All-electron and pseudopotential study of the spin-polarization of the V(001) surface: LDA versus GGA

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(Received 2 October 2000; published 3 April 2001)

The spin-polarization at the V(001) surface has been studied by using different local [local spin-density approximation (LSDA)] and semilocal [generalized gradient approximation (GGA]) approximations to the exchange-correlation potential of DFT within two *ab initio* methods: the all-electron tight-binding linear muffin-tin orbital atomic-sphere approximation and the pseudopotential linear combination of atomic orbitals code SIESTA (Spanish initiative for electronic simulations with thousands of atoms). A comparative analysis is performed first for the bulk and then for a N-layer V(001) film ($7 \leqslant N \leqslant 15$). The LSDA approximation leads to a nonmagnetic V(001) surface with both theoretical models in agreement (disagreement) with magneto-optical Kerr (electron-capture spectroscopy) experiments. The GGA within the pseudopotential method needs thicker slabs than the LSDA to yield zero moment at the central layer, giving a high surface magnetization (1.70 Bohr magnetons), in contrast with the nonmagnetic solution obtained by means of the all-electron code.

DOI: 10.1103/PhysRevB.63.172406 PACS number(s): 75.70.−i, 75.70.Rf, 73.20.−r

I. INTRODUCTION

The understanding and prediction of the magnetic behavior of vanadium-based systems has motivated numerous experiments and calculations over the last 15 years. Vanadium is one of those paramagnetic metals[1] that can exhibit magnetism under certain conditions (loss of coordination, hybridization with a ferromagnet), due to its large paramagnetic susceptibility.[2,3] For instance, Akoh and Tasaki[4] have reported large localized magnetic moments in hyperfine particles of V, and several experimental groups have demonstrated the existence of an induced magnetization at the V interface for V overlayers on Fe substrates[5–7] and Fe/V multilayers.[8–10] Although these trends are clear, in other aspects there has not been consensus. One controversial aspect concerns the short- or long-range induced spin-polarization in V. Two of us have reported on this problem in a recent work[11] where the reader can find a complete review. Another unclear aspect, that gave rise to an interesting discussion more than ten years ago, was the magnetic character of the V(001) surface. Rau *et al.*[12] through electron-capture spectroscopy concluded the existence of ferromagnetic order at the V(001) $p(1\times1)$ surface and on the V monolayer supported on Ag(001), whereas Fink *et al.*[13] through magneto-optical Kerr measurements did not find magnetization in ultrathin epitaxial films of V on Ag substrates. *Ab initio* full-potential linearized augmented plane-wave (FLAPW) calculations within the density-functional framework using the von Barth-Hedin[14] local spin-density approximation (LSDA) for the exchange and correlation (XC) potential found no surface magnetization,[15] which was since then admitted and corroborated using other all-electron methods with LSDA [linear muffin-tin orbital atomic-sphere approximation (LMTO-ASA)].[16]

Very recently, Bryk *et al.*[17] performed an *ab initio* calculation for a seven layer V(001) film using the plane-waves method with the ultrasoft (US) non-normconserving pseudopotential (PP) of Vanderbilt,[18] and the generalized gradient approximation (GGA) of Perdew[19] (PW91) for the XC potential, obtaining a magnetic moment of $1.70\mu_B$ at the unrelaxed surface plane ($1.45\mu_B$ if relaxed). These authors believe that their prediction of a magnetic V(001) surface is more likely to be correct than the contrary result obtained earlier[15] from local spin-density approximation (LSDA), and consequently they request new measurements to test the prediction. Besides, although they correctly find the paramagnetic bulk ground state for V at the calculated equilibrium lattice constant, they also obtain, at the experimental lattice constant, the ferromagnetic phase, with $0.15\mu_B$ per atom, lying only 0.7 meV below the paramagnetic one. In the opinion of the authors, this energy is small compared with the difference between the calculated magnetic and nonmagnetic surface energies, concluding that the GGA overestimates the magnetization of the interior layers, but does not alter their prediction of magnetic V(001) surface. An even more recent calculation of the magnetic structure of V(001) surface using the *all-electron* FLAPW method and the PW91 form of GGA,[19] by Bihlmayer, Asada, and Blügel,[20] conclude that ''in very thin V films a surface magnetic moment can be stabilized, while for thicker and relaxed films no surface magnetism can be found.''

The suspicion that the PW91 form of GGA might incorrectly tip metals with large LSD spin-susceptibility enhancements, like Pd and V, into the ferromagnetic state, was posed in one paper testing the PW91 functional.[21] Subsequent calculations using all-electron[22–25] and/or pseudopotentials[23–26] methods coincide pointing out the trend of GGA's to enhance magnetism of magnetic materials and susceptibilities of nonmagnetic materials when compared with results from analogous LSDA calculations. Singh and Ashkenazi[22] using the all-electron FLAPW method confirmed that bulk V and Pd are correctly predicted as paramagnetic by the PW91 GGA approximation, but conclude also that GGA's do not have greater precision than the LSDA for studying transition metals (TM's) and especially for magnetic materials. In Ref. 20 it is also noted that there are considerable differences between the predictions of the GGA's from Langreth, Mehl, and Hu (LMH) (Ref. 27) and PW91, which gives room for more consistent improvements on the LSDA. Ozolins and Körling,[23] using the full-potential linear muffin-tin orbital

(FP-LMTO) method,[28,29] found that the PW91 GGA predicts more accurately than the LSDA the structural properties of nonmagnetic $3d$, $4d$, and $5d$ TM's. Also in Ref. 21 it is suggested that a full-potential treatment, instead of the atomic-sphere approximation (ASA), is important for GGA calculations, because the inaccuracies introduced by the ASA are of the same magnitude as the gradient corrections. Apparently, an ASA GGA calculation average out the angular parts of the GGA and thus is missing what could be a portion of the GGA contribution. Norm conserving and ultrasoft pseudopotentials has been compared for first-row and transition elements by Kresse and Hafner[30] from the point of view of numerical performance achieving good convergence and transferability properties. The extreme softening of nonnorm-conserving Vanderbilt pseudopotentials without loss of accuracy compared to very hard and accurate pseudopotentials (working at much more higher cutoff energy) has been demonstrated recently by Furthmüller *et al.*[31] On the other hand, the use of pseudopotentials, particularly the US-PP of Vanderbilt,[18] has been tested by Holzwarth *et al.*[24] and by Kresse and Joubert[25] against all-electron (AE) FLAPW and projector augmented wave (PAW) (Ref. 32) results for structural properties of several metals, including vanadium[24,25] and the magnetic properties of Fe, Co, and Ni.[25] Whereas Holzwarth *et al.*[24] conclude that the structural properties of bcc V are represented equally well by the PAW, LAPW, and PP methods, Kresse and Joubert[25] point out that for TM at the left side of the Periodic Table it is very desirable to include semicore states as valence states in the pseudopotentials. The LSDA (GGA) magnetic moments of bcc Fe calculated in Ref. 23 are slightly (considerably) larger within the PP method than within the AE methods FLAPW and PAW. On the other hand, in both PP and AE calculations, the GGA magnetic moments of Fe, Co, and Ni are systematically larger than the LSDA ones. The same trends are obtained in Ref. 24 by comparing calculations using the PP linear combination of atomic orbitals (LCAO) code SIESTA (Ref. 26) with available AE results for the magnetic moment of bulk bcc Fe, the (001) Fe surface, and small clusters of Fe on the (001) Ag surface.

The work of Bryk *et al.*[17] opens again clearly the discussion about the magnetic character of V(001) and besides, from the theoretical point of view, it offers a different benchmark to test different *ab initio* methods and different XC functionals. Therefore the need of further calculations is evident. In this work, calculations have been done using two different *ab initio* methods based on the density-functional theory (DFT),[33] namely, (i) AE tight-binding linear muffin-tin orbitals (TB-LMTO) method, in the scalar relativistic version and the ASA,[28,29] and (ii) the SIESTA LCAO method,[34] using the Troullier-Martins pseudopotentials.[35] For the XC functional, we have used within TB-LMTO four different approximations: two LSDA versions—the Hedin-Barth[14] and the Vosko-Wilk-Nusair[36]—and two GGA's—the PW91 (Ref. 19) and the Langreth-Mehl-Hu (LMH) (Ref. 27). The XC functionals used within the pseudopotential code SIESTA (Ref. 34) are the Perdew-Zunger (PZ) parametrization for the LSDA (Ref. 37) and the Perdew-Burke-Ernzerhof (PBE) (Ref. 38) form of GGA. The soft ionic pseudopotential used in SIESTA is generated according to the procedure of Troullier and Martins[35] from the atomic configurations $[\mathrm{Ar}]3d^3 4s^2$ for V with core radii for the *s*, *p*, and *d* components of 2.35, 2.70, and 2.35 a.u., respectively. The partial core correction for nonlinear XC (Ref. 39) has been included. A careful study of the optimum core-correction radius leads to a value of 0.8 a.u.

Let us first discuss the bulk bcc case. The GGA's equilibrium lattice constants are, within the TB-LMTO (in a.u.), 5.68 (5.79) from the LMH (PW91) calculations and 5.71 for the SIESTA-PBE calculation. The LSDA's equilibrium lattice constant is 5.61 a.u. for the different LSDA approximations in both TB-LMTO and SIESTA calculations. With both AE and PP methods, and for all the XC approximations used we obtain a paramagnetic ground state at the experimental lattice constant (5.73 a.u.), in agreement with the experimental findings.[1] This contrasts with the GGA result of Bryk *et al.*[17] where bulk V at the experimental lattice constant is ferromagnetic (FM) with $0.15\mu_B$ per atom, although they find the paramagnetic state at the equilibrium lattice constant in their calculations. It is a general trend that when expanding the lattice, the electronic localization increases and the kinetic energy of the system decreases so that spin polarization is favored. It is therefore expected to find a magnetic phase transition in V bulk in this context. Moruzzi and Marcus[40] studied ten years ago this magnetic transition in V bulk through total-energy band calculations using the LSDA in the augmented-spherical-wave (ASW) method. They found that the paramagnetic solution is the ground state of V bulk for the experimental lattice constant and for lattice expansions of less than 12%. For this expansion they find a transition to the antiferromagnetic (AF) solution (always more stable than a low-spin FM solution). Earlier spin-polarized augmented plane-wave (APW) calculations for bcc vanadium[3] found also that a nonmagnetic-to-ferromagnetic transition occurs abruptly for a lattice constant about 25% larger than the equilibrium value. We have also tested volume expansions and within all XC functionals considered in our TB-LMTO and SIESTA calculations, the paramagnetic ground state persists at least up to an expansion of 10%.

In the case of the seven-layer V(001) film at the bulk experimental lattice constant, the LSDA gives no surface magnetization in both our AE and PP calculations, in agreement with previous first-principles LSDA results.[15,16] Concerning the GGA, our all electron results are reported in Fig. 1 for both the PW91 and LMH versions of GGA. Here a surface magnetization is obtained, although it is much lower than the value reported by Bryk *et al.*[17] using pseudopotentials. They obtain $1.70\mu_B$ at the surface plane in contrast with our values of $0.66\mu_B$ for the PW and $0.25\mu_B$ for the LMH cases (Fig. 1). Notice also the large difference obtained with different versions of GGA, as already observed in Ref. 20, and that for volume expansions of the order of 2% that difference become negligeable [Fig. 1(b)]. We see then that the AE surface magnetization is still far from the PP value of $1.7\mu_B$ obtained by Bryk *et al.*[17] This system constitutes a good test for an *ab initio* pseudopotential calculation in order to see whether or not the pseudopotential code give rise to an overestimation of the V magnetic moment compared with a

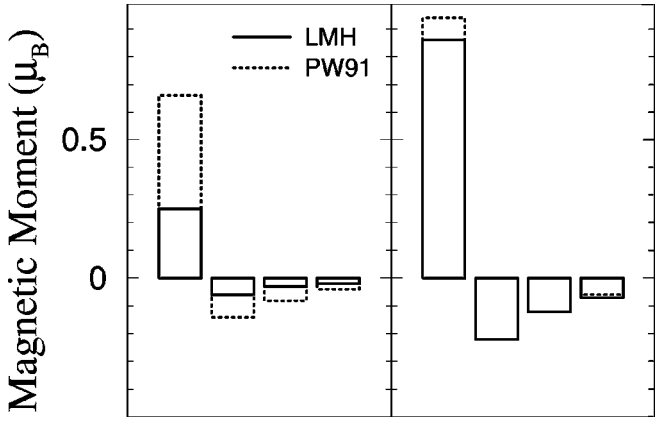

FIG. 1. Magnetic moments profile for the seven-layer V(001) film obtained with TB-LMTO method and two GGA versions [LMH (Ref. 27) and PW91 (Ref. 19)]. The left panel corresponds to the experimental lattice constant whereas the right panel corresponds to a lattice expansion of 2%.

typical AE method. For this purpose we have repeated the same seven-layer calculations with SIESTA and the PP of Troullier and Martins. The LSDA again leads to the paramagnetic solution whereas the GGA leads to a magnetic moment of $1.77\mu_B$ which is similar to the value reported by Bryk *et al.*[17] These results indicate that the GGA within the pseudopotential calculations enhances even more than within AE methods the V(001) magnetic moment. We note, however, a difference between our PP-GGA results and those of Bryk *et al.*[17] for the seven-layer V film. At the experimental lattice constant, they achieve in the central layer the convergence of the magnetic moment to their bulk value ($0.15\mu_B$) and, consequently, they use the surface layer to discuss the V(001) surface. However, our results for the central layer do not converge to our paramagnetic bulk with just seven layers. As we increase the number of layers in the film, the calculated magnetic moment at the center decreases. For 15 layers the local moment at the center is zero as in the bulk and we can discuss then the V(001) surface magnetism in terms of the surface layer. The interesting result is that when we consider more than seven layers in the slab the V(001) surface is nonmagnetic with the all-electron TB-LMTO method, independently of the approximation used for the XC potential (LDA or GGA), whereas with the pseudopotential code SIESTA, even for calculations with 15 layers of V the GGA still produces a high magnetic moment at the surface (see Table I), comparable with that obtained by Bryk *et al.*[17] (with LDA we obtain the nonmagnetic surface).

TABLE I. Local magnetic moment obtained at the surface of a seven-layer and 15-layer V(001) film with the different versions of the GGA in the all-electron TB-LMTO and pseudopotential SIESTA methods for the experimental bulk lattice constant of vanadium. For slabs thicker than seven layers the TB-LMTO yields nonmagnetic ordering at the V(001) surface.

	TB-LMTO (LMH)	TB-LMTO (PW91)	SIESTA (PBE)
7 layers	0.25	0.66	1.77
15 layers	0.00	0.00	1.70

In summary, our results indicate the well known tendency[22,26] of GGA to produce larger magnetic moments than the LSDA, but also that the convergence of GGA to the bulk value at the central layer of a slab is slower than for LSDA. Taking care of these convergence problems, the V(001) surface is nonmagnetic with both the LSDA and GGA within the all-electron TB-LMTO method, whereas the pseudopotential code with GGA still produces a high magnetic moment. It is interesting to note that our pseudopotentials and basis in SIESTA are different from those of Bryk *et al.*[17] To conciliate our all-electron and pseudopotential GGA results for V(001) we think that the treatment of semicore states as valence states should be needed. This is a well-known recipe to improve the pseudopotential description of transition metals at the left of the Periodic Table (see, e.g., Ref. 25). However, this procedure increases largely the computational costs. On the other hand, in view of the controversial theoretical predictions, new experiments concerning the magnetic character of the (001) surface of vanadium are needed to confirm or to correct the earlier findings of Rau and co-workers.[12]

ACKNOWLEDGMENTS

We acknowledge financial support of DGICYT of Spain (Grant PB98-0368-C02) and of Junta de Castilla y León (Grant VA70/99). J.I. and R.R. acknowledge the F.P.U. grants from M.E.C. of Spain.

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