Induced magnetic order in ultrathin vanadium films on Fe(100)

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The magnetic ordering of vanadium overlayers on Fe(100) was studied using spin-polarized electron-energy-loss spectroscopy. Net magnetic moments of the V surface were observed for one and two monolayers of vanadium, while no magnetic ordering of the surface was observed for thicker films. The vanadium monolayer couples antiferromagnetically to the Fe substrate, while the surface of two monolayers of vanadium aligns ferromagnetically with the substrate. The magnetic moment of the V monolayer is estimated to be less than $1\mu_B$.

Magnetism at surfaces and interfaces is a most interesting field of study. In general, theory predicts different moments for surfaces, free monlayers, and monolayer overalyers of the same element.[1] In addition to the reduction of crystal symmetry at these interfaces, structural effects play an important role in determining the magnetism of these systems. Epitaxial deposition of thin films on substrates with a different crystal lattice than the deposited material can produce thin films that are structurally different from the bulk form. The ability to create magnetic materials at surfaces and in thin films leads one to the exciting prospect of creating a magnetic system from a material that is nonmagnetic in the bulk.

Although interesting, recent attempts to observe magnetic ordering in vanadium systems have led to controversy. Although bulk vanadium is nonmagnetic, early calculations indicated that slight changes at the surface such as the reduction in the coordination number or relaxations may induce magnetic ordering.[2] Additionally, early magnetic susceptibility measurements of hyperfine (100–1000 Å) vanadium particles showed a magnetic response that scaled with the surface area of the particles.[3] The ensuing research focused on surfaces of both bulk vanadium and epitaxial thin films of vanadium on Ag(100).[4–9] While calculations for both of these systems have yielded magnetic ordering, theoretical studies disagree on the form of this ordering. Several studies favor ferromagnetic surface ordering[4] while other groups predict an antiferromagnetic alignment.[5] Experimental studies have also resulted in disagreement. Rau *et al.* have used electron capture spectroscopy (ECS),[6] an extremely surface sensitive probe, to observe ferromagnetically ordered surfaces both for bulk vanadium and for 1–7 monolayers (ML) of vanadium of Ag(100). A critical temperature of 475 K is reported for five atomic layer films while the Curie temperature of thinner films is below room temperature. Small oxygen contaminations were found to greatly reduce the spin polarization at the V(100) surface. These studies are contradicted by the magneto-optic Kerr effect (MOKE) (Ref. 7) and by spin-polarized photoemission spectroscopy (SPPES) (Ref. 8) studies, neither of which found any indications of ferromagnetic ordering for the V/Ag(100) system at temperatures as low as 30 K. Core-level photoemission spectroscopy studies,[9] while yielding no long-range magnetic information, identified a surface magnetic feature of V on graphite that disappeared with 1-L (1 L $=10^{-6}$ Torr s) exposure to residual gas. Both theory and experiment have yielded conflicting results.

The V/Fe(100) system is a good alternative to the V/Ag(100) system. Both the Fe and Ag(100) substrates provide essentially the same surface net with a difference in lattice constant of only 0.8%. Therefore the structure of the overlayers in both systems should be nearly identical. Differences in the magnetism of the two systems should be due primarily to the presence of the magnetized Fe interface. This interface would tend to magnetically order the vanadium overlayers. In the case of the V/Fe(100) system, the predictions of theory are unambiguous. Calculations by Vega *et al.* predict layer-by-layer antiferromagnetism in the vanadium overlayers with small magnetic moments that rapidly die out by about 5 ML.[10] In this paper we report investigations of the magnetic ordering of V overlayers on Fe(100) utilizing spin-polarized electron-energy-loss spectroscopy (SPEELS) techniques.

Clean Fe substrates were obtained by evaporating 60 Å of Fe onto a bulk Cr(100) crystal at temperatures of 210–250 °C. Fe evaporations were performed at rates of 4–6 Å/min and pressures of less than 8×10^{-10} mbar, while V evaporations were performed at rates of 0.1–0.4 Å/min and pressures below 3×10^{-10} mbar. The base pressure of the vacuum chamber was less than 5×10^{-11} mbar. Both low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) were used to monitor sample quality. A quartz oscillator thickness monitor was used to monitor the thicker films and to calibrate the AES data for accurate measurements of the thinner film thicknesses. LEED studies showed strong, sharp (1×1) patterns for all Fe substrates, and that the V maintained the (1×1) structure out to 5 or 6 ML. Beyond this thickness, no LEED patterns were observed, indicating a substantial amount of surface disorder, possibly due to the 5% lattice mismatch between bulk V and Fe. This observation is consistent with previous growth studies of V on Ag(100).[7,8]

Neither the Fe substrates nor the V films showed any signs of carbon contaminations, as determined by AES.

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We found that any oxygen contamination in the Fe substrates migrated to the surface, yielding atomically pure bulk films, with surface contaminations of about 8% of a monolayer. The vanadium films were found to have less than 3% oxygen contamination, however more accurate determinations were not possible since the 503-eV oxygen AES peak has near perfect overlap with the 509-eV vanadium peak. Auger spectra showed no signs of V/Fe intermixing for low-temperature grown vanadium films annealed up to 250 °C. Both LEED studies and magnetic measurements indicated an optimal anneal temperature of 80–100 °C for the V films. This was true for low-temperature (−100 °C) grown films as well as room-temperature grown films. All films grown below 90 °C and annealed to 90–100 °C showed the same behavior as films grown at 90–100 °C. Subsequent studies were performed on V films grown at 90–100 °C.

Briefly, the SPEELS experiment consists of spin-polarized electrons incident on the sample with scattered electrons collected 20° off specular using energy and spin resolution capability. Incident electrons of 31.5 eV and an energy resolution of 300 meV were routinely used, however the resolution was reduced to 150 meV for some studies to provide measurements closer to the elastic peak. We should note that when a spin-polarized electron source is used in conjunction with scattered electron polarization analysis, as in the SPEELS experiment, the limited scattering current determines the level of uncertainty in the measurements. Improving the energy resolution to measure the spin scattering closer to the elastic peak has the inherent trade off of reduced intensities. Since the V overlayers have a limited lifetime before residual gas contaminates the surface and since the SPEELS signal of the V overlayers is relatively weak, accurate SPEELS measurements of a given V film were effectively limited to an energy resolution of 150 meV. All measurements were performed on in-plane remanently magnetized samples. In the SPEELS experiment the polarization and intensity of the scattered electrons are measured as a function of energy loss. The exchange asymmetry is commonly defined as the normalized difference between scattering intensities for incident spin-up and spin-down electron beams.

Figure 1 shows the exchange asymmetry of a 0.8-ML V/Fe(100) sample measured at −80 °C as well as the clean Fe(100) surface spectrum. The large negative values of the Fe asymmetry are typical for a ferromagnet magnetized to saturation. The 0.8-ML V spectrum shows features from both the V overlayer and the Fe substrate. This spectrum demonstrates the extreme sensitivity of the SPEELS experiment. With the addition of only 0.8 ML V, the Fe asymmetry at a 2 eV loss is attenuated by a factor of 6. The resulting asymmetry spectrum is due to two overlapping features with opposite signs. That is, the V contributes a low-energy feature of positive asymmetry, while the Fe provides a higher energy-loss feature of negative asymmetry. The existence of a nonzero asymmetry for the V feature proves that the V monolayer has a net in-plane magnetic moment, while the difference in sign between the V and the Fe features indicates that the V monolayer is coupled antiferromagnetically to the Fe substrate.

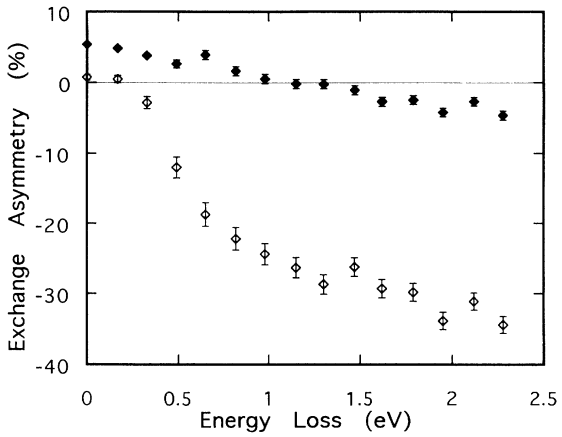

FIG. 1. The exchange asymmetry vs energy loss for the Fe(100) surface (open symbol) and 0.8 ML V/Fe(100) (filled symbol). Statistical error bars are shown.

The V asymmetry feature is small in magnitude and not well peaked. The interpretation of the data is much more difficult than in the Cr and Mn overlayer studies, where the monolayer signal clearly dominated over any substrate effects. The V feature is localized at low energy. Studies of thicker films (up to 2.3 ML) have shown that the V asymmetry feature is peaked at about a 0.85-eV loss. The partial scattering rates for spin-flip and nonflip scattering events for both incident spin-up (parallel) and spin-down (antiparallel to the Fe majority spin direction) electrons are shown in Fig. 2. The Fe substrate contributes to the 0.8-ML V/Fe spectrum an excess of flip-down scattering that can be seen at energy losses greater than 1 eV. The spectrum for the bare Fe substrate clearly shows that Fe should contribute an excess of flip-down scattering at lower energy losses as well. It can therefore be concluded that the V overlayer must be contributing an excess of flip-up scattering that cancels the Fe substrate flip-down scattering excess at lower energies. Studies of thicker films have shown this V flip-up excess to be peaked at about a 0.85 eV energy loss.

In addition to asymmetry in the flip scattering rates, the V overlayer also contributes more non-flip-up than non-flip-down scattering at low-energy losses. This feature is significant only near the elastic peak and is completely gone for 1-eV energy loss. Curiously, the V spectrum appears to show a greater asymmetry in the nonflip scattering feature than in the flip scattering feature. That is, the difference between the two nonflip scattering channels is greater than the difference between the flip scattering channels. This result is different from previous SPEELS studies of ferromagnetic systems. This difference is due solely to the weak nature of the V flip asymmetries. The magnitude of the nonflip asymmetries are consistent with previous SPEELS studies while the difference between the flip scattering rates are significantly smaller than in previous studies.[11–13] The very weak character of the spin-flip scattering asymmetries of the 0.8-ML V overlayer indicates that the V

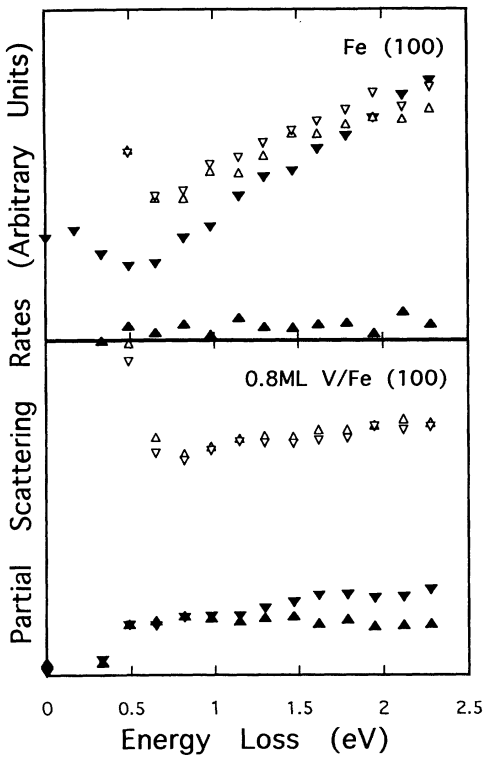

FIG. 2. The partial scattering intensities for the clean Fe(100) surface (upper panel) and 0.8 ML V/Fe(100) (lower panel). Spin-flip rates (filled symbols) and nonflip rates (open symbols) are shown for incident spin-up electrons (up arrows) and incident spin-down electrons (down arrows).

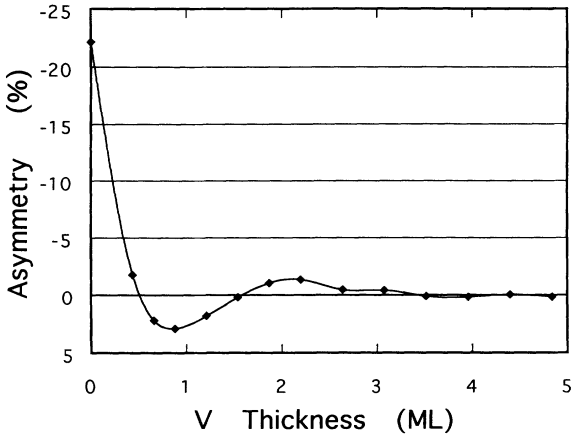

FIG. 3. The exchange asymmetry measured at a 0.85 eV energy loss of V/Fe(100) vs overlayer thickness. Note the inverted y axis. Statistical errors are contained within the symbol size.

monolayer on Fe is only weakly magnetic and has a small moment.

Generally, the energy loss of the flip feature of a ferromagnet roughly equals the exchange splitting of the magnetic system, and the exchange splitting of magnetic systems correlates with the magnetic moment of the material, with a relationship of roughly 1 eV/1μ_B. Even though correlations between the flip feature energy loss and the magnetic moment are generally associated with systems that show much larger flip-induced asymmetries, they are still relevant to the study at hand. Thus, the V flip feature location of less than 1 eV indicates that the V monolayer on Fe has a magnetic moment of less than 1μ_B.

Films as thick as 2.3 ML V show a V asymmetry peak with a maximum at about a 0.85-eV loss. In order to probe the magnetic ordering of the thicker V overlayers, the energy loss was held constant at a 0.85 eV loss and the exchange asymmetry of the V surface measured at $-80\,^{\circ}$C as a function of total vanadium thickness (Fig. 3). The nonzero values of the exchange asymmetry clearly demonstrate that the V surface layer has in-plane ferromagnetic order for thicknesses up to 2 ML V/Fe(100). Since all polarizations are defined with respect to the Fe majority-spin direction, negative asymmetries correspond to alignment with the Fe substrate, while positive asymmetry values result from a surface antiferromagnetically aligned with the substrate. Thus the data clearly show that the V monolayer is antiferromagnetically coupled to the substrate, while the surface of 2 ML V/Fe is ferromagnetically aligned with the substrate. The measurements between 2 and 3 ML coverage are consistent with the second layer remaining magnetic and being covered with a nonmagnetic third layer, giving an exponential tail. All asymmetries for thicker films are measured to be zero, within the uncertainty of the experiment (about 0.8%).

If the magnetic moment of the V surface layer changes as the film thickness is varied, then the energy loss of the asymmetry maximum would shift. In order to preclude the possibility that the constant energy loss of the data in Fig. 3 does not adequately probe the magnetic ordering due to possible energy shifts of the asymmetry maximum, energy-dependent data were taken for several thicknesses. Energy-loss spectra for thicknesses up to 2.3 ML V were all consistent with a feature location at about a 0.85 eV loss, however, the magnitude of the signal decayed with increasing thickness, resulting in greater uncertainty in the determination of the energy loss for the second layer. Films thicker than 2.3 ML showed zero exchange asymmetries for all energy losses, within the experimental error of the spectra of roughly 1.5%.

Since sample cleanliness considerations limit the measurement time of a given film and therefore the energy resolution used, the current experiment is insensitive to very small magnetic moments. A small moment system would have a small energy loss of the spin-flip feature. The elastic scattering feature is very intense and dominated by nonflip scattering and, therefore, the limited energy resolution used cannot adequately resolve features of less than a 0.4 eV loss from the elastic peak. The current SPEELS experiment is therefore insensitive to moments below about 0.4μ_B. Figure 3 indicates that no magnetic ordering for V films thicker than 2 ML is found and that any ordering present would have moments less than 0.4μ_B.

The effects of temperature should also be considered. While no magnetic ordering of the thicker films was measured, it is possible that V exhibits long-range order with

an ordering temperature below our experimental limit of $-100\,^{\circ}C$, and that the one and two monolayer films exhibit magnetism induced by the presence of a magnetic Fe interface. Fe has a Curie temperature of 1043 K, and any magnetism induced in a paramagnetic V overlayer should show roughly the same temperature dependences of the interface layer of the Fe substrate. This analysis is consistent with temperature-dependent measurements. No significant changes in the measured asymmetries for the V monolayer on Fe were noted throughout the temperature range -100–$200\,^{\circ}C$.

This type of behavior can be contrasted to previous SPEELS measurements of overlayers of both Cr (Ref. 12) and Mn (Ref. 13) on Fe(100), in which layer-by-layer antiferromagnetic behavior out to tens of monolayers was observed. The Mn overlayers were found to have an ordering temperature of about $35\,^{\circ}C$ while the Cr overlayers maintained magnetic ordering to above $200\,^{\circ}C$. The fact that the V overlayers exhibit magnetic ordering in only the first two layers in conjunction with the lack of significant temperature dependences implies that within the temperature range considered, the magnetic order observed was in fact induced by the Fe substrate, however it is possible that an ordering temperature exists below $-100\,^{\circ}C$.

The data are in good qualitative agreement with the recent self-consistent tight-binding calculations of Vega *et al.* for the V/Fe(100) system.[10] The calculations predict in-plane weakly magnetic V surface layers showing a layer-by-layer antiferromagnetic ordering that dies out within the first few monolayers. Moments of $-1.67\mu_B$ and $1.26\mu_B$ are predicted for the 1 and 2 ML V surfaces, respectively, while thicker films are predicted to have much smaller surface moments. They find a V surface aligned antiferromagnetically (ferromagnetically) for the 1 ML (2 ML) V/Fe system, in qualitative agreement with our measured exchange asymmetries (Fig. 3).

These results provide interesting implication concerning the V/Ag(100) system. Since the surface net provided by Fe(100) and Ag(100) differ only by a 0.8% expansion, one would expect that the structural differences would have little effect on the magnetism of V overlayers on these substrates. If the magnetic ordering was inherent to the V thin film rather than induced by the Fe substrate, the V/Ag system would then be limited to the magnetic ordering observed in the V/Fe films. That is, the first two layers would have small net magnetic moments and would be coupled antiferromagnetically to each other, while any layers thicker than two monolayers would have moments below the practical limit of the current experiment of perhaps $0.4\mu_B$. However, it is most likely that the V ordering was induced by the presence of the magnetic Fe interface and that the V/Ag system has no long-range magnetic ordering. While, like the SPPES (Ref. 8) and MOKE (Ref. 7) studies, we do not see any magnetic ordering for V films thicker than 2 ML, it is possible that the ECS technique (Ref. 6) is sensitive to small magnetic moments that we cannot detect.

In conclusion, we have measured the exchange asymmetry of vanadium overlayers on Fe(100) and have found evidence for a net magnetic moment at the surface for one and two monolayer V films. Further, the monolayer was found to couple antiferromagnetically to the Fe, while the surface of a 2 ML film was coupled ferromagnetically to the substrate. The magnetic moment of the V monolayer on Fe(100) was determined to be less than $1\mu_B$, and since no surface magnetic ordering was detected for films over 2 ML, any moments would have to be less than the practical limit of this experiment of about $0.4\mu_B$.

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