Condition for the appearance of a live magnetic layer on paramagnetic pure transition metals

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Self-consistent real-space calculations in the unrestricted Hartree-Fock approximation of the Hubbard Hamiltonian are performed for slabs of metallic systems with unfilled d shells in order to investigate a possible appearance of a live magnetic surface plane on paramagnetic bulk. These results can also be obtained qualitatively within a flat-band model, which gives a simple relation between the appearance of magnetism and the coordination number. Within this model, vanadium is shown to have a ferromagnetic surface plane, as observed experimentally.

Since 1930,[1] it has been well known that magnetism in metals can be well represented by a splitting of the d bands. In this scheme, ferromagnetism can appear when the intrasite exchange integral J, which, following Bethe,[2] is related to the extension of valence orbitals, is positive. Some years later Stoner[3] proposed his famous criterion which relates J to the inverse of the density of states at the Fermi level. This criterion has been discussed recently in relation with a spin-polarized total-energy band calculation of fcc Fe.[4]

Freeman et al.[5] have developed a full potential linearized augmented-plane-wave method (FLAPW) for the description of the electronic and magnetic structure of solid surfaces. Later on this program was used by Blügel and Dederichs[6] for the appearance of ferromagnetism and antiferromagnetism of $3d$ metal overlayers on noble-metal substrates. So far, most of the theoretical studies on the magnetic properties of transition-metal multilayers were performed using this first-principles method. These type of calculations do provide the highest precision and reliability one can reach nowadays, but require a great deal of computational effort.

On the other hand, recent experimental advances make it possible to explore the magnetic and electronic properties of artificially structured ultrathin films not found in nature. An exciting challenge concerns bcc vanadium which is paramagnetic in the bulk but has been found magnetic by Akoh and Tasaki[7] in their work on hyperfine particles. An isolated vanadium atom possesses a permanent magnetic moment of $3.0\mu_B$ in the ground state whereas bulk solid vanadium does not exhibit ferromagnetism. In the case of surface atoms where the coordination number (number of the nearest neighbors), which is known to strongly influence magnetic ordering, is reduced, one might expect ferromagnetic behavior.

Electron-capture spectroscopy has been used to investigate magnetic order at the topmost atomic layer of atomically clean and flat (100) surfaces of bulk paramagnetic vanadium.[8] These authors[8] find unambiguously that long-ranged ferromagnetic order exists at atomically clean and flat surfaces of $V(100)p(1 \times 1)$.

Allan[9] has presented a condition for the existence of a magnetic instability localized near the surface of bulk paramagnetic transition metals. He was able to derive a magnetic moment at the surface of vanadium as a function of the surface Coulomb exchange integral U_S. Unfortunately, his derivation was performed in the first-order perturbation theory. The electronic structure and spin polarization of five-layer vanadium (100) thin films have been calculated using the self-consistent charge spin-polarized discrete variational X_α method (Yokoyama et al.[10]). They found that the surface layer has a magnetic moment of $0.24\mu_B$ and that the relaxation of the surface affects the spin polarization. Grempel and Ying[11] have derived a finite-temperature susceptibility at the (100) surface of vanadium by means of spin fluctuation theory. A Néel temperature of about 4 K and a magnetic moment of $2.4\mu_B$ are obtained. More recently the FLAPW method was applied to the derivation of magnetism of V(001).[12] This method does not yield ferromagnetic order for the V(100) surface, but does for a V(100) monolayer.

In this paper, we propose to investigate a possible appearance of a live ferromagnetic surface layer within a self-consistent tight-binding approach. This model is based on recent investigation on the magnetism of V(001).[13] In this model the size and structural dependence of magnetic properties of vanadium slabs are determined by using a tight-binding Hubbard Hamiltonian in the unrestricted Hartree-Fock approximation. This

method has given reasonable results in the case of small Cr_n, Fe_n, and Ni_n clusters[14] and iron slabs.[15]

Following[14,15] the use of the Hubbard Hamiltonian for d electrons, we derive the electronic structure for slabs of bcc V. In this model, the hopping integrals are spin independent, whereas the spin-dependent diagonal terms are given by

$$\varepsilon_{i\sigma} = \varepsilon_d^0 + U\Delta N_i - \sigma\frac{J}{2}\mu_i , \tag{1}$$

where i is the index of the ith atomic plane and σ is the spin. ε_d^0 is the d level of vanadium and can be chosen as zero. The exchange and effective direct intra-atomic Coulomb integrals denoted by J and U, respectively, are taken to be independent of the size of the slab. U is taken from Ref. 16. The local magnetic moment is given by

$$\mu_i = N_{i\uparrow} - N_{i\downarrow} , \tag{2}$$

whereas the numbers of electrons $N_{i\sigma}$ are determined by

$$N_{i\sigma} = \int^{\varepsilon_F} n_{i\sigma}(\varepsilon)d\varepsilon . \tag{3}$$

The spin-polarized local densities of states (SPLDOS) $n_{i\sigma}(\varepsilon)$ are calculated by using the recursion method[17] with ten levels of the continuous fraction and canonical hopping integrals.[18] We allow charge transfer ΔN_i between different atomic planes by requiring global charge neutrality for the N_L layer slabs of V(001).

The calculation proceeds in two steps. The first step consists of a calculation of the bulk magnetic moment μ_b of V in terms of the parameter J. Bulk vanadium displays a magnetic moment for an unrealistically high value of 1.45 eV (Fig. 1): This is consistent with the absence of magnetism in bulk vanadium. For $J > 1.5$ eV the magnetic moment converges rapidly to 4.0 μ_B. This is exactly what Hund's rule,[19] or its solid-state equivalent "strong ferromagnetism," is supposed to give us.

The second step of the calculation consists of a study of 1–3- and 11-layer slabs of V(001) in order to find the J value which gives a transition from paramagnetism to ferromagnetism on the surface plane. As shown by the results displayed in Fig. 1 the appearance of magnetism is related to the coordination number. Therefore, we may explain this appearance of magnetism with a simple model, considering rectangular bands for up and down spins,[20] and a "strong ferromagnetism" model for the magnetism..

In this model, the minimum value J_{min} of J for appearance of strong ferromagnetism is given by $W/5$. In a tight-binding model the width W of the band is related to the square root of the second moment of the local density of states:[17,21]

$$W \propto \sqrt{Z_{eff}} , \tag{4}$$

where the effective coordination number Z_{eff}, for a bcc structure is given by:[22]

$$Z_{eff} = Z_1 + 0.4Z_2 . \tag{5}$$

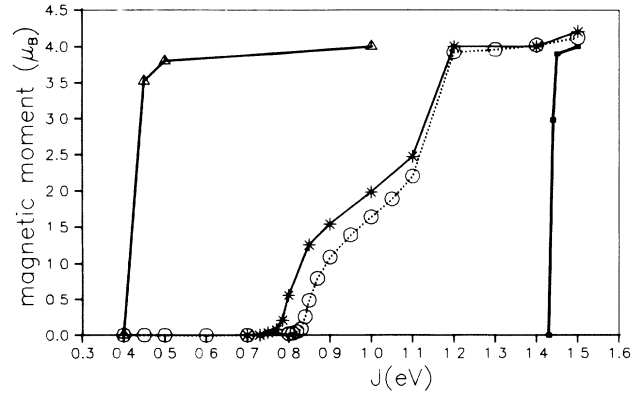Z_1 and Z_2 are the number of first and second neighbors.

FIG. 1. Magnetic moment per atom for slabs of vanadium in terms of the exchange parameter J: $\triangle$, a monolayer; $\bigcirc$, a three-layer slab; $*$, an eleven-layer slab; $\blacksquare$, an infinite slab (bulk). The bulk magnetic moment is obtained at the center of the infinite slab whereas, for slabs of finite thickness, the magnetic moment is taken at the surface.

In the bulk, the vanadium atom has eight nearest (N) and six next-nearest (NN) neighbors. Therefore, for the bulk, $Z_{eff} = 10.4$; for a monolayer (001) we have just 4 NN neighbors so that $Z_{eff} = 1.6$ and for a (001) surface (or a slab with three layers or more), $Z_{eff} = 6$.

The preceding estimation shows that, in this simple semiquantitative model, the appearance of magnetism is clearly related (i) to the number of effective coordination numbers and (ii) to the crystallographic orientation of the surface.

For example, in the case of bcc, $Z_{eff} = 1.6$ for a (001) monolayer whereas $Z_{eff} = 4$ for a (011) monolayer. This model is in agreement with the magnetic moments obtained in a self-consistent derivation and reported in Fig. 1. The minimum value of J for the appearance of magnetism in the bulk is almost three times that necessary for the monolayer (001). The case of 3 and 11 layers is intermediate. The bulk bandwidth being 7.5 eV,[18] the simple model predicts a value of 1.5 eV for J which is astonish-
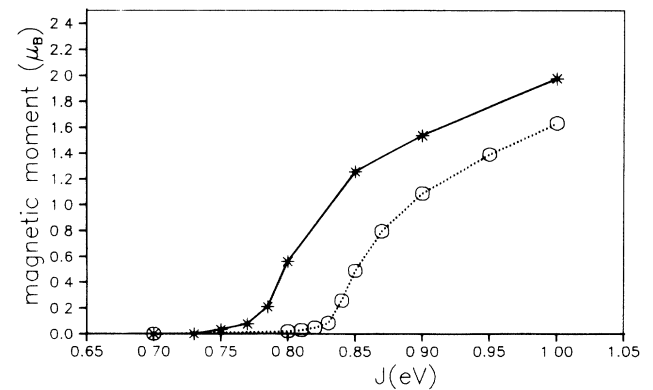

FIG. 2. Magnetic moment per surface atom for 3- and 11-layer slabs of vanadium in terms of the exchange parameter J: $\bigcirc$, a three-layer slab and $*$, an eleven-layer slab.

ingly near 1.45 eV, the value found within our full self-consistent scheme for the appearance of magnetism. For the monolayer which also presents strong ferromagnetism, the simple model leads to a slightly higher value of 0.58 eV. On the other hand, for semi-infinite slabs, the appearance of weak ferromagnetism is observed when J is of the order of 0.7 eV. For a (001) semi-infinite crystal, strong ferromagnetism is reached for $J \propto 1.05$ eV which is only slightly smaller than 1.12 eV, the value conjectured by the simple model.

The results of our self-consistent derivation are in agreement with the ferromagnetic order observed by electron-capture spectroscopy[8] for a J between 0.7 and 0.8 eV, which in spite of the fact that an exact value cannot be obtained in a tight-binding framework,[15] is very reasonable. Let us point out that only the surface layer is magnetic. In any case, the other planes are paramagnetic due to unphysical values of J_{min}, which are of the order

of magnitude of the threshold value for the bulk. Also, the appearance of magnetism depends on the thickness of the layer slab (Fig. 2).

We believe that our simple model will yield predictions concerning other systems with unfilled d shells. If we consider the width of the d bands,[18] Sc, Ti, Y, and Pd may be good candidates for the appearance of magnetism at the surface. However, our feeling must be supported by a self-consistent derivation in terms of reasonable values of J. Results are planned to be given in due course.

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