Structural, electronic and magnetic properties of V_2O_{5-x} : An *ab initio* studyZ. R. Xiao and G. Y. Guo^{a)}*Department of Physics and Center for Theoretical Sciences, National Taiwan University, Taipei 106, Taiwan*

(Received 15 October 2008; accepted 5 May 2009; published online 1 June 2009)

Pure V_2O_5 is a diamagnetic layered semiconductor with many applications such as catalysis. In this paper, we study oxygen vacancy-induced changes in the atomic and electronic structures as well as magnetic properties of V_2O_{5-x} within spin density functional theory with generalized gradient approximation. Both the supercell approach and virtual crystal approximation are used to simulate the oxygen-deficient V_2O_{5-x} with vacancy concentration x up to 0.5. The $1 \times 2 \times 2$ supercell calculations with one O vacancy predict that the formation energies of the apical (O^1), bridge (O^2), and chain (O^3) oxygen vacancies are, respectively, 2.48, 4.17, and 4.44 eV/vacancy, and hence that the O vacancies in V_2O_{5-x} would be predominantly of the O^1 type. The local structural distortions of the V atoms next to the O vacancies are found to be large for high vacancy density $x(x > 0.25)$, and for $x \sim 0.5$, even the crystal lattice changes from the orthorhombic to monoclinic symmetry. In all the cases considered, an O vacancy-induced stable or metastable ferromagnetic state with spin magnetic moment of $\sim 2.0\mu_B$ /vacancy is found. For x below ~ 0.13 and $0.19 < x < \sim 0.45$, the ferromagnetic state would be the ground state, while for $0.45 \leq x \leq 0.5$, the antiferromagnetic state with the V spins on neighboring rungs (AF-2) being antiparallel is the ground state. Importantly, this suggests that undoped V_2O_{5-x} with $x \leq 0.13$ and $0.19 < x < \sim 0.45$ would be a diluted ferromagnetic semiconductor. The AF-2, however, disappears for $x \leq 0.25$, while the antiferromagnetic state with the V spins on neighboring ladders being antiparallel (AF-1) occurs for the entire range of x studied. Nevertheless, the AF-1 is energetically more favorable than the ferromagnetic state only in $0.13 < x < \sim 0.19$. For low O vacancy concentrations ($x < 0.25$), the electronic structure of V_2O_{5-x} is very similar to that of the perfect bulk V_2O_5 , except that $2x$ electrons now occupy the low V d_{xy} dominant conduction bands which are exchange split. Majority of the magnetization is located on the d_{xy} -orbitals of the V atoms near the O vacancy site. For larger x values, however, the electronic structure may change significantly, and, in particular, the V d -orbital character of the low conduction bands can be altered completely. Analysis of the calculated electronic structure reveals that the oxygen vacancy-induced magnetization in V_2O_{5-x} results primarily from the Stoner mechanism. © 2009 American Institute of Physics.

[DOI: [10.1063/1.3146790](https://doi.org/10.1063/1.3146790)]**I. INTRODUCTION**

Transition-metal oxide (TMO) materials are one of the most important categories of room temperature diluted magnetic semiconductors (DMSs).¹⁻³ The origin of the ferromagnetism in ion-doped TMO-DMS is a complex issue. The magnetism might be induced by the doped ions or oxygen vacancies or in the phase separated from the DMS.^{4,5} Previous first principles studies⁴ show that in some TMO-DMS systems the oxygen vacancies have significant effects on the electronic structure and thus enhance the magnetic moments. For most cases of TMO with magnetism, the presence of doped ions results in the magnetization. Nevertheless, experimental and theoretical research indicates that it is possible to have magnetism merely by intrinsic defects or oxygen vacancy.^{6,7} Recently, the oxygen vacancy-induced magnetization in V_2O_5 was observed.⁸ These results show that the magnetic moments can be generated on the vanadium atoms near the oxygen vacancies without any external

$3d$ transition-metal cation. In fact, it was reported earlier that vanadium pentoxide ribbons could interact with the external magnetic field, indicating the existence of magnetic moments in the vanadium pentoxide.⁹

In the modern chemical industry, the variability in geometrical and electronic structures of surface vanadium oxides plays an important role in the field of catalytic applications.¹⁰ Vanadium ions have various kinds of oxidation states, such as V^{3+} to V^{5+} , which can be influenced by the coordination environment of vanadium. This is why one often uses the vanadium oxide, particularly vanadium pentoxide (V_2O_5), as a catalytic material. Therefore, many experimental and theoretical studies have been focused on the [001] surface¹¹⁻¹³ or the clusters¹⁴⁻¹⁶ of V_2O_5 . It is well known that under ambient conditions, bulk V_2O_5 has a layered structure with atomic layers extending in the xy plane (see Fig. 1) and the inter-layer coupling being weak. Bulk V_2O_5 is also known to be a semiconductor with the energy gap (E_g) of 2.2–2.3 eV.^{17,18} Several characteristics of the electronic structure of V_2O_5 have been investigated theoretically in Refs. 12, 19, and 20. Band structure calculations by Yin *et al.*¹⁹ and Chakrabarti

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FIG. 1. (Color online) The $1 \times 2 \times 2$ SC of the perfect V_2O_5 crystal. The lattice constants and atomic positions are theoretically determined.

*et al.*¹² show that the structural and electronic properties of bulk V_2O_5 are very similar to that of a single slab structure of V_2O_5 . Due to the different geometrical relations between the oxygen and neighboring vanadium atoms, the oxygen atoms can be classified into three types, namely, apical (O^1), bridge (O^2), and chain (O^3) oxygens (see Fig. 1). The splitting off of the $\text{V } d_{xy}$ bands is primarily induced by the O^3 in-plane displacements. Previous first principles calculations indicate that the chemical properties, such as the charge population¹⁹ and the vacancy formation energy,¹³ of different kinds of oxygen atoms on the surface are distinct. Concerning the defect geometrical arrangement on the crystal surface, the apical oxygen vacancies are found along $[010]$ direction in the previous experiments¹¹ and also first principles calculations.¹³ Recent theoretical results of combined density functional theory (DFT) calculations and Monte Carlo simulations on the oxygen-depleted V_2O_5 surface also corroborated the interesting experimental results of *in situ* band gap mapping.²¹ Furthermore, first principles calculations indicate the possibility of spin-polarized states either on the oxygen-vacated V_2O_5 surface¹³ or in the bulk V_2O_5 .²²

The origin of the magnetism due to the oxygen vacancy in bulk vanadium pentoxide still needs further inquiries. Therefore, in order to investigate the relation between the oxygen vacancy and magnetic properties in bulk V_2O_5 systems, we have performed *ab initio* structural optimization and electronic structure calculations based on spin DFT for both perfect and oxygen-vacated V_2O_5 crystals. We consider bulk V_2O_5 in the $\alpha\text{-V}_2\text{O}_5$ phase.²³ The supercell (SC) approach with several different SC sizes is used to simulate the oxygen-deficient V_2O_5 crystal with different O vacancy concentrations. The relative stability of all three types of O vacancies is investigated by calculating the vacancy formation energy. Indeed, we find that all the O vacancies would induce considerable local structural distortions, electronic structure changes, and especially formation of the magnetic moments on the neighboring V atoms. The calculated electronic band structure of the O-vacated V_2O_5 indicates that the predicted ferromagnetism is consistent with Stoner model.²⁴ In order to discuss the possible magnetic ordering in V_2O_{5-x} , the approach of virtual crystal approximation (VCA) is also used. These interesting findings will be presented in details in

Sec. III after a brief description of the computational details is given in Sec. II. Finally, main conclusions will be presented in Sec. IV.

II. COMPUTATIONAL DETAILS

Our *ab initio* calculations are based on spin DFT with generalized gradient approximation (GGA).²⁵ We used the accurate full-potential projector augmented-wave (PAW) method,²⁶ as implemented in the VASP code.^{27–29} The core radii of the vanadium and oxygen atoms are 1.2 and 0.8 Å, respectively. A large cutoff energy of 800 eV for plane wave expansion is used to ensure the numerical accuracy. The criterion for the convergence of the electronic self-consistency cycles is 10^{-6} eV. The changes in the lattice constants and atomic structure distortions induced by the oxygen vacancy are determined by using the conjugate-gradient technique. The equilibrium structure is obtained when all the forces acting on the atoms and the components of the stress tensor on the SC are less than 0.02 eV/Å and 0.5 kBar, respectively.

The size of the SC in the present calculations depends on the concentration of oxygen vacancies in the crystal. There are four vanadium and ten oxygen atoms for each primitive unit cell of the perfect bulk V_2O_5 , in which the numbers of O^1 , O^2 , and O^3 atoms are 4, 4, and 2, respectively. We consider the cases of oxygen concentrations $x=0.5$, 0.25 and 0.125, by using the $1 \times 1 \times 1$, $1 \times 2 \times 1$ (or $1 \times 1 \times 2$), and $1 \times 2 \times 2$ SCs with one oxygen atom removed, respectively. In the present calculations, the Γ -centered Monkhorst-Pack³⁰ k -meshes are used for Brillouin zone integration. For the $1 \times 1 \times 1$, $1 \times 2 \times 1$, $1 \times 1 \times 2$, and $1 \times 2 \times 2$ SCs, the k -meshes of $3 \times 10 \times 8$, $3 \times 5 \times 8$, $3 \times 10 \times 4$, and $3 \times 5 \times 4$ are chosen, respectively. To investigate the relative stability of all three types of oxygen vacancies in V_2O_{5-x} , we calculate the oxygen vacancy formation energy for each case. The formation energy for each oxygen vacancy E_{vac} may be defined as

$$E_{\text{vac}} = \frac{1}{N} \left(E_x + \frac{1}{2} E_{\text{O}_2} - E_0 \right), \quad (1)$$

where N , E_x , E_{O_2} , and E_0 represent the number of the oxygen vacancies in the SC, total energy of the V_2O_{5-x} SC, the free single oxygen molecule, and the perfect V_2O_5 SC, respectively.

III. RESULTS AND DISCUSSION

A. O vacancy-induced structural distortions

To understand how the oxygen vacancy in the V_2O_5 crystal affects its physical properties, we first performed *ab initio* calculations for the perfect V_2O_5 crystal. Figure 1 shows our theoretically determined structure of the perfect V_2O_5 crystal. The calculated lattice constants are $a = 11.556$ Å, $b = 3.575$ Å, and $c = 4.760$ Å, with a and b being in very good agreement with the corresponding experimental values³¹ (within 0.5%). Furthermore, the calculated bond lengths $d_{\text{V-O}^1} = 1.60$ Å, $d_{\text{V-O}^1'} = 3.16$ Å, $d_{\text{V-O}^2} = 1.79$ Å, $d_{\text{V-O}^3} = 1.89$ Å, and $d_{\text{V-O}^3'} = 2.04$ Å also agree

TABLE I. Calculated lattice parameters and O vacancy formation energy (E_{vac}) (eV/vacancy) for several different SCs of V_2O_{5-x} . Angles α and γ are always 90° and thus, only angle β is listed. The E_{vac} calculated by using the unrelaxed structures are given in brackets

SC	Vacancy	a (Å)	b (Å)	c (Å)	β (deg)	E_{vac}
$1 \times 2 \times 2$	O^1	11.559	7.175	9.106	89.56	2.48(4.68)
$1 \times 2 \times 2$	O^2	11.807	7.214	8.510	90.00	4.17(5.74)
$1 \times 2 \times 2$	O^3	11.596	7.169	9.068	89.99	4.44(5.04)
$1 \times 1 \times 2$	O^1	11.431	3.614	9.163	89.44	2.36(4.44)
$1 \times 2 \times 1$	O^1	11.552	7.209	4.656	87.96	3.89(4.46)
$1 \times 1 \times 1$	O^1	10.277	3.724	5.644	105.38	2.30(4.33)

very well with the corresponding measured values. Nonetheless, the calculated lattice constant c is larger than the experimental one by 9% because of the failure of the GGA to properly describe the weak interlayer van der Waals interaction. Our results are in good agreement with the *ab initio* calculations by Ganduglia-Pirovano and Sauer.¹³

We have performed both spin-unpolarized and spin-polarized calculations for all the SCs considered here and find that a ferromagnetic solution can be stabilized in all the cases. Furthermore, the ferromagnetic state is always lower in total energy than the nonmagnetic one. Therefore, in the following discussion on the structural distortions and electronic structure changes induced by the oxygen vacancies, we always refer to the results of the spin-polarized calculations for simplicity, unless stated otherwise. We list in Table I the theoretical lattice parameters for the different SCs.

When an oxygen atom is removed from the lattice of V_2O_5 , the bonding changes would induce the forces that act on the atoms in the vicinity of the oxygen vacancy site. In order to understand how the forces drive the geometrical distortions, we introduce one O^1 or O^2 or O^3 vacancy in the $1 \times 2 \times 2$ SC and calculate the forces on the ions in each case before the process of structural relaxation. The forces induced by the O vacancy are shown in Fig. 2. In the O^1 vacancy case [Fig. 2(a)], the vanadium atom that loses the O^1 atom [denoted as V_9 in Fig. 2(d)] would feel the force, generated by the vacancy, that pulls the vanadium down toward the position of the $\text{O}^{1'}$ atom. In the meantime, the nearby O^2

FIG. 2. (Color online) The structure of V_2O_{5-x} before [(a)–(c)] and after [(d)–(f)] relaxation in the $1 \times 2 \times 2$ SC with one oxygen vacancy. Three types of oxygen vacancy sites, namely, O^1 [(a) and (d)], O^2 [(b) and (e)], and O^3 [(c) and (f)], are considered. The blue, orange, yellow, and green spheres represent V, O^1 , O^2 , and O^3 atoms, respectively. In (a)–(c), the red arrows show the O vacancy-induced forces before the structural relaxation. In (d)–(f), the numbers label different vanadium atoms, while the blue and purple surface represent the isosurfaces of the positive and negative spin densities (majority spin-minority spin), respectively.

atoms would be attracted toward and influenced by the vanadium cation V_9 . After the process of relaxation [Fig. 2(d)], the V_9 atom would share an apical oxygen ($O^{1'}$) with the V_{11} atom. The calculated distances of $V_9-O^{1'}$ and $V_{11}-O^{1'}$ are 1.79 and 1.75 Å, i.e., the $d_{V_9-O^{1'}}$ is now shorter while the $d_{V_{11}-O^{1'}}$ becomes longer. These results are consistent with the previous calculations of the vacancy effect on the surface.¹³ On the other hand, if the O^2 site is vacant [Fig. 2(b)], the two vanadium atoms (V_1 and V_{13}) sharing the bridge O^2 would be pushed away from the vacant site, while the O^1 atoms surrounding the defect would contract together slightly. The zigzag geometry is then generated by the forces acting on these vanadium ions and O^1 atoms [Fig. 2(e)]. The bond lengths $d_{V_1-O^{1'}}$ and $d_{V_{13}-O^{1'}}$ both become 2.09 Å. The $O^1-V-O^{1'}$ angle on both the vanadium atoms changes from 177.5° to 141.4° after the structural relaxation. In the case of the O^3 vacancy, the vacancy-induced forces on the neighboring V atoms would again point away from the O vacancy but in the y direction [Fig. 2(c)]. Again, the nearby two O^3 atoms would be pulled toward the vacant hole. According to Fig. 2(f), if the $O^{3'}$ site of V_{11} is vacant, the $O^3-V_{11}-O^3$ angle changes from 141.8° to 128.3°. At the same time $d_{V_{11}-O^2}$ and $d_{V_{11}-O^3}$ become 1.75 and 1.83 Å, respectively. Therefore, we may conclude from the above analysis that, in general, an oxygen vacancy would attract its neighboring oxygen atoms but repel the neighboring V atoms. We notice that the driving force of the vacancy-induced relaxation is mainly electrostatic in nature. An oxygen vacant site has less electrons compared to the other oxygen positions in the crystal, and consequently, it repels the cations (V) but attracts the anions (O). For the O^1 and O^2 vacancy cases, the structural relaxation would lead the crystal to form certain interlayer bondings while, in contrast, no new bonding is found in the case of the O^3 vacancy.

To determine the relative stability of the three types of the oxygen vacancies, we perform the vacancy formation energy calculations via Eq. (1) by using the $1 \times 2 \times 2$ SC. The calculated O vacancy formation energies (E_{vac}) in V_2O_5 both before and after relaxation are listed in Table I. Interestingly, we find that the E_{vac} for the O^2 vacancy is the highest in the unrelaxed structure, but the E_{vac} for the O^3 vacancy is highest after the structural relaxation. In both relaxed and unrelaxed cases, the E_{vac} of the O^1 vacancy is lowest. As may be expected, the relaxation processes substantially reduce the E_{vac} , especially for the O^1 and O^2 vacancies by about 2.2 and 1.6 eV, respectively, and also for the O^3 vacancy by somewhat a smaller amount of 0.6 eV. Inspection of the structural distortions due to the O vacancies (Fig. 2) indicates that the new bonds ($V-O^{1'}$) formed in both the O^1 and O^2 cases may be the main source of the reduction in the vacancy formation energy. Table I also indicates that without structural relaxations, the calculated O^1 vacancy E_{vac} increases as the vacancy concentration decreases, suggesting that the vacancies would attract each other. On the other hand, since the vacancy-induced structural distortions are large, a large SC would be needed to fully accommodate these structural distortions. Therefore, when O^1 vacancy concentration decreases from $x=0.5$ to $x=0.25$, the E_{vac} in-

creases (see Table I) because of the weakened vacancy-vacancy attraction. However, when the x further is reduced further, the energy lowering due to the structural relaxation becomes dominant and hence the E_{vac} decreases again (Table I).

In Ref. 13, *ab initio* GGA calculations for V_2O_{5-x} in the $1 \times 2 \times 3$ SC with one O^1 vacancy were performed and the calculated E_{vac} is 1.97 eV/vacancy. However, our calculated E_{vac} for O^1 , O^2 , and O^3 vacancies in $1 \times 2 \times 2$ SC are about 0.5–0.6 eV larger than those on the V_2O_5 surfaces. To understand the difference in E_{vac} between the present and previous calculations, we have also calculated the E_{vac} for single O^1 vacancy in the $1 \times 2 \times 3$ SC. We found that $E_{\text{vac}} = 1.87$ eV/vacancy, being in good agreement with Ref. 13. Therefore, the systematic increase in E_{vac} for the vacancies in the $1 \times 2 \times 2$ SC might reflect stronger distortions induced by the vacancies inside the $1 \times 2 \times 2$ SC compared with those on the surface. The decrease in E_{vac} for the $1 \times 2 \times 3$ SC case might be due to the further relaxation accommodated by the additional V_2O_5 layer. Nonetheless, the E_{vac} values from these *ab initio* GGA calculations are larger than the estimated E_{vac} of 1.3–1.5 eV/vacancy from conductivity experiments.³² One possible origin of this discrepancy between the experimental estimates and GGA calculations may be that the $1 \times 2 \times 3$ SC used in the GGA calculations is still not sufficiently large. On the other hand, in the oxygen-deficient V_2O_{5-x} , the conduction electrons occupying the V 3d states can be significantly correlated. Consequently, the LDA (local density approximation) and GGA may become inadequate because the self-interaction errors in them can become rather significant when they are applied to the strongly correlated TMOs (see, e.g., Ref. 33). Nonetheless, the main purpose of the E_{vac} calculations in this work is to find out which type of the oxygen vacancies is energetically favorable. Indeed, the recent B3LYP hybrid functional calculations,³⁴ which gave rather reliable formation energies, showed that DFT-GGA calculations do reproduce the trend of V=O bond dissociation energies of V_2O_5 clusters correctly, although they may yield errors in absolute values.

In the following, we will focus only on the structural distortions induced by the O^1 vacancies with several different vacancy densities and orderings since the O^1 vacancy is more stable than the O^2 and O^3 ones, as discussed above. The theoretical crystal structures of V_2O_5 with larger O^1 vacancy concentrations are shown in Fig. 3. For an O^1 vacancy in the $1 \times 1 \times 1$ SC [Fig. 3(a)], the local structural distortions of V_1 are large when the O^1 is removed. After the structural relaxation, the out-of-plane force pushes the V_1 toward the O^1 owned by the V_4 in the next layer, resulting in the formation of the interlayer $V_1-O^1-V_4$ bonding. In this new structure, the V_1 and V_4 atoms form a zigzag interlayer linkage along the [001] direction with the O^2 and O^1 atoms owned by V_4 in the original structure. The original layer structure thus gives away to a three-dimensional one. The lengths of $d_{V_1-O^1}$, $d_{V_4-O^1}$, $d_{V_1-O^2}$, and $d_{V_4-O^2}$ are about 1.77 Å. Furthermore, the structural distortions are so large that even the crystal lattice is altered dramatically. The original orthorhombic lattice becomes the monoclinic one with the β angle being increased from 90° to 106° (Table I).

With the same oxygen vacancy density, the different va-

FIG. 3. (Color online) The relaxed structure of V_2O_{5-x} in (a) $1 \times 1 \times 1$, (b) $1 \times 2 \times 1$, and (c) $1 \times 1 \times 2$ SCs with one O^1 vacancy. The blue, orange, yellow, and green spheres represent V, O^1 , O^2 , and O^3 atoms, respectively. The blue and purple surfaces represent the isosurfaces of the positive and negative spin densities (majority spin-minority spin), respectively. The numbers label the V atoms.

cancy orderings can have different effects on the crystal structure. When the O^1 vacancy is in the $1 \times 2 \times 1$ SC structure [Fig. 3(b)], the vanadium atom next to the vacancy site (V_8) has no $V-O^1$ bond. The vacancies form a O vacancy chain along the $[001]$ direction and this prevents V_8 from forming a common $V-O^1-V$ interlayer structure. For the O^1 vacancy in the $1 \times 1 \times 2$ SC structure, on the other hand, two vanadium atoms (V_7 and V_8) share one O^1 atom. The bond lengths $d_{V_7-O^1}$ and $d_{V_8-O^1}$ near the vacancy site are 1.76 and 1.77 Å, respectively. The O^1 vacancies form a O vacancy chain in the $[010]$ direction, being similar to the missing-row structure reported in Ref. 13. Interestingly, the calculated vacancy formation energies (Table I) show that the $1 \times 1 \times 2$ SC with the missing-row structure is more stable than the $1 \times 2 \times 1$ SC, suggesting that it saves energy to maintain the layer structure. However, the layer crystal structure would disappear completely as the vacancy density becomes higher, as can be seen by comparing Fig. 2(d) with Fig. 3.

B. Electronic structure

The pure V_2O_5 crystal is a diamagnetic semiconductor with a layer structure. When the oxygen vacancies are introduced, not only the crystal structure changes but also the electronic properties are altered. To understand these changes in the electronic properties, we display the total and V-site decomposed density of states (DOS) spectra of V_2O_{5-x} with several different O vacancy concentrations in Fig. 4. In the simple ionic picture, in the pure V_2O_5 crystal, the electrons on the vanadium atoms are transferred to the neighboring oxygen atoms to form the ionic bonds. If an oxygen vacancy is introduced in the V_2O_5 crystal, it would effectively release two electrons per each vacancy. The top of the occupied states would move from the O $2p$ states to the V d_{xy} states, according to the band structure of the pure V_2O_5 . This would imply a significant reduction in vanadium when the oxygen vacancies appear. The other major effect due to the introduction of the O vacancies would be the dramatic alternations of the local structure of the V atoms next to the O vacancy sites,

as described in Sec. III A. These V local structure changes would subsequently affect the electronic structure of the V_2O_{5-x} .

When an oxygen vacancy is introduced, not only the Fermi level would move to the V d -dominant bands but also the local structure of the neighboring V atoms may be altered dramatically, as mentioned before. The changes in the local coordination of the V atoms would shift the energy levels of the different d -orbitals differently, and this energy level shifting would also depend on the vacancy configuration. When an O^1 atom is removed from the $1 \times 2 \times 2$ SC, the V atom next to the vacancy site [V_9 in Fig. 2(d)] would lose the $V-O^1$ bond but would move downward [Fig. 2(a)] to form the interlayer bonding with the O^1 and V (V_{11}) atoms on the neighboring layer. Despite this dramatic local structural distortion near the O vacancy, the calculated total DOS is very similar to that of the perfect V_2O_5 crystal, except the occupation of the lowest d_{xy} -dominant conduction band that is exchange split by about 0.3 eV [Fig. 4(a)], perhaps due to the low O vacancy concentration ($x=0.125$). The partial occupation of the $Vd_{xy}-O^3-Vd_{xy}$ ladder orbital-based conduction bands comes from the charge transfer of the reduction. The occupied conduction bands are actually made up of the V_1-V_2 , $V_{13}-V_{14}$, V_3-V_4 , $V_{15}-V_{16}$, V_5-V_6 , V_9-V_{10} , V_7-V_8 , $V_{11}-V_{12}$ ladder orbitals, V_5-V_9 , V_7-V_{11} rung orbitals, and $V_9-O^1-V_{11}$ interlayer bonding orbital [see Fig. 2(d) for the atomic positions]. The vacancy-induced interlayer bonding of the $V_9d_{yz}-O^1p_y-V_{11}d_{yz}$ orbitals manifests itself as a pronounced V d_{yz} -DOS peak in Fig. 4(a). In Fig. 4(a) we can observe the remarkable contribution of d_{yz} orbitals below the Fermi level due to the $V_9-O^1-V_{11}$ bonding. Furthermore, this interlayer bonding reduces the $d_{3z^2-r^2}$ occupancy on V_9 and V_{11} by 0.08/V atom. In addition, a discernable increased d_{xy} occupation (by 0.1 per orbital) on V_5 and V_7 which form a rung orbital with V_9 and V_{11} , respectively, is also found.

In the $1 \times 1 \times 2$ SC, the number of the O vacancy-induced interlayer $V-O^1-V$ bonds would be increased. In fact, the O^1 vacancies would form a vacancy column along the $[010]$ direction (see Sec. III A). Therefore, the

FIG. 4. (Color online) Total, site, and orbital decomposed DOS of (a) $1 \times 2 \times 2$, (b) $1 \times 1 \times 2$, (c) $1 \times 2 \times 1$, and (d) $1 \times 1 \times 1$ SCs with one O^1 vacancy. The dotted vertical lines represent the Fermi level.

$V d_{yz}$ -DOS peak just below the Fermi level becomes more pronounced [Fig. 4(b)], and it is now comparable to that of the $V d_{xy}$ -DOS. The occupied conduction band just below the Fermi level are mainly composed of the V_1-V_7 , V_2-V_8 , V_3-V_5 , V_4-V_6 ladder orbitals and $V_7-O^1-V_8$ interlayer bonding orbital [see Fig. 3(c) for the atomic positions]. Note that the $V_7 d_{yz}-O^1-V_8 d_{yz}$ orbitals would couple the V_1-V_7 and V_2-V_8 ladder orbitals. We find that the exchange splitting (~ 0.5 eV) of the lowest conduction band is not sufficiently large such that the majority conduction band is able to accommodate two electrons per vacancy, i.e., the conduction electrons would not be fully spin-polarized in the $1 \times 1 \times 2$ SC.

In the $1 \times 2 \times 1$ SC, on the other hand, the O vacancies would form the vacancy row along the $[010]$ direction [Fig. 3(b)]. This O vacancy row produces a distinct $V_8 d_{3z^2-r^2}$ band between -0.5 and -1.0 eV below the $V d_{xy}$ -dominant conduction band [Fig. 4(c)]. Interestingly, although the exchange splitting (~ 0.3 eV) of the d_{xy} conduction band could only allow its majority-spin band to contain 1.0 electron, the large exchange splitting of about 1.6 eV for the $d_{3z^2-r^2}$ -dominant band would allow its majority spin band to accommodate another 1.0 electron, i.e., the electrons in the conduction bands would be fully spin polarized in this case. The occupied d_{xy} -dominant conduction band consists mainly of V_1-V_2 , V_7-V_8 ladder orbitals and also $V_3-V_4-V_5-V_6$ lad-

TABLE II. Calculated ferromagnetic magnetic moment (m_s) (μ_B /vacancy), magnetization energy (E_{mag}) (meV/vacancy), the averaged local DOS of the V atoms next to the O¹ vacancy at the Fermi level $N_V(E_F)$ (states/eV/V atom), and $N_V(E_F)I_V$ in V_2O_{5-x} with several different O¹ vacancy densities (x) and configurations.

SC	x	m_s	E_{mag}	$N_V(E_F)$	$N_V(E_F)I_V$
$1 \times 2 \times 2$	0.125	2.00	86	3.22	1.14
$1 \times 1 \times 2$	0.25	1.79	78	4.28	1.52
$1 \times 2 \times 1$	0.25	2.00	293	3.26	1.15
$1 \times 1 \times 1$	0.5	1.93	133	3.54	1.25

der orbitals with the contributions from the former ladder orbitals being twice as much as that of the latter ladder orbitals.

As the O vacancy density is further increased, as in the $1 \times 1 \times 1$ SC ($\text{V}_2\text{O}_{4.5}$), greater distortions to the local structure of the V atoms next to the O vacancy site [see V_1 and V_4 in Fig. 3(a)] occur. In particular, V_1 and V_4 now form a $\text{V}_1\text{—O}^1\text{—V}_4\text{—O}^2\text{—V}_1$ continual zigzag structure along [001], and the original V_1 and V_4 associated ladder becomes a two-dimensional grid. This topological change to the local V_1 and V_4 structures would certainly alter the electronic structure greatly especially the V d -dominant conduction bands, as may be seen from Fig. 4(d). For example, the formation of the zigzag structure along [001] gives rise to a strong hybridization of the V_1 and V_4 $d_{3z^2-r^2}$, $d_{x^2-y^2}$, and d_{zx} orbitals in the conduction bands just below the Fermi level. Because of this, the minority spin conduction band is partially occupied even though the exchange splitting is as large as ~ 0.9 eV.

C. Magnetic property

The self-consistent density functional calculations for V_2O_5 in all the SCs with the different oxygen vacancy sites presented in the preceding paragraphs are actually spin-polarized ones. In all the cases, the self-consistent spin-polarized calculations converged to a ferromagnetic solution. The calculated spin density distribution (i.e., the difference between the majority and minority electron number densities) is displayed in Figs. 2(d) and 3. The obtained magnetic moments (m_s) and also ferromagnetic magnetization energies (E_{mag}) for all the O¹ vacancies are listed in Table II. The magnetization energy per vacancy is defined as

$$E_{\text{mag}} = \frac{E_{\text{NM}} - E_{\text{M}}}{N}, \quad (2)$$

where E_{NM} and E_{M} are the total energy of the SC in the nonmagnetic and magnetic states, respectively, and N is the number of vacancies in the SC. In principle, each oxygen vacancy would provide two electrons. If all these electrons occupy the majority spin states, we would get a magnetic moment of exactly $2.0\mu_B$ per O vacancy. This is indeed the case in the $1 \times 2 \times 1$ and $1 \times 2 \times 2$ SCs, although the calculated magnetic moment per O vacancy is slightly smaller than $2.0\mu_B$ in the $1 \times 1 \times 1$ and $1 \times 1 \times 2$ SCs (Table II).

Interestingly, the GGA calculated magnetic moment or the highest occupied state does not localize on the O vacancy site,^{13,34} but rather comes mainly from the contributions of

the V atoms near the O vacancy, as demonstrated by the calculated spin density distributions displayed in Figs. 2(d)–2(f), and also Fig. 3. This may be expected since each oxygen vacancy would modify mainly the local electronic structure of the V atoms next to the vacancy, as has been discussed above. In particular, a major contribution to the spin moment results from the occupation of the d_{xy} orbital of the neighboring V atoms by the electrons released from the O vacancy. For example, in the $1 \times 2 \times 2$ SC, the calculated local magnetic moments on V_5 , V_7 , V_9 , and V_{11} are $0.34\mu_B$, $0.19\mu_B$, $0.43\mu_B$, and $0.30\mu_B$, respectively. The local moments of about $0.12\mu_B$ – $0.17\mu_B$ are also found on V_6 , V_8 , V_{10} , and V_{12} , while the other vanadium sites have a local moment being less than $0.08\mu_B$. Not surprisingly, the d -orbitals on the V atoms next to the vacancy site host about a half of the magnetization.

As pointed out in Sec. III B, the conduction electrons occupying the V $3d$ states in the oxygen-deficient V_2O_{5-x} can become rather strongly correlated. Consequently, the GGA may become inadequate because its self-interaction errors may become rather significant when applied to the strongly correlated TMOs. The methods going beyond the LDA or GGA, such as the B3LYP hybrid functional³⁴ and LDA/GGA plus on-site Coulomb interaction U [LDA(GGA)+ U] (Ref. 35) schemes, might become necessary. To examine the effect of the on-site Coulomb interaction of the V $3d$ electrons on the calculated magnetic properties, we have also performed the rotationally invariant GGAU (Ref. 35) ($U=3.0$ eV and $J=0.9$ eV for the V atoms) calculations for V_2O_{5-x} in the $1 \times 2 \times 2$ SC with one O¹ vacancy. However, we find that the main magnetic properties from the GGA and GGA+ U calculations are rather similar. For example, the calculated magnetic moment is still $2.0\mu_B$ per O vacancy, and the calculated E_{mag} is 70 meV/vacancy, being rather close to the GGA result (86 meV/vacancy) (Table II). Nonetheless, compared with the GGA results, the occupation of the d_{xy} orbital and the local magnetic moment on the V atoms near the vacancy site [V_9 and V_{11} in Fig. 2(d)] are increased, while they are decreased on the V atoms further away from the vacancy site. For instance, the magnetic moments on V_5 , V_7 , V_9 , and V_{11} become $0.50\mu_B$, $0.35\mu_B$, $0.58\mu_B$, and $0.51\mu_B$, respectively. The local moments of about $0.06\mu_B$ – $0.18\mu_B$ are also found on V_6 , V_8 , V_{10} , and V_{12} , while the other V atoms have a small local moment of $\sim 0.01\mu_B$. Similar findings from the B3LYP calculations for the V_2O_{5-x} surface were recently reported.³⁴ Finally, a small band gap of ~ 0.1 eV is opened at the Fermi level in the GGA+ U calculations, although other main features of the DOS spectra are more or less the same in both cases.

In order to understand the nature of the magnetization induced by the oxygen vacancy, let us turn to the Stoner theory.²⁴ According to this theory, the exchange-enhanced susceptibility for a V atom is given by

$$\chi = \frac{N_V(E_F)}{1 - N_V(E_F)I_V}, \quad (3)$$

where $N_V(E_F)$ is the nonmagnetic local DOS per V atom at the Fermi level for the V atoms next to the O vacancy and

$I_V=0.354$ eV is the Stoner exchange parameter for V.²⁴ If $N_V(E_F)I_V \geq 1$, the nonmagnetic state would become unstable, leading to the formation of magnetization. In Table II, we list the calculated $N_V(E_F)$ averaged over the V atoms next to the O¹ vacancy in several SCs together with the resultant $N_V(E_F)I_V$ values. The V atoms next to the O¹ in the $1 \times 2 \times 2$, $1 \times 1 \times 2$, $1 \times 2 \times 1$, and $1 \times 1 \times 1$ SCs are, respectively, V₉ and V₁₁, V₇ and V₈, V₈, and V₁ and V₄ [see Figs. 2(d) and 3]. Clearly, in all the O¹ vacancy cases, the $N_V(E_F)I_V$ value is larger than 1.0. This indicates that the magnetism in V₂O_{5-x} results from the large local DOS at the Fermi level on the V atoms next to the O vacancy, being consistent with the large spin density found surrounding these V atoms [Figs. 2(d)–2(f) and 3]. The large $N_V(E_F)$ values for the V atoms next to the O¹ vacancy may also be seen indirectly from Fig. 4.

Intercalating V₂O₅ with alkali metals such as Na is, to some extent, equivalent to the reduction of V₂O₅ due to the presence of the O vacancies. Previous studies on the electronic and magnetic properties of NaV₂O₅ indicated that the reduction of V₂O₅ by the intercalation of Na would induce local magnetic moments on the rung orbitals with antiferromagnetic (AF) coupling along the ladder.³⁶ Therefore, we may expect the AF magnetic ordering also to occur in V₂O_{5-x}. In the case of a single O vacancy per SC, previous study showed that the AF configuration with the initial magnetic moments on the two V atoms next to the vacancy being antiparallel, always converges to the FM state.²² However, when we extended the structure of the $1 \times 1 \times 1$ SC along y-direction and performed the calculation with the AF coupling between the rungs within each ladder, we found that it converges to a metastable state with $E_{\text{mag}}=83$ meV/vacancy. This result inspired us to investigate the possible magnetic ordering in V₂O_{5-x}.

Here we discuss the possible AF ordering in V₂O_{5-x} in two ways: one is to construct an initial AF ordering in the perfect V₂O₅ lattice with various degree of reduction by artificially adding electrons to the lattice (VCA), and the other is to introduce two O¹ vacancies in the $1 \times 2 \times 2$ SC of V₂O₅ while keeping the inversion symmetry. The VCA results of the AF calculations in the former way are shown in Fig. 5. The AF coupling could be either between the ladders (AF-1) or between the rungs within each ladder (AF-2) [Fig. 5(a)]. We find that the E_{mag} in the AF-1 state increases with x , and also it is similar to that of the FM state. In fact, in the small window of $0.13 < x < 0.19$, the E_{mag} of the AF-1 state is slightly larger than that of the FM state [Fig. 5(a)]. In contrast, the E_{mag} for the AF-2 state is zero when $x \leq 0.25$, because the AF-2 state could not be stabilized in this x region [Fig. 5(b)]. However, the AF-2 appears when $x \geq 0.25$, and the E_{mag} increases dramatically with x . When $x=0.5$, the reduction state of the V₂O_{5-x} crystal would be equivalent to NaV₂O₅. Indeed, we notice that the total energy of the AF-2 state is lower than that of both the FM and AF-1 states (Fig. 5), being consistent with the AF-2 ordering observed in NaV₂O₅.³⁶ Furthermore, Table II shows that the E_{mag} of the FM state obtained from the single O vacancy SC calculations is very similar to that displayed in Fig. 5, except for the $1 \times 2 \times 1$ SC. The E_{mag} in the $1 \times 2 \times 1$ SC case is found to be

FIG. 5. (Color online) The VCA results of the magnetization energy (E_{mag}) (a) and the sum of the spin magnetic moments (M_s) on the V and O ions per formula unit (f.u.) (b), of V₂O_{5-x} in the FM and AF states as a function of O vacancy concentration x . In the inset in (a), the AF-1 and AF-2 structures are illustrated. The arrows represent the spins on the V atoms while the dots denote the O² and O³ atoms.

especially large, being about 300 meV per vacancy, and this is due to the exceptionally large exchange splitting of the $d_{3z^2-r^2}$ orbital on the V atoms next to the O vacancy, as can be seen in Fig. 4.

In order to examine the reliability of our VCA results based on the fixed crystal cell, we performed further calculations for the structural optimizations within the VCA scheme. We found that the electronic structure and magnetization energy hardly change, even though some discernable geometrical changes were observed. The VCA calculations on the V₂O_{5-0.25} with structure optimization exhibited that the lattice constants (a, b, c) become 11.21, 3.66, and 8.45 Å. The optimized bond lengths d_{V-O^1} , d_{V-O^2} , d_{V-O^3} , and $d_{V-O^3'}$ are 1.61, 1.81, 1.93, and 2.01 Å, respectively. The magnitude of the structural changes is less than 3% except the lattice constant c ($\sim 77.5\%$). The VCA result of lattice constant c cannot reflect the real structure compared with the SC approach due to the absence of the interlayer bondings. We also found that the $E_{\text{mag}}(\text{FM})$, $E_{\text{mag}}(\text{AF-1})$, and $E_{\text{mag}}(\text{AF-2})$ for structurally optimized V₂O_{5-0.25} VCA results are 92.6, 87.6, and 0.0 meV/vacancy, respectively. Our results show that the magnetic ordering for $x=0.25$ remains unchanged, and the deviations of the magnetization energies between the optimized cases and unrelaxed cases are less than 4 meV/vacancy. Therefore, the magnetic properties for the structurally optimized VCA results are very similar to the structurally unoptimized results. For that reason, we believe that the magnetization energies from the VCA calculations without structural optimization are appropriate to describe the in-plane magnetic interactions.

The results of the AF calculations by introducing two

TABLE III. The calculated vacancy formation energy (E_{vac}) (in eV/vacancy) and magnetization energy (E_{mag}) (in meV/vacancy) of V_2O_{5-x} ($x=0.25$) in the FM or AF-1 state with either type I or type II O vacancy structure (see text).

SC	E_{vac} (FM)	E_{mag} (FM)	E_{mag} (AF-1)	E_{mag} (AF-3)
Type I	2.55	77	73	48
Type II	2.41	78	73	45

single O^1 vacancies in the $1 \times 2 \times 2$ SC are summarized in Table III. The two O^1 vacancies may have two kinds of defect configurations. In the first defect configuration, the two vacancy-induced interlayer V–V bondings appear on the same side of the V_2O_5 slab (type I). In the second configuration, the two interlayer V–V bondings appear on the opposite side of the V_2O_5 slab (type II). Since the interlayer bondings are present in type I and type II structures, unlike the VCA cases, we also consider the AF states with the antiparallel spin configurations between V_2O_5 slab (AF-3). We find that the initial AF-2 state in both type I and type II defect configurations always converged to the AF-1 configuration after some self-consistent cycles, indicating that the AF-2 state is unstable. Therefore, only the results for the FM, AF-1, and AF-3 states are listed in Table III. As in Fig. 5(a), the E_{mag} for the FM is larger than that of the AF-1 and AF-3 states, indicating that the FM would be the ground state. Nonetheless, the difference in the E_{mag} between the AF-1 and FM states is small, being 4–5 meV per vacancy, and this may reflect the similarity of the electronic structures between the two magnetic states and also the weak interladder coupling of the V d -orbitals in the conduction bands. With respect to the AF-1 state, the AF-3 states are unstable. The magnetization energies E_{mag} (AF-3) for type I and type II are 48 and 45 meV/vacancy, respectively. Note that the difference in the E_{mag} between the AF-1 and FM states at $x=0.25$ in Fig. 5(a) is 4.5 meV per vacancy. By comparing the results of the magnetic configurations from SC calculations with those from the VCA calculations, we found that both approaches predict the possible existence of the FM and AF-1 states but absence of AF-2 state about $x \leq 0.25$, while the values of E_{mag} (FM) and E_{mag} (AF-1) are similar.

IV. CONCLUSIONS

To summarize, we have investigated oxygen vacancy-induced changes in the structural, electronic, and magnetic properties of oxygen-deficient V_2O_{5-x} within spin DFT with GGA by using the accurate PAW method. Both the SC approach and VCA were used to model V_2O_{5-x} with vacancy concentration x up to 0.5. The $1 \times 2 \times 2$ SC calculations with one O vacancy show that the formation energies of the apical (O^1), bridge (O^2), and chain (O^3) oxygen vacancies are, respectively, 2.48, 4.17, and 4.44 eV/vacancy, and hence that the O vacancies in V_2O_{5-x} would be predominantly of the O^1 type. The local structural distortions of the V atoms next to the O vacancies are found to be large for high vacancy density ($x > 0.25$), and for $x \sim 0.5$, even the crystal lattice changes from the orthorhombic to monoclinic symmetry. In all the cases considered, an O vacancy-induced stable or

metastable ferromagnetic state with spin magnetic moment of $\sim 2.0\mu_B$ /vacancy can be found. Both of SC and VCA approaches predict the existence of the FM and AF-1 states but absence of AF-2 state about $x \leq 0.25$, while the values of magnetization energies E_{mag} (FM) and E_{mag} (AF-1) are similar. Metastable or possible stable AF-2 states appears only when $x > 0.25$. Based on the VCA results, for x below ~ 0.13 and $0.19 < x < 0.45$, the ferromagnetic state would be the ground state, while for $0.45 \leq x \leq 0.5$, the AF state with the V spins on neighboring rungs (AF-2) being antiparallel is the ground state. Importantly, this suggests that undoped V_2O_{5-x} with $x \leq 0.13$ and $0.19 < x < 0.45$ would be a diluted ferromagnetic semiconductor. The AF-2, however, disappears for $x \leq 0.25$, while the AF state with the V spins on neighboring ladders being antiparallel (AF-1) occurs for the entire range of x studied. Nevertheless, the AF-1 is energetically more favorable than the ferromagnetic state only in $0.13 < x < 0.19$. For low O vacancy concentrations ($x < 0.25$), the electronic structure of V_2O_{5-x} is very similar to that of the perfect bulk V_2O_5 , except that $2x$ electrons now occupy the low V d_{xy} dominant conduction bands which are exchange split. Majority of the magnetization is located on the d_{xy} -orbitals of the V atoms near the O vacancy site. For larger x values, however, the electronic structure may change significantly, and, in particular, the V d -orbital character of the low conduction bands can be altered completely. Analysis of the calculated electronic structure indicates that the oxygen vacancy-induced magnetization in V_2O_{5-x} results primarily from the Stoner mechanism.

ACKNOWLEDGMENTS

The authors thank J. A. C. Huang, H. S. Hsu, and P. H. Lee for stimulating discussions. The authors acknowledge the financial supports from the National Science Council, TSMC under TSMC JDP Grant No. NTU-0806 and NCTS. They also thank the Computer and Information Networking Center (CINC) of National Taiwan University and the National Center for High-performance Computing (NCHC) for the computing time.

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