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Magnetism of the vanadium surfaces

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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.

Keywords: Electronic structure; surface magnetism; surface states.

Analizamos la actividad magnética en las superficies (001), (110), y (111) del vanadio. Tratamos de manera especial la dirección (001) debido a que aún persiste la controversia sobre su actividad magnética entre estudios teóricos y resultados experimentales. No encontramos ninguna actividad magnética en la dirección (110). La superficie (111) es interesante en el sentido de que los átomos en esta dirección están más alejados entre ellos comparado con las otras dos direcciones. Esto, en principio, debe mostrar un momento magnético más alto. Para este estudio usamos el método de acoplamiento de funciones de Green de superficie para calcular la densidad local de estados y el modelo de Stoner para obtener el momento magnético.

Descriptores: Estructura electrónica; magnetismo de superficie; estados de superficie.

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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 at 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.

A similar effect occurs in the FeRh alloy, this system has the unusual property of being antiferromagnetic at low temperatures and of undergoing a phase transition to a ferromagnetic state at ~ 320 K and is accompanied by a volume increase of about 1% [6, 7]. This phase transition was discovered by Fallot and Hocart [8]. In 1992 Moruzzi and Marcus, calculated the total energy of FeRh as a function of volume for different magnetic structures, using spin polarized density functional theory in the framework of the local density approximation and the augmented spherical wave formalism [9]. They found that the AF-II spin structure is the ground state, whereas the FM structure is another stable solution with higher energy and a large volume, in agreement with experimental results [10]. The magnetism on a FeRh alloy is a very subtle and interesting problem that is still under study. We do not deal with it in this paper, although we refer to it in the sense that we find a paramagnetic to ferromagnetic transition on a vanadium surfaces upon expansion of the first-layer to surface distance. We do not pretend to say that the two phenomena have the same physics behind but we do point to the possible consequences of an expansion on the magnetic behavior of the surface layer in vanadium and, in general, to the relationship between expansion and magnetism.

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 Å) [11]. 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

We decribe the electron bands with the tight-binding method of Slater and Koster [12]. To set up the hamiltonian for the surface we assume ideal truncation. With this hamiltonian we obtain the Green's function form

$$(\varepsilon I - H)\, G = I, \tag{1}$$

where ε is the energy and I is the unit matrix. We adopt the customary description in terms of principal layers. We label them with positive numbers and zero for the surface atomic layer. Let $|n\rangle$ be the principal layer wave function describing the n^{th} principal layer. It is a LCAO wave function with five d-like, three p-like and one s-like atomic functions per spin on each atom. If we take matrix elements of Eq. (1) in the Hilbert space generated by this system of wave-functions $|n\rangle$, we get

$$\langle n|\, (\varepsilon I - H)\, G|m\rangle = \delta_{mn}. \tag{2}$$

The identity operator (from the definition of principal layer) can be cast as

$$I = |n-1\rangle\langle n-1| + |n\rangle\langle n| + |n+1\rangle\langle n+1|, \tag{3}$$

inserting Eq. (3) in Eq. (2) we get

$$\begin{aligned}(\varepsilon I - H_{n,n})\, G_{n,m} - H_{n,n-1}G_{n-1,m}\\ - H_{n,n+1}G_{n+1,m} = \delta_{mn}.\end{aligned} \tag{4}$$

Using Eq. (4) for $m = n$, and $m = 0$ for the surface, it is straightforward to get the surface Green's function

$$G_s^{-1} = \varepsilon I - H_{00} - H_{01}T, \tag{5}$$

and the principal layer projected bulk Green's function

$$G_b^{-1} = G_s^{-1} - H_{10}\tilde{T}, \tag{6}$$

where $H_{0,-1} = 0$, H_{00} and H_{01} are the in-layer (surface) and interlayer interaction Hamiltonians respectively, and T is the matrix defined as

$$G_{k+1p} = TG_{kp}, \qquad k \geq p \geq 0, \tag{7}$$

$$G_{ij+1} = \tilde{T}G_{ij}, \qquad j \geq i \geq 0, \tag{8}$$

where $G_{10} = TG_{00}$, G_{10} is the propagator from the principal layer 0 to the first one. $G_{00} \equiv G_s$ is the propagator with in the surface principal layer. This matrices can be calculated by the quick algorithm of López-Sancho *et al*. [13], recalculated by Baquero [14–16]. They get

$$T = t_0 + \tilde{t}_0 t_1 + \ldots + \tilde{t}_0 \tilde{t}_1 \ldots \tilde{t}_{i-1} t_i + \ldots, \tag{9}$$

$$\tilde{T} = \tilde{t}_0 + t_0 \tilde{t}_1 + \ldots + t_0 t_1 \ldots t_{i-1} \tilde{t}_i + \ldots, \tag{10}$$

where

$$\begin{aligned} t_0 &\equiv (\varepsilon - H_{00})^{-1}\, H_{01}^{\dagger}, & \tilde{t}_0 &\equiv (\varepsilon - H_{00})^{-1}\, H_{01}, \\ t_i &\equiv M_{i-1} t_{i-1}^2, & \tilde{t}_i &\equiv M_{i-1} \tilde{t}_{i-1}^2, \end{aligned}$$

with $M_{i-1} = \left(1 - t_{i-1}\tilde{t}_{i-1} - \tilde{t}_{i-1}t_{i-1}\right)^{-1}$. A very important quantity for our application here is the LDOS projected onto the surface, this is given by

$$N(\varepsilon) = -\frac{1}{\pi} \int \mathrm{Im}\left[\mathrm{Tr}G\,(\varepsilon, k)\right] dk. \tag{11}$$

The numerical integration was realized by the Cunningham's method [17] in the 2D first Brillouin zone.

2.2. The magnetic moment

The magnetic moment is calculated using first the Hubbard [18] and then the Stoner model [19]. Both give the same result for a ferromagnetic system. The magnetization, in units of Bohr magnetons, μ_B, is given by

$$\mu\,(\Delta) = \int_{-\infty}^{\varepsilon_F} \left[n_d^+(\varepsilon) - n_d^-(\varepsilon)\right] d\varepsilon = \int_{\varepsilon_F - \frac{\Delta}{2}}^{\varepsilon_F + \frac{\Delta}{2}} n_d\,(\varepsilon)\, d\varepsilon, \tag{12}$$

where Δ is the magnetic band splitting. $n_d^{\pm}(\varepsilon)$ indicates $n_d\,(\varepsilon \pm \Delta/2)$, and $n_d(\varepsilon)$ is the paramagnetic density of states per atom, per spin, per eV for d-band. We check that the total d-band electronic occupation, n_d, is conserved at each step,

$$n_d = \int_{-\infty}^{\varepsilon_F} \left[n_d^+(\varepsilon) + n_d^-(\varepsilon)\right] d\varepsilon. \tag{13}$$

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

$$E\,(\Delta) = \int_{-\infty}^{\varepsilon_F} \left[n^+(\varepsilon) + n^-(\varepsilon)\right] \varepsilon d\varepsilon + \frac{J\mu^2}{4}, \tag{14}$$

where $n^{\pm}(\varepsilon) = n_s(\varepsilon) + n_p(\varepsilon) + n_d^{\pm}(e)$, with $n_s(\varepsilon)$ and $n_p(\varepsilon)$ the contributions to the LDOS from de 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 done by Janak [20]. The magnetic moment is calculated from the minimum of the energy curve.

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 [21]

$$H_{ll'}(r) = H_{ll'}(r_o)\left(\frac{r_o}{r}\right)^{\alpha}, \tag{15}$$

where r_o is the original lattice constant and r is the new lattice constant. For α was used the well known Harrison rule [22]. Finally, ll' run over the basis of atomic states considered in our calculations.

3. Results and conclusions

Our results are presented in three tables, we devote one to each direction. 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 I we report the (001) direction case. We use the experimental lattice value of 3.02 Å 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* [23].

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 I).

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 (see Table II).

In Table III 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 magnetic 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 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].

TABLE I. Results for V(001) surface. The first column corresponds to the lattice constant [Å], the second 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 spin^{-1} eV^{-1} atom^{-1}].

Lattice constant	Magnetic Moment	Band splitting	$E_F(n_d)$	$E_F(n_{sp})$
3.02	0.00	0.00	1.2849	0.0205
3.05	0.00	0.00	1.3526	0.0196
3.08	0.28	0.19	1.4247	0.0201
3.11	0.48	0.34	1.5446	0.0206
3.14	0.59	0.42	1.6475	0.0204
3.17	0.68	0.48	1.6630	0.0199
3.20	0.79	0.56	1.7761	0.0205
3.23	0.97	0.68	1.8589	0.0213

TABLE II. Results from V(110) surface. The meaning of the symbols is the same as in Table I.

Lattice constant	Magnetic Moment	Band splitting	$E_F(n_d)$	$E_F(n_{sp})$
3.02	0.00	0.00	0.8779	0.0552
3.05	0.00	0.00	0.9397	0.0563
3.08	0.00	0.00	0.9559	0.0531
3.11	0.00	0.00	1.0306	0.0538
3.14	0.00	0.00	1.0418	0.0517
3.17	0.00	0.00	1.0621	0.0485
3.20	0.00	0.00	1.1271	0.0490
3.23	0.00	0.00	1.1410	0.0467

TABLE III. Results from V(111) surface. The meaning of the symbols is the same as in Table I.

Lattice constant	Magnetic Moment	Band splitting	$E_F(n_d)$	$E_F(n_{sp})$
3.02	0.05	0.0353	1.4247	0.0789
3.05	0.88	0.6227	1.4828	0.0787
3.08	1.23	0.8701	1.5457	0.0788
3.11	1.40	0.9902	1.5949	0.0784
3.14	1.57	1.1100	1.6566	0.0792
3.17	1.78	1.2590	1.7227	0.0805
3.20	2.16	1.5282	1.7604	0.0788
3.23	2.77	1.9602	1.8249	0.0808

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, $0.707\,a^2$, and $1.732\,a^2$ 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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