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Effect of band hybridization on the electronic structure of V(100) at interfaces

R. DE COSS
Departamento de Física Aplicada
Centro de Investigación y de Estudios Avanzados del IPN
Apartado postal 73 Cordemex, 97310 Mérida, Yucatán, México

AND

R. BAQUERO
Departamento de Física
Centro de Investigación y de Estudios Avanzados del IPN
Apartado postal 14–740, 07000 México, D.F., México

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ABSTRACT. We have investigated the role of *s*-*p*-*d* hybridization on the interface electronic structure of V(100)–M single interfaces, where M is a nonmagnetic metal having *s*, *sp*, or *sd* electrons near the Fermi level; in the *sd* case we consider two different configurations with full and partially filled *d*-bands. We have calculated the interface local density of states, using an empirical tight-binding hamiltonian within the Green-function-matching formalism. We find that if M is a metal not having *p* or *d* electrons at the Fermi level, the interface local density of states at the vanadium side retains the features of the surface local density of states. Surface electronic properties of V(100) are expected in the vanadium side for these interfaces.

RESUMEN. Estudiamos el papel de la hibridación *s*-*p*-*d* en la estructura electrónica de las interfaces V(100)–M, donde M es un metal no-magnético con electrones *s*, *sp*, o *sd* cerca del nivel de Fermi, en el caso con electrones *sd* consideramos dos diferentes configuraciones; banda *d* parcial y completamente llena. Calculamos la densidad local de estados en la interface, usando un hamiltoniano de enlace fuerte empírico dentro del formalismo de acoplamiento de funciones de Green. Encontramos que si M es un metal que no tiene electrones *p* ni *d* alrededor del nivel de Fermi, la densidad local de estados de la interfaz en el lado del vanadio retiene las características de la densidad local de estados de superficie. Por lo tanto, se espera que el lado del vanadio de tales interfaces presente propiedades electrónicas semejantes a las de la superficie V(100).

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1. INTRODUCTION

The idea that magnetism could manifiest itself in different ways at the surface and in the bulk of some transition metals is not new [1]. Magnetism on a surface of a paramagnetic transition metal was first predicted by Allan [2] for V(100), using a very simplified tight-binding model that only included the *d*-bands. More recently Mokrani *et al.* [3] found the V(100) surface to be ferromagnetic using a self consistent tight-binding approach, in agreement with the experimental results of Rau *et al.* [4]. Various methods [2, 5–9] based on one-electron band theory, have been used to calculate the surface electronic structure of V(100), all these calculations predict a large peak in the local density of states (LDOS) near the Fermi level (E_{F}), this highly populated LDOS is responsible for the magnetic behaviour of the V(100) surface. Magnetism at this surface is essentially the consequence of the localization of the *d*-electrons on the surface sites due to lower atomic coordination, which narrows the band width, increasing the surface LDOS at the E_{F}, and of course depends on the particularities of the crystal potential itself.

In recent years the formation of magnetic monolayers and multilayers in metals which are normally nonmagnetic has attracted considerable interest [10–13]. One interesting example is the formation of magnetic moments in monolayers of V on the surface of noble metals (Ag and Au) [13] as a result of the weak *d-sp* hybridization between the monolayers and substrate. Very recently [14] measurements of weak antiferromagnetism in multilayers of up to 16 atomic layers of V on Au have been reported. In transition metal monolayers on a substrate, the controlling parameter of the electronic structure and therefore the magnetism is the band hybridization between the monolayers and substrate.

The electronic properties of metal interfaces are basically determined by the electronic states localized at the interface, which are modulated by the band hybridization of the two metals at the interface. Since it is essentially the localization of the *d*-electrons at the surface atomic layer of V(100) that renders it magnetic, the same can occur at certain interfaces. Whenever the *d*-electrons of the V(100) semi-infinite medium do not have available states from which to tunnel into the adjacent medium, they might behave like those on the surface and interface magnetism would be possible. Since recent results shows that phenomena is posssible in the V–Ag interfaces.

From an electronic structure calculation which includes only *d*-electrons Baquero *et al.* [15] find that in the vanadium side of V–Ta(100) and V–Nb(100) interfaces the LDOS have high values, 1.26 and 1.22 ($\mathrm{eV}^{-1}\cdot\mathrm{atom}^{-1}\cdot\mathrm{spin}^{-1}$) respectively, at E_{F} and features like the surface LDOS of V(100). From that result Baquero *et al.* [15] conclude the possible existence of magnetism in the V–Ta(100) and V–Nb(100) interfaces, *i.e.*, magnetic interfaces of paramagnetic metals. In contrast with this result, we found a low value of LDOS at E_{F} (0.84–0.92 $\mathrm{eV}^{-1}\cdot\mathrm{atom}^{-1}\cdot\mathrm{spin}^{-1}$) for the V–Ta(100) interface including *s-p-d* orbitals [16]. We, thus concluded that magnetism is not expected in the V–Ta(100) interface, where the *d-d* and *sp-d* hybridization at the interface is significantly large [16]. On the other hand, superconducting quantum interference device (SQUID) magnetometer experiments of V layers sandwiched in Ag(111) layers [17], have been interpreted as due to some magnetic moment in the V layer. The magnetization decreases with increasing number of V layers. This experimental result show that magnetic interfaces of paramagnetic metals is possible in V–Ag interfaces.

As a first approach to the problem of magnetic interfaces of paramagnetic metals, we present a study on the conditions under which the features of surface LDOS of V(100) remain when vanadium is at the interface. We do not intend to predict magnetism in any specific system but only to study in a systematic way the influence of the electronic character (*s*, *sp*, and *pd*) of the neighbor of vanadium on the interface electronic structure. The outline of this paper is as follows: In Sect. 2 we present the interface models and the method of calculation. In Sect. 3 we discuss our results, and the conclusions are in the Sect. 4.

2. THE MODEL AND METHOD

To examine the interface electronic structure we have built four hypothetical systems which cover the most important possibilities in real situations. All four systems are interfaces with vanadium oriented in the (100) direction on one side and a body-centered cubic hypothetical foreign medium on the other. We take the adjacent medium to have the same (100) orientation. Vanadium has a nominal atomic configuration $[\mathrm{Ar}]3d^34s^2$. For the foreign medium we consider a Ca–like ($[\mathrm{Ar}]4s^2$) metal with electronic states of predominantly *s*-symmetry, an Al–like ($[\mathrm{Ne}]3s^2p^1$) metal with *p*-states that can hybridize with the vanadium *d*-states and diminish the localization effect, a Nb–like ($[\mathrm{Kr}]4d^45s^1$) metal whose electronic structure resembles that of vanadium, and a Au–like ($[\mathrm{Xe}]4f^{14}5d^{10}6s^1$) metal with the important *d*-band full. Our systems are hypothetical in the sense that we take Ca, Al and Au to be body-centered cubic (bcc) instead of face-centered cubic (fcc) and assume the same lattice constant for all. We use this simplification to avoid stress or other considerations, such as the details of the growth, which are not central to the essential idea developed in this paper.

We describe our systems by empirical tight-binding Hamiltonians with an *s*-*p*-*d* basis in the orthogonal two-center version [18,19]. We consider the interaction up to third nearest neighbors and use the tight-binding parameters given by Papaconstantopoulos [19]. The Green function is calculated with the Green-function-matching method [20]. This method provides an exact solution for the interface Green function, since it takes into account the true two semi-infinite media forming the interface, avoiding undesirable slab effects. Practical details of the application of the Green-function-matching method to the study of electronic properties of layered systems have been explained elsewhere [21] and need not be repeated here. The method also can be applied to surfaces [22], overlayers [23], sandwiches [24], and superlattices [25]. In all our LDOS curves we take charge neutrality into account and find E_F in the usual way [15,16].

3. RESULTS

This is the first systematic calculation of the effects of band hybridization on the interface LDOS of V(100) at interfaces. In all our LDOS curves the common origin is at E_F. We have studied the V(100) surface for reference.

In Fig. 1 we show the surface and the bulk projected LDOS for V(100). The bulk projected LDOS shows the typical features for the bcc transition metals, the bonding (~ -2.0–0.0 eV) and the anti-bonding (~ 1.5–3.0 eV) states separated by the pseudogap (~ 1.5–3.0 eV). The minimum just above E_F is associated with the stability of the bcc structure. In contrast, the surface LDOS has three main peaks close to E_F (~ 0.0–1.5 eV), and exactly one around E_F, this highly populated LDOS is responsible for the magnetic behaviour of the V(100) surface [2]. We can see that the surface LDOS is almost twice the bulk projected LDOS at E_F. This is a manifestation of the localization of the *d*-electrons and it occurs essentially at the surface atomic layer [26]. Notice also that the band width becomes narrower at the surface as a consequence of lower coordination.

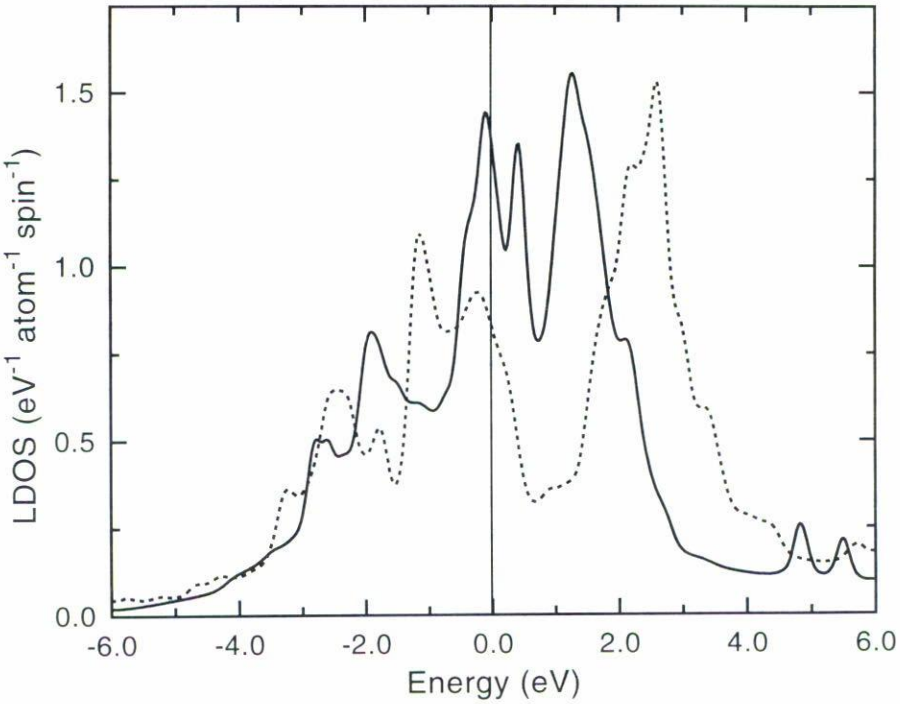

FIGURE 1. LDOS for vanadium bulk (dashed line) and surface (solid line) layer projected in the (100) direction. Notice the difference in the LDOS value at the Fermi level. This is an essential feature to explain the V(100) surface magnetism.

In Fig. 2 we show the LDOS for the vanadium interface layer for our V/Ca–like, V/Al–like, V/Nb–like, and V/Au–like models. In Table I we show the value of the interface LDOS at E_F for all the interfaces, projected on the vanadium side. The different values define the behavior of the outermost vanadium atomic layer in front of the neighboring medium (Ca, Al, Nb and Au). We give the percentage of the surface LDOS that each interface LDOS and the bulk projected LDOS represents, all taken at E_F. This is an important parameter. The bulk LDOS is only 61% paramagnetic. From now on, whenever we refer to a value of any LDOS curve we mean always at E_F, compared with the V(100) surface LDOS (SLDOS).

In Fig. 2a we can see that the interface LDOS for the V/Ca–like case is similar to V(100) surface LDOS, although they differ in some details. Although smaller, the enhancement of the interface LDOS at the vanadium side of the interface is of the same order as in the surface (90%, see Table I), and the band width is only ~ 1.0 eV wider that in the surface. This case illustrates the behaviour of the vanadium atomic layer in front of a material containing only *s*-electrons. The V/Al–like model (Fig. 2b) illustrates the behaviour of the *p*-states which are seen to hybridize with the vanadium *d*-states, diminishing the localization, as we already mentioned. The interface LDOS on the vanadium side is only 67%. This has to do with an important hybridization of the *s*- and *p*-states of the Al with the *d*-states of V at the interface. This result is in qualitative agreement with a recent study of Al overlayers on Fe(001) performed by Hong *et al.* [27], who found

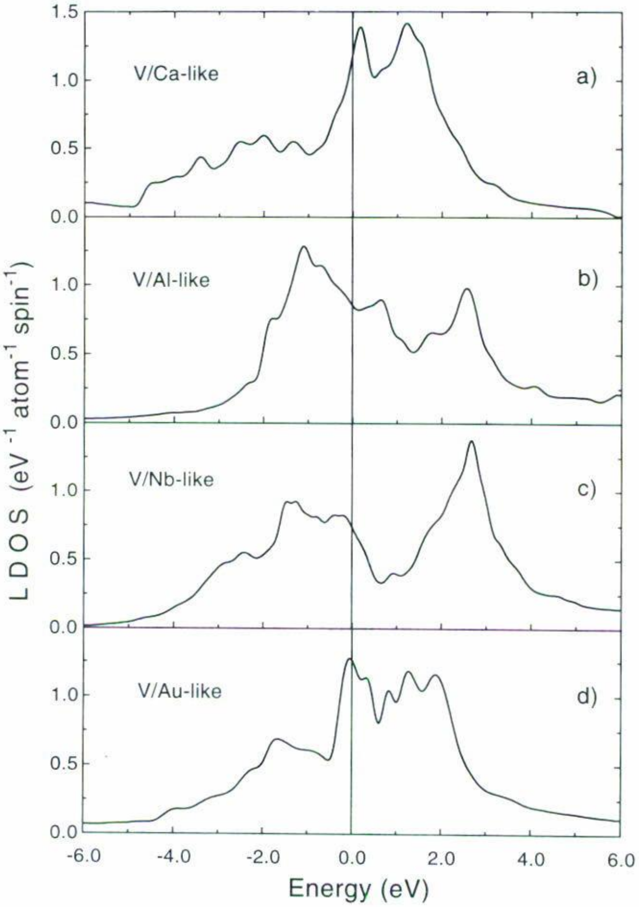

FIGURE 2. LDOS for the vanadium side in the four model interfaces: a) V/Ca–like, b) V/Al–like, c) V/Nb–like, and d) V/Au–like (see text).

that the magnetic moment at the Fe(001) surface covered by Al is reduced from that of clean Fe(001) by 54%, as a consequence of the strong hybridization of Al *s*, *p*- and Fe *d*-electrons.

In the V/Nb–like model (Fig. 2c) the interface LDOS on the vanadium side is 55% lower than the bulk LDOS (61%). The features of the interface LDOS in this model resemble the vanadium bulk LDOS, indicating that the *d*-*d* and *sp*-*d* hybridizations at the interface V–Nb(100) are significantly large. This agrees with the result of Ref. [16] who found a very similar behaviour for the V–Ta(100) interface and contrasts with the results of Ref. [15] who found a surface-like behaviour in the vanadium side of both interfaces, V–Nb(100) and V–Ta(100), as we already mentioned. The V/Au–like model (Fig. 2d) illustrates the role of the completely-filled *d*-band; the band width in this case is practically the same as in the V(100) surface. The interface LDOS on the vanadium side is 94%; this is the highest value in our models (see Table I), showing that the electronic surface properties of V(100) can be retained at interfaces with noble metals.

TABLE I. Value at the Fermi energy, E_F, of the Interface Local Density of States (ILDOS) projected on the vanadium side. The values on the right hand side are the percentage of the ILDOS at E_F with respect to the V(100) surface local density of states (SLDOS) at the same energy.

System	$N(E_F)$	% of V(100) SLDOS
V(100)–bulk	0.82	61
V(100)–surface	1.34	100
V/Ca–like	1.20	90
V/Al–like	0.90	67
V/Nb–like	0.73	55
V/Au–like	1.26	94

4. CONCLUSIONS

We have studied the conditions under which the surface electronic structure of V(100) can be retained when vanadium is at the interface. For that purpose we have built four model interfaces with vanadium. Our models have the atomic electronic characteristics of Ca, Al and Nb to represent materials with only *s*, *s* and *p*, or *s* and *d* electrons, respectively. A Au–like model was also built to study the behavior of a full *d*-band. We construct ideal interfaces in the sense that we take all the elements to be of bcc crystal structure and to have the same lattice constants as vanadium. We find that in V(100) interfaces with metals having *p* or *d* electrons at E_F the hybridization is large and so suppresses the localization of the *d*-electrons in the vanadium side. On the contrary, for interfaces with *s*-electrons and with noble-metal-like electronic structure, the interface LDOS at the vanadium side retains the features of the surface LDOS of V(100). Consequently, surface electronic properties of V(100) can be expected in the vanadium side of V(100)-noble metal interfaces. To make further predictions a detailed study of a real interface is necessary.

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