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VO_2: Orbital Competition, Magnetism, and Phase Stability

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The relative phase stability of VO_2 is one of the most fundamental issues concerning the metal-insulator transition in this material but has so far largely unexplored theoretically. We investigate the relative stability of various phases of VO_2 using different levels of energy functionals within density functional theory (DFT). It is found that straightforward applications of several popular energy functionals, including the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional, result in a wrong prediction for the ground state of VO_2. In particular, although the HSE and DFT+U methods are able to produce a band gap in the M_1 phase, they strongly favor the formation of local magnetic moments, a result that clearly disagrees with experiments. We also examine the effect of the occupation and the redistribution of the d derived t_{2g} (i.e., d_{xz}, d_{yz} and $d_{x^2-y^2}$) orbitals of V atoms on the calculated relative phase stability of VO_2. We find that a small change in d-occupation can result in a drastically different theoretical prediction. With the introduction of an orbital-dependent potential, a complete separation between the $d_{x^2-y^2}$ derived valence band and d_{xz} and d_{yz} derived conduction bands in the M_1 phase is achieved, resulting in a slight redistribution of the d occupation and a more faithful account of the polarization of the t_{2g} orbitals. This slight rearrangement of the d occupation also leads to a relative phase stability of VO_2 (including structural and magnetic phases) that agrees well with experiment.

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I. INTRODUCTION

Vanadium dioxide (VO_2), a transition-metal oxide that undergoes a metal-insulator transition (MIT) at $T_{\mathrm{MIT}} = 340\mathrm{K}$),[1] has been investigated extensively for decades for its great technological potentials[2, 3] and the intriguing physics [4] behind the MIT. The electronic phase transition is accompanied by a (nearly) simultaneous structural distortion from a high temperature metallic phase with a rutile (R) structure to a low temperature insulating phase with a monoclinic structure (M_1) as shown in Fig. 1. Under hole-doping [5] or stress[6], another monoclinic phase (M_2) shows up with antiferromagnetically (AFM) coupled V chains (denoted as V_1 in Fig. 1). [5, 7–9] Interestingly, no local magnetic moments were observed in the M_1 phase, [10, 11] implying that Peierls bonding mechanism dominates the localization effects of d electrons. However, it is generally agreed that the structural changes and the Peierls mechanism alone cannot be fully responsible for the insulating nature of the M_1 phase.[12–15]

Much previous effort has been focused on understanding the physics behind the MIT, especially the role electron-electron correlation and electron-lattice coupling play in driving the simultaneous structural and electronic phase transition. [14, 16–20] Whether the insulating M_1

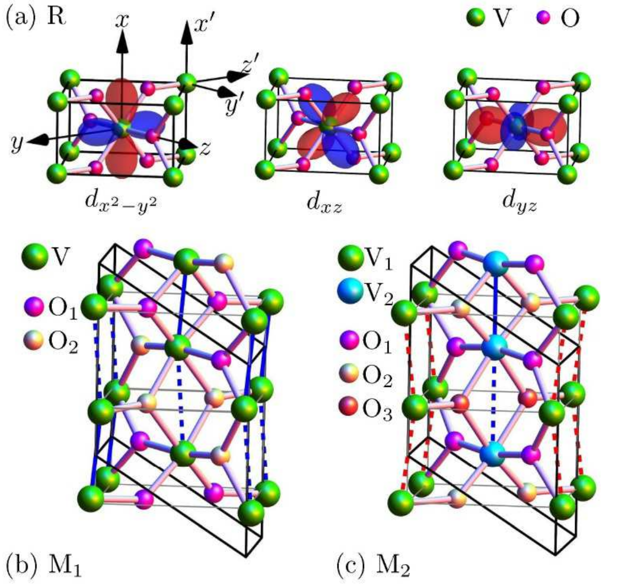

FIG. 1. (color online) Structures of different VO_2 phases. (a) High-temperature R phase and three t_{2g} orbitals (i.e., d_{xz}, d_{yz}, and $d_{x^2-y^2}$). Local coordinate systems on V atoms are defined with the x and x' axes directing along the c_r direction and the z axis pointing to the nearest O atom in the $(001)_r$ plane. (b) M_1 phase. All V atoms are dimerized and zigzagged along the c_r direction. (c) M_2 phase. Half of the V atoms (denoted as V_1) are zigzagged whereas the other half (V_2) are dimerized.

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phase should be described as a correlated Mott-Hubbard insulator or a Peierls band insulator has been a subject of unabated discussions. Unfortunately, despite decades of efforts, a unified theory remains elusive. Electronic structure calculations based on density functional theory (DFT) within the local density approximation (LDA) or the generalized gradient approximation (GGA) fail to reproduce the insulating nature of the M_1 phase. [4, 21] More sophisticated methods such as the LDA+U[22], hybrid functionals[23–25], GW[26, 27] or dynamical mean field theory (DMFT) [12, 28, 29] have been applied to this system. Interestingly, although these methods attempt to address different aspects of the electron-electron correlation, they are all able to predict an insulating gap develops in the M_1 phase. However, it should be pointed out that the LDA (or GGA) often fails to open a gap in narrow-gap semiconductors such as Ge, InN, etc., which are weakly correlated materials. This "band-gap" problem alone shall not be over-interpreted. The fact that LDA (or GGA) calculations fail to open a gap in a narrow-gap material does not necessarily mean that the material under investigation is strongly correlated. Conversely, being able to reproduce the band gap of an insulator does not guarantee that a method or functional is able to correctly capture the underlying physics of the system.

In this paper, we show that hybrid functionals (such as HSE) and the LDA+U (or GGA+U) method, although being able to predict an insulating gap for the M_1 phase, incorrectly produce a magnetic, either ferromagnetic (FM) or AFM, ground state. The spin-polarized solution for the M_1 phase is lower in energy than the spin-unpolarized (i.e. nonmagnetic, NM) one by more than 0.5 eV using the HSE functional . Since one of the most important measures of the success of an energy functional is its ability to predict the ground state properties of a system, the wrong magnetic ground state predicted by hybrid functionals or the LDA+U (or GGA+U) method raises a serious issue regarding the applicability of these methods to study the electronic properties of VO_2. There are multiple competing instabilities (e.g., magnetic, structural, and orbital) arising from the subtle interplay among various degrees of freedom in this system. It appears that VO_2 is an extreme case in which the relative stability of various states (phases) depends sensitively on the energy functional used in theoretical calculations, and none of the functionals used in this work are able to reproduce the experimentally observed results. In addition, we find that the redistribution of the d occupation plays a central role in determining the stability of difference phases of VO_2. By suppressing the occupation of d_{xz} and d_{yz} orbitals through the introduction of a simple orbital-biased potential, the correct energy ordering is restored.

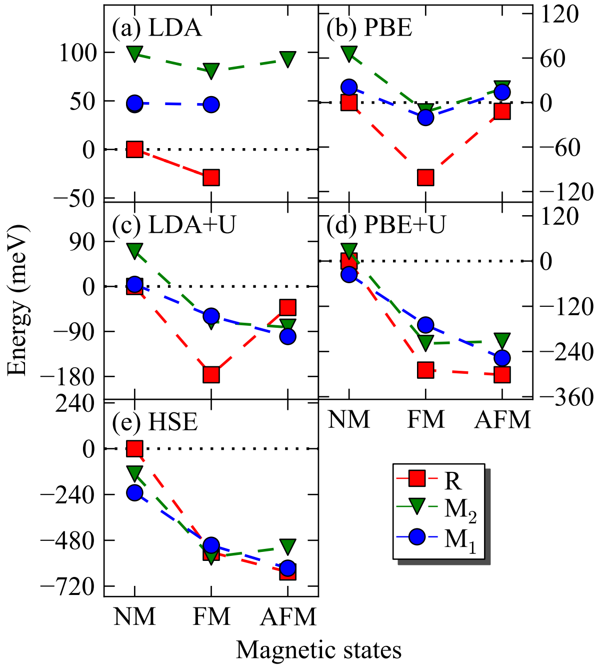

FIG. 2. (color online) Calculated total energies of different VO_2 phases (including structural and magnetic phases) using different energy functionals. We use a small on-site Coulomb energy of $U_{\text{eff}} = 2.0$ eV in the LDA+U and PBE+U calculations. Within each method, the energy of the NM R phase is set to zero. All energies are rescaled for one VO_2 formula unit.

II. COMPUTATIONAL DETAILS

All calculations in this work are carried out using the projected augmented wave (PAW) method [30, 31] implemented in the VASP code [32]. We use experimental structures [33–35] for all calculations. The plane wave kinetic energy cut-off (E_{cut}) is set at 600 eV, and a $6 \times 6 \times 6$ uniform Monkhorst-Pack k-grid is used for the M_1 phase. A k-grid with a similar density is used for the R and M_2 phases. To demonstrate that VO_2 is an extreme system whose (theoretical) phase stability and electronic structure depend sensitively on the energy functional used in the calculation, we consider five different functionals (methods), namely, the LDA, GGA (PBE[36]), LDA+U, PBE+U, and HSE[37, 38]. We use a simplified version of the rotationally invariant L(S)DA+U method [39], with a small effective on-site Coulomb energy U_{eff} of 2.0 eV for the vanadium d electrons [40]. Calculations using the original formulation of the rotationally invariant LDA+U method [41, 42] are also carried out, the results are found to be almost the same. For the HSE functional, the exact exchange mixing parameter is chosen to be 0.25, and the screening parameter μ is 0.4.

III. RESULTS AND DISCUSSION

A. Structural and magnetic instabilities

Vanadium ions in VO_2 have nominally one d electron. These lone d electrons may assume various and distinct roles. For example, they may form a dispersive band and contribute to the metallic bonding as in the case of the R phase VO_2; they may also form singlet bonding pairs as in the case of the M_1 phase. In addition, being $3d$ electrons, they are substantially localized and may develop local magnetic moments (e.g., in the M_2 phase) if on-site Coulomb correlations dominate other bonding mechanisms. The competition between these bonding and localization tendencies may result in multiple competing instabilities and ultimately determines the electronic, magnetic, and structural properties of VO_2. Surprisingly, the subtle interplay between the magnetic and structural instabilities has not been carefully investigated. In fact, most previous investigations on VO_2 were restricted within spin-unpolarized solutions. In evaluating the applicability and accuracy of various energy functionals (methods), it is important to include spin-polarized solutions. For example, it was pointed out very recently[25] that the HSE functional gives wrong ground state solutions for both the R and the M_1 phase if spin-polarization is allowed, in contrary to a recent claim [23] that the HSE functional is able to predict the electronic properties of both phases.

The complexity of the physics of VO_2 goes beyond that of d electrons: The behavior of d electrons in this system also depends sensitively on the underlying crystal structure, and seemingly minor structural changes may result in profound changes in electronic properties. This poses a stringent test to the accuracy and applicability of DFT based electronic structure methods, and subtle differences in energy functionals may result in drastically different theoretical predictions. In the following, we first examine the relative phase stability (including different magnetic and structural phases) within DFT using different levels of energy functionals.

Figure 2 shows the relative total energy (rescaled for one VO_2 formular unit) calculated using different energy functionals for the R, M_1, and M_2 phases of VO_2 with different magnetic (i.e., NM, FM, and AFM) structures. Corresponding numerical values are listed in Table I. Local magnetic moments for magnetic phases are also listed in the table. Within each method, the energy of the NM solution for the R phase is taken as the reference. Different magnetic states of the R, M_1, and M_2 phases are realized using initial charge densities with different spin-polarization. Note that we do not consider temperature effects, therefore phonon contributions to free energy is neglected. Phonon contribution to free energy is expected to be small [43] compared with the energy differences listed in Table I.

Several rather unexpected and surprisingly aspects are worth mentioning. With the exception of the LDA result for the M_1 phase, a strong tendency of forming local magnetic moments is observed, especially with the DFT+U and HSE functional. The LDA gives an FM solution for the M_1 phase with a local magnetic moment of about 0.4 μ_B/V atom, but with a slightly higher energy (by about 1.5 meV) than the NM solution. Also, within the LDA, the AFM solution is not stable for both the R and the M_1 phases. If we start the calculation with an AFM charge density, it converges to a NM solution. However, the LDA does give a low energy ground state solution with local magnetic moments for the R and M_2 phases.

All other functionals strongly favor the formation of local magnetic moments for all three phases. Formation of local magnetic moment results in an energy gain ranging from about 40 meV (PBE) to about 400 meV (HSE) for the M_1 phase with either FM or AFM ordering. For the R phase, allowing the formation of local magnetic moments lowers the energy of the system by about 30 meV calculated with the LDA, 100 meV with the PBE functional, and over 600 meV with the HSE functional. The LDA+U or PBE+U method, even with a fairly small U value ($U_{\text{eff}} = 2.0$ eV), also greatly enhances the tendency of magnetic moment formation for all three phases investigated.

We mention that the large energy difference between the FM and the AFM solution for the R and M_1 phases calculated using the PBE or the DFT+U functionals ($U_{\text{eff}} = 2.0$ eV) is not due to a strong magnetic coupling between local moments, but rather that the value of the local magnetic moments are very different for the two solutions. This suggests that the magnetic moments associated with these magnetic structures are not very localized compared with local moments in late transition metal oxides such as CoO or NiO. Finally, although the LDA+U, PBE+U, and HSE methods predict an insulating band gap for the M_1 phase, they all predict an FM or AFM ground state for the M_1 phase with a local magnetic moment of about 1.0 μ_B/V atom. This is clearly inconsistent with experiment. As it is pointed out in a recent paper [25], the HSE functional *cannot* describe the electronic structure of the insulating VO_2, contrary to an earlier claim [23].

As we mentioned earlier, although there are no fundamental arguments against the possibility of forming local magnetic moments in VO_2, so far only the M_2 phase has been confirmed to possess local magnetic moment. It appears that the lone d electrons of V atoms in the M_1 phase tend to form conventional singlet bonding pairs (analogous to an H_2 molecule), which prevents the formation of local moments. This bonding tendency in the M_1 phase is enhanced by a few factors, i.e., a local pairing structural distortion, a substantial pd hybridization, and by the fact that the vanadium $3d$ electrons are substantially more delocalized than those of late transition metals such as Co or Ni. It was also pointed out that the local Coulomb interaction might also join forces with the dimerization which enhances the bonding anti-bonding splitting. [44]

TABLE I. Calculated total energy of different VO_2 phases and magnetic states. Within each method (functional), the NM state for the R phase is set as a reference (i.e., set to zero). Corresponding local magnetic moments (M) are also listed. Note that only the V_1 atoms in the M_2 phase have magnetic moments.

		LDA			LDA+U			PBE			PBE+U			HSE		
		NM	FM	AFM	NM	FM	AFM	NM	FM	AFM	NM	FM	AFM	NM	FM	AFM
R	E (meV)	0.0	-29.0	–	0.0	-176.6	-42.1	0.0	-101.2	-11.8	0.0	-289.3	-301.7	0.0	-542.5	-645.5
	M (μ_B)	0.0	0.94	–	0.0	1.13	0.75	0.0	1.05	0.59	0.0	1.12	0.93	0.0	1.06	0.95
M_1	E (meV)	46.2	47.7	–	4.1	-59.4	-100.1	20.7	-20.2	14.0	-35.7	-169.7	-257.4	-230.9	-505.9	-626.0
	M (μ_B)	0.0	0.38	–	0.0	1.10	0.78	0.0	1.03	0.48	0.0	1.15	0.87	0.0	1.04	0.91
M_2	E (meV)	97.9	80.2	92.4	69.8	-70.4	-81.6	65	-12.5	18.3	25.3	-218.8	-212.7	-133.2	-567.6	-516.5
	M (μ_B)	0.0	0.88	0.54	0.0	1.09	0.91	0.0	0.99	0.80	0.0	1.14	0.95	0.0	1.05	0.98

Although possible magnetism in the R phase is less discussed so far, temperature dependent magnetic susceptibility measurement [45] of VO_2 shows a sudden jump at the MIT which cannot be attributed to simple Pauli susceptibility from conducting electrons. Formation of local magnetic moments in the R phase would naturally explain this sudden jump in magnetic susceptibility. Therefore, it is plausible that the R phase VO_2 is a paramagnetic metal with local moments or a weak ferromagnet with a T_C well below the MIT temperature. Further experiments will help to clarify this issue.

Regardless of the possibility of local moment formation in the R phase VO_2, none of the methods (i.e., LDA, PBE, LDA+U, PBE+U, and HSE) are able to reproduce a correct low temperature ground state (i.e., NM M_1 phase) for VO_2. Another intriguing observation from these results is that subtle differences in energy functionals (e.g., LDA v.s. PBE, or LDA+U v.s. PBE+U) may give rise to drastic different conclusion about the relative phase stability. These results further strengthen the notion that VO_2 is on the verge of multiple instabilities with comparable (and small) stabilization energies. These rather surprising and unexpected results prompt us to examine in more detail the electronic structure of VO_2 and the competition between various degrees of freedom and energy stabilization mechanisms, with the hope that these intriguing and contradicting results can be reconciled.

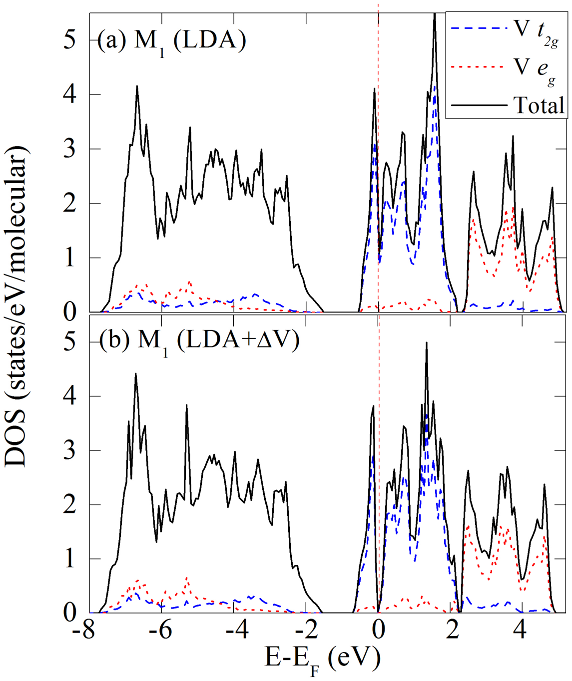

FIG. 3. (color online) The projected and total DOS of NM M_1 phases calculated within the LDA and the LDA+ΔV method with $\Delta V = 0.5$ eV as discussed in the text.

B. Electronic structure of VO_2 revisited

A simple model for the band structure of VO_2, first proposed by Goodenough [46], is still very useful in understanding qualitative features of the electronic properties of this material. In the R phase, crystal field effects splits the V $3d$ levels into higher and unoccupied e_g states (derived from d_{xy} and $d_{3z^2-r^2}$) and lower partially occupied t_{2g} states (derived from $d_{x^2-y^2}$, d_{xz}, and d_{yz} orbitals), see Fig. 1. Note that since VO_2 does not have the full symmetry of a regular octahedron, these notations are only approximate. The V-V dimerization in the M_1 phase enhances the bonding of the $d_{x^2-y^2}$ orbitals to form fully-filled valence bands. As a result, a band gap develops between the $d_{x^2-y^2}$ derived occupied states and the d_{xz} and d_{yz} derived unoccupied states, which has been qualitatively verified by experiments.[15] Even in this simple model, it is evident that cooperative changes in structural and electronic properties, i.e., pairing distortions and rearrangement of degenerate orbitals and their occupation, are the key driving force behind the MIT. In particular, the occupation of the $d_{x^2-y^2}$, d_{xz}, and d_{yz} states plays a central role.

In its simplest picture, the $d_{x^2-y^2}$ derived state shall be fully occupied, whereas d_{xz} and d_{yz} shall be unoccupied. However, this simple model does not take into account the pd hybridization and the mixing between d derived e_g and the t_{2g} states due to the symmetry lowering as shown in Fig. 3 (a), which shows the density-of-states (DOS) and the projected DOS (PDOS) for the M_1 phase calculated within the LDA. These hybridizations distort the simple band structure described in this model. Still, the occupation of the aforementioned d orbitals must be carefully examined. Errors in the calculated d-occupation will have several consequences. First, a small uncertainty in d-occupation directly results in an uncertainty in the calculated total energy through the definition of the energy functional. Second, a change in the d occupation will modifies the nature and the strength of the bonding in this system. Since the energy involved in determining the relative phase stability is rather small (a few tens of meV), it is not surprising that a small error (or uncertainty) will result in a completely different conclusion about the relative stability of various phases of this system.

The deviation in the calculated d occupation may be a direct result of the approximation made in the energy functional. It may also be a result of the well-known band gap problem related to local or semi-local energy functionals (e.g., LDA or PBE). This is because in the case of small band gap materials like the M_1 phase of VO_2, the well-known "band-gap" problem may result in a small overlap between the valence and the conduction bands, thus the occupation of low-lying conduction bands, as shown in Fig. 4. Within the LDA functional (or the PBE functional), an energy gap nearly develops for the M_1 phase (see Fig. 4 (a)). However, there is still a substantial overlap between the valence and the conduction bands. This overlap results in the occupation of a small portion of conduction bands, and the deoccupation of a small portion of the valence bands, which naturally leads to an error in the occupation of the d orbitals, especially the three t_{2g} orbitals (i.e., $d_{x^2-y^2}$, d_{xz}, and d_{yz}). This erroneous occupation of relevant bands may not have significant effects for sp semiconductors such as Ge, but could pose a serious problem for more localized d systems. Again, the extremely small energy scale involved in this problem poses a daunting challenge to existing electronic structure methods (functionals).

C. Tuning the orbital occupation through an orbital-dependent potential

Here we do not attempt to improve the *accuracy* of a particular energy functional. Instead, we propose a practical mean to adjust (tune) the d-occupation and investigate the relative phase stability as the d-occupation is varied. As discussed earlier, the redistribution of the d-occupation of $d_{x^2-y^2}$, d_{xz}, and d_{yz} orbitals is critical for the development of a band gap in the M_1 phase. Therefore, we introduce an energy functional with an additional term that will bias the occupation of selected d orbitals, in particular, the d_{xz} and d_{yz} orbitals:

$$E_{\mathrm{DFT}+\Delta V} = E_{\mathrm{DFT}} + \Delta V \cdot (n_{xz} + n_{yz}), \tag{1}$$

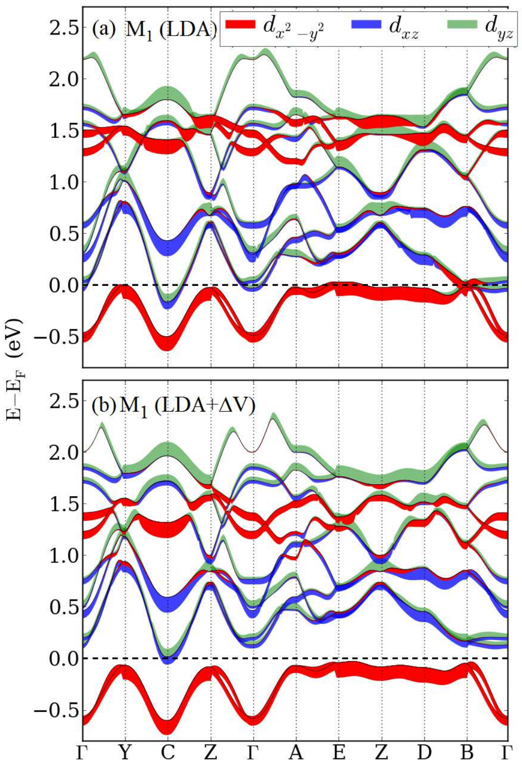

FIG. 4. (color online) Projection of band wave functions on to the three t_{2g} orbitals (i.e., $d_{x^2-y^2}$, d_{xz}, and d_{yz}) of the M_1 phase of VO_2 calculated within (a) the LDA and (b) the LDA+ΔV (ΔV = 0.5 eV) method as discussed in the text. The width of the shaded thick lines indicates magnitude of the projection.

where n_{xz} and n_{yz} are the occupation of the d_{xz} and d_{yz} orbitals. This corresponds to introducing an additional potential to the Kohn-Sham equation:

$$\begin{aligned}(H_{\mathrm{DFT}} + \Delta V(|d_{xz}><d_{xz}| + |d_{yz}><d_{yz}|)\psi_{nk}> \\ = \epsilon_{nk}|\psi_{nk}> .\end{aligned} \tag{2}$$

In the following, we will call this revised functional LDA+ΔV. Obviously, if ΔV in eq. (1) is positive, this functional will suppress the occupation of d_{xz} and d_{yz} orbitals by shifting the relevant states upwards.

This potential is similar to a scissors-shift operator used in some small gap semiconductors for which DFT-based calculations are not able to open an energy gap. However, the potential we introduced focuses in particular the d_{xz} and d_{yz} derived states. The hope is that, with this orbital-biased potential, the slight overlap between the valence and conduction band can be removed, and the d-occupation can be more faithfully reproduced. In fact, with a reasonable ΔV ($\sim$ 0.5 eV), an energy gap does develop for the M_1 phase, as shown in Fig. 4 (b) and Fig. 3 (b). This band gap opening naturally removes the occupation of the lowest conduction bands and restores the full occupation of valence bands of the M_1 phase. If this procedure indeed improves the calculated charge

TABLE II. Occupation of the three t_{2g} orbitals in the M_1 phase of VO_2.

	$E < E_F - 1.5eV$			$E_F - 1.5eV < E < E_F$			$E < E_F$		
	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xz}	d_{yz}	$d_{x^2-y^2}$
M_1(LDA)	0.338	0.381	0.233	0.118	0.083	0.601	0.456	0.464	0.834
M_1(LDA+U)	0.316	0.355	0.242	0.042	0.019	0.702	0.358	0.374	0.944
M_1(LDA+ΔV)	0.315	0.354	0.236	0.047	0.023	0.691	0.362	0.377	0.927

density of the system, we would then expect a better description of the ground state properties within DFT. And hopefully, a correct description of the relative phase stability of VO_2, i.e., $E(M_1) < E(R) < E(M_2)$, can be achieved.

Table II shows the occupation of the three t_{2g} orbitals of the M_1 phases calculated with the LDA, LDA+U ($U_{\text{eff}} = 2.0$ eV), and LDA+ΔV ($\Delta V = 0.5$ eV) functionals. We first integrate the d-occupation up to the pd gap. This d-occupation arises from oxygen p derived bands due to pd hybridizations. The occupations from the d derived bands are shown in middle columns, and the last three columns show the total d-occupation. As it can be seen from the table, the introduction of an orbital-biased potential slightly depresses the occupation of the d_{xz} and d_{yz} orbitals, and enhances the occupation of the $d_{x^2-y^2}$ orbitals. Although these changes seem insignificant, they have profound effects on the calculated relative phase stability.

Interestingly the LDA+U method gives very similar occupations as those calculated from the LDA+ΔV method. The LDA+U functional also enhances the occupation of the $d_{x^2-y^2}$ orbital in the NM M_1 phase, as shown in Table II. The changes in d-occupation calculated within the LDA+U method are nearly the same as those realized within our proposed LDA+ΔV scheme. However, the screened on-site HF-like exchange included in the LDA+U method strongly favors the formation of magnetic moment in this system, a result that clearly disagrees with experiment. Therefore, one justification for the introduction of the ΔV term is to produce a more faithful d-occupation without resorting to a (screened) Hartree-Fock (HF) exchange potential such as that included in the LDA+U or the HSE method.

Figure 5 shows the calculated energy for all three phases of VO_2 with and without spin-polarization within the LDA with the introduction of an orbital-biased potential discussed above. Note that we use the energy of the FM R phase as the reference (i.e., we set $E_{\text{R/FM}} = 0$ in the plot). As discussed earlier, the LDA ($\Delta V = 0$) clearly gives the wrong ordering of the relative phase stability, predicting the R phase to be the most stable phase at low T. As ΔV increases, the occupation of the d_{xz} and d_{yz} derived states is gradually reduced, and the energy of the M_1 phase decreases monotonically with respect to the R phase. Similar trend is observed for the M_2 phase. With a reasonable value of ΔV ($0.4 \sim 0.6$ eV), we recover the correct ordering of the phase stability, i.e., $E(M_1) < E(R) < E(M_2)$, as shown in Fig. 5 with the shaded area. In particular, the ground state solution for the M_1 phase is now NM and the ground state solution for the M_2 phase is the AFM state. However, the FM solution for the R phase remains lower in energy than the NM solution, and futher investigation (both theoretical and experimental) is needed before this issue can be resolved. Moreover, the energy difference between the M_1 and the R phase is now less than 50 meV. This is consistent with the experimental latent heat of about 44 meV including phonon contributions. [43]

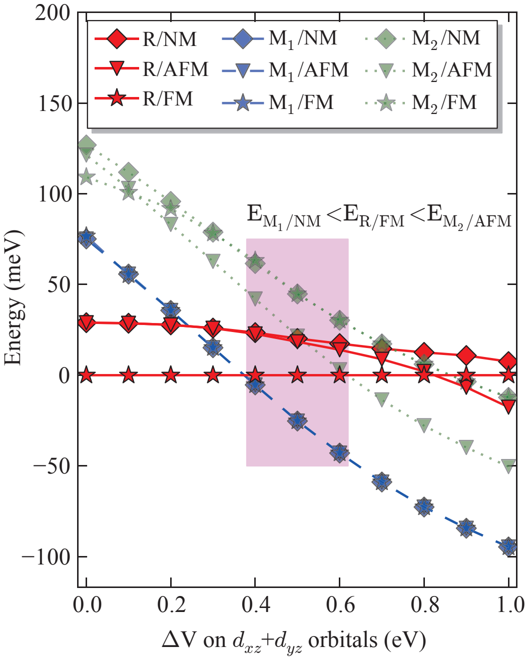

FIG. 5. (color online) The relative energetic stability of all VO_2 phases with different magnetic states with respect to perturbations on d_{xz} and d_{yz} orbitals based on LDA functional. The energies of FM R phase are set as references. The shaded area indicates the region in which a correct ordering of the relative phase stability is recovered.

We would like to mention that another hint for this orbital-dependent potential comes from a study by Tomczak *et al.*. [44] In their study, Tomczak *el al.* showed that by introducing static shifts (with parameters calculated using a cluster DMFT method) to the a_{1g} and the e_g^{π} states, the calculated DOS within their LDA+Δ scheme resembles that calculated using a more sophisticated cluster DMFT method. The magnitude of the static shift Δ used in their work is comparable to the value used here. Note that our calculation, although being phenomenological in nature, goes beyond an effective low energy description. In addition, the *pd* hybridization effects are fully included in our calculation.

In a very recent work, Zhu *et al.* [47] studied the relative phase stability of VO_2 using a modified Becke-Johnson (mBJ) exchange potential. [48] It was shown that using this functional, the magnetic solutions are not stable (in other words, they have a higher energy than the spin-unpolarized solution). In this regard, the mBJ potential might be a better choice than the LDA or GGA potential for calculating the electronic properties of VO_2. However, Zhu *et al.* did not investigate the M_2 phase of VO_2, which has an AFM ground state. In fact, we have done a calculation of the M_2 phase VO_2 using the mBJ functional. Surprisingly, the mBJ functional wrongly predicts an NM ground state for the M_2 phase (which, again, has an AFM ground state), with the NM soultion being lower in energy than the AFM solution by about 160 meV. So it appears that the mBJ functional indiscriminatly supress the formation of magnetic moments, at least in the case of VO_2. Therefore, although there is some interest in this newly proposed potential, it has certain limitations. In fact, it has already been pointed out that the mBJ functional sometimes give worse results than the LDA or GGA functional [49, 50]. More work is needed before we can have a better understanding of this new potential.

IV. SUMMARY

In summary, we have investigated the relative phase stability of various phases (including structural and magnetic) of VO_2. We find that none of the functionals (i.e., LDA, PBE, LDA+U, PBE+U, and HSE) are able to reproduce the correct low temperature ground state of VO_2. Although the LDA+U, PBE+U, and HSE methods are able to open a band gap for the M_1 phase, they all predict a magnetic (either FM or AFM) ground state. These results suggest that the HSE and DFT+U method overestimate the localization effects of the d electrons in this system. We further investigate the implication of the d-occupation on the calculated relative phase stability. We suggest that a more faithful d-occupation (thus the overall charge density) can be achieved by introducing an orbital-biased potential in the calculation. The introduction of such a potential removes the overlap between the valence and conduction bands, thus avoiding the erroneous occupation of the d_{xz} and d_{yz} derived conduction bands. It also restores the full occupation of the $d_{x^2-y^2}$ derived valence band. With such a procedure, the correct ordering of the energy of difference phases of VO_2 is reproduced. It appears that VO_2 is such a delicate system in which a subtle change in d occupation can result in profoundly different theoretical results.

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