Empirical tight-binding description of surfaces: is it meaningful?

R. Baquero and A. Noguera*

Departamento de Física, Instituto de Ciencias, Universidad Autónoma de Puebla,
Apartado postal J-48, Puebla, Pue. 72570, México

(Recibido el 13 de diciembre de 1988; aceptado el 31 de mayo de 1989)

Abstract. By describing the (001)-Vanadium surface with a seven-parameter tight-binding hamiltonian for the d-electron band, we obtain a description of the (001)-Vanadium surface that compares well with more sophisticated calculations. We take into account charge neutrality in a simple way that justifies itself due to the extreme localization of the surface effects. We present here the bulk, the surface and the inner-layer-projected local density of states. By analyzing and comparing our calculations, we conclude that this simple method gives meaningful results and can be used in other similar cases. This is of great interest since due to the sharp contradiction between the state-of-the-art calculation and experiment, new sources of magnetism for the (001)-Vanadium surface need to be studied.

PACS: 73.20.At; 71.20.Cf

1. Introduction

There is a growing interest in the study of transition metal surfaces [1] because of their special chemical and physical properties and because they may manifest themselves differently both in the bulk and in the surface, *i.e.*, the electronic structure and the magnetic properties [2]. Take for example the enhanced magnetic moment that presents the (001)-surface of Fe with respect to the bulk. It is known that it diminishes as the dimensionality increases: 4.0 for the free electron, 3.3 for the linear chain, 2.89 for the (001)-surface and 2.27 for the bulk (in Bohr magnetons) [3]. Another interesting example of transition metal surface is the (001)-Ni where the question was whether the surface layer is 'dead' or 'alive' [4]. There has been quite a few experimental and theoretical work on this point. Recent results lead to the conclusion that (001)-Ni is not magnetically dead [3].

These conclusions were arrived at with first principles calculations that constitute a state-of-the art work. They are, however, time consuming and as the complexity of the systems described increases, approximate methods that give good results become more and more necessary and important. The aim of this paper is

---

*Post-doctoral fellow. Permanent address: Departamento de Física, Universidad de los Andes, Mérida Venezuela.

to analyze in detail how the simplest possible description of a system compares to complex calculations when a good approximate method of calculation is used.

The effect of a surface of a given crystal is to narrow the bandwidth due to the few number of nearest neighbors. This effect is sharper in the (001)-face of the *bcc* crystals, where 50% of the nearest neighbors are lost. In transition metals, where the d-electrons play the most important role, the narrowing of the bandwidth could build a magnetic moment on the surface even if the bulk is paramagnetic. Vanadium is an example of it. This situation occurs because the peak in the local surface density of states turns out to be very near the Fermi level.

There are some studies on this respect. The first one was made by Allan [4], who has found that the surface layer adquires a magnetic moment if the Coulomb integral $U_s > 0.5$. The Local Density of States (LDOS) surface peak, characteristic of the $3d$-transition metals with *bcc* structure, was found almost right at the Fermi level. Grempel *et al.* [5] devoted themselves to the calculation of the paramagnetic properties of the Vanadium surface based on a tight-binding description and have found an enhanced paramagnetism at the surface layer. More recently, Onishi, Fu and Freeman [6] reported a total energy first principles calculation for the (001)-Vanadium surface and have found that the ground state is paramagnetic instead of magnetic as was proposed by Allan. The surface peak is found to lie about 0.3 eV from the Fermi level.

In what follows, we set up the simplest reasonable description of (001)-Vanadium surface, *i.e.,* a tight-binding Hamiltonian accounting for the d-bands only. Afterwards, we review the recent results of Baquero *et al.* [7] for (001)-Vanadium with the specific purpose of comparing in detail, at each step, these results to the ones of Ref. [6]. The results of Ref. [7] are based on a generalization of the Surface Green Function Matching (SGFM) method [8] specially suited to deal with the physics of layered structures as described in an empirical tight-binding Spirit [9]. Below we shall obtain significant results that give a good description of the (001)-Vanadium surface. It is encouraging that, once we have included the correction for charge neutrality, we get the LDOS main peak about 0.19 above the Fermi Level; this compares very well with the 0.3 eV obtained in Ref. [6]. Moreover, a reasonable fit to the band structure calculated by Yasui *et al.* [10] is obtained and our bulk LDOS coincide with theirs. Furthermore, also in agreement with Ref. [10], the Fermi level turns out to be close to the main minimum of the bulk LDOS. On the other hand, our surface LDOS agrees with the results of Grempel *et al.* [5]. Its features are those characteristic for the (001)-surface of *bcc* transition metals. The effect of the surface is mainly localized at the first atomic layer and this is a striking fact in these structure [4,5].

The rest of the paper is organized as follows: section 2 is devoted to a brief review of the method. In section 3, we analyze our results and the last section 4 is dedicated to summarize our conclusions.

2. The method [7]

We use five nonzero parameters to describe the bulk d-electron bands in the two center approximation within the language of Slater and Koster [9]. To set up the hamiltonian for the (001)-Vanadium surface we assume ideal truncation, and so we use the same tight binding parameters. This approximation seems reasonable because the (001)-Vanadium surface does not reconstruct as it is well known [11].

With this hamiltonian we obtain the Green's function from

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

where ω is the energy eigenvalue and I is the unit matrix. We adopt the customary description in terms of principal layers. We will label them with positive numbers and zero for the surface. 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 atomic functions on each atom and two atomic layers, *i.e.*, it is a 10-dimensional vector. If we take matrix elements of Eq. (1) in the Hilbert space generated by the complete system of wave-functions $|n\rangle$, we get

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

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

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

since there is only nearest-neighbor interactions between principal layers and therefore $H_{m,m+i} \equiv 0$ for $|i| \geq 2$. By inserting (3) in (2) we get

$$(\omega - H_{nn})G_{nm} - H_{nn-1}G_{n-1m} - H_{nn-1}G_{n+1m} = \delta_{mn}. \tag{4}$$

The matrix elements of the hamiltonian, H_{nm}, that appear in this formula are 2×2 supermatrices (each principal layer contains two atomic layers) each of whose elements is a 5×5 matrix (since we a re using five d-wave functions for each atom as a basis). For example

$$H_{01} = \begin{pmatrix} h_{0-2} & h_{0-3} \\ h_{-1-2} & h_{-1-3} \end{pmatrix}. \tag{5}$$

Notice that the rows are labeled with the index of the surface principal layer zero (containing atomic layers 0 and -1) while the columns are indexed with the first principal layer (atomic layers -2 and -3). We label principal layers with positive numbers and atomic layers with negative numbers. The surface is labeled with zero in both cases. We shall adopt the hypothesis of an ideal, non reconstructed surface and then $H_{00} = H_{nn}$ for any n. Also $h_{0-2} = h_{-1-3}$ and $h_{-1-2} = h_{0-1}$. For second-nearest neighbors interactions $h_{0-3} = 0$. To calculate H_{00} and H_{01} we need to know only h_{00}, h_{0-1} and h_{0-2} which are 5×5 matrices as stated before. These three matrices are readily written in a tight-binding language and can be calculated with the bulk parameters mentioned above. They depend on the energy, ω, and on the wave vector $\mathbf{k}$. The lattice constant is 3.02 Å.

Using (4) for $m = n$ it is straightforward to get the surface Green's function [7]

$$G_s^{-1} = \omega I - H_{00} - H_{10} T, \tag{6}$$

and the principal-layer-projected bulk Green's function

$$G_b^{-1} = G_s^{-1} - H_{01}^{+} \widetilde{T}. \tag{7}$$

Furthermore, we make use of a Surface Green Function Matching formulae to get the principal-layer-projected Green's function on the layers next down form the surface

$$G_{nm} = G_b + T^n (G_s - G_b) \widetilde{S}^n. \tag{8}$$

It is customary to define the transfer matrices as

$$G_{ij+1} = T G_{ij}, \qquad G_{ij+1} = G_{ij} S \quad j \geq i \geq 0, \tag{9.a}$$

$$G_{k+1p} = \widetilde{T} G_{kp}, \qquad G_{k+1p} = G_{kp} \widetilde{S} \quad k \geq p \geq 0, \tag{9.b}$$

These matrices can be calculated by the quick algorithm of Lopez-Sánchez *et al.* [12] and Baquero [13]. They get

$$T = t_0 + \widetilde{t}_0 t_1 + \ldots + \widetilde{t}_0 \widetilde{t}_1 \cdots t_{i-1} + \ldots, \tag{10.a}$$

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

$$S = s_0 + s_1 \widetilde{s}_0 + \ldots + s_i \widetilde{s}_i \widetilde{s}_{i-1} \cdots \widetilde{s}_1 \widetilde{s}_0 + \ldots, \tag{10.c}$$

$$\widetilde{S} = \widetilde{s}_0 + \widetilde{s}_1 \widetilde{s}_0 + \ldots + \widetilde{s}_i s_{i-1} \cdots s_1 s_0 + \ldots, \tag{10.d}$$

where,

$$t_0 \equiv (\omega - H_{00})^{-1} H_{01}^{+}, \quad \widetilde{t}_0 \equiv (\omega - H_{00})^{-1} H_{01}, \tag{11.a}$$

$$t_i \equiv M_{i-1} t_{i-1}^2, \quad \widetilde{t}_i \equiv M_{i-1} \widetilde{t}_{i-1}^2, \tag{11.b}$$

with $M_{i-1} = (1 - t_{i-1} \widetilde{t}_{i-1} - \widetilde{t}_{i-1} t_{i-1})^{-1}$,

$$s_0 \equiv H_{01}^{+} (\omega - H_{00})^{-1}, \quad \widetilde{s}_0 \equiv H_{01} (\omega - H_{01})^{-1}, \tag{11.c}$$

$$s_i \equiv s_{i-1}^2 N_{i-1}, \quad \widetilde{s}_i \equiv \widetilde{s}_{i-1}^2 N_{i-1}, \tag{11.d}$$

with $N_{i-1} \equiv (1 - s_{i-1} \widetilde{s}_{i-1} - \widetilde{s}_{i-1} s_{i-1})^{-1}$.

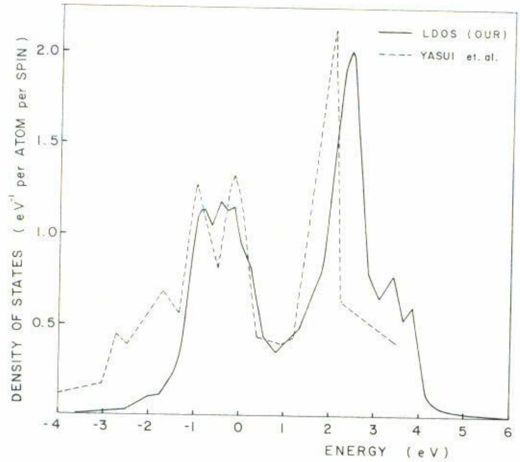

FIGURE 1. Our calculated bulk LDOS compared to the schematic one by Yasui *et al.* [10]. The origin is at the bulk Fermi level. They describe the s- and d- band while we describe only the d-band.

The i^{th} term in (10) is of the order of $2^{i+1}-1$ in H_{01} and it vanishes rapidly. Thus a good approximation is obtained for the transfer matrices. Once they are known we can compute the G_s, G_b and G_{nn} in an straightforward way from the formulae given above.

At the moment of practical calculations one has to take into account that a small imaginary part, ϵ, is to be added to the energy in all the matrices. To calculate transfer matrices our criterium for convergency was based on the matrices obtained by taking the difference between two iterations. The sum of all its elements, divided by the sum of all the elements of the corresponding transfer matrix during the same iteration, has to be lower than a certain small number, δ ($\simeq 0.000001$).

3. Results

For any of the Green's functions given above, the corresponding density of states at a given layer can be calculated from the usual formula

$$N(\mathbf{k},\omega) = -\frac{1}{\pi}\,\mathrm{Im}(\mathrm{tr}\,G(\mathbf{k},\omega)). \tag{12}$$

Since G is a 10×10 matrix that describes two atomic layers, the trace is to be taken only in the upper half of the diagonal or in the lower part of it, according to which atomic layer is desired. The density of states is then integrated in the two-dimensional first Brillouin zone using the method of Cunningham [14].

In Fig. 1 we show our calculated [7] bulk density of states and the equivalent one from Ref. [10], in both curves the Fermi level is taken at the origin. Our density

	Main Peak s (eV)		Main Minimun
Yasui *et al.*	-1.72 -0.96	-0.18 2.09	0.986
This Work	-0.95 -0.43	-0.15 2.45	0.9700

TABLE I. The position of the most important peaks (eV) for the bulk LDOS of Yasui *et al.* [10] are compared to those obtained in this work. The origin is taken at the Fermi level.

This work		Yasui et al.
5. (only d-bands)	$\int_{-\infty}^{\epsilon_f} N_{\text{bulk}}(\omega)d\omega$	6. (s and d bands)
1.5	V_e (see Eq. 13)	2.5
2.00	Intensity of the highest peak states/eV/spin	2.26.
89.	Rel. Intensity	100.
0.97	Intensity at ϵ_f	1.19

TABLE II. Detailed comparison of the main properties of the bulk LDOS of Ref. [10] and of those this work.

of states is normalized to 5 electrons (d-electrons only) and theirs to 6 (s and d electrons). We calculated the Fermi level, ϵ_f, from the usual equation

$$\int_{-\infty}^{\epsilon_f} N(\omega)d\omega = V_e, \tag{13}$$

where V_e is the number of single spin valence electrons. Because the electronic configuration of Vanadium is Ar $3d^3 4s^2$, Yasui *et al.* [10] use $V_e = 2.5$ (s and d electrons) while we take $V_e = 1.5$ (only d electrons). It is to be noticed that the bulk LDOS passes through a minimum on going to higher energies away from the Fermi level before it reaches the main peak. This minimum is characteristic of the *bcc* transition metals and has been associated with the stability of the crystal structure in transition metals like W and Mo [15,16]. This minimum is located at 0.986 eV in the work of Yasui *et al.* [10] to be compared to 0.97 eV, in our case. Their main peak is located at 2.09 eV and ours at 2.44 eV.

In Tables I and II these values are listed for comparison, along with the position of the rest of the peaks. The intensity of the bulk LDOS at ϵ_f is 1.19 states $\text{eV}^{-1}\text{atom}^{-1}\text{spin}^{-1}$ whereas our values is 0.97 in the same units. In conclusion, fitting only the d-bands gives a reasonable description of the bulk LDOS. A certain intuition about what is important has to be used since the two LDOS cannot be compared directly to each other. Here we take into account, as a point of reference, the minimum in the bulk LDOS near the Fermi level because it is usually located close to the surface LDOS maximum. This surface peak is crucial for the appropriate description of the physics of the (001)-Vanadium surface.

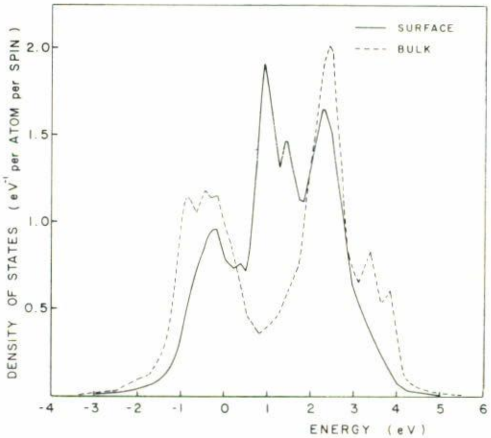

FIGURE 2. The bulk and surface LDOS. The surface curve is not yet corrected for charge neutrality. The origin is taken at ϵ_f.

The Fig. 2 displays our computed surface —and the bulk— LDOS, with the origin again at the Fermi level. The surface curve shows the main peak characteristic of the (001)-surface in *bcc* transition metals. This peak is as intense as the bulk main peak and is located below in energy, 0.98 above ϵ_f. This value is much higher than the 0.3 eV reported in Ref. [6] and even higher than the findings of Ref. [4], where this peak was found right at the Fermi level (we shall come back to this point later). One of the reasons for the disagreement is that our calculated surface LDOS does not conserve charge neutrality. Notice that $\int_{-\infty}^{\epsilon_f} N_s(\omega)d\omega = 0.91$. This is, of course, less than 1.5 and we have therefore less negative charge at the surface than we should.

In Fig. 3 we show the evolution of the LDOS as one goes into the bulk in the (001)-direction. Observe that the first layer away from the surface presents most of the characteristics of the bulk and for the third atomic layer the bulk LDOS is almost reached. This strong localization of surface effects allows us to correct for charge neutrality in a very simple way. Charge neutrality has been dealt with by several authors [17]; in Ref. [7] this correction was done by finding the energy of the capacitor produced by the difference of charge between the first and the second atomic layers. Here, this correction is done in a slightly different way, we merely shift the surface LDOS until the integral from the bottom of the d-band up to the bulk ϵ_f reaches 1.5 (the bulk value). This shift has been first proposed by Allan [18].

We present in Fig. 4 our final result for the bulk and the corrected surface LDOS for the (001)-Vanadium surface. Observe that the main peak in the surface LDOS occurs now at 0.19 eV above the Fermi level, in good agreement with a recent band structure calculation [6]. This is a big success for such a simple description of the system.

Finally, one question remains to be discussed. Why in the simple calculation presented in the pioneer work by Allan [4] the surface LDOS-peak is at the Fermi

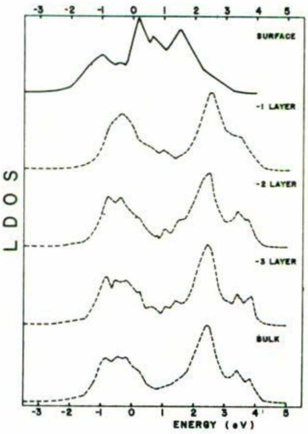

FIGURE 3. Evolution of the LDOS into the bulk in the (001) direction.

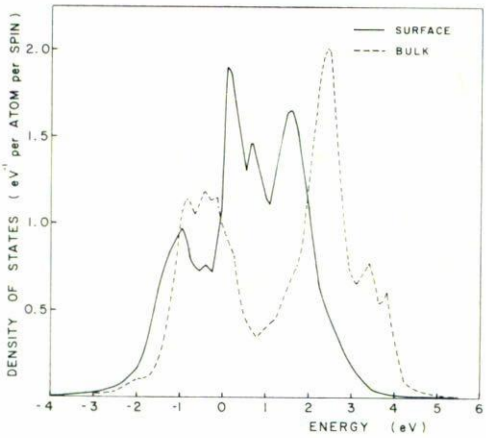

FIGURE 4. The bulk and the surface LDOS corrected for by charge neutrality. Final result.

level? This point must be clarified because the position of this peak is crucial to explain the magnetic properties at the surface. Actually, Allan [4] had found that a magnetic moment exists on the (001)-Vanadium surface if the Coulomb integral $U_s > 0.5$ eV (a condition that seems easy to achieve for Vanadium). However in Ref. [6], the ground state of (001)-Vanadium surface is found to be paramagnetic. Although in Ref. [4] the tight-binding parameters of Cr have been used to describe V, this simplification can be justified. The real approximation is elsewhere. Looking carefully at Fig. 4 in Ref. [4] (showing the single spin bulk LDOS) we see that the integral under the curve is 5 electrons spin^{-1}atom^{-1} (only d-states are considered).

If we make the integration up to the Fermi level we see that the occupied states sum up to 2.5 electrons $\text{spin}^{-1}\text{atom}^{-1}$ as if the s and d electrons were included all together. This implies a big $s-d$ transfer. This $s-d$ electron transfer of 1 electron $\text{spin}^{-1}\text{atom}^{-1}$ is the highest possible in this system. We have not consider any $s-d$ electron transfer in our calculation as we have not any support for such a big transfer.

4. Conclusions

We have calculated the bulk, the (001)-surface, and the inner-layer-projected Local Density of States (LDOS) for the transition metal Vanadium. The calculation uses the simplest tight-binding description of the d-bands for the (001)-Vanadium surface. The purpose of this paper is to see how this approach remains meaningful at each step, and how close is the final result compared to the first principle calculation of Ref. [6]. Our work shows that while there is a lost of precision in the bulk LDOS, the most significant information about the surface calculation is given by our model by taking d-electrons only. Our description of the surface- and inner-layers-projected LDOS is also very satisfactory. In particular, we have found a strong localization of the surface effects which allowed us to use a one-parameter correction for charge neutrality. After having included this correction, the highest peak in the surface LDOS turns out to be a 0.19 eV above the Fermi level in very good agreement with the very accurate calculation of Ref. [6]. The position of this peak is important to explain the magnetic properties of this surface.

The first conclusion is then that a tight-binding model for the surface of a transition metal is meaningful.

The extension of the method to describe interfaces, quantum wells and superlattices looks suggestive.

A natural extension of this work is to calculate the magnetic properties of transition metal surfaces. In particular the (001)-Vanadium surface which has been found to be ferromagnetic by electron spectroscopy [11] in sharp contradiction with the state-of-the-art-calculation of Ref. [6], where the ground state has been found to be paramagnetic. This discrepancy has been suggested to be attributable to the negligible anisotropic spin-orbit part of the hamiltonian.

It is appealing that our method can be extended to include anisotropy without representing a large computational effort. The interesting point would be to see if within this model anisotropy it can be shown that the ground state is the ferromagnetic one. It has been reported that anisotropy induces magnetism in a single atomic layer of Vanadium grown on Ag(100) substrat [19].

An interesting situation should arise if it is confirmed that the paramagnetic state lies lower in energy than the ferromagnetic one but the ground state is given by the anisotropy. If this were the case, magnetism in the (001)-Vanadium would have been properly predicted but not for the right reason. This will be the subject of a future work.

Acknowledgements

One of us (A.N.) would like to thank the Departamento de Física, Universidad de los Andes, Mérida, Venezuela for its financial support. Part of this work was done while one of us (R.B.) was visiting the Consejo Superior de Investigaciones Científicas, Madrid, España. Their hospitality and financial support is gratefully acknowledged.

References

1. See, for example, *Magnetic Properties of Low-Dimensional Systems*, ed. by L.M. Falicov and J.L. Moran-López, Springer Proceedings in Physics **14** (1986).
2. J.E. Inglesfield, *Electronic Properties of Surfaces*, ed. M. Prutton, Adam Hilger Ltd. Bristol (1984) p.34.
3. A.J. Freeman and C.L. Fu, Ref. [1] pag. 16 and references therein.
4. G. Allan, *Phys. Rev.* **B19** (1979) 4774.
5. D.R. Grempel and S.C. Ying, *Phys. Rev. Lett.* **45** (1980) 1018.
6. S. Onishi, C.L. Fu and A.J. Freeman, *J. Magn. Mat.* **50** (1985) 161.
7. R. Baquero, V.R. Velasco and F. García-Moliner, *Physica Scripta* (in Press).
8. F. García-Moliner and V.R. Velasco, *Progress in Surface Science* **21** (1986).
9. J.C. Slater and G.F. Koster, *Phys. Rev.* **94** (1954) 1498.
10. M. Yasui, E. Hayashi and M. Shimizu, *J. Phys. Soc. Jpn.* **29** (1970) 1446.
11. C. Rau, E. Lin, A. Schmalzbauer and G. Xing, *Phys. Rev. Lett.* **57** (1986) 2311.
12. M.P. López-Sancho, J.M. López-Sancho and J. Rubio, *J. Phys. F:Met. Phys.* **14** (1984) 1205; *J. Phys. F: Met. Phys.* **15** (1985) 855.
13. R. Baquero, ICTP-preprint IC/88/185, sent to *Nuovo Cimento.*
14. S.L. Cunnningham, *Phys. Rev.* **B10** (1974) 4988.
15. M. Posternack, H. Krakauer, A.J. Freemann and D.D. Koelling, *Phys. Rev.* **B21** (1980) 5601.
16. G.P. Kacker, K.M. Ho and M.L. Cohen, *Phys. Rev.* **B18** (1978) 5473.
17. See for example, O. Bisi and C. Calandra, *Nuovo Cimento* **B38** (1977) 81.
18. See, for example, *Surface Magnetism*, G. Allan in Ref. [1].
19. J.G. Gay and R. Ritcter, *Phys. Rev. Lett.* **56** (1986) 2728.

Resumen. Al describir la superficie (001) de Vanadio con un hamiltoniano de siete parámetros de "tight-binding" para la banda de electrones d, obtenemos una descripción de dicha superficie que se compara satisfactoriamente con la derivada de cálculos más sofisticados. La neutralidad de carga se toma en cuenta en una forma sencilla que se justifica por sí misma debido a la extrema localización de los efectos de superficie. Aquí presentamos la densidad de estados para el volumen, la superficie y su proyección a capas internas. Al analizar y comparar nuestros cálculos, concluimos que este método sencillo da resultados significativos y que puede, a su vez, ser usado en otros casos similares. Esto es de mucho interés, debido a que la gran contradicción existente entre el cálculo de primeros principios y el experimento necesita que nuevas formas de magnetismo para la superficie (001) de Vanadio sean estudiadas.