

Surface transition metal magnetism

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In this work, we investigate the magnetic activity of the (001), (110), and (111) vanadium surfaces. The (001) orientation is particularly interesting since some controversy persists about its magnetic activity between the theoretical studies and the experimental results. On the (110) surface there is no magnetic activity. The (111) surface is interesting in the sense that the atoms in this plane are the most distant from each other as compared to the other two planes. This, in principle, should give the largest magnetic moments as we, indeed, find. We used the Surface Green's Function Matching method to calculate the local density of states and the Stoner model to obtain the magnetic moment. This method has proven to be accurate enough in this situation.

Keywords: Electronic structure; Surface magnetism; Surface states

1. Introduction

The problem whether the surface of vanadium is or is not magnetic has been discussed intensely. Allan [1] suggested that the V(001) surface could be magnetic even if bulk vanadium is paramagnetic. Studies by Onishi *et al.*, [2] have predicted a paramagnetic state for the V(001) surface using the FLAPW method. Yokoyama *et al.*, [3] calculated the magnetic polarization on the V(001) surface and found $0.2\mu_B$ per atom. These authors used the self-consistent charge spin polarized discrete variational X_α method. Rau, *et al.* [4] obtained a finite magnetic moment for the V(001) surface. García-Cruz *et al.*, [5] calculated the ideal V(001) surface and found a paramagnetic state. However, when they applied an expansion of the topmost layer-substrate distance, they found magnetic activity.

In this work, we investigate magnetism on the (001), (110), and (111) vanadium surfaces using the Surface Green's Function Matching method to calculate the local density of states and the Stoner model to obtain the magnetic moment.

We study the effect on magnetism of an isotropic expansion by up to 7% starting from the experimental value of lattice parameter (3.02 \AA). [6] We look for magnetism at the surface and in the bulk. All the situations here considered give rise to paramagnetism in the bulk.

2. Method

2.1 The Surface

For the surface the well known surface Green's function matching method (SGFM) [7-11] was used together with the tight-binding Hamiltonians for the calculation of the

local density of states (LDOS) for the free vanadium surfaces. The SGFM surface Green's function G_s^{-1} is given by

$$G_s^{-1} = \epsilon I - H_{00} - H_{01} T, \quad (1)$$

where ϵ is the energy, I is the unit matrix, H_{00} and H_{01} are the in-layer (surface) and interlayer interaction Hamiltonians, respectively, and T is the matrix defined by $G_{10} = T G_{00}$, where G_{10} is the propagator from the principal layer 0 to the first one. $G_{00} \equiv G_s$ is the propagator within the surface principal layer. These matrices are readily written in the tight-binding Slater-Koster language. [12]

A very important quantity for our application here is the LDOS projected onto the surface, this is given by

$$N(\mathbf{e}) = \frac{1}{p} \int \text{Im}[\text{Tr}G(\mathbf{e}, \mathbf{k})] d\mathbf{k} \quad (2)$$

The numerical integration was realized by the Cunningham's [13] method in the 2D first Brillouin zone.

1.2 The magnetic moment

The magnetic moment is calculated using first the Hubbard [14] and then the Stoner model [15]. Both give the same result for a ferromagnetic system. The magnetization, in units of Bohr magnetons, μ_B , is given by

$$\mathbf{m}(\Delta) = \int_{-\infty}^{e_F} [n_d^+(\mathbf{e}) - n_d^-(\mathbf{e})] d\mathbf{e} = \int_{e_F - \frac{\Delta}{2}}^{e_F + \frac{\Delta}{2}} [n_d(\mathbf{e})] d\mathbf{e}, \quad (3)$$

Table 1. Results for V(001) surface. The first column corresponds to an isotropic expansion [%], the second column to the lattice constant [\AA], the next column to the magnetic moment [μ_B], the next gives the corresponding magnetic band splitting [eV], and the last two to the partial contribution from the d , s and p states to the density of states at the Fermi level [states $\text{spin}^{-1}\text{eV}^{-1}\text{atom}^{-1}$].

| (001) expansion | Lattice constant | Magnetic moment | Band splitting | $N_d(E_F)$ |
|-----------------|------------------|-----------------|----------------|------------|
| 0.1 | 3.02 | 0.00 | 0.00 | 1.2849 |
| 1.0 | 3.05 | 0.00 | 0.00 | 1.3526 |
| 2.0 | 3.08 | 0.28 | 0.19 | 1.4247 |
| 3.0 | 3.11 | 0.48 | 0.34 | 1.5446 |
| 4.0 | 3.14 | 0.59 | 0.42 | 1.6475 |
| 5.0 | 3.17 | 0.68 | 0.48 | 1.6630 |
| 6.0 | 3.20 | 0.79 | 0.56 | 1.7761 |
| 7.0 | 3.23 | 0.97 | 0.68 | 1.8589 |

where Δ is the magnetic band splitting. $n_d^\pm(\mathbf{e})$ indicates $n_d\left(\mathbf{e} \pm \frac{\Delta}{2}\right)$ and $n_d(\epsilon)$ is the d -band paramagnetic density of states per atom, per spin, per eV. We checked that the total d -band electronic occupation number, n_d , is conserved at each step,

$$n_d = \int_{-\infty}^{e_F} [n^+(\mathbf{e}) + n^-(\mathbf{e})] d\mathbf{e}. \quad (4)$$

The total energy, E , of the magnetic system in this approximation is calculated from

$$E(\Delta) = \int_{-\infty}^{e_F} [n^+(\mathbf{e}) + n^-(\mathbf{e})] \mathbf{e} d\mathbf{e} + \frac{Jm^2}{4}, \quad (5)$$

where $n^\pm(\epsilon) = n_s(\epsilon) + n_p(\epsilon) + n_d^\pm(\epsilon)$, with $n_s(\epsilon)$ and $n_p(\epsilon)$ being the contributions to the LDOS from the s and p states, respectively.

In these equations the only independent variable is Δ ; J is the Stoner parameter. Extensive calculations of this parameter were realized by Janak [16]. The magnetic moment is calculated from the minimum of the energy curve as a function of Δ . [17]

The effect of an isotropic expansion on the electronic band structure and in the magnetic moment is studied expanding the experimental lattice constant by 0 up to 7%. To calculate the change in the interatomic distance was used the bulk stress tensor. To scale the tight-binding Slater-Koster parameters, $H_{ll'}$, was used [18]

$$H_{ll'}(r) = H_{ll'}(r_0) \left(\frac{r_0}{r}\right)^\alpha,$$

where r_0 is the original lattice constant and r is the new lattice constant. For α was used the well known Harrison

rule. [19] Finally, ll' run over the basis of atomic states considered in our calculation.

3. Results and conclusions

Our results are presented in two tables. We devote one to each direction, where either we find magnetism or it can be switched on by small expansion. Each table reports the results for the magnetic moment that we get, the corresponding band splitting and the d -band paramagnetic density of states at the Fermi level. First we consider an ideal surface with the bulk lattice parameter. This is what corresponds to the 0% expansion line in the tables.

In Table 1 we report the (001) direction case. We use the experimental lattice value of 3.02\AA and do not get any magnetic moment. This agrees with the theoretical calculation of Onishi *et al.*, [2] but does not agree with the experimental finding of Rau *et al.*, [4] and the recent calculation of Iskander *et al.* [20]

We want to look at a possible cause of disagreement between experiment [4] and theory. [2] For that purpose we redid the calculation but now considering expansion. In the V(001) a case, 2% expansion is enough for a magnetic moment of the order of the one seen by Rau to appear. (see Table 1)

For the (110) orientation a zero magnetic moment persists even if we expand the lattice up to 7%. This surface seems to be definitely not magnetic. In Table 2 we present our results for the (111) direction where the nearest neighbors atoms are separated by the biggest distance. This case is very interesting since at the bulk equilibrium lattice constant, a agnetic moment of $0.05\mu_B$ appears. At 2% expansion it reaches a value bigger than $1\mu_B$. We find the (111) surface to be the most magnetically active. No experiments on this direction are known to us.

In conclusion, the magnetic activity of the vanadium surfaces were studied in three crystallographic orientations, (001), (110), and (111).

The magnetic moment of the ideal (001), (110) and (111) surfaces with the experimental value as the lattice

Table 2. Results for V(111) surface. The meaning of the symbols is the same as in Table 1.

| (111) expansion | Lattice constant | Magnetic moment | Band splitting | $N_d(E_F)$ |
|-----------------|------------------|-----------------|----------------|------------|
| 0.0 | 3.02 | 0.05 | 0.0353 | 1.4247 |
| 1.0 | 3.05 | 0.88 | 0.6227 | 1.4828 |
| 2.0 | 3.08 | 1.23 | 0.8701 | 1.5457 |
| 3.0 | 3.11 | 1.40 | 0.9902 | 1.5949 |
| 4.0 | 3.14 | 1.57 | 1.1100 | 1.6566 |
| 5.0 | 3.17 | 1.78 | 1.2590 | 1.7227 |
| 6.0 | 3.20 | 2.16 | 1.5282 | 1.7604 |
| 7.0 | 3.23 | 2.77 | 1.9602 | 1.8249 |

parameter, is different from zero only on the (111) surface. An isotropic expansion of the lattice by as low as 2% from the experimental value is enough to produce a magnetic moment on the (001) surface. In the (001) orientation, we reproduced the results already obtained by García-Cruz *et al.* [5]

We have tried to find a geometrical parameter that governs the switching on of the magnetic activity. If the three directions are compared, the area at disposal per atom is, a^2 , $0.707a^2$, and $1.732a^2$ in (001), (110), and (111) surfaces, respectively. μ is highest on the (111) orientation and lowest on the (110)-one. The nearest neighbors atoms on this plane are farther away as compared to the other two directions. So we can use either the area at disposal per atom in each direction or the nearest neighbors distance as a geometrical parameter. It would be interesting to see to which extend each one of these parameters is universal.

Nevertheless, the physics underlying the switching on of magnetism on a vanadium surface is a d -band transfer of electronic states to the Fermi energy region. This enhances the paramagnetic density of states at the Fermi level in a very important way, a phenomenon that clearly, switches on magnetism as can be judged from the stoner criterium.

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