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Summary Abstract: Magnetic order at (100)$p(1\times1)$ surfaces of bulk and thin-film vanadium

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I. INTRODUCTION

The surface magnetic properties of bulk and thin-film materials are presently of great experimental and theoretical interest. Among the $3d$-transition metals, vanadium is of particular interest because of its importance in heterogeneous catalysis, hydrogen storage, and superconductivity.

Beyond that, bcc vanadium sets an exciting challenge for the search for possible *ferromagnetic* order at the surface of the bulk material. Solid vanadium possesses a high paramagnetic susceptibility, but does not exhibit ferromagnetism in the bulk. Isolated vanadium atoms, however, possess a permanent magnetic moment of $3\mu_B$ in the ground state. In the intermediate situation, e.g., for vanadium surface atoms, where the coordination number (number of nearest neighbors) is reduced compared to that of the bulk, one might expect ferromagnetic behavior.

Furthermore, by using the appropriate technique, vanadium atoms can be deposited on metallic substrates in the form of ultrathin superlattices, which allows us to study thin-film magnetism in vanadium possessing a lattice constant *different* from that of the bulk.

Recently, a series of theoretical calculations on the surface magnetic properties of bulk and thin-film vanadium has been performed and striking and unusual magnetic properties, both for the surfaces of bulk and thin-film vanadium, have been predicted.[1–6]

At present, there is, besides one experiment on the existence of localized magnetic moments at the surface of hyperfine particles of V,[7] a lack of experimental information on the surface magnetic properties of well-defined, atomically clean, and flat surfaces of bulk and thin-film vanadium.

Using electron capture spectroscopy (ECS)[8] which is sensitive to the magnetic order existing at the *topmost* layer of a surface, we find that long-ranged ferromagnetic order exists at the surface of well-defined, atomically clean, and flat surfaces of magnetized V(100) single crystals. We have further deposited ultrathin films of vanadium on surfaces of Ag(100) substrate single crystals and find that long-ranged ferromagnetic order exists at the surface of these films.

II. EXPERIMENT AND RESULTS

The technique of electron capture spectroscopy and experimental details are described in Ref. 8: During specular reflection of fast ions, spin-polarized electrons are captured at the surface of magnetic single crystals. In grazing-angle surface reflection, the distance of closest approach of the ions is about 1–2 Å (reflection angle: 0.2°), showing that the ions probe only the topmost surface layer of the sample.

Atomically clean and flat (100) surfaces of vanadium single crystals are prepared with a surface orientation better than 0.01°. From our low-energy electron diffraction measurements, we find a $p(1\times1)$ surface structure.[9,10] Our method to obtain impurity-free V(100)$p(1\times1)$ surfaces is described in Ref. 11. For the measurement of surface magnetic order, a specimen is magnetized along the [001] direction in a magnetic field H ranging between 103 and 515 Oe. The electron-spin polarization P is determined with electron capture spectroscopy, using a reflection angle of 0.2°.

At 300 K, P amounts to -34% ($-$ sign: predominance of minority-spin electrons[8]), which unambiguously demonstrates the existence of *long-ranged ferromagnetic order* at the topmost surface layer of V(100)$p(1\times1)$.[11] With increasing temperature, the electron spin polarization decreases almost *linearly* and disappears at an approximate surface Curie temperature $T_{Cs} = 540$ K. P remains zero above T_{Cs}. Varying the magnetizing field between 115 and 515 Oe, no change of P is observed within experimental errors.

For the deposition of ultrathin vanadium superlattices, we have prepared atomically clean and flat (100) surfaces of Ag single crystals with a surface orientation better than 0.01°. (At 300 K, the lattice mismatch between bulk V and bulk Ag is approximately 4.8%). In first ECS experiments, using electron beam evaporation under ultrahigh vacuum conditions, we have deposited five atomic layers of vanadium on Ag(100) substrates. At 300 K, the electron-spin polarization amounts to approximately -20%, which clearly demonstrates the existence of long-ranged ferromagnetic order

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at the topmost surface layer of a five-layer-thick V(100) film on Ag(100).

Our experimental findings are in agreement with the theoretical predictions of Allan[1] [on surface ferromagnetic order of bulk V(100)] and of Kambara *et al.*[2] [on ferromagnetic order at surfaces of five monolayers of V(100)]. Our results are not confirming the predictions of Grempel and Ying[3] who find large localized moments at V(100) surfaces which are antiferromagnetically coupled up to 2 K. Regarding the work of Freeman and co-workers, there is an apparent discrepancy. These authors predict that the surface of bulk V(100) is not ferromagnetic,[5] and that the surface of one or two monolayers V(100) on Ag(100) is ferromagnetic.[4] However, the surface of a more than two-monolayer-thick V(100) film on Ag(100) is found not to be ferromagnetic. Gay and Richter predict that one monolayer of V(100) is ferromagnetic with the interesting finding that for one monolayer V(100), the easy direction of magnetization is perpendicular to the surface plane.

Work is in progress to investigate the surface magnetic order of V(100) on Ag(100) as function of film thickness, temperature, and applied magnetizing field which allows us to obtain surface critical exponents and to record the surface Curie temperature as a function of film thickness.

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