Calculated electronic and magnetic structure of rutile phase $V_{1-x}Cr_xO_2$

M. E. Williams,[1] W. H. Butler,[2,3] C. K. Mewes,[2] H. Sims,[2,3] M. Chshiev,[2] and S. K. Sarker[2,3]
[1]*Math and Computer Science, University of Maryland Eastern Shore, Princess Anne, Maryland 21853, USA*
[2]*MINT Center, University of Alabama, Tuscaloosa, Alabama 35487–6609, USA*
[3]*Department of Physics and Astronomy, University of Alabama, Tuscaloosa, Alabama 35487–0324, USA*

(Presented 11 November 2008; received 26 September 2008; accepted 20 November 2008; published online 12 March 2009)

Recent experiments indicate that films of $V_{1-x}Cr_xO_2$ may be obtained which retain the tetragonal rutile phase to low temperature. In order to better understand this system we have calculated its electronic structure using density functional theory in the generalized gradient approximation and density functional theory with empirical on-site Coulomb correlations (LDA+U). Within these approximations we find that the ground state of rutile phase $V_{1-x}Cr_xO_2$ is quite simple. Both V and Cr are in the +4 state, implying that the V and Cr ions have moments of $1\mu_B$ and $2\mu_B$, respectively. Similar to CrO_2, $V_{1-x}Cr_xO_2$ is predicted to be ferromagnetic and half-metallic. Our results appear to be consistent with the experimental observations that VO_2 is paramagnetic and metallic for temperatures above 340 K where it is stable. It is not clear, however, that these results are completely consistent with recent experimental observations of ferromagnetism at low temperature in $V_{1-x}Cr_xO_2$ for $x=0.1$ and $x=0.2$. © *2009 American Institute of Physics*.
[DOI: 10.1063/1.3072033]

I. INTRODUCTION

Above approximately 340 K, vanadium dioxide usually takes the rutile structure (similar to rutile TiO_2 and CrO_2),[1] although other phases are possible.[2] As the temperature is reduced below 340 K, metallic rutile structure VO_2 transforms into an insulating nonmagnetic monoclinic phase characterized by a dimerization of the V atoms. This metal to insulator phase transformation has been the subject of much speculation with most interest directed at understanding the nature of the insulating phase.[3–6] Here we focus on rutile structure VO_2 and on alloys obtained by partial substitution of V ions by Cr ions. Our interest is motivated in part by recent experiments,[7] which indicate that films of $V_{1-x}Cr_xO_2$ ($x=0.1$ and $x=0.2$) may be obtained which retain the tetragonal rutile phase to low temperature. It should be noted that earlier work on single crystal $V_{1-x}Cr_xO_2$ for these phases[8] found a structure with monoclinic symmetry not greatly distorted from Rutile.

II. CALCULATED ELECTRONIC STRUCTURE OF RUTILE VO_2

The electronic structure of rutile phase VO_2 was calculated using the generalized gradient approximation to density functional theory (GGA-DFT) as implemented in the VASP code.[9–12] The experimental lattice constants ($a=b=4.5546$ Å and $c=2.8514$ Å) and internal parameter ($u=0.3001$) were used in the calculation. Structural relaxation changed these parameters by less than 1%. The calculated density of states (DOS) is shown in Fig. 1. As expected, the bands with primarily O-p character are completely filled. The V atoms are ions in the +4 valence state with each of the V ions having 1d electron. The approximate local octahedral symmetry of the V site causes the V d states to split into a lower energy group (with three states per atom) and a higher group (with two states per atom). The ground state is found to be a ferromagnetic half-metal very similar to CrO_2.[13] The minority d states are empty.

Previous calculations of rutile VO_2 (Refs. 4 and 14) seem to have focused on the nonmagnetic rutile phases. Our calculations, however, find the ferromagnetic phase to be lower in energy than the nonmagnetic phase by 135 meV/f.u. The ferromagnetic phase was also calculated to be lower in energy by 79 meV/f.u. compared to an antiferromagnetic phase in which moments on the two V atoms in the tetragonal cell were antiparallel.

III. CALCULATED ELECTRONIC STRUCTURE OF V(CR)O_2

The effect on the electronic structure of Cr substitution on the V sites was investigated using supercells containing

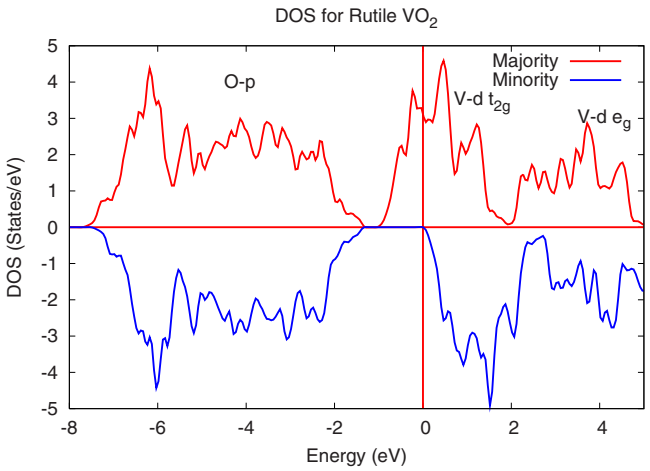

FIG. 1. (Color online) Calculated DOS for VO_2. Energy is measured from the Fermi energy. The DOS is calculated from the smallest periodic cell which contains 2 f.u.

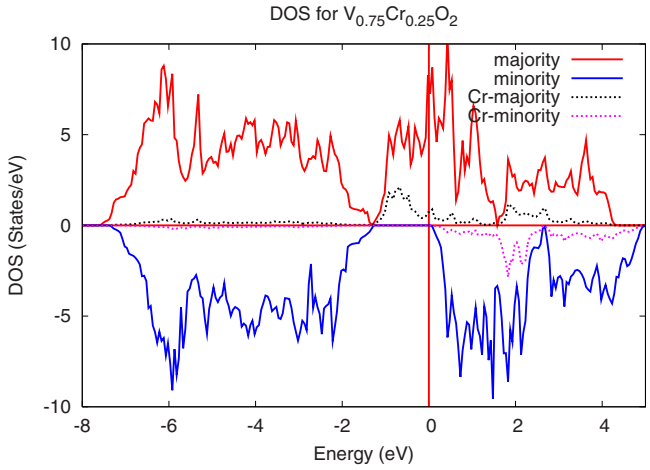

FIG. 2. (Color online) Calculated DOS for $V_{0.75}Cr0_{.2}5O_2$ using GGA-DFT. Energy is measured from the Fermi energy. The DOS is calculated using a cell containing 4 f.u. The dashed lines show the density of states within a sphere with radius of 0.55 Å on the Cr ion site.

eight oxygen ions and four cations which could be either V or Cr. The results were quite simple. The systems were all half-metallic, with the magnetic moment per cell being equal to $4+n$, where n is the number of Cr ions that replaced a V ion. In other words, the V ions carry $1\mu_B$ each while the Cr ions carry two. Addition of Cr rapidly leads to filling of the gap between the oxygen p states and the cation d states in the majority spin channel. On the other hand, the Fermi energy remains at the top of the minority band gap for 25%, 50%, and 75% Cr. For 100% Cr, the Fermi energy lies more than 0.6 eV below the top of the gap (Fig. 2).

The calculated energy of the ferromagnetic phase of $V_{0.75}Cr_{0.25}O_2$ was lower than that of the nonmagnetic phase by 190 meV/f.u. It was also lower than that of several antiferromagnetic phases that we tried using the 12 atom cell.

IV. EXCHANGE INTERACTIONS IN VO_2 AND $V(CR)O_2$

The GGA-DFT result that rutile VO_2 is a half-metallic ferromagnet (within this approximation) raises the question of whether this could be the actual ground state of rutile structure VO_2. Recall that the rutile structure is typically accessible only above room temperature. Experimentally, rutile VO_2 is a metal with a resistivity of 230 $\mu\Omega$ cm at the transition, increasing linearly to approximately 500 $\mu\Omega$ cm at 800 K.[15] It is also paramagnetic with a susceptibility that increases with decreasing temperature.[3] The extrapolation of the susceptibility to 0 K from above the transition yields a finite value, however, unlike typical Curie–Weiss behavior.

One can hypothesize that the GGA-DFT result for the ground state of rutile VO_2 is correct, but that the ferromagnetic state is not realized because the structural and electronic phase transition which occurs at 340 K precludes the observation of the ferromagnetic state. In order to investigate this hypothesis, the exchange interactions in VO_2 and $V(Cr)O_2$ were investigated using both supercell and spin spiral calculations. In a spin spiral calculation the Bloch theorem that relates the phase of the wave functions in adjacent cells is generalized to include a rotation of the wave function in spin space.[16] Table I gives the relative energies when successive V moments along the (100) direction have a relative rotation of 0, $\pi/4$, $\pi/2$, $3\pi/4$, and π radians. The energy difference between the 0 and π radian rotations was confirmed by performing a collinear spin calculation starting from parallel and antiparallel moments.

TABLE I. Energy of spin spiral in the (100) direction.

Angle (rad)	Energy (eV)
0	0.00
$\pi/4$	0.031
$\pi/2$	0.111
$3\pi/4$	0.155
π	0.158

Comparison of the calculated exchange energies for VO_2 with those calculated for CrO_2 (Ref. 17) indicates that exchange interactions are weaker in VO_2 by a factor of approximately 2 compared to CrO_2 leading to an estimate of the VO_2 Curie temperature of approximately 200 K within GGA-DFT. It should be emphasized that VO_2 is only approximately a Heisenberg ferromagnet. In particular, the V magnetic moment decreases by about 40% as the angle between the magnetic moments at the corner and the center of the cell are torqued from parallel to antiparallel.

V. ELECTRONIC STRUCTURE USING LDA+U

In GGA-DFT calculations, each electron moves in an average potential due to all of the other electrons. One consequence of this is that in a periodic system, the wave functions are delocalized regardless of the width of the energy bands. This is clearly not correct in the limit of a very narrow band because it neglects the increased energy cost of having two electrons on the same site and because it includes an incorrect interaction of the electron with itself. In VO_2, the t_{2g} subband is only about 2 eV wide. Thus the bandwidth is comparable to or possibly even less than the local Coulomb correlation energy.

These errors in the treatment of the local Coulomb correlations can sometimes be accounted for semiempirically by a scheme called LDA+U or GGA+U,[18] which effectively adds an energy penalty to partially occupied local orbitals. The typical effect is to push occupied levels down relative to unoccupied levels. We performed GGA+U calculations using the Dudarev formulation[19] which utilizes a single empirical parameter, U-J, where U is an onsite Coulomb energy and J is an exchange energy usually estimated to be approximately 0.9 eV. In the following we denote $U'=U-J$.

Figure 3 shows the calculated DOS using GGA+U with a U' parameter of 2 eV for VO_2. Figure 4 is a similar DOS plot for $V_{0.75}Cr_{0.25}O_2$ but with $U'=5$ eV. Using LDA+U or GGA+U we find that the ferromagnetic phase remains lower in energy than the nonmagnetic phase or any antiferromagnetic phases that we have tried. As expected, LDA+U and GGA+U for sufficiently large U pushes the occupied d states down into the top of the O-p band and opens a gap between the occupied and unoccupied d levels.

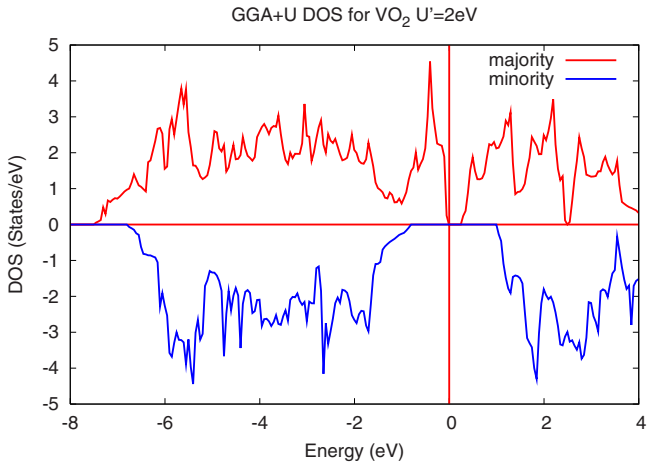

FIG. 3. (Color online) DOS for VO_2 calculated with GGA+U for $U'=2$ eV.

In contrast with GGA-DFT, GGA+U tends to make rutile VO_2 a magnetic insulator. The moment remains $1\mu_B$/V as in GGA-DFT, however, the occupied states are pushed down relative to the unoccupied states and for sufficiently large U, a gap opens between the majority occupied d states and the unoccupied d states. The minority gap remains with all minority d states empty. The energy of the antiferromagnetic phase in which the two V moments in the usual tetragonal cell are antiparallel was calculated. It was higher than the energy of the ferromagnetic phase, but the energy difference was significantly less than for $U'=0$. We found that the ferromagnetic state was more stable relative to antiferromagnetic by 135 meV for $U'=0$, 46 meV for $U'=3$ eV, 19 meV for $U'=5$ eV, and 16 meV for $U'=7$ eV. The energy of the nonmagnetic phase is much higher than that of the ferromagnetic phase, 135 meV/f.u. for $U'=0$, 370 meV/f.u. for $U'=3$ eV, 1738 meV for $U'=5$ eV, and 2563 meV for 7 eV.

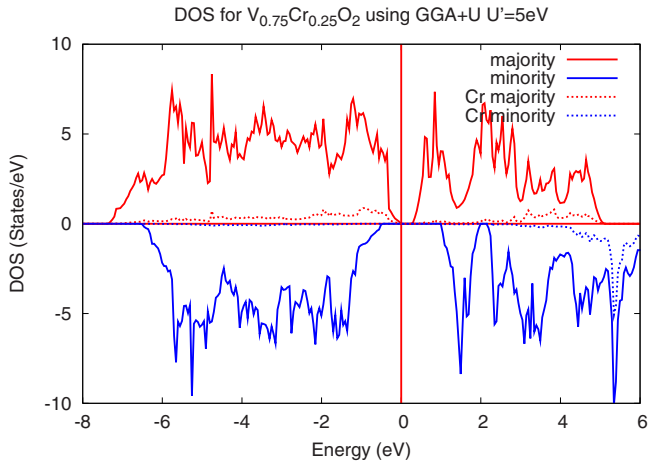

FIG. 4. (Color online) DOS for $V_{0.75}Cr_{0.25}O_2$ using GGA+U with $U'=5$ eV.

VI. CONCLUSIONS

We have presented a summary of extensive calculations of the electronic structure of VO_2 and $V_{0.75}Cr_{0.25}O_2$ using GGA-DFT and GGA+U. It must be admitted, however, that the electronic structure of rutile VO_2 and rutile $V_{1-x}Cr_xO_2$ remains a puzzle. GGA-DFT correctly predicts that the high temperature phase is a paramagnetic metal. However, it also predicts that it is a half-metallic ferromagnet at 0 K, a result for which there is still no experimental confirmation. Recent results for VO_2 doped with 10% or 20% Cr (Ref. 7) indicate that it is a ferromagnet with a moment of $1\mu_B$ per substituted Cr ion at the very lowest temperatures. By 50 K this value drops to a fraction of its low temperature value. Our calculations using either GGA-DFT or GGA+U suggest that the moment should be much larger if it is ferromagnetic. Although the measured resistivity of the $V_{1-x}Cr_xO_2$ is orders of magnitude lower than that of the undoped VO_2 at low temperature, its temperature dependence is not that of a metal but is more appropriate to variable range hopping.

ACKNOWLEDGMENTS

This work was supported by NFS Grant Nos. DMR-0706280 and DMR-0213985. We thank M. Marsman for help with the spin spiral calculations.

[1] F. J. Morin, Phys. Rev. Lett. **3**, 34 (1959).
[2] C.-Z. Wu, Z.-P. Hu, W. Wang, M. Zhang, J.-L. Yang, and Y. Xie, Chem. Commun. (Cambridge) **2008**, 3891.
[3] A. Zylbersztejn and N. F. Mott, Phys. Rev. B **11**, 4383 (1975).
[4] V. Eyert, Ann. Phys. **11**, 650 (2002).
[5] S. Biermann, A. Poteryaev, A. I. Lichtenstein, and A. Georges, Phys. Rev. Lett. **94**, 026404 (2005).
[6] M. Gatti, F. Bruneval, V. Olevano, and L. Reining, Phys. Rev. Lett. **99**, 266402 (2007).
[7] K. G. West, J. Lu, L. He, D. Kirkwood, W. Chen, T. P. Adl, M. S. Osofsky, S. B. Qadri, R. Hull, and S. A. Wolf, J. Supercond. Novel Magn. **21**, 87 (2008).
[8] J. B. Goodenough and H. Y.-P. Hong, Phys. Rev. B **8**, 1323 (1973).
[9] G. Kresse, J. Furthmüller, G. Kresse, and J. Hafner, Phys. Rev. B **47**, 558 (1993).
[10] G. Kresse and J. Hafner, Phys. Rev. B **49**, 14251 (1994).
[11] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
[12] G. Kresse and J. Furthmüller, Phys. Rev. B **55**, 11169 (1996).
[13] S. P. Lewis, P. B. Allen, and T. Sasaki, Phys. Rev. B **55**, 10253 (1997).
[14] R. M. Wentzcovitch, W. W. Schulz and P. B. Allen, Phys. Rev. Lett. **72**, 3389 (1994).
[15] P. B. Allen, R. M. Wentzcovitch, and W. W. Schulz, Phys. Rev. B **48**, 4359 (1993).
[16] M. Marsman and J. Hafner, Phys. Rev. B **66**, 224409 (2002).
[17] H. Sims (unpublished).
[18] V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, J. Phys.: Condens. Matter **9**, 767 (1997).
[19] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B **57**, 1505 (1998).