RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 62, NUMBER 18 1 NOVEMBER 2000-II

Electronic and magnetic structure of the (001) surfaces of V, Cr, and V/Cr

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(Received 14 July 2000)

We investigate the magnetic and structural properties of the (001) surfaces of V, Cr, and one monolayer V on Cr in density-functional theory in the local spin-density and the generalized gradient approximation. For both exchange-correlation potentials the surface magnetic moment of Cr is very large ($2.6\mu_B$) and the V surface is nonmagnetic. One monolayer V on Cr exhibits also a large magnetic moment ($2.1\mu_B$) but reduces the Cr moment drastically. The importance of the surface moment on the spin-density wave of Cr is discussed. While some of the discrepancies between theory and experiment are cured by the generalized gradient corrections, several difficulties remain.

I. INTRODUCTION

After 20 years of intense research in surface magnetism, the magnetism of the V(001) surface is still controversial and there seems to be considerable disagreement between theory and experiment on the Cr(001) surface. Both V and Cr are bcc $3d$ transition metals (TM) with about half-band filling. From band theory[1] we expect antiferromagnetism (AF) along the (001) direction which will convert at the (001) surfaces to ferromagnetic (001) planes which couple antiferromagnetically from layer to layer, called layered antiferromagnetism (LAF). Whether magnetism actually occurs depends on several factors, e.g., the strength of the exchange interaction, the lattice constant, or the coordination number.

Bulk V is nonmagnetic. Hattrox *et al.*[2] found that (nonmagnetic) bulk V becomes ferromagnetic (FM) when the lattice constant is enlarged by 25%. (The spin susceptibility of V favors an AF ground state for large volumes. Since this early calculation was restricted to FM solutions, the AF state[3] was not found for the enlarged volumes.) Magnetism was reported for V monolayers (ML) on magnetic and nonmagnetic substrates[4–7] and thin films on Fe(001).[8–14] Indeed, early calculations[15–17] suggested that the V(001) surface might also be magnetic and experimental investigation with electron capture spectroscopy by Rau *et al.*[18] seemed to confirm these findings. But measurements of thicker V(001) films on Ag (Ref. 19) and a density-functional theory (DFT) calculation in the local spin-density approximation (LSDA) by Ohnishi *et al.*[20] found no magnetic moment in the surface layer of V(001). LMTO calculations by Turek *et al.*[21] confirmed this result.

With the advent of the generalized gradient approximation (GGA) the predictive power of DFT for magnetic $3d$ TM improved considerably. The major differences to the LSDA results are increased lattice constants closer to the experimental equilibrium values[22,23] and, consequently, higher magnetic moments. This motivated a reinvestigation of the V(001) surface by Bryk *et al.*,[24] who now found that, within GGA, the relaxed V surface had a magnetic moment of $1.45\mu_B$. This pseudopotential calculation employed a seven layer film and an inward relaxation of the surface layer by -6.25%. A projector-augmented wave (PAW) calculation with GGA of the nonmagnetic V(001) surface[14] found a relaxation of -13.3%, but did not mention any attempts to investigate a magnetic surface layer.

The ground state of bulk Cr is a spin-density wave (SDW) state where the LAF structure is modulated by a wave vector $\mathbf{q}=(2\pi/a_0)(0,0,q)$; $q=0.952\approx\frac{19}{20}$. Also for bulk Cr the LSDA calculations suffer from some deficits: at the theoretically determined LSDA lattice constant of Cr, with[25] and without[3] SDW, bulk Cr is found to be nonmagnetic. The bulk modulus turns out to be too high or too small,[3] depending on the magnetic state. But at the experimental lattice constant, the bulk magnetic moment is in reasonable agreement with the experimental values, therefore these discrepancies posed no further problems for the surface calculations. On the Cr(001) surface, in comparison to V, the debate about magnetism seems to be more settled. Experimental[26–28] and theoretical[28–31] investigations indicate that the surface is magnetic and that the magnetic moment is enhanced as compared to the bulk value. But even then LSDA calculations of the Cr(001) surface seem to predict a somewhat too strongly enhanced magnetic moment of $2.5\mu_B$. Artificially reducing this value to $1.75\mu_B$ brought a reasonable agreement with tunneling spectroscopy measurements of the surface state of Cr(001).[28] Until now it is not clear whether this is an error of the LSDA, a neglect of the surface relaxation of the Cr(001) surface, or due to finite temperature. Concerning GGA, Singh and Ashkenazi[32] realized that, although improving the bulk Cr lattice constant, it yields far too large magnetic moments that might spoil the predictive power of GGA calculations on Cr. The effect of GGA on the Cr(001) surface has not yet been investigated.

The purpose of this paper is to present a rather thorough investigation of V(001) and Cr(001) surfaces by both LSDA and GGA and with a full optimization of interlayer relaxation. We investigate first the bulk phase of V and Cr, where the consequence of GGA on SDW state is partly studied. Next we investigate the V(001) surface which involves the studies of the effects of film thickness, interlayer relaxation, and **k**-space sampling. Finally, we investigate the Cr(001) surface where the possibility of the SDW in the thin-film geometry is tested.

TABLE I. Lattice constant a_0 and bulk modulus B of V and Cr in LSDA and GGA as compared to the experimental values. Experimental data (a) was taken from Ref. 32 and (b) from Ref. 3.

	a_0 (Å)			B (GPa)		
	LSDA	GGA	Expt.	LSDA	GGA	Expt.
V	2.93	2.99	3.02$^{(a)}$	197	197	159$^{(a)}$
Cr	2.79	2.85	2.88$^{(a)}$	282	198	192$^{(b)}$

II. METHOD

The results were obtained with the full-potential linearized augmented plane-wave method (FLAPW) in bulk and film geometry,[33] as implemented in the computer code FLEUR, based on density-functional theory in LSDA or GGA. For LSDA we used the exchange-correlation (XC) potential of von Barth and Hedin,[34] but with the parameters as chosen by Moruzzi, Janak, and Williams (MJW).[35] For GGA we used either the version of Perdew and Wang (PW91)[36] or the form of Perdew, Burke and Ernzerhof (PBE).[37]

The surfaces were modeled by 15- and 23-layer films for V and Cr, respectively, embedded in infinite vacuum. Throughout this paper all total-energy results presented are calculated using 70–80 basis functions per atom. The calculations of the bulk moduli and the force[38] appear to be a bit more critical with respect to the cutoff parameters and we used 110 basis functions. The forces were minimized down to a maximum force of 3 meV/a.u. per atom. For the integration in the Brillouin-zone (BZ) we used a special **k**-point set of 36 points for V and 28 points for Cr within the two-dimensional irreducible wedge (1/8) for the film calculations. The bulk calculations were performed with an equivalently dense mesh in the three-dimensional BZ. The SDW of bulk Cr was approximated by calculating tetragonal unit cells with one atom in the (001) plane and 24 or 28 atoms in the unit cell corresponding to spin-density waves with wave vectors $q=\frac{11}{12}$ and $q=\frac{13}{14}$, respectively.

III. RESULTS

As a first step of our calculations we determined the lattice constants for bulk V and Cr in LSDA and GGA. For V we found for the PW91 form of the GGA a lattice constant of $a_0=2.99$ Å or 1% smaller than the experimental value. The same lattice constant was also found by Moruzzi and Marcus[3] in LSDA and Bryk *et al.*[24] in GGA. In Table I we give a comparison between calculated and experimental data; note that for V, unlike for other $3d$ metals, GGA gives no improvement of the bulk-modulus as compared to LDA. We found that in GGA antiferromagnetic Cr without SDW has a lattice constant of 2.85 Å (or 1% smaller than the experimental value) and determined the bulk modulus to be 198 GPa, i.e., in good agreement with the experimental value of 192 GPa.[3] A summary of these data is again given in Table I. While these results agree favorably with the experimental values, the magnetic moment of bulk Cr obtained with the PW91 form of the GGA was $0.99\mu_B$ or 50% higher than the amplitude of the SDW found experimentally. Using the PBE form at the same lattice constant, the magnetic moment was 3% smaller, but in LSDA (MJW) at the GGA lattice constant the magnetic moment dropped to a mere $0.44\mu_B$.

TABLE II. Calculated GGA relaxations of the (001) surfaces of V, Cr, and FM and hypothetical NM Fe. Δd_{ij} gives the relaxation of the layers i and j as compared to the ideal (bulk truncated) interlayer distance of 1.50 Å for V, 1.43 Å for Cr, and 1.38 Å for Fe. $i=1$ indicates the surface layer.

	V(001) (%)	Cr(001) (%)	Fe(001) FM (%)	Fe(001) NM (%)
Δd_{12}	-11.1	-3.7	-0.6	-20.7
Δd_{23}	$+0.7$	$+4.3$	$+4.3$	$+9.5$
Δd_{34}	$+3.1$	-0.2	$+1.2$	$+0.8$

To see whether the SDW of Cr would change these results, we calculated spin-density waves for $q=\frac{11}{12}$ and $q=\frac{13}{14}$ with the PW91 XC potential at the GGA lattice constant. While these wavelengths are smaller than the experimentally observed one ($q\approx\frac{19}{20}$), they can be used to extrapolate the results to the experimental SDW. In our GGA calculations we found that the energy difference between the SDW and the commensurate AF structure, $\Delta E=E(q)-E_{AF}$, is $\Delta E=9.7$ meV/atom for $q=\frac{11}{12}$ and $\Delta E=-4.8$ meV/atom for $q=\frac{13}{14}$ ($\Delta E<0$ means that the SDW is energetically favored). The energy difference between these two SWD's is large as compared to the LSDA-KKR calculations of Hirai,[25] that were carried out at the experimental lattice constant. Hirai found magnetic moments at $q=\frac{11}{12}$ and $q=\frac{13}{14}$ of $0.41\mu_B$ and $0.53\mu_B$, 39% and 22%, respectively, smaller than the amplitude for the experimentally observed **q** vector. We find moments which are too large: the amplitudes of the SDW's are $0.85\mu_B$ and $0.96\mu_B$ for $q=\frac{11}{12}$ and $q=\frac{13}{14}$, respectively. Thus, even when we would calculate bulk Cr with the experimentally observed SDW, we would get far too large magnetic moments within GGA. By fitting $E(q)$ to a quadratic function of $(q-1)^2$ we predict a SDW ground state with $q\approx\frac{18}{19}$ which is remarkably close to the experimental value. This indicates that, despite other discrepancies, the Fermi surface and the Fermi-surface nesting, respectively, responsible for the SDW, is reasonably well reproduced by the GGA. When we estimate the effect of the relaxational (strain) wave induced by the SDW from the calculated forces on the atoms, we would expect even (slightly) larger moments: the Cr layers tend to contract around the nodes of the spin-density wave and expand around the antinodes. This magnetovolume effect tends to magnify the amplitude of the SDW.

We now turn to the surfaces using the in-plane lattice constants obtained from the bulk calculations. Starting with a nonmagnetic (NM) seven layer V film we relaxed the layers and found a contraction for the interlayer distance between the surface and the subsurface layer of -10.4% while the distance of the second and third layer from the surface expanded by 1.8%. A recent PAW calculation[14] found relaxations of -13.6% and 1.0% for the first two interlayers, respectively; experimentally, -6.7% and 1.0% were found.[39] In a 15-layer V film these relaxations did not change very much as can be seen from Table II. It might be interesting to compare these relaxations with results of hypothetical NM Fe also included in this table. In this case an even stronger inward relaxation can be observed, but the ferromagnetism pushes these relaxations back and only a small inward relaxation remains. In the case of AF Cr this inward relaxation can also be found, with an oscillatory decay into deeper layers.

One might wonder, whether magnetism could also reduce the inward relaxation of V. When we spin-polarize the relaxed seven layer V film, we find a small magnetic moment of $+0.04\mu_B$ at the surface that couples antiferromagnetic to even smaller sub- and subsubsurface moments. At the center of the slab a small net moment of $+0.01\mu_B$ remains. This LAF coupling can be considered as a remnant of the AF behavior[3] of expanded bulk V. In an unrelaxed 15-layer V film the surface magnetic moment was only $0.19\mu_B$ and the magnetic moment vanishes below the subsubsurface layer. Relaxation of the 15-layer film finally quenches the magnetism completely. In an older LSDA investigation, we studied the magnetism of (unrelaxed) 1-, 3-, and 5-layer V films in a $c(2\times2)$ unit cell, i.e., with two atoms per film plane. While the unsupported monolayer was clearly antiferromagnetic, the magnetic trilayer system was on the border of stability, while the 5 layer system was always nonmagnetic. In contrast to the calculations of supported monolayers,[7] the ferromagnetic solutions were always more stable than the antiferromagnetic ones. From these results we 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. Naturally, the results also depend sensitively on the **k**-point sampling in the BZ. For an unfortunate choice of the **k**-point set that was not evenly distributed over the BZ, we found an (unrelaxed) magnetic surface with magnetic moments of $1.5\mu_B$ in the top layer, just as in the work of Bryk *et al.*[24] Otherwise, we could not obtain such a large magnetic moment, even with the relaxation assumed in this reference. Concerning magnetism, one possible critical issue of the ultrasoft pseudopotential method 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.

GGA calculations of the Cr(001) surface predict surface magnetic moments of $2.6\mu_B$ that decay rapidly to the bulk value (see top of Fig. 1). Unfortunately, the overestimation of the surface magnetic moment is not the only discrepancy between theory and experiment at this surface: in recent surface x-ray diffraction measurements[40] an outward relaxation of the topmost layer was found, but our results indicate an inward relaxation. The relaxations of the LAF Cr surface are given in Table II. Similar trends have been reported in a tight-binding study[41] on magnetic and nonmagnetic Cr(001) and Fe(001) surfaces. Note that a reduced surface moment would only make the discrepancy with experimental data worse, since—as can be seen from Fe in Table II—magnetism pushes the topmost layers outwards.

As we already did for the bulk Cr, we can also introduce a (compressed) film-SDW in our 23-layer film. Two antinodes are located at the surfaces and have moments of $2.4\mu_B$, while the magnetic moments in the middle of the film are similar to the bulk values of the $q=\frac{11}{12}$-SDW (Fig. 1, full circles). This film SDW is a (meta)stable magnetic configuration since it is 12.7 meV higher in energy than the LAF state, but is a stable solution. Interestingly, this energy is close to what could be expected from the $E(q)$ curve of bulk Cr. Since the enhancement of the magnetic moments at the surface is much larger in LSDA than in GGA, we expect a clear deviation, extending the stability of the LAF state to larger Cr thicknesses.

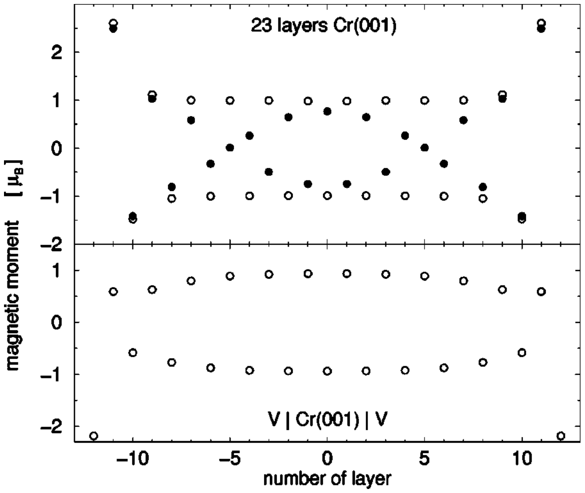

FIG. 1. Magnetic moments in a central-symmetric 23-layer Cr film with (bottom) and without (top) a V cap layer on each side. Layer number 0 defines the center of the film. Full circles denote calculations for a stable SDW, empty circles are for a LAF structure.

To study the role of the surface moment on the SDW, we deposited 1 ML V on the Cr surface. V and Cr have similar lattice constants and this should be experimentally possible. We find V couples layered antiferromagnetically to Cr. The surface moment of V is $2.1\mu_B$ and surprisingly the Cr moment at the V/Cr interface is reduced to $0.6\mu_B$. In this case, the Cr forms the onset of a node at the interface. Introducing a SDW in this system leads to an unstable magnetic arrangement that decays into the LAF state, which is energetically very close.

IV. SUMMARY

We have shown that GGA tends to overestimate the magnetic moments in bulk and at a (001) surface of Cr. If this overestimation is also true for V, we suspect that the absence of magnetism we found for the plain V(001) surface will reflect the physical reality. Since some GGA results are still at variance with experimental findings, further experimental work on the possible magnetism of this surface would be desirable. Scanning tunneling spectroscopy of the V(001) surfaces state could be an experiment that provides the necessary information. We note that the magnetism of V is very delicate and it is still possible that stepped V surfaces show a nonvanishing magnetic moment. We speculate that the large moments of the Cr surface extend the thickness range of Cr films for which the LAF state is stable over the SDW state. A ML V cap layer on Cr reduces drastically the Cr interface moment to a value smaller than the bulk value.

ACKNOWLEDGMENTS

The authors gratefully acknowledge support from the TMR network Contract No. FMRX-CT98-0178.

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