Effect of Iron on Vanadium (001) Strained Surface Magnetism

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Abstract. The magnetism of the vanadium (001) surface has been a controversial subject on both theoretical and experiment fronts. Both strongly ferromagnetic and paramagnetic phases were reported. We have used the first principle full-potential linearized-augmented plane waves (FP-LAPW) as implemented in WIEN2k package to study the magnetic properties of strained surfaces of vanadium films as a function of film thickness. We found that for films thicker than about 11 monolayers, the magnetism of the strained surfaces converge to a constant value of about 0.15μB. Introduction of Fe monolayers and impurities at the centre of the films affects the magnetic structure of thin films but has no influence on the surface magnetism of thicker films. For Fe monolayers positioned at the centre of thick films, the Fe atoms maintain magnetic moment of order 0.86μB, a quadruple splitting of order -0.3 mm/s and a small negative isomer shift, while an Fe impurity has vanishing hyperfine fields and magnetic moment. In addition we have varied the location of the Fe monolayer and impurity within the V films and found that their position affects the surface magnetism.

1. Introduction
Vanadium is a paramagnetic metal with a large magnetic susceptibility that lies at the border just below the magnetic 3d transition metals. Vanadium atoms are easily polarized when introduced into a magnetic material. On expansion, it was found that vanadium metal undergoes a transition from the paramagnetic to antiferromagnetic phase at a Wigner-Seitz radius of about 3.15 a.u. [1]. On the other hand, the magnetism of transition metals also depends on the coordination number. Reduction in atomic bonding as happens at surfaces is expected to lead to formation of atomic magnetic moments. Thus vanadium has the potential to exhibit surface magnetism.

Rau et al using electron-capture spectroscopy reported ferromagnetic order of V atoms at the V(001)p(1×1) surface for bulk vanadium [2] and for ultra thin vanadium films deposited on silver [3]. However, later measurements using other techniques could not detect any magnetic order to within 0.05μB per V atom neither for the surface of bulk vanadium nor for the surface of thin films on silver (see reference 4 and references therein).

The electronic and magnetic structures of the surface vanadium thin films have been calculated using different computational techniques with contradictory results. In particular, a big discrepancy exists between the results obtained using the all-electron methods and the pseudopotential methods

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Bihlmayer et al [7] using the full-potential all electron method in the linearized-augmented plane-wave approach (FP-LAPW) concluded that in ultra thin V films a surface magnetic moment can be stabilized, while for thicker and relaxed films no surface magnetism is obtained. On the other hand, Bryk et al [8] using the pseudopotential methods obtained magnetic moments of order 1.5μB even for relaxed surfaces.

At the interface between vanadium and the 3d magnetic transition metals, V atoms are found to couple antiferomagnetically to the neighboring 3d atoms. In particular, for V-Fe (001) interface an antiferromagnetically coupled V moment was obtained theoretically [9] and reported experimentally [10]. Thin overlayers are completely polarized; however for thick overlayers polarization is confined to the interface region.

In this contribution we use the first principle FP-LAPW method to study the magnetism of 3 to 27 layers of vanadium (001) surface with and without introduction of iron impurities and monolayers at various depths in the vanadium films. The magnetic moment, the contact magnetic hyperfine field and the electric field gradient of Fe impurities were found to vanish except when the impurity is close to the surface of the V film. A negative small isomer shift is retained at all positions. The effect of deep Fe impurities on the V surface magnetic moment is minor. For an Fe monolayer a local Fe magnetic moment of order 0.9μB, a magnetic hyperfine field of order 2 T and an electric field gradient of order $-2 \times 10^{21} \text{V/m}^2$ are retained except close to the surface. The computational method used is presented in the following section and results are presented and discussed in section 3.

2. Computational Method

The density functional L/APW+lo method as implemented in WIEN2k package [11] is used to calculate the electronic and magnetic structures of vanadium films with and without iron. Systems with a Fe monolayer in V are represented by $1 \times 1 \times (N+NV)$ supercells, where N is the number of monolayers and NV is the width of vacuum, while Fe impurities in V are represented by $2 \times 2 \times (N+NV)$ supercells.

In the L/APW+lo method the Kohn-Sham orbitals are expanded in terms of atomic orbitals inside the atomic muffin-tin (MT) sphere of radius $R_{MT}$ and in terms of plane waves in the interstitial regions. The Kohn-Sham equations were solved using Perdew-Burke-Ernzerhof GGA approximation. Core and valence states were separated by an atomic energy of -6.0 Ry. In this case V 3s orbitals belong to the valence states, while Fe 3s orbitals belong to the core states. It is found that when the cut off energy is increased to -7.0 Ry to include the Fe 3s orbitals among the valence states, no major change results. The calculations were carried out using the bulk V lattice constant of 5.66 a.u as determined through volume optimization, a value that agrees with reported results [6]. Touching MT spheres having radii of 2.44 a.u are used. For the valence electrons the potential and charge density are expanded in spherical harmonics up to $L = 4$, while the wavefunctions are expanded inside the MT sphere up to $l = 10$ partial waves. Mixed basis set are used depending on the partial wave $l$, with APW+lo being used for $s, p$ and $d$ valence orbitals, whereas LAPW is used for the remaining $l$ values.

For the plane wave expansion in the interstitial region we have used a wavenumber cut off $K_{max}$ such that $R_{MT} K_{max} = 7$ and the potential and charge density are Fourier expanded up to $G_{max} = 12$. The mesh size and the number of points in the Brillouin zone were tested for small supercells using the convergence of the values of the electric field gradient and the total energy as indicators [12]. It is found that a $k$ sampling with a $30 \times 30 \times 1$ Monkhost-Pack mesh gives good results in case of Fe monolayers and a mesh of $15 \times 15 \times 1$ in case of Fe impurities. An equivalent of 8 monolayers of vacuum size (about 12 Å) is determined to give a well converged work function, which is taken as a measure of the quality of vacuum. The results reported here are for strained surfaces using the calculated V lattice constant.
3. Results and discussions

The calculated local properties at a Fe site in a monolayer of Fe at the centre of strained V films as function of the number of layers N, in addition to the surface magnetic moment of V in films with and without Fe are shown in table 1. Results for small number of layers oscillate strongly with the number of layers and are not shown here. For the lattice constant used in this calculation, the Fe monolayer is expanded by about 4% relative to the corresponding α-Fe configuration. We note in general that the hyperfine field parameters at the Fe site saturate very quickly to constant values as the number of layers increases. In addition the V surface magnetic moment approaches the corresponding values of Fe-free films, which are comparable to the results of the 15 layer strained film reported in [7]. The V layers immediately neighboring the Fe monolayer was found to gain sizeable negative moment (of order -0.25 \( \mu_B \)), while further layers are weakly polarized with negligible local moment. As the thickness of the V film increases above about 15 layers, the V surface does not feel the presence of the deep Fe monolayer. The Fe local magnetic moment within the MT sphere converges to about 0.86 \( \mu_B \).

The axial electric field gradient at the Fe site leads to quadruple splitting of order -0.3 mm/s, while the contact charge density results in isomer shifts less than about -0.1 mm/s.

| N  | \( \mu_{Fe} (\mu_B) \) | \( B_{hf} \) (T) | \( V_{zz} \times 10^{21} \) (V/m\(^2\)) | \( \rho \) (a.u) | \( \mu_V \) with Fe | \( \mu_V \) without Fe |
|----|----------------|-------------|---------------------|-----|----------------|----------------|
| 7  | 0.96           | -1.9        | -1.8                | 7.13| -0.14          | 0.04           |
| 11 | 0.90           | -2.1        | -2.6                | 7.17| 0.01           | 0.15           |
| 15 | 0.83           | -1.6        | -2.1                | 7.22| 0.10           | 0.14           |
| 23 | 0.85           | -1.7        | -2.1                | 7.21| 0.13           | 0.15           |
| 25 | 0.86           | -1.7        | -2.1                | 7.20| 0.14           | 0.15           |
| 27 | 0.86           | -1.7        | -2.1                | 7.21| 0.15           | 0.15           |

Table 1. The atomic magnetic moments \( \mu \) (in Bohr Magneton), the contact hyperfine fields \( B_{hf} \) (in Tesla), the axial electric field gradients \( V_{zz} \) (in volts per meter square) and the contact charge density \( \rho \) (in atomic units) at the Fe site in an iron monolayer at the centre of strained V film with total number of layers N. The last two columns give the V magnetic moment per atom at the surface of the thin film with and without iron monolayer at the centre.

The introduction of a Fe impurity at the centre of the strained V films has similar effects on the magnetic structure of V surface. However, the local Fe magnetic moment, hyperfine field and electric field gradient vanish in this case as happens for a Fe impurity in bulk vanadium. For the supercell and the P4/mmm (123) space group used for the Fe impurity representation, the V surface has three independent atomic sites in some films. The magnetic moments of the three V atoms at the surface are found to couple ferromagnetically for the cases of Fe impurity at the centre of the V film. The values of their magnetic moments are different but remain close to those reported for Fe monolayer in table 1 above.

We have also varied the location of the Fe monolayer and impurity within the strained V film for systems with 7, 11 and 23 layers. Table 2 shows the results for a Fe monolayer at different location in the 23 layers film. Only results for locations at the five positions below the surface are shown. Results for deeper position are similar to those of a Fe monolayer at the centre and hence are not presented here. The V surface magnetic moment is observed to vary with the location of the Fe monolayer reflecting oscillatory trends. It is in general coupled ferromagnetically to Fe even when the Fe monolayer is directly below the surface. It worth noting the respective decrease (increase) of the magnitudes of the electric field gradient (magnetic hyperfine field) at the Fe site as the Fe monolayer approaches the surface. Similar trends were found in the 7 and 11 layers thick films. Also the Fe impurity reflected the same features culminating in a large and positive electric field gradient at the surface. A Fe impurity at one V surface produces antiferromagnetic structures on the same surface and also on the opposite Fe-free surface. The magnetic moment of the Fe atom at the surface is large (of
order 2.7μB). The magnetic hyperfine field of an Fe atom at the surface is of order -10 T, which is relatively large as compared to that of the interior positions. The electric field gradient is also large and positive.

Table 2. The atomic magnetic moments μ (in Bohr Magneton), the contact hyperfine fields Bhf (in Tesla), the axial electric field gradients Vzz (volts per meter square) and the contact charge density ρ (in atomic units) at the Fe site in an iron monolayer at position S-I of strained V film with 23 layers. The last column gives the V magnetic moment per atom at the corresponding the surface of V film.

| Depth below surface | μFe (μB) | Bhf (T) | Vzz x10^21(V/m^2) | ρ (a.u) with Fe | μV |
|---------------------|----------|---------|-------------------|----------------|-----|
| S-5                 | 0.88     | -1.70   | -2.08             | 7.21           | 0.26|
| S-4                 | 0.82     | -1.50   | -2.13             | 7.20           | 0.03|
| S-3                 | 0.90     | -1.80   | -1.94             | 7.20           | 0.03|
| S-2                 | 1.26     | -1.80   | -1.70             | 7.24           | 1.01|
| S-1                 | 1.05     | -3.60   | -1.52             | 7.22           | 0.22|

We have made a limited study of the effect of surface relaxation on the magnetism of V films with and without Fe. For example for the 23 layers thick film a reduction of the top surface layer interplanar distance by 10% leads to zero surface magnetic moment of V with or without centrally positioned Fe.

In summary, we have calculated the local magnetic moment, the contact magnetic hyperfine field, the electric field gradient and the contact charge density at the Fe site in an iron monolayer and Fe impurity in vanadium films as a function of film thickness and also as a function of location within the films. The influence of the Fe on the magnetic structure of the V surface was determined. It is found that neither a centrally positioned Fe monolayer nor Fe impurity has any effect on the V surface for thick films. However, Fe monolayers and Fe impurities at locations closer to the surface result in significant changes in the V surface magnetic structure with possibility of induction of antiferromagnetic configuration.

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