclear polarization by hyperfine interaction. The resulting nuclear polarization can be determined by the asymmetry in the angular distribution of the emitted ${}^4\text{He}$ particles and provides a direct measure of the spin polarization P of the captured electrons. Because the electrons captured by different deuterons originate at *widely separated points* on the target surface, observation of a nonzero spin polarization indicates the presence of *long-ranged* ferromagnetic order. Defining P along the

direction of the magnetizing field yields

$$P = (n^+ - n^-)/(n^+ + n^-) = 12(1 - N)/(N + 2), \quad (1)$$

with n^+ and n^- the numbers of up(majority)- and down(minority)-spin electrons and N the count-rate ratio of the emitted ${}^4\text{He}$ particles counted in two ${}^4\text{He}$ -particle detectors. The experimental errors of P are solely due to the counting statistics of the ${}^4\text{He}$ particles emitted in the reaction $T(d,n){}^4\text{He}$.

For the measurement of *short-ranged* ferromagnetic order at unmagnetized surfaces, we investigate *two-electron* capture processes yielding D^- ions which are only stable in the $1s^2{}^1S$ state. Consequently, D^- ions can only be formed by capture of electrons of *antiparallel* spin orientations. For 150-keV deuterons, the characteristic length (spin-spin correlation length) within which two electrons are captured by *one* deuteron is approximately $10\text{--}20 \text{ \AA}$ [time scale of $(3\text{--}6) \times 10^{-16} \text{ s}$]. Two-electron capture is therefore strongly suppressed at surfaces where, on an atomic scale, only electrons with parallel spin orientations can be captured. Thus, the reduction in the D^- yield in the reflected beam, relative to that observed for a nonmagnetic sample such as Cu, provides a measure of the short-ranged surface magnetic order. The D^- and the D^+ (used for normalization purposes) ion currents are measured with an accuracy of $\pm 1\%$ by means of two Faraday cups. These can be replaced by two surface-barrier solid-state detectors for which the experimental errors are only due to counting statistics. The reader is referred elsewhere for further details.^{9,10}

For the deposition of ultrathin fcc γ -Fe films, *atomically clean and flat* Cu(111) substrate crystals are prepared under ultrahigh-vacuum conditions in a target preparation chamber.⁹ The accuracy of the surface orientation of the substrate crystals is better than 0.01° . When we apply our standard cleaning and annealing procedures,⁹ and use Auger-electron spectroscopy with a cylindrical-mirror analyzer, the residual C and O contaminations are found to be less than 1% of a monolayer. The single-crystalline (1×1) state of the surfaces is detected by means of low-energy electron diffraction.

To obtain reliable experimental results, the fcc γ -Fe films must be deposited *homogeneously* and *island free* by layer-by-layer growth on the Cu substrate crystals. We selected Cu as the substrate, because it has been noted that fcc γ -Fe can be deposited pseudomorphically on fcc Cu up to a thickness of approximately 10 \AA , below which no misfit dislocations occur.^{6,11} The critical parameters are the substrate temperature and the evaporation rate.

In our experiments, electron-beam evaporation at $8 \times 10^{-10} \text{ mbar}$ is used. For evaporation rates between 0.01 and 0.2 \AA/s , and for a substrate temperature of 393 K , we find homogeneous and island-free growth of fcc

γ -Fe(111) on fcc Cu(111) for layer thicknesses between 2 and 23 Å. The homogeneous growth of the films is carefully checked by our monitoring the Auger intensities of the substrate (Cu, at 61 eV) and of the films (Fe, at 47 eV) as a function of film thickness (see Fig. 2), as described by Seah¹² and Chang.¹³ To do so, six films of thickness 1.4, 2, 3.5, 8.1, 15, and 23 Å are evaporated on Cu(111) substrates. The film thickness is determined with a calibrated quartz oscillator and with data obtained from calibrated Auger signals.¹³ Figure 2 shows normalized low-energy (Cu, 61 eV; Fe, 47 eV) Auger-electron signals measured as a function of the Fe film thickness on the Cu substrate. For layer-by-layer film growth, the Cu Auger-electron (Fe Auger-electron) signal is predicted^{12,13} to decrease (increase) exponentially [$I_{\text{Cu}} = \exp(-d/d_0)$; $I_{\text{Fe}} = 1 - \exp(-d/d_0)$]. The two curves shown in Fig. 2 are plotted with use of $d_0 = 6.8$ Å.¹⁴ Our experimental Auger-electron data points are in good agreement with the predictions for island-free growth. The deviation of the first pair of data points is probably due to the unreliability of the thickness monitor for such low film thickness. Island-free growth can be further investigated by more detailed Auger measurements¹⁵ and by reflection electron diffraction.¹⁶

Our low-energy electron-diffraction measurements on the epitaxial and island-free fcc γ -Fe(111) films exhibit a $p(1 \times 1)$ structure that is identical (no change in symmetry and intensity of the electron-diffraction pattern) to that of the fcc Cu(111) substrates (lattice constant = 3.615 Å), implying the pseudomorphic growth of fcc γ -Fe(111) on fcc Cu(111). No indications were found for a low-energy electron-diffraction pattern of bcc α -Fe.¹⁴

After preparation, the *uncoated* films are transported *in situ*, with use of a linear and rotary manipulator drive, from the target preparation chamber to the main

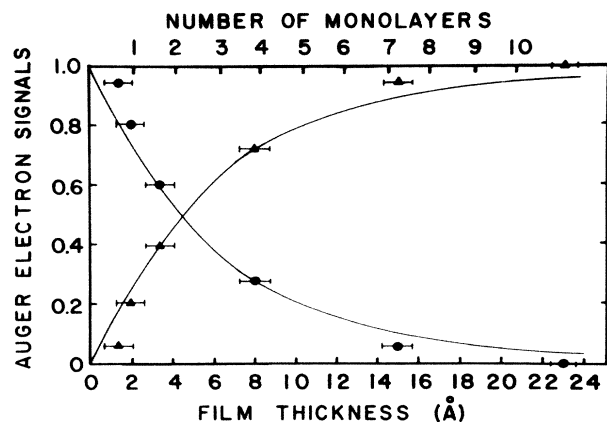


FIG. 2. Auger-electron signals (Cu, circles; Fe, triangles) as a function of the fcc γ -Fe(111) film thickness on the Cu(111) substrate.

chamber⁹ which operates at a base pressure in the low- 10^{10} -mbar region, and the magnetic order is measured within 20 min.

For the measurement of long-ranged surface magnetic order, a specimen is magnetized along the [110] direction in a magnetic field of 34 kA/m (427 Oe), and the long-ranged electron-spin polarization at the topmost surface layer is determined with electron-capture spectroscopy, with use of a reflection angle of 0.2° . The temperature of the specimen is kept constant within 0.03° , by means of an automatic-control device. The absolute temperature is calibrated to within 0.5° .

At the surface of 8.1-Å-thick thin films of fcc γ -Fe(111) on Cu(111), which correspond to four atomic layers of fcc γ -Fe, the long-ranged, net electron-spin polarization is $+ (11 \pm 5)\%$ at 373 K and increases to $+ (16 \pm 5)\%$ when the temperature is lowered to 298 K (see Table I). This clearly establishes, for this temperature range and film thickness (four monolayers), the existence of *long-ranged* ferromagnetic order at the surface of the films.

With *two-electron* capture processes at the surface of 3.5-Å-thick (\approx two atomic layers) and 1.4-Å-thick (\approx one atomic layer) *unmagnetized* fcc γ -Fe(111) films on Cu(111), we find that the short-ranged electron-spin polarization between 300 and 400 K is 12%: This clearly demonstrates the existence of *short-ranged ferromagnetic* order at the surface of these films (see Table I). Upon increasing the temperature to 640 K, where interdiffusion between Fe and Cu is still negligible,¹⁷ and which is presumably *above* the Curie temperature for one- and two-monolayer thick Fe films,⁶ it was observed that the short-ranged electron-spin polarization does not vanish. Similar behavior is found at surfaces of the *ferromagnetic* 3d transition-metal Ni.¹⁰

From the above nonzero electron-spin-polarization data (see Table I), it is therefore established that long-ranged and short-ranged ferromagnetism exists at the *topmost* surface layer of fcc γ -Fe, in the form of pseudomorphic ultrathin (*111*)-*surface-oriented films* which is in agreement with the results of Refs. 5 and 6 reported for surface-coated fcc γ -Fe(111) films. This is in contrast to earlier claims according to which surface-coated fcc γ -Fe(111) films possessing an *island structure* were *paramagnetic* at 300 K.⁷

TABLE I. Electron-spin polarization at surfaces of ultrathin fcc γ -Fe(111) films on Cu(111) substrates.

Film thickness (monolayers)	Electron-spin polarization (%)		Temperature (K)
	Long-ranged	Short-ranged	
4	$+16 \pm 5$...	298
4	$+11 \pm 5$...	373
2	...	12 ± 1	300-400
1	...	12 ± 1	300-400

We note that the present electron-spin-polarization data may represent the lowest limits for the "intrinsic" electron-spin polarization at the surface of *unsupported* fcc γ -Fe(111) films. It is well known that substrate-overlayer hybridization and charge transfer can reduce the intrinsic magnetization of overlayers. In previous electron-capture spectroscopy experiments at surfaces of seven-atomic-layer thin Ni(100) films, we found that the long-ranged electron-spin polarization is reduced from -64% to -33% when Cu(100) substrates are used instead of *nonmetallic* NaCl(100) substrates.¹⁸

In a recent theoretical study, Fu, Freeman, and Oguchi¹ investigated thin-film magnetism in an *unsupported* Fe(100) monolayer with the lattice constant of Cu, and in a single pseudomorphic monolayer of Fe deposited on Cu(100). These authors find a reduction of the magnetic moment of a Fe monolayer when supported by a metallic substrate. No evidence for antiferromagnetism was found for this monolayer system. Unfortunately, there are no theoretical predictions for the lattice-parameter dependence of ferromagnetism in ultrathin fcc γ -Fe(111) films.

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