Enhancement of the Curie Temperature of Epitaxial Fe Films on W(110) Caused by Adsorption of Submonolayers of Fe, Pd, Ag, and O

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We have determined the Curie temperature T_C of an epitaxial monolayer of Fe(110) on a W(110) substrate by means of spin-polarized low-energy-electron diffraction. Adsorption of submonolayer amounts of Fe causes T_C to increase distinctly. An *enhancement* of T_C by about the same amount is also found upon adsorption of *submonolayers* of Pd, Ag, and O_2.

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The magnetism of ultrathin films in the monolayer (ML) range is currently under close scrutiny.[1] Theoretically,[2,3] the interest has focused on the exact value of the magnetic moment μ of Fe, Ni, and Co atoms arranged in a variety of two-dimensional structures, such as the "free-standing" monolayer, the monolayer atop a nonmagnetic substrate, or the monolayer sandwiched between two nonmagnetic films. A consensus has emerged that μ for the free-standing monolayer is enhanced with respect to the bulk value and any contact with nonmagnetic atoms is found to slightly reduce the magnetic moment. This reduction depends on parameters like the degree of d-band hybridization between film and substrate and the exact monolayer-substrate geometry. For example, the moment of Fe monolayers on Ag(001) is calculated[3] to be less than that of those on W(110).[4] Experimentally, one is slowly moving toward the verification of this fundamental picture of metallic magnetism. A slight enhancement of μ (14%) over the bulk value has been reported for an Fe monolayer on W(110) coated with Ag.[5] Co films sandwiched between Cu did not show any significant enhancement,[6] although the value of μ in the monolayer range is at least as large as in the bulk. Actually, more interest has been focused on the experimentally easier accessible quantities, such as the temperature dependence of the magnetization,[7] magnetic anisotropies,[8] and the value of the Curie temperature T_C as a function of thickness.[9,10] Critical exponents[9,11] and anisotropy constants[8,12] have been reported that are in the range predicted for truly two-dimensional systems. T_C, quite generally,[13] is found to decrease from the bulk value when the thickness approaches the monolayer range. Here we report a new phenomenon, the *enhancement* of T_C of a pseudomorphic monolayer of Fe on W(110) caused by adsorbing submonolayer amounts of nonmagnetic impurity atoms Pd, Ag, and O. The very same adsorbates which are believed to cause a reduction of the magnetic moment[2,14] (or at least to leave it unaffected) are found to *increase* the Curie temperature.

We were stimulated to systematically search for an effect of adsorbates on T_C of thin films by an early ob-

servation of Przybylski and Gradmann,[15] who reported the Curie temperature of their Fe films on W(110) to be larger when the films were coated with Ag. In addition to Ag, Pd was also chosen because it is believed to acquire a small magnetic moment when in contact with Fe.[16] Finally, O_2 was used because of the absence of both d electrons and conduction electrons, which are present in both Ag and Pd. Clearly, judging from the radical differences in electronic structure between Pd, Ag, and O, we were expecting T_C to behave quite differently upon adsorption: Most surprisingly, in all cases T_C was found to increase by a similar amount.

The experimental procedure was as follows. First, an Fe film of thickness 1.3 ± 0.3 ML was deposited by molecular-beam epitaxy on a clean single-crystal W(110) substrate. During the deposition the substrate was held at room temperature and the pressure in the UHV chamber did not rise above 1×10^{-10} mbar (base pressure, 4×10^{-11} mbar). Under such conditions the films are known[17,18] to grow in registry (pseudomorphically) with the underlying substrate for thicknesses up to 2 ML. The quality of the pseudomorphic, layer-by-layer growth has been confirmed by studies using LEED, Auger, and, most conclusive, Mössbauer spectroscopies.[17] This was confirmed by our 1.3-ML film showing a sharp $p(1 \times 1)$ low-energy-electron diffraction (LEED) pattern. A common contaminant of the films was found to be oxygen: Thin films of Fe on W(110) are so sensitive to O that exposing the films to an amount as low as 1% of a langmuir resulted in clearly distinguishable $p(2 \times 2)$ extra spots. All the results presented in this Letter for "clean" films refer to the $p(1 \times 1)$ LEED structure, with contaminant level below 1% of a ML. At about 2 ML, clean films develop satellites near some LEED spots: This fact was used to obtain an approximate calibration of the deposition rate. A more accurate estimate of film thickness was obtained by a method using the known probing depth of the spin-polarized low-energy-electron diffraction (SPLEED) electrons.[19] This method was used to estimate the above value of 1.3 ± 0.3 ML.

Magnetic order was measured in *real time* during film growth by SPLEED. In this technique, low-energy electrons (in the present case, 31.0-eV kinetic energy) are detected after elastically scattering from the remanently magnetized sample. The magnetizing of the sample is achieved by a field pulse of about 100 Oe produced *in situ* by a Helmholtz coil. The magnetizing of the sample is performed at the taking of every data point. As the incident beam is spin polarized, the scattered intensities $I\uparrow$ and $I\downarrow$ for incident electrons with spin parallel and antiparallel to the sample magnetization, respectively, are different if the sample is ferromagnetically ordered. A so-called[20] exchange asymmetry $A_{ex} = (I\uparrow - I\downarrow)/(I\uparrow + I\downarrow)$ arises, which in the single-scattering limit is proportional to the number of spontaneously magnetized atoms within the probing depth of the SPLEED electrons (about 2.5 ML in the present case; see Ref. 19). In particular, when the temperature is raised, A_{ex} varies as the magnetization, vanishing at the Curie temperature. Recorded as a function of the Fe deposition time—as displayed in Fig. 1—A_{ex} remains zero up to just below the 1.3-ML thickness and then suddenly reaches a finite value (see Fig. 1). This means that the Curie temperature T_C of the clean film has exceeded room temperature (see first entry in Table I). Right after this sharp onset the Fe deposition is stopped and T_C of the clean film is measured (see Fig. 2, circles). The sharpness of the drop of the A_{ex}-vs-T curve near T_C is affected by impurities and film defects. For example, films produced under poorer vacuum conditions exhibit a less sharp phase transition. As suggested in Ref. 9, the sharpness of the transition itself can be taken as a stringent criterion for the film quality. We notice that the phase transition measured on such a film is among the sharpest ever recorded in thin-film magnetism. In view of the extreme sharpness of the onset in Fig. 1, T_C for films prepared in different runs cannot be reproduced exactly (on the scale of Fig. 1, adding or subtracting 1 s to the deposition

TABLE I. Values of the Curie temperature for clean Fe films and for Fe films with adsorbates as determined by the vanishing of A_{ex}. T_C for the 1.5-ML Pd-covered film is larger than 392 K (we explicitly avoided higher temperatures to minimize the risk of interdiffusion and/or clustering).

T_C (K) of clean films (± 5 K)	T_C (K) of films with adsorbates (± 5 K)
300	360 (+0.05 ML Fe)
369	431 (+0.1 ML Pd)
351	395 (+0.1 ML Ag)
353	402 (+0.1 L O_2)
351	422 (+1.0 ML Ag)
357	> 392 (+1.5 ML Pd)
379	376 (+1.0 L O_2)

time—corresponding to less than 1% of ML—makes a sizable difference in the value of T_C). To separate unambiguously the effect on T_C produced by the adsorbates and by uncertainties in the thickness we found it necessary to measure T_C of the clean film prior to deposition of each adsorbate (see first column in Table I). On the other hand, the extreme sensitivity of T_C to minute disturbances of the system is the key ingredient of these experiments.

After the sample has cooled down to room temperature, about 0.1 ML Pd is evaporated onto the Fe films. As for the Fe films, the evaporation rate of the Pd oven (about 0.2 ML/min) is also estimated by the method using the known probing depth of the SPLEED electrons. By this method, because of the small amounts involved, the coverage is only known to within an accuracy of 50%. After deposition of this small amount of Pd onto the Fe film no change in the LEED pattern could be observed. But a subsequent determination of T_C, see Fig. 2 (stars), shows a surprising result: T_C has risen by as much as 62
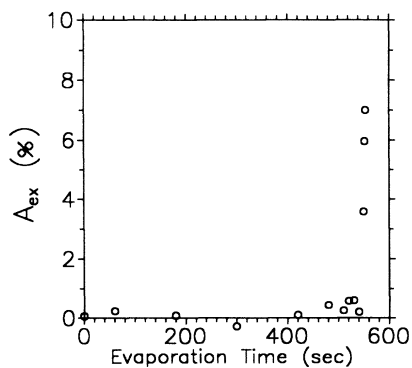

FIG. 1. Dependence of A_{ex} (specularly reflected beam) on the Fe deposition time: Electron kinetic energy, 31 eV; angle of incidence, 22°. The substrate during deposition and measurement of A_{ex} was held at *room temperature*.
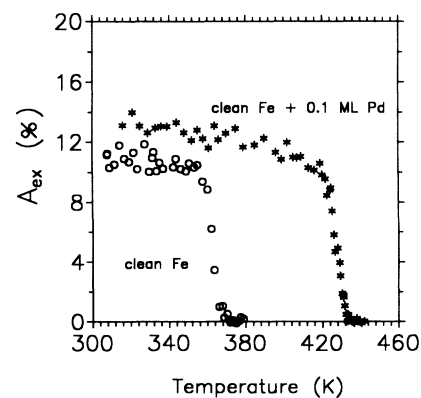

FIG. 2. Temperature dependence of A_{ex} (specularly reflected beam) for a clean, 1.3-ML-thick film (circles) and for the same film covered with 0.1 ML Pd. Electron kinetic energy and angle of incidence as in Fig. 1. The curves were found to be reversible within the accuracy of the experiment.

K with respect to its value for the clean Fe film. Nearly the same result is obtained when the experiment is performed with Ag instead of Pd. Again, a coverage of only 0.1 ML of Ag leads to a clear rise of the Curie temperature, although no change of the LEED pattern is observed. A third experiment involved exposing the clean Fe film to 0.1 L ($1 \text{ L} = 10^{-6}$ Torrs) O_2 In this case the LEED pattern evolved from the sharp $p(1 \times 1)$ structure of the clean epitaxial film to an equally sharp $p(2 \times 2)$ structure. Although different in this respect, there is no qualitative difference between Pd, Ag, and O concerning their effect on the Curie temperature of the Fe film. As Table I shows, an exposure of 0.1 L of O_2 also causes a sizable enhancement of T_C.

Our results for Ag agree with the earlier observation of Ref. 15, which reports an increase in T_C from 210 to 296 K upon coating a monolayer Fe film on W(110) with an unspecified amount of Ag. The somewhat thicker films measured here have correspondingly higher Curie temperatures. Later results reported by Gradmann et al.[18] for Ag-coated Fe films with thicknesses in the range 0.4–1.1 ML are also in agreement with our finding that the Curie temperature of the 1.3-ML Fe film is above room temperature. A T_C of 340 K for a W(110)/Fe/Ag sandwich with an Fe thickness of 1.1 ML is also, to within the accuracy of both experiments, a sign that the two systems prepared under similar conditions but in different laboratories have essentially the same magnetic properties. In the cases of Pd and O we know of no previous studies that would suggest the type of behavior observed here.

As summarized in Table I, we have observed an enhancement of the Curie temperature of a pseudomorphic Fe film on W(110) upon adsorption of submonolayer amounts of nonmagnetic impurity atoms. It does not seem to matter whether these atoms are Pd, Ag, or O, although their electronic structure is quite different. The enhancements observed are even of the same order of magnitude as those obtained when Fe adatoms adsorb on an Fe film (compare to first line in Table I). Notice that the adsorption of such quantities of Pd, Ag, and O_2 was always accompanied by an *enhancement of the coercive field* necessary to switch the magnetization, as measured with SPLEED using the method described in Ref. 21. Simiar rises in T_C were observed when an amount of Pd or Ag atoms corresponding to about 1 ML were deposited (see Table I). However, we attribute more significance to values measured for submonolayer contaminants, which should be a true measure of the extra interatomic exchange brought about by the adsorbates. Upon approaching the 1-ML range (or above), we cannot exclude that some amount of interdiffusion or clustering in the Pd(Ag)-Fe occurs, thus affecting the structure of the underlying Fe film (and with it the direct interatomic exchange between the Fe atoms). At such coverages as low as 0.1 ML, in con-

trast, it is more likely that the adsorbed atoms remain statistically randomly distributed *on top* of the Fe film.

In the following we suggest two possible reasons for this T_C enhancement:

(a) Mediated by the impurity atoms, an indirect exchange interaction is added to the direct exchange interaction between the Fe atoms. If there is no perturbation of the direct exchange interaction due to the impurity atoms diffusing into the Fe or oxidizing it, then this additional interaction could lead to an enhanced Curie temperature. Such an indirect exchange interaction is known to occur, e.g., between Fe layers separated by Cu (Ref. 22) and between Co layers separated by Cu.[19]

(b) Structural changes of the pseudomorphic Fe film in the presence of impurities may, in principle, lead to a change of the Curie temperature. Although we did not see any structural change of the $p(1 \times 1)$ structure upon adsorption of Pd and Ag, we cannot exclude the possibility of a minute relocation of the Fe atoms. To clarify this point, methods that can detect the smallest structural changes should be used, such as high-resolution electron-energy-loss spectroscopy.[23] In the case of 0.1 L of oxygen we observed a $p(2 \times 2)$ pattern, which may be connected with the enhancement of T_C.

Whatever explanation applies, it is clear from the present experimental results that the exact value of T_C in ultrathin films is not simply a matter of reduced dimensionality: As adsorbates can enhance T_C, so could the substrate. The observed enhancement, not previously considered by theory, should stimulate new research into the origin of *inter*atomic exchange interactions.

[1]See the collection of papers, *Magnetism in Ultrathin Films*, edited by D. Pescia [Appl. Phys. A **49**, Nos. 5 and 6 (1989)], and the numerous references therein.

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