Magnetism of the V(001) surface: Contradictory results from pseudopotential and linearized augmented plane-wave calculations

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Recently using a pseudopotential and the generalized gradient approximation (GGA) we determined that V(001) with the experimentally determined surface relaxation has a strongly ferromagnetic surface. More recently, others also using the GGA found that with full-potential linearized augmented plane-wave (FLAPW) calculations, the unrelaxed surface is only weakly magnetic and the relaxed surface is nonmagnetic. We report here other pseudopotential and FLAPW calculations. The FLAPW results are consistent with the previous ones except that the surface relaxation is much smaller. A nonmagnetic pseudopotential calculation yields a -13.5% surface relaxation, slightly larger than the FLAPW calculation, while the ground state has a -12.5% surface relaxation with a surface magnetization of $0.75\mu_B$. The unrelaxed surface has a $1.77\mu_B$ magnetization in good agreement with our previous calculation. Thus we are forced to conclude that what are usually assumed to be the most accurate methods of electronic structure calculation are in complete disagreement insofar as the magnetic nature of the V(001) surface is concerned. We speculate on the source of this disagreement.

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Although local spin-density approximation calculations[1] found the V(001) surface to be paramagnetic it had been our feeling that the generalized gradient approximation (GGA) might yield a magnetic surface. Therefore using Perdew's form[2] of the GGA, Bryk, Bylander, and Kleinman[3] (BBK) performed a first-principles pseudopotential calculation of a seven-layer film and found that for the unrelaxed surface a state with $1.705\mu_B$ per surface atom was 8.2 mRy below the paramagnetic state,[4] while surface relaxations of $\Delta_{12}=-6.25\%$ and $\Delta_{23}=0.0\%$, within the uncertainty of the experimental values,[5] resulted in a reduction of the surface magnetization to $1.452\mu_B$. The subsurface planes had -0.875, -0.220, and $-0.118\mu_B$ in the unrelaxed case and -0.698, -0.352, and $-0.149\mu_B$ in the relaxed case, i.e., they were oppositely polarized with respect to the surface.

Bihlmayer, Asada, and Blügel[6] (BAB) have very recently reported full-potential linearized augmented plane-wave (FLAPW) calculations of V(001) using both the PW91[2] and the PBE forms[7] of the GGA. Since they did not always specify which form was used in any particular calculation, we assume their results were not strongly dependent upon which one was used. They found that a relaxed seven-layer film ($\Delta_{12}=-10.4\%$) had a surface magnetization of only $0.04\mu_B$ and an unrelaxed 15-layer film had a surface magnetic moment of $0.19\mu_B$, but upon relaxation ($\Delta_{12}=-11.1$, $\Delta_{23}=0.7$, and $\Delta_{34}=3.1\%$) it became nonmagnetic. They found for an ''unfortunate'' choice of the **k**-point set that was not evenly distributed over the Brillouin zone an unrelaxed surface magnetic moment of $1.5\mu_B$. Since this almost certainly is the magnetic moment within a muffin-tin sphere, it may actually correspond to a larger magnetization than that found by BBK. However, we would like to assure the reader that the **k**-point sample used by BBK was evenly distributed. BAB also state, ''Concerning magnetism, one possible critical issue of the ultrasoft pseudopotential is the choice of the treatment of the overlap between core and valence charge density to calculate the XC potential, which is not approximated in the FLAPW method.'' In Ref. 3 BBK used the norm conserving[8] and not the ultrasoft[9] form of the Vanderbilt pseudopotential. Furthermore the ionic pseudopotential was obtained by subtracting the total core plus valence exchange-correlation (XC) potential as well as the valence Coulomb potential from the atomic pseudopotential. It is well known that excess magnetism can occur because of nonlinearities in the XC potential if the core and valence contributions are separated.[10]

Thus the question arises, did one of the two groups make a computational error or, using the same form of the GGA potential, does one actually find that the ground state of V(001) is either paramagnetic or does it have a large in-plane ferromagnetism depending upon whether one performs a FLAPW or a pseudopotential calculation? To answer this question we have performed several calculations using different computer codes than those used in Refs. 3 and 6. BAB used the FLAPW code FLEUR whereas here we use the WIEN97 code[11] with one modification. Rather than having the Broyden scheme for updating the input spin densities operate on $\rho_\uparrow$ and $\rho_\downarrow$, we had it operate on $\rho_s=(\rho_\uparrow+\rho_\downarrow)/2$ and $\rho_a=(\rho_\uparrow-\rho_\downarrow)/2$, resulting in approximately 20% more rapid convergence.[12] In Table I we compare results for bulk vanadium and note that the four calculations are in fairly good agreement with one another and with experiment.

The first seven FLAPW calculations listed in Table II were performed on unrelaxed seven-layer films. The first column lists the number of **k** points sampled in the irreducible wedge of the surface Brillouin zone (SBZ) corresponding to 100, 196, and 256 points in the full SBZ. The second lists the type of GGA (Refs. 2 and 7), the third lists the energy of the

TABLE I. GGA vanadium lattice constants and bulk moduli for BAB (Ref. 6) and present FLAPW calculations compared with BBK (Ref. 3) and present pseudopotential calculations, and with experiment.

	BAB	FLAPW	BBK	Pseudopotential calculations	Experiment
a (bohr)	5.65	5.66	5.65	5.77	5.73
B (GPa)	197	201	183	195	162

TABLE II. Results obtained for various FLAPW calculations of seven-layer V(001) films. The first column lists the number of **k** points sampled in the irreducible wedge of the SBZ. The asterisk indicates that an 8-mRy broadening of the eigenvalues was used; 2 mRy was used otherwise. The second column lists the type of GGA density functional that was used. The third column lists the all-electron energy (per seven-atom unit cell) of a nonmagnetic film, and the fourth column lists the energy of the magnetic film below the nonmagnetic. The remaining columns list the magnetization in bohr magnetons within the inscribed spheres associated with the surface to center planes. Only the results in the last row, indicated by an *R*, are for a relaxed film.

k	GGA	$(E+13\,290)$ Ry	$-\Delta E$ (mRy)	m_s	m_s-1	m_s-2	m_c
15*	PBE	−0.254 68	1.83	0.386	−0.144	−0.086	0.021
15	PBE	−0.254 85	0.25	0.242	−0.118	−0.047	−0.052
15	PW91	−4.173 78	0.35	0.163	−0.066	−0.038	−0.028
28	PW91	−4.172 80	0.45	0.087	−0.026	−0.017	0.000
28	PW91	−4.172 80	−0.08	0.766	−0.284	−0.110	−0.026
36	PW91	−4.172 86	0.30	0.141	−0.045	−0.028	−0.010
36	PW91	−4.172 86	0.17	0.277	−0.116	−0.057	−0.034
28*R*	PW91	−4.195 32	0.28	0.010	−0.001	−0.001	0.005

nonmagnetic film, and the fourth lists the magnetic energy, i.e., the energy of the magnetic film (with two surfaces) relative to the nonmagnetic. The last four columns give the magnetization within the inscribed sphere of atoms from the surface to the central planes. A 2 mRy gaussian broadening[13] of all the eigenvalues was used except for the first PBE calculation where 8 mRy was used.

The 2-mRy broadening is more reasonable for the larger **k**-point samplings but it also results in making the 15 **k**-point results more consistent with the others. There is not much difference between the PBE and PW91 results with 15 **k** points and 2-mRy broadening; the PBE has the larger magnetization but the smaller magnetic energy $-\Delta E$. The changes in ΔE that occur with the changing number of **k** points look relatively large but that is because ΔE is so small. Note also that they are occuring in the ninth significant figure of the total energy. The calculations converged to ten significant figures and only fluctuated in the eleventh; however we are troubled by an inconsistency that occurred with the WIEN97 code. We calculated the nonmagnetic film using the magnetic version of the code. When we zeroed the magnetization and started iterating from the charge density of the 28 **k**-point magnetic ground state, we obtained a nonmagnetic state 0.17 mRy below that obtained with the nonmagnetic code, independent of whether we used a simple iteration scheme, the Broyden scheme, or our modified Broyden scheme. Since WIEN97 does not calculate the energy variationally (until the charge density is correctly converged), there is no reason to prefer the lower energy, and since the nonmagnetic version seems to be more accurate[14] all nonmagnetic energies listed in Table I were obtained from the nonmagnetic version. We found two magnetic energy minima with the 28 and 36 **k**-point samples, where the metastable state has the larger magnetization. There may be one with 15 **k** points but we did not search for it. The last row of Table II lists the results for a film whose magnetic (nonmagnetic) equilibrium[15] relaxations were found to be $\Delta_{12}=-6.2$ (-6.2), $\Delta_{23}=-1.4$ (-1.5), and $\Delta_{34}=-1.7\%$ (-2.1%). The magnetization has practically vanished while the magnetic energy has only fallen from the 0.45 mRy of the unrelaxed film to 0.28 mRy. It would be only 0.11 mRy, which is more reasonable, if we were to assume that all magnetic calculations contain the −0.17-mRy discrepancy found in the nonmagnetic energy obtained from the magnetic code. The surface relaxation is in good agreement with the experimental value[5] of $\Delta_{12}=-6.7\pm1.5\%$ but is far from the -11.1% of BAB (Ref. 6) $(-10.4\%$ for a seven-layer film), the -13.6% relaxation of a nonmagnetic GGA projector-augmented wave calculation,[16] and the -12.5% and -13.5% we report in Table IV for our magnetic and nonmagnetic pseudopotential calculations. Our FLAPW calculations were performed using the experimental lattice constant. If the smaller calculated lattice constant in Table I had been used, an even smaller inward relaxation would have been obtained. In spite of this, our FLAPW calculations and those of BAB yield similar magnetic properties for the V(001) surface.

The results of our pseudopotential calculation for an unrelaxed nine-layer film at the calculated lattice constant (in Table I) are compared in Table III with those of BBK for a seven-layer film with the experimental lattice constant. There are several other differences. BBK used the 15 **k**-point sample while we used 28, although in preliminary calculations we did not find much difference between the two samples. We used a 3.33-mRy full width at half maximum energy broadening;[13] BBK used 2.0 mRy. BBK obtained their pseudopotentials from a $V^{+0.5}$ ion, pulling in the nodes of the *s* and *p* functions, which allowed them to use smaller pseudopotential cutoff radii than our $r_s=2.37$, $r_p=2.83$, and $r_d=2.15$ bohr. They used projectors[8,9] at both the $3d$ and $4d$ energies whereas we used an ordinary $3d$ pseudopotential. We use the PBE form of the GGA while BBK used Perdew's. We used a partial core correction[17] with $r_c=1.0$ bohr; BBK used the full core. And in spite of our large pseudopotential cutoff radii, we required all plane waves up to 60 Ry to obtain satisfactory convergence; BBK required a cutoff of only 40 Ry. Nevertheless the results in Table III are remarkably similar. In particular both surface magnetizations[18] are nine times larger than that reported by BAB for a 15-layer unrelaxed film. A recent tight-binding pseudopotential calculation[19] that used the PBE functional and expanded in atomic pseudofunctions found for an unrelaxed seven-layer film $M_s=1.77\mu_B$, while for a 15-layer film $M_s=1.70\mu_B$. They also performed all electron linear muffin-tin-orbital calculations with Perdew's XC potential

TABLE III. Comparison of the results of our pseudopotential calculation for an unrelaxed nine-layer V(001) film with those of BBK (Ref. 3) for a seven-layer film. The M's are planar magnetizations, ΔE is the energy relative to a nonmagnetic film, and E_s is the surface energy.

M_s	$1.77\mu_B$	$1.705\mu_M$
M_2	$-0.61\mu_B$	$-0.875\mu_B$
M_3	$-0.23\mu_B$	$-0.220\mu_B$
M_4	$-0.10\mu_B$	$-0.188\mu_B$
M_c	$-0.13\mu_B$	
ΔE	-0.135 eV	-0.112 eV
E_s	1.371 eV/a^2	1.477 eV/a^2

and found for unrelaxed films a surface magnetization of $0.66\mu_B$ for a seven-layer film but zero magnetization for 15 layers. Thus the pseudopotential surface magnetization is nearly independent of film thickness, which does not seem to be the case for nonpseudo calculations.

Table IV lists the interplanar relaxation,[15] the planar magnetization, the energy relative to the relaxed nonmagnetic film, and the surface energy for the nine-layer film. The planar average of the densities of the two different spin directions is plotted in Fig. 1 for the relaxed film. Because the coupling between the surface and subsurface planes is antiferromagnetic, the magnetic pressure is very weak and the only difference between the nonmagnetic and magnetic relaxations is that the nonmagnetic Δ_{12} is -13.5%. This large relaxation causes the surface magnetization to be reduced from 1.77 to $0.75\mu_B$ and the magnetic energy from -135 to -3.47 meV. Twice the -51-meV difference between the relaxed and unrelaxed surface energies is the energy reduction of the film due to relaxation. That reduction is -234 meV for the nonmagnetic film.

In conclusion, three entirely different pseudopotential calculations[3,19] within the GGA for unrelaxed V(001) films have found a surface magnetization of about $1.7\mu_B$, independent of film thickness and other details of the calculation. Our calculation also found a surface relaxation of 12.5%, consistent with two other calculations,[6,16] but not with the experimental 6.7% or the 6.2% we obtained using the WIEN97 code. This large relaxation caused a reduction in the surface magnetization to $0.75\mu_B$, but with a relaxation closer to the experimental value the surface magnetization would be much larger.[3] BAB found small magnetizations in unrelaxed seven- and 15-layer films that became negligible or zero upon relaxing the surface. In spite of its much different surface relaxation our FLAPW calculation was consistent with BAB's for the seven-layer film. Thus the FLAPW and pseudopotential calculations consistently agree among themselves and disagree with each other insofar as surface magnetization is concerned. We do not believe that this disagreement can arise because the FLAPW calculation is an all-electron method (i.e., it does not use the rigid core approximation) while the pseudopotential is not. Both methods include the core charge density in evaluating the exchange-correlation potential and both assume the core charge density of each atom is spherical although either could treat the outer-core electrons on an equal footing with the valence electrons. Having eliminated the linear dependence of the logarithmic derivative of a wave function on its energy, both also neglect its remaining energy dependence. The two-projector method used by BBK considerably reduces the error caused by this. The only explanation that seems likely to us is the following. Because the pseudopotential is norm conserving, with all else being unchanged, we would expect the integrated $3d$ spin densities and pseudospin densities within a sphere of radius r_{3d}, the $3d$ pseudopotential cutoff radius, to be equal. However, we would expect the $3d$ pseudospin density to be larger than the $3d$ spin density in the outer regions of the sphere. Because of the nonlinearity of the density-functional exchange potential, the exchange interaction between the d electrons is reduced almost to zero where the core charge density is large. Because the pseudospin density within r_{3d} is larger than the spin density where the core density is becoming small, the exchange interaction between $3d$ pseudofunctions is less ''screened'' by the core electrons than that between $3d$ functions, accounting for their greater propensity to be magnetic. This ''screening'' is completely unphysical but there are errors in the LSDA and GGA correlation functionals that favor magnetism so one cannot say whether the slight reduction in this unphysical ''screening'' of the $3d$ exchange should yield improved results. In fact, it could vary from case to case. If this explanation is correct, the Vanderbilt ultrasoft pseudopotential,[9] which uses a charge density that it constructs from the pseudocharge density, should yield results closer to the FLAPW results than to those of other pseudopotentials.

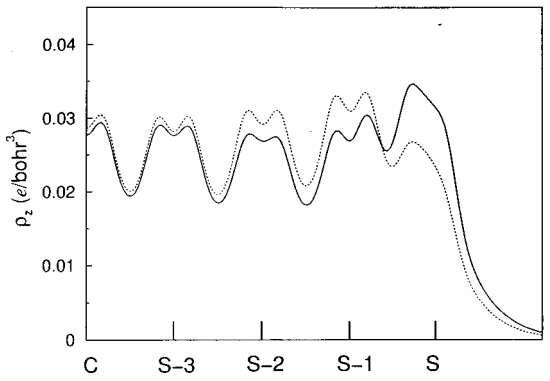

FIG. 1. Planar average of the two pseudospin densities of the relaxed nine-layer V(001)-film ground state.

TABLE IV. Pseudopotential calculation of the interplanar relaxation (in %), planar magnetizations (in μ_B), energy relative to relaxed ($\Delta_{12}=-13.5\%$) nonmagnetic film (in meV), and surface energy (in eV/a^2).

Δ_{12}	Δ_{23}	Δ_{34}	M_s	M_2	M_3	M_4	M_c	ΔE	E_s
-12.5	0.9	2.5	0.75	-0.26	-0.27	-1.10	-0.09	-3.47	1.320

We know of only one experiment to determine the magnetic nature of the V(001) surface. This experiment favors the magnetic surface but much more work needs to be done to verify or refute this. Electron-capture spectroscopy[20] yields an electron-spin polarization of -34% at 300 K that decreases linearly until it vanishes at a surface Curie temperature of 540 K. Ordinarily negative polarization means that the electron capture has occurred far enough outside the crystal that minority-spin *s* electrons dominate but in this case it may imply that the subsurface layers are polarized oppositely to the surface layer and have a larger total magnetization. In Table IV we note that the total subsurface magnetization is slightly less than that of the surface layer (it could be larger for a thicker film) and of opposite sign. Because of the near cancellation of the surface and subsurface magnetizations, any new experiments must, like electron-capture spectroscopy, see only the surface plane. This would seem to eliminate the Kerr effect and spin-polarized photoemission; however, angle-resolved spin-polarized photoemission should be able to detect the magnetic surface state predicted in Ref. 3, if it exists.

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[12] Because of charge sloshing and the fact that ρ_s screens the Coulomb potential, only small changes in the long-range part of ρ_s can be made in each succeeding iteration; whereas, because ρ_a antiscreens the exchange potential, large changes in ρ_a are required to obtain rapid convergence. Of course, a perfect Broyden scheme could operate with equal efficiency on either $\rho_\uparrow$ and $\rho_\downarrow$ or ρ_s and ρ_a.

[13] Specifically, we chose $\sqrt{2}\sigma = 2$ mRy in the gaussian $(2\pi\sigma^2)^{-1/2}\exp[1/2(\Delta E/\sigma)^2]$, which yields a full width at half maximum of 3.33 mRy.

[14] Once we started iterating the 28 **k**-point magnetic code with a superposition of nonmagnetic atomic charge densities we converged to an energy 0.23 mRy higher. However we were not able to repeat this result, perhaps because we iterated in a different manner or perhaps we had not converged. We subsequently found that the energy could appear to be converged when the charge density was not, although iterating the charge density to convergence in no other case caused a change of more than 0.06 mRy in the energy. If the higher minimum is real, i.e., not merely a failure to converge, it is very strange. Although it is not impossible, we know of no other case where, at fixed magnetization and atomic position, two energy minima were found. In any event, all other nonmagnetic calculations using the magnetic code resulted in the energy being 0.17 mRy below that obtained from the nonmagnetic code. We performed the same test for a bulk crystal and found that the magnetic code had a nonmagnetic energy 0.044 mRy below that of the nonmagnetic code. This discrepancy is actually larger than the 0.17/7 mRy/atom found for the seven-layer film. To further test the WIEN97 code we inserted the nonmagnetic ground-state charge density obtained from the magnetic code into the nonmagnetic code. The first iteration resulted in an energy 0.008 (0.169) mRy above that obtained from the nonmagnetic (magnetic) code. On further iteration it converged back to the energy previously obtained from the nonmagnetic code. When we entered the charge density from the nonmagnetic program into the magnetic program, the first iteration energy was 0.008 mRy below and the converged result was 0.004 mRy above the nonmagnetic ground-state energy previously calculated with the magnetic code. Furthermore, both codes yielded energies that were stable to ± 0.003 mRy when they were converged. These facts lead us to the conclusion that the 0.17 Ry discrepancy between the two codes lies in the calculation of the total energy itself and not in the diagonalization of the Hamiltonian or the calculation of the charge density. Although the nonvariational nature of the code cannot by itself be the source of the error, it results in many more required iterations to obtain convergence and makes error detection much more difficult.

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