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Lack of evidence for ferromagnetism in the vanadium monolayer on Ag(001)

M. Stampanoni, A. Vaterlaus, D. Pescia,* M. Aeschlimann, and F. Meier
Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule Zürich—Hönggerberg, CH-8093 Zürich, Switzerland

W. Dürr and S. Blügel
Institut für Festkörperforschung der Kernforschungsanlage Jülich G.m.b.H., D-5170 Jülich, Federal Republic of Germany

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Spin-polarized photoemission has been used as a probe of the ferromagnetism of thin films of V on Ag(001) consisting of 1–3 monolayers. The measured electron-spin polarization at 30 K and applied magnetic fields up to 18 kOe is less than 2% for all film thicknesses. No evidence for ferromagnetism of V on Ag(001) is found. Available model calculations claiming ferromagnetism of V on Ag(001) are in disagreement with the experiment.

A remarkable result of computational solid-state physics is the prediction of ferromagnetic order for the single monolayer (ML) of vanadium on a Ag(001) substrate,[1-4] in contrast to the paramagnetism of the bulk. These theoretical predictions are supported by non-spin-polarized inverse photoemission spectroscopy.[5] In this work, two structures in the unoccupied density of states are tentatively assigned to spin-exchange splitting. However, it is pointed out—to our opinion, correctly—that a spin-polarized spectroscopy is necessary for an unambiguous assignment.

On the other hand, the prediction of ferromagnetism for a similar prototype system, Cr/Au(100), has been withdrawn because of the discovery that the antiferromagnetic state lies lower in the energy than the ferromagnetic one.[6] Very recently, a detailed study by Blügel, Weinert, and Dederichs[7] predicts the general trend of light transition-metal monolayers to order antiferromagnetically on the heavy $3d$, $4d$, and $5d$ transition-metal substrates.

In this paper, we have used a well-established experimental technique[8]—spin-polarized threshold photoemission—to test the predictions of ferromagnetism in this system. The measured electron-spin polarization (ESP) is less than 2%. In contrast, the value calculated according to Ref. 18 for the ferromagnetic monolayer of V on Ag(001) is five to six times larger. The ferromagnetism of V on Ag(001) as predicted by self-consistent theoretical calculations is therefore not confirmed by our experimental results.

The experimental technique used in the present experiment utilizes the spin polarization P of the electrons emitted near the photothreshold as a probe of ferromagnetism. $P=(N^{\uparrow}-N^{\downarrow})/(N^{\uparrow}+N^{\downarrow})$ where $N^{\uparrow}$ ($N^{\downarrow}$) is the number of electrons, irrespective of their kinetic energy or angle, with spin magnetic moment parallel (antiparallel) to the surface normal. In order to force the sample into saturation, an externally variable magnetic field is applied perpendicularly to the film plane. As a light source, the full spectrum of a Hg-Xe lamp ($h\nu < 5.5$ eV) was used. The photothreshold of all films was 4.25 ± 0.05 eV, that of the clean silver crystal 4.35 ± 0.05 eV. The sample was held at a temperature of around 30 K and the pressure in the measuring chamber was 2×10^{-10} Torr. Recently, spin-polarized photoemission has been successfully applied to discover the ferromagnetism of films of Fe and Co on Cu as thin as 1 monolayer.[9,10] In particular, this technique combines the very short probing depth [less than 10 Å (Refs. 9 and 10)] with the availability of low temperatures and high magnetic fields, a decisive aspect when dealing with very thin films for which low Curie temperatures and perpendicular magnetic anisotropy have been found to occur.[9-11]

The Ag(001) crystal used as substrate was mechanically polished and subsequently, after insertion into the vacuum system, treated with cycles of argon sputtering (800 eV, 10 μA, 6×10^{-5} Torr) and heating up to 700 °C. The last argon bombardment was followed by flash annealing at 700 °C. After this treatment the $p(1\times1)$ low-energy electron diffraction (LEED) pattern was perfectly sharp and no traces of any contaminant were recorded in the Auger spectra. The thin vanadium films were prepared by evaporation from a resistively heated V filament.[12] Ex-

tensive outgassing was necessary to minimize hydrogen and carbon contamination and to obtain a pressure of less than 3×10^{-9} Torr during evaporation. Different procedures were used to improve the LEED quality of the vanadium films and the best results were found using a silver substrate which had been heated up to 300 °C just before starting the evaporation. With an evaporation rate between 0.05 and 0.2 Å/min the sample temperature at the end of this procedure was around 100 °C. For coverages up to 2 ML the $p(1\times1)$ LEED pattern was still distinguishable, despite a gradual rise in background intensity. For thicker films the LEED pattern became indistinct, indicating that there is no perfect epitaxial growth. Films prepared by evaporation at room temperature showed a slightly worse quality of the LEED pattern. No traces of impurities were recorded in the Auger spectra of the measured films. For films up to 3 ML we have also followed the Auger peak-to-peak amplitudes for V and Ag as function of the evaporation time. The resulting curves are roughly exponential. We conclude that the films are homogeneous, i.e., island formation or interdiffusion[13] can be excluded, although the LEED pattern suggests a large amount of disorder on an atomic scale. In an independent Auger and LEED study on V/Ag(001) performed in Jülich[14] the same results were found.

The thickness of the films was determined by Auger spectroscopy. Because of the homogeneous growth mode, the thickness can be calculated from the ratio of the peak-to-peak Auger amplitudes (I_V,I_{Ag}) of the V (475 eV) and Ag (355 eV) peaks. According to[15]

$$d=\lambda\ln\left[1+\frac{I^0_{Ag}}{I^0_V}\frac{I_V}{I_{Ag}}\right], \tag{1}$$

where I^0_{Ag} and I^0_V are the Auger peak-to-peak amplitudes for pure Ag and V, respectively, and λ is the mean free path of the Auger electrons, we found $I^0_{Ag}/I^0_V=2.8$ and for λ we used the value of 3.5 ML=5 Å.[16] We estimate the error of λ not to be larger than ±1 Å, which gives a relative error of 20% (the uncertainty of I^0_{Ag}, I^0_V is negligible).

The dependence of the polarization P versus applied magnetic field is shown in Fig. 1 for four different films. The thicknesses have been all chosen around 1 ML because only in this range the occurrence of ferromagnetism is expected. The 0.8 and 1.3 ML films have been prepared by evaporating on a hot substrate as described above, while for the 0.9 and 2.8 ML films the silver crystal was at room temperature. The average statistical absolute error of each measurement is 1% as indicated with error bars. Except for two data points in Fig. 1(d) the ESP is below 2% over the whole magnetic field range. In view of the fact that the remaining eighteen points are within this range, we regard the two data points in Fig. 1(d) as statistical accidents.

In order to estimate the relevance of this experimental upper limit as a test for the possible existence of ferromagnetism in V/Ag(001) we have calculated the majority and minority spin density of states (DOS) for the ferromagnetic V layer on Ag(001). The calculation is performed using the full-potential linearized augmented-plane-wave method in film geometry.[17] A nine-layer (001) film consisting of seven layers of Ag and one V monolayer on each surface is considered. The results are

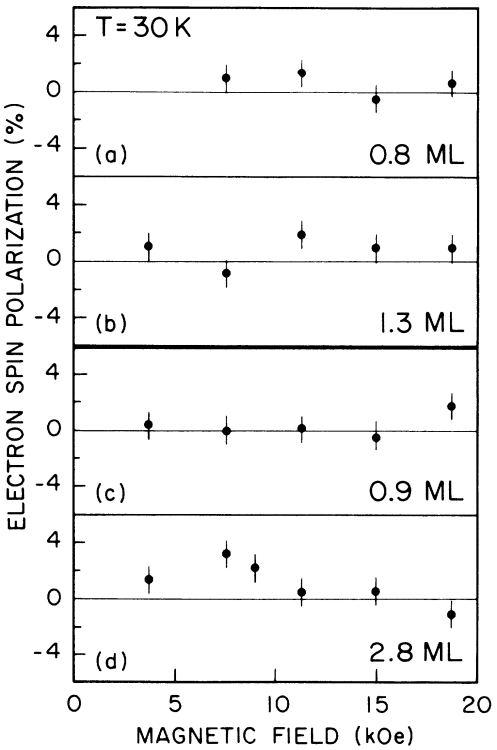

FIG. 1. Electron-spin polarization P versus perpendicularly applied magnetic field H for four thicknesses of the V overlayer. The films were prepared by evaporation onto a hot substrate for (a) and (b), and by evaporation at room temperature for (c) and (d). The error bars indicate the statistical error.

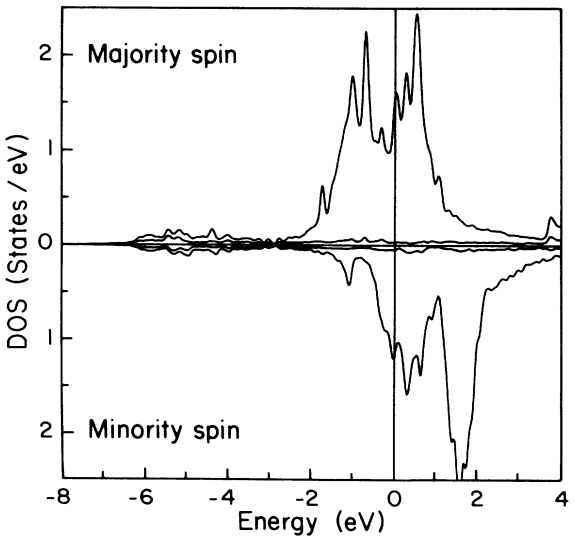

FIG. 2. Majority and minority spin DOS for the V monolayer on Ag(001). The s- and p-electron contribution to the DOS over the d bandwidth is negligible. The DOS is smoothed by a Gaussian broadening function of 0.1 eV full width at half maximum. The origin of the energy scale is the Fermi level E_F of the system.

plotted in Fig. 2. The details are explained in a forthcoming publication.[18] Essential for our purposes is that in this type of experiment, where a wide cone around the surface normal is sampled and no energy resolution is performed, the number of photoemitted electrons $N^{\uparrow\downarrow}(h\nu)$ is determined by the integrated DOS $\mathcal{D}$ near the Fermi level E_F, namely[19]

$$N^{\uparrow\downarrow}(h\nu) \propto \int_{E_F-(h\nu-\phi)}^{E_F} \mathcal{D}^{\uparrow\downarrow}(E)dE \ , \tag{2}$$

ϕ being the photothreshold. As a consequence, $P(h\nu)$ can be calculated from the DOS given in Fig. 2. Since the full spectrum of the Hg-Xe lamp is used, the resulting polarization is obtained by weighting $P(h\nu)$ with the measured photocurrent $I(h\nu)$:

$$P_{\text{tot}} = \frac{\int I(h\nu)P(h\nu)d(h\nu)}{\int I(h\nu)d(h\nu)} \ . \tag{3}$$

For the V layer, we find $P_{\text{tot}} = 35\%$. This value does not take into account the unpolarized contribution from the Ag substrate. From our previous work on the Fe/Ag(001) system,[20] we know that the contribution of the substrate to the photocurrent is about $\frac{2}{3}$. This gives an expected value for the polarization of about 12%. The measured ESP is less than 2%! To account for this evident discrepancy several possibilities are open, among which are (1) the Curie temperature is below 30 K; (2) the magnetic moment is smaller than the calculated one;[1,21,22] (3) apart from ferromagnetism, other types of magnetic order—neglected so far in theoretical arguments—could indeed turn out to be energetically favored (see Refs. 6 and 7); (4) the V layer could retain the paramagnetism of the bulk: note that the energy difference between paramagnetic and ferromagnetic states is smaller than, for instance, in Fe/Ag(001).[1]

Clearly, further work is needed in order to distinguish between these possibilities.[23] However, the results reported in this paper put a severe limit to the hypothesis of ferromagnetism in V/Ag(001).

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*Permanent address: Institut für Festkörperforschung der Kernforschungsanlage Jülich G.m.b.H., D-5170 Jülich, Federal Republic of Germany.

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