Ferromagnetic order and critical behavior at surfaces of ultrathin V(100)$p(1\times1)$ films on Ag(100)

C. Rau and G. Xing
Physics Department, Rice University, Houston, Texas 77251

M. Robert
Department of Chemical Engineering, Rice University, Houston, Texas 77251

(Received 17 September 1987; accepted 9 October 1987)

The magnetic order and critical behavior of well-defined $(100)p(1\times1)$ surfaces of ultrathin (1–7 monolayers) vanadium films deposited on atomically clean and flat Ag(100) substrates is studied by electron capture spectroscopy, a novel method which probes electron spin polarization (ESP) at the topmost surface. For all investigated films, the long-ranged ESP is nonzero, demonstrating the existence of long-ranged ferromagnetic order at the film surface. For a 5-monolayer-thick film, ferromagnetic order sets in at a critical surface temperature $T_{Cs} = 475.1$ K. In the temperature range from 200 to 475.1 K, the ESP of the topmost surface layer follows the power law $(T_{Cs} - T)^{\beta}$, with $\beta = 0.128 \pm 0.01$. This result is in good agreement with the exact value $\beta = \frac{1}{8}$ of the two-dimensional Ising model.

I. INTRODUCTION

Recent progress in experimental methods enables us to investigate in detail the magnetic properties of well-characterized surfaces, interfaces, and thin films, as well as the various phase transitions occurring in them.

On the other hand, the theoretical studies of such systems have been initiated many years ago.

The central role played by the Ising model[1] of a ferromagnet in the modern theory of phase transitions is well known.[2] It is the first model which established[3] the essential role played by the dimension of space in the existence of a phase transition, and it is exactly solvable in two dimensions, as first shown by Onsager.[4]

Identical expressions for the spontaneous magnetization of the two-dimensional Ising model with nearest-neighbor forces were calculated exactly nearly 40 yr ago by Kaufman and Onsager,[5] and, from a different evaluation of long-distance order, by Yang.[6] The equivalence of these two definitions of magnetic order to the "true" spontaneous magnetization defined as the derivative of the free energy with respect to the external field, was later established by Benettin *et al.*[7]

With T the temperature and T_C its critical value, the spontaneous magnetization m has, near T_C, the exact form[5,6]

$$m = \text{const}(T_C - T)^{1/8}. \tag{1}$$

In contrast to these most remarkable theoretical achievements, the prediction (1) for the critical behavior of the spontaneous magnetization of a two-dimensional uniaxial ferromagnet could not be tested experimentally for real, truly two-dimensional ferromagnets. It is the purpose of this paper to report such an experimental test.

Originally proposed by Lenz[8] as a model for ferromagnetism, the Ising model can also be used to describe a uniaxial antiferromagnet and can readily be transcribed into a simple model fluid, the lattice gas. For bulk three-dimensional antiferromagnets such as K_2NiF_4 and especially Rb_2CoF_4, in which the magnetic couplings in one direction are much smaller than in the other two, thus making them quasi-two-dimensional, neutron scattering measurements[9] have shown that the critical behavior is quite close to that of the two-dimensional Ising model. However, crossover effects from two-dimensional to three-dimensional critical behavior were observed in these systems. For fluids, high-resolution heat capacity measurements of monolayer methane adsorbed on graphite have recently revealed that this system behaves like the two-dimensional Ising model.[10]

Whether the surface of a given element exhibits magnetic order or not clearly cannot be predicted by statistical mechanics: the appropriate theory is purely quantum mechanical, based on the evaluation of the exchange integral. In that respect, one-electron band theories predict that the surface of bulk vanadium and of thin films of vanadium are ferromagnetically ordered in the ground state.[11–14] This is supported by recent experimental findings.[15]

In this paper, the magnetic behavior of truly two-dimensional magnetic films consisting of a few monolayers of $V(100)p(1\times1)$ on Ag(100) substrates is studied using the method of electron capture spectroscopy (ECS).

It is first found that the surface of these ultrathin films orders ferromagnetically at low temperatures, as had been previously reported for the surface of bulk vanadium.[15] This is in contrast to bulk vanadium itself which, as is well known, is paramagnetic at all temperatures. It is equally well known that for isotropic two-dimensional continuous spin systems with short-ranged forces, no spontaneous magnetization can occur at nonzero T, as proved by Mermin and Wagner.[16] However, the slightest anisotropy is sufficient to induce a spontaneous magnetization, as shown by Malyshev,[17] and as seen in the present experiment.

Next, it is found that in the neighborhood of the Curie temperature of the surface T_{Cs}, the magnetization of the topmost layer behaves like $(T_{Cs} - T)^{\beta}$, with $\beta = 0.128 \pm 0.01$, in good agreement with the exact result[4,5] [Eq. (1)] of the two-dimensional Ising model.

Finally, V(100) films of varying thickness, ranging from 1

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to 7 monolayers, were also studied, and the Curie temperature of the surface was observed to increase with film thickness.

The preparation of atomically clean and flat substrates and the deposition of well-ordered and well-characterized films represent major difficulties in experimental studies of ultrathin epitaxial films. These obstacles can now be overcome for an increasingly large number of interesting systems. Details for the case V(100)/Ag(100) will be described below.

II. EXPERIMENTAL

The present experimental results were obtained using electron capture spectroscopy. This method has been discussed in detail in Ref. 18, and we shall only briefly describe its essential features. This technique is based on the capture of one spin-polarized electron during grazing-angle surface reflection of fast deuterons D^+.[18] At specular reflection, the distance of closest approach of the deuterons is 1–2 Å, establishing that the ions probe only the topmost surface layer of the sample.

After reflection, the atomic part of the beam consists of D^0 atoms with polarized electron spin. The electrons then transfer their polarization to the D^0 nuclei by hyperfine interaction. The nuclear polarization thus measures the electron spin polarization, and is determined from the asymmetry in the angular distribution of the ^{4}He particles emitted in the reaction $T(d,n)^4$He.

Because the electrons captured by different deuterons originate at widely separated points on the target surface, observation of a nonzero spin polarization indicates the existence of long-ranged surface ferromagnetic order. Defining the electron spin polarization P along the direction of the magnetizing field yields

$$P = (n^+ - n^-)/(n^+ + n^-) ,$$

with n^+ and n^- the numbers of up(majority)- and down (minority)-spin electrons.

For the deposition of ultrathin vanadium films, atomically clean and flat Ag(100) substrate crystals are prepared under ultrahigh vacuum in a target preparation chamber.[18] The surface orientation of the Ag(100) crystals is better than 0.01°, and is monitored by use of a precision x-ray diffractometer.

Applying standard cleaning and annealing procedures developed in our earlier studies, and using Auger electron spectroscopy with a cylindrical-mirror analyzer, residual C and O contaminations are measured to be $< 1\%$ of a monolayer. The single-crystalline (1×1) state of the Ag(100) surface is detected by low-energy electron diffraction.

The vanadium films are deposited by electron-beam evaporation at 8×10^{-10} mbar. For a substrate temperature of 373 K and an evaporation rate of 0.04 Å/s, homogeneous and island-free growth of the V films are obtained. Further details of this procedure can be found in our earlier study of epitaxial Fe films on Cu single-crystal substrates.[19]

Low-energy electron diffraction measurements show a $p(1\times1)$ structure for all films studied. No changes in symmetry and intensity of the electron-diffraction patterns are found, implying the epitaxial growth of V(100) on Ag(100). The thickness of the films is determined with a calibrated quartz oscillator and with calibrated Auger electron signals.[19]

TABLE I. Electron spin polarization P (%) at surfaces of ultrathin V(100)$p(1\times1)$/Ag(100); applied magnetic field $H = 300$ Oe.

Film thickness (monolayers)	Electron spin polarization P(%)	Temperature (K)
7	-18 ± 2	308
6	-12 ± 2	318
5	See Figs. 1 and 2	250–613
3	-12 ± 2	215
3	0 ± 2	306
2	-15 ± 2	238
1	-12 ± 2	220

After preparation and characterization, the V/Ag samples are studied *in situ* at 2×10^{-10} mbar. Electron capture spectroscopy is finally used to measure the long-ranged surface ferromagnetic order, the specimens being magnetized along the [001] direction in magnetic fields ranging between 75 and 600 Oe, and the temperature of the samples being kept constant within 0.05°. Such applied fields have a negligible effect on the electron spin polarization in the investigated temperature range.[20,21]

III. RESULTS AND DISCUSSION

Results of the measurements are presented in Table I. For films of five layers, the temperature variation of the electron spin polarization is shown in Figs. 1 and 2.

For all film thicknesses, nonzero values of the electron spin polarization are observed, clearly establishing that long-ranged ferromagnetic order exists at the topmost layer.

Figure 1 shows the temperature dependence of the normalized long-ranged electron spin polarization P/P_0 at the surface of five-layer-thick V(100) films on Ag(100), as a function of T/T_{Cs}, with $T_{Cs} = 475.1$ K the surface Curie

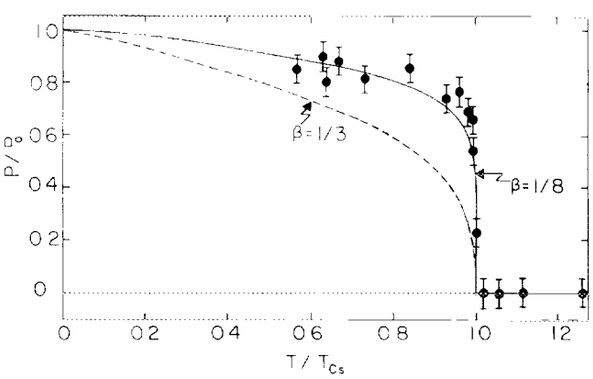

FIG. 1. Electron spin polarization P/P_0 as function of T/T_{Cs} for a 5-monolayer film of V(100) on Ag(100). The solid and dashed lines represent, respectively, the theoretical predictions for the spontaneous magnetization of the two-dimensional Ising model and the three-dimensional Ising model or the isotropic XY and Heisenberg models.

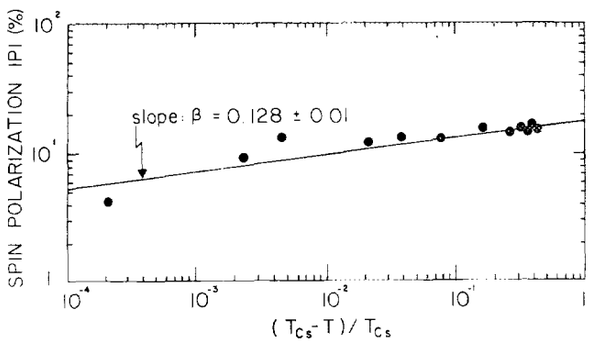

FIG. 2. Log–log plot of the electron spin polarization data shown in Fig. 1.

temperature of the film and $P_0 = -17.8\%$ the calculated electron spin polarization at $T = 0$. In Fig. 2 a logarithmic plot is given of the electron spin polarization P as function of the reduced temperature $(T_{Cs} - T)/T_{Cs}$.

The surface Curie temperature T_{Cs} and the critical exponent β for a five-layer film are determined by a linear least-squares fit of the polarization data under the assumption of a power law behavior of the form $(T_{Cs} - T)^{\beta}$, and are shown in Figs. 1 and 2. The value of β is found to be $\beta = 0.128 \pm 0.01$ giving the slope of a straight line in the log–log representation of the polarization data given in Fig. 2. The solid curve in Fig. 1 corresponds to $\beta = 0.125$, which cannot be distinguished from 0.128 on the scale of the figure.

The value we obtain for the critical exponent β agrees well with the exact value [Eq. (1)] of the two-dimensional Ising model of a ferromagnet. For comparison, we also show in Fig. 1 the temperature behavior of the three-dimensional Ising, XY, or Heisenberg models for which β is very close to $\frac{1}{3}$.[2]

From Table I, which gives the ESP as a function of film thickness and temperature, we can conclude that the critical temperature of a film decreases with film thickness, as expected. This is particularly apparent from the ESP data of a 3-monolayer-thick film, and from the fact that below a film thickness of three layers, the samples had to be cooled below room temperature to exhibit ferromagnetism.

The present results are consistent with ground-state one-electron band calculations of Yokoyama *et al.*, who studied unsupported five-layer-thick V(100) films, of Fu, Freeman, and Oguchi, who analyzed one and two layers of V(100) on Ag(100), and of Gay and Richter who considered an unsupported monolayer of V(100).

The effect of fluctuations on these ground-state results have, to our knowledge, not been determined and represent a challenge for future research.

Finally, it is of interest to note that for a Gd monolayer in the paramagnetic region, Ising critical behavior was very recently observed by Farle and Baberschke using electron spin resonance.[22]

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation, the Robert A. Welch Foundation, the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and by a Joseph H. DeFrees Grant of Research Corporation.

[1] E. Ising, Z. Phys. **31**, 253 (1925).
[2] For a review, see M. E. Fisher, in *Proceedings of The Robert A. Welch Foundation Conferences on Chemical Research, XXIII, Houston, TX, 1979*, edited by W. O. Milligan (Pyoung, Houston, 1980).
[3] R. Peierls, Proc. Cambridge Philos. Soc. **32**, 477 (1936).
[4] L. Onsager, Phys. Rev. **65**, 117 (1944).
[5] B. Kaufman and L. Onsager, unpublished work referred to in L. Onsager, Nuovo Cimento Suppl. **6**, 261 (1949).
[6] C. N. Yang, Phys. Rev. **85**, 808 (1952).
[7] G. Benettin, G. Gallavotti, G. Jona-Lasinio, and A. L. Stella, Commun. Math. Phys. **30**, 45 (1973). See also A. Martin-Löf, Commun. Math. Phys. **24**, 253 (1972).
[8] W. Lenz, Phys. Z. **21**, 613 (1920).
[9] R. J. Birgeneau, H. J. Guggenheim, and G. Shirane, Phys. Rev. Lett. **22**, 720 (1969); Phys. Rev. B **1**, 2211 (1970); E. J. Samuelsen, Phys. Rev. Lett. **31**, 936 (1973); H. Ikeda, M. Suzuki, and M. T. Hutchings, J. Phys. Soc. Jpn. **46**, 1153 (1979).
[10] H. K. Kim and M. H. W. Chan, Phys. Rev. Lett. **53**, 170 (1984); H. K. Kim, Q. M. Zhang, and M. H. W. Chan, Phys. Rev. B **34**, 4699 (1986).
[11] G. Allan, Phys. Rev. B **19**, 4774 (1979); Surf. Sci. Rep. **1**, 121 (1981).
[12] G. Yokoyama, N. Hirashita, T. Oguchi, T. Kambara, and K. I. Gondaira, J. Phys. F **11**, 1643 (1981).
[13] C. L. Fu, A. J. Freeman, and T. Oguchi, Phys. Rev. Lett. **54**, 2700 (1985); C. L. Fu and A. J. Freeman, J. Magn. Magn. Mater. **54–57**, 777 (1986).
[14] J. G. Gay and R. Richter, Phys. Rev. Lett. **56**, 2728 (1986).
[15] C. Rau, C. Liu, A. Schmalzbauer, and G. Xing, Phys. Rev. Lett. **57**, 2311 (1986).
[16] N. D. Mermin and H. Wagner, Phys. Rev. Lett. **17**, 1133 (1966).
[17] V. A. Malyshev, Commun. Math. Phys. **40**, 95 (1975).
[18] C. Rau, J. Magn. Magn. Mater. **30**, 141 (1982).
[19] C. Rau, C. Schneider, G. Xing, and K. Jamison, Phys. Rev. Lett. **57**, 3221 (1986).
[20] J. Balberg and J. S. Helman, Phys. Rev. B **18**, 303 (1978).
[21] C. Rau and S. Eichner, Phys. Rev. B **34**, 6347 (1986).
[22] M. Farle and K. Baberschke, Phys. Rev. Lett. **58**, 511 (1987).