

Ferromagnetic Order at $(100)p(1 \times 1)$ Surfaces of Bulk Paramagnetic Vanadium

C. Rau, C. Liu, A. Schmalzbauer,^(a) and G. Xing

Physics Department, Rice University, Houston, Texas 77251

(Received 18 July 1986)

Electron-capture spectroscopy has been used to investigate magnetic order at the *topmost* atomic layer of atomically clean and flat (100) surfaces of bulk paramagnetic vanadium. From low-energy electron-diffraction measurements, we find a $p(1 \times 1)$ surface structure. At 300 K, the long-ranged electron-spin polarization amounts to $\sim 34\%$, clearly demonstrating the existence of *ferromagnetic* order at the $V(100)p(1 \times 1)$ surface. With increasing temperature, the electron-spin polarization decreases almost linearly and disappears at a surface Curie temperature $T_{Cs} \approx 540$ K.

PACS numbers: 75.50.Cc, 73.20.Cw, 79.20.Nc

Experimental and theoretical studies of the magnetic structure of surfaces play a central role in the investigation of the surface properties of materials. A better understanding of the magnetic and electronic properties of vanadium surfaces is of particular interest because of their importance in heterogeneous catalysis, hydrogen storage, and superconductivity. Moreover, bcc vanadium, which is *paramagnetic* in the bulk, sets an exciting challenge for the search for possible *two-dimensional (2D) ferromagnetic* behavior localized at the surface.

Isolated vanadium atoms possess a permanent magnetic moment of $3.0\mu_B$ in the ground state, whereas bulk solid vanadium does not exhibit ferromagnetism (though its paramagnetic susceptibility is large).¹ In the intermediate situation, e.g., for vanadium *surface* atoms, where the coordination number (number of nearest neighbors), which is known to strongly influence magnetic ordering, is reduced from 8 to 4, one might expect ferromagnetic behavior. Moreover, surface relaxation effects (changes of the bulk lattice constant near the surface) can modify the electron density of states near the Fermi level and eventually stabilize a ferromagnetic surface layer on top of the otherwise paramagnetic material.^{2,3}

Various methods, based on one-electron band theory, have been used to calculate the ground-state surface magnetic structure of $V(100)$.²⁻⁵ On the one hand, ferromagnetism^{2,3} or large localized magnetic moments⁴ have been predicted. Another approach indicates that the (100) surface of bulk vanadium may be at most very weakly ordered⁵ (magnetic moment less than $0.1\mu_B$). All these calculations predict a large peak in the electron density of states near the Fermi level, making the $V(100)$ surface a promising candidate to exhibit a transition from paramagnetic to ferromagnetic behavior. This feature is known to be characteristic of the (100) surfaces of elements with bcc structure and is rather insensitive to the details of the surface potential.⁴

At present, there is a lack of experimental information on the surface magnetic structure of well-defined, atomically clean and flat vanadium surfaces. To our knowl-

edge, the only related experiment for vanadium is that of Akoh and Tasaki,⁶ who reported the existence of large localized magnetic moments in hyperfine particles (100 to 1000 Å in diameter) of vanadium metal. These authors found the magnitude of the magnetic moment to be nearly proportional to the area of the particles, from which they suggested that the magnetic moment originated from their surface region. In 1981, using the (100) surface of Cr, another bulk nonferromagnetic bcc transition metal with nearly half-filled *d* bands, two more closely related magnetic experiments were reported.^{7,8} In the first one, long-ranged ferromagnetic order was detected at the topmost surface layer of $Cr(100)$ for temperatures below the bulk Néel temperature $T_{Nb} = 310$ K of Cr.^{7,9} In the second one, using spin-polarized photoemission spectroscopy at nitrogen-stabilized, unreconstructed $Cr(100)$ surfaces, Meier, Pescia, and Schriber⁸ found that highly diluted oxygen, incorporated into the bulk Cr lattice, induces long-ranged surface ferromagnetic order up to 500 K, whereas oxygen adsorbed on the surface does not. No indication of ferromagnetism was found at the oxygen-free, nitrogen-stabilized $Cr(100)$ surface.

In this Letter, we report the first measurements of the long-ranged (macroscopic) and short-ranged (microscopic) electron-spin polarization at well defined and well characterized $V(100)$ surfaces. The major aim of our experiments is to settle the key issue of ferromagnetic versus paramagnetic order at $V(100)$ surfaces. Using electron-capture spectroscopy¹⁰ we find unambiguously that long-ranged ferromagnetic order exists at atomically clean and flat surfaces of $V(100)p(1 \times 1)$. At 300 K, the long-ranged electron-spin polarization amounts to $\sim 34\%$ and decreases quasilinearly until it vanishes at an approximate surface Curie temperature $T_{Cs} \approx 540$ K. The short-ranged ferromagnetic order, measured at unmagnetized surfaces, is found to be nonzero and nearly T independent between 200 and 640 K.

The fundamental process of electron-capture spectroscopy (ECS) is the capture of one or two spin-polarized electrons during grazing-angle surface reflection of fast deuterons.¹⁰ The extreme *real-space* sensitivity of this

spin spectroscopy is due to the fact that for specular reflection (incidence angle 0.2°), the distance of closest approach of the deuterons is about 1 to 2 Å, so that the ions only probe the spin-polarized electron density of states at the *topmost* surface layer. One-electron capture processes are used to investigate long-ranged ferromagnetic order, whereas two-electron capture processes are used to detect short-ranged ferromagnetic order (local spin-spin correlations). Based on typical electron-loss cross sections, the probing distance in a two-electron capture process is within roughly 10 to 20 Å along the surface.¹¹ For further details, please consult Refs. 7, 10, and the works of Rau and Sizmann.¹²

For the investigation of long-ranged ferromagnetic order, a sample magnetizing field is applied to align randomly oriented magnetic domains, thereby producing a macroscopic magnetization which defines a preferred direction along which both sign and magnitude of the spin polarization $P = (n^+ - n^-)/(n^+ + n^-)$ of the captured electrons can be measured; n^+ and n^- are the fractional numbers of electrons with spin moment antiparallel (majority spin electrons) and parallel (minority spin electrons), respectively, to the target magnetizing field.

The V(100) crystals are prepared with a surface orientation better than 0.01° , which is monitored by use of a precision x-ray diffractometer. The pretreatment of the crystal surfaces consists of a mechanical polishing with diamond powder down to a grain size of 0.1 μm. The surfaces are then annealed for 10 h at 1500 K in a hydrogen atmosphere of 10^{-4} mbar which yields an additional surface-flattening effect (thermal surface smoothing).

This procedure (mechanical polishing using a 0.1-μm diamond grain size per thermal annealing) is repeated 3 times. During each cycle, surface-segregated bulk impurity atoms (mostly S, Cl, C, and O) are removed. After the third cycle (annealing temperature 640 K), the residual surface contamination is less than one monolayer; it is monitored with a cylindrical mirror analyzer for Auger-electron analysis. The Auger spectra contain peaks due to S (149 eV), Cl (181 eV), C (272 eV), and O (512 eV; overlaps the V peak at 509 eV), and V (31 eV, 399 eV, 411 eV, 437 eV), and a peak at 489 eV caused by O in V₂O₅.¹³ For the quantitative impurity analysis of V surfaces, we use a method proposed by Szalkowski and Somerjai¹⁴ and find an O surface contamination of 0.35 monolayer.

Further cleaning of the V(100) surfaces consists of cycles of argon bombardment (4 keV, 15 μA, 3 h at 640 K) and subsequent annealing at 640 K. After the third cycle, the S, Cl, C, V₂O₅, and O Auger peaks have completely disappeared, and the Auger spectrum consists only of V Auger peaks at 31, 399, 411, 437, and 509 eV, which characterize clean V surfaces.

From our low-energy electron-diffraction measurements, we find a $p(1 \times 1)$ surface structure.^{15,16} This method to obtain impurity-free V(100) $p(1 \times 1)$ surfaces is only successful if, during ion bombardment and anneal-

ing, a titanium sublimation pump and a cooling trap, held at liquid-nitrogen temperature, are used. Without the cooled shroud, the O surface contamination (Auger peak at 512 eV) could not be completely removed. After these treatments, the V samples are transported *in situ*, by use of a linear and rotary manipulator drive, from the target preparation chamber to the main ECS chamber¹⁰ which operates at a base pressure in the low 10^{-10} -mbar range.

For the determination of long-ranged ferromagnetic order, a specimen is magnetized along the [001] direction in a magnetic field H ranging between 103 and 515 G, and the electron-spin polarization is determined with electron-capture spectroscopy, using a reflection angle of 0.2° . The temperature of the samples is kept constant within 0.03° , by use of an automatic control device. The absolute temperature is calibrated within 0.5° .

Figure 1 shows the electron-spin polarization $P(T)$ measured for $H = 515$ G, at atomically clean and flat V(100) $p(1 \times 1)$ surfaces. At 300 K, P amounts to $-(34 \pm 2)\%$. This clearly demonstrates the existence of *long-ranged ferromagnetic order* at the topmost surface layer. With increasing temperature, P decreases almost linearly and disappears at a surface Curie temperature $T_{Cs} \approx 540$ K; it remains zero above T_{Cs} . The error bars are only due to counting statistics. For calibration of the detectors for zero polarization, we use a nonmagnetic Cu surface. Each measuring sequence consists of two runs with the Cu target, four runs with the magnetic sample, and again two runs with the Cu target. For further information, the reader is referred to Refs. 10 and 12.

It is interesting to note that $P(T)$ data of stepped V(100) $p(1 \times 1)$ surfaces (surface orientation between 0.05° and 0.5°) are within the experimental errors of $P(T)$ data for unstepped surfaces. Lower $P(T)$ data are only obtained for surfaces slightly contaminated with oxygen. $P(T = 317 \text{ K})$ is *reduced* from -30% to -22% by an oxygen contamination of 0.06 monolayer. At 300 K, the magnetizing field has been varied between 103 and 515 G, with no change of $P(T)$ observed within experi-

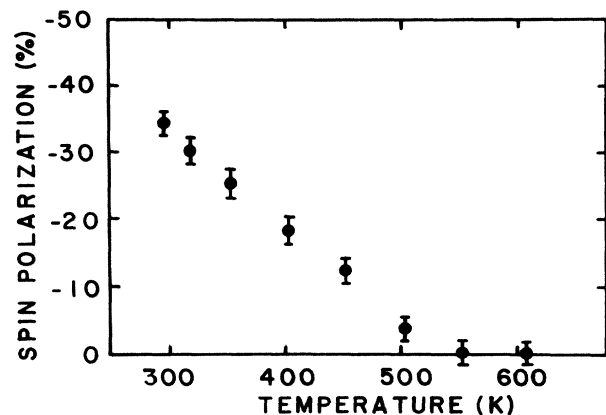


FIG. 1. Temperature dependence of the long-ranged electron-spin polarization at V(100) $p(1 \times 1)$ surfaces.

mental errors. This suggests that these H values are sufficient to overcome a surface anisotropy as predicted recently by Gay and Richter.¹⁷

Using two-electron capture processes (measurement of short-ranged spin-spin correlations) at nonmagnetized $V(100)p(1\times 1)$ and slightly contaminated (0.03 monolayer oxygen, 0.1 monolayer carbon) surfaces, we find that the short-ranged electron-spin polarization is *non-zero* and nearly temperature independent between 200 and 640 K, amounting to $(8 \pm 3)\%$. We interpret these data as probable lowest limits for the intrinsic short-ranged magnetic order existing at uncontaminated $V(100)p(1\times 1)$ surfaces.

From the above findings, it can be concluded that the topmost atomic layer of the $V(100)p(1\times 1)$ surface of bulk paramagnetic vanadium is ferromagnetic.

As noted above, the theoretical studies of the surface magnetic properties of vanadium yield slightly different results depending on the methods used. Our experimental findings are in accord with the results of Allan² and Kamar *et al.*³ In contrast to the findings of Gempel and Ying,⁴ we observe ferromagnetic rather than paramagnetic order in the temperature range 300–540 K. As regards the work of Freeman, Fu, and Oguchi,⁵ it may be noted that the predictions of these authors disagree with our experimental findings: Their techniques do not yield ferromagnetic order for the $V(100)$ surface, but do for a $V(100)$ monolayer.

We believe that these theoretical methods, if suitably modified, would yield predictions in accordance with our experimental results. In particular, it may be necessary to include surface anisotropy effects. To test the theory further, we are presently preparing a new experiment to determine the magnetic properties of a variable number of vanadium monolayers deposited on silver and gold single-crystal substrates.

One of us (C.R.) is very grateful to G. Allan, A. S. Arrot, A. J. Freeman, C. L. Fu, and M. Robert for valuable discussions. This work was supported in part by the Na-

tional Science Foundation, under Grant No. DMR-8406975, and by the Donors of the Petroleum Research Fund, administered by the American Chemical Society.

^(a)Present address: Sektion Physik, University of Munich, Federal Republic of Germany.

¹T. M. Hattox, J. B. Conklin, Jr., J. C. Slater, and S. B. Trickey, *J. Phys. Chem. Solids* **34**, 1627 (1973).

²G. Allan, *Phys. Rev. B* **19**, 4774 (1979), and *Surf. Sci. Rep.* **1**, 121 (1981).

³G. Yokoyama, N. Hirashita, T. Oguchi, T. Kambara, and K. I. Gondaira, *J. Phys. F* **11**, 1643 (1981).

⁴D. R. Gempel and S. C. Ying, *Phys. Rev. Lett.* **45**, 1018 (1980).

⁵C. L. Fu, A. J. Freeman, and T. Oguchi, *Phys. Rev. Lett.* **54**, 2700 (1985); C. L. Fu and A. J. Freeman, *J. Magn. Magn. Mat.* **54–57**, 777 (1986).

⁶H. Akoh and A. Tasaki, *J. Phys. Soc. Jpn.* **42**, 791 (1977).

⁷C. Rau and S. Eichner, *Phys. Rev. Lett.* **47**, 939 (1981).

⁸F. Meier, D. Pescia, and T. Schriber, *Phys. Rev. Lett.* **48**, 645 (1982).

⁹Long-ranged ferromagnetic order was detected, both for the $c(2\times 2)$ and $p(1\times 1)$ surface structure, the $p(1\times 1)$ surface structure exhibiting a slightly lower spin polarization compared to the $c(2\times 2)$ surface structure.

¹⁰C. Rau, *J. Magn. Magn. Mater.* **30**, 141 (1982).

¹¹M. C. Cross, *Phys. Rev. B* **15**, 602 (1977); we refer also to Ref. 3 in the preceding article.

¹²C. Rau and R. Sizmann, *Phys. Lett.* **43A**, 317 (1973), and in *Atomic Collisions in Solids*, edited by S. Datz *et al.* (Plenum, New York, 1975), Vol. 1, p. 295.

¹³L. Fiermans and J. Vennik, *Surf. Sci.* **24**, 541 (1971), and *Surf. Sci.* **35**, 42 (1973).

¹⁴F. J. Szalkowski and G. A. Somorjai, *J. Chem. Phys.* **56**, 6097 (1972).

¹⁵V. Jensen, J. N. Andersen, H. B. Nielsen, and D. L. Adams, *Surf. Sci.* **116**, 66 (1982).

¹⁶J. S. Foord, A. P. C. Reed, and R. M. Lambert, *Surf. Sci.* **129**, 79 (1983).

¹⁷J. G. Gay and Roy Richter, *Phys. Rev. Lett.* **56**, 2728 (1986).