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Theoretical study of the new compound VO_2 (D)

B.Y. Qu [a], Liang Liu [b,c], Y. Xie [b,c], B.C. Pan [a,c,*]

[a] Department of Physics, PR China
[b] Department of Chemistry, PR China
[c] Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026, PR China

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ABSTRACT

The structural feature and the electronic properties of the newly synthesized compound VO_2 (D) are theoretically studied. Our calculations reveal that all of the V ions in VO_2 (D) form two types of chains. One of the chains contributes to the electronic states near the Fermi level, but the other one almost does not yet. Such discrepancy is attributed to the different strength of the V–O bonds belonging to the different chains. Furthermore, it is found that one type of the V–V chains characters the antiferromagnetic feature, whereas the other one is almost non-magnetic. So, the compound VO_2 (D) is of one-dimensional antiferromagnetic ordering. In addition, we propose that the structural transition from VO_2 (D) to the rutile-type VO_2 (R) is driven by three vibrational modes. The transition temperature is estimated to be about 600 K, being consistent with experiment.

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1. Introduction

The vanadium dioxide (VO_2) has been attracted widespread attentions for about half a century due to its reversible metal-insulator transition (MIT) at 340 K [1]. It has been established that this phase transition underwent a structural change from the high-temperature rutile-type VO_2 (R) which possessed the tetragonal structure to the low-temperature monoclinic VO_2 (M). The underlaying mechanisms, whether the Peierls transition or (and) the electron-correlation-driven Mott transition, associated with this MIT were under intensive study [2–7]. On the other hand, such a phase transition accompanied a significant change in optical and transport properties [8,9]. This makes it promising applications in electric switches, smart optical windows, and the other electronic devices [10,11].

Except for VO_2 (R) and VO_2 (M), several other phases such as VO_2 (A) and VO_2 (B) were found during producing the precursors of the vanadium dioxide compounds. More recently, Liu and coauthors [12] have observed a new phase of VO_2, which was notated as VO_2 (D). Experiments indicated that this new phase possessed the monoclinic structure with an energy gap of about 0.3 eV, and characterized an antiferromagnetic feature. In addition, it is found that VO_2 (D) could transform to VO_2 (R) at about 593 K. Obversely, this is another metal-insulator phase transition in the family of vanadium dioxide. However, experiments could not provide more detailed intrinsic properties such as the atomistic structural feature and the electronic structures. Especially, the driving force associated with the phase transition from VO_2 (D) to VO_2 (R) is also a puzzle. Apparently, revealing the detailed structural features and the electronic structures around the Fermi level as well as the origin of the phase transition from VO_2 (D) to VO_2 (R), is of benefit to gain deep insight into the diversity of the structure and the physical properties for the vanadium dioxide compounds.

In this work, by performing the first-principle calculations, we study the structural, electronic and the vibrational properties of VO_2 (D). Our calculations suggest that the V ions in the new phase have different local bonding features and these bonding features sensitively affect the hybridizations between the V and O ions, resulting in a larger difference in the electronic and the magnetic properties of the V ions. More importantly, we propose that the phase transition from VO_2 (D) to VO_2 (R) is probably driven by three vibrational modes.

2. Computational details

The density functional theory (DFT) calculations are performed using the projector augmented wave (PAW) pseudopotentials as implemented in the VASP code [13,14]. The electronic exchange and correlation potential is expressed using the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) formula [15]. Since DFT within the local density approximation (LDA) or GGA often yields qualitatively incorrect results for the narrow d band electron systems, it is necessary to employ the DFT+U methodology to improve the theoretical predictions of the d electron systems. Here, the scheme suggested by Liechtenstein et al.

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[*] Corresponding author at: Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026, PR China. Tel.: +86 0551 3606385.

E-mail address: bcpan@ustc.edu.cn (B.C. Pan).

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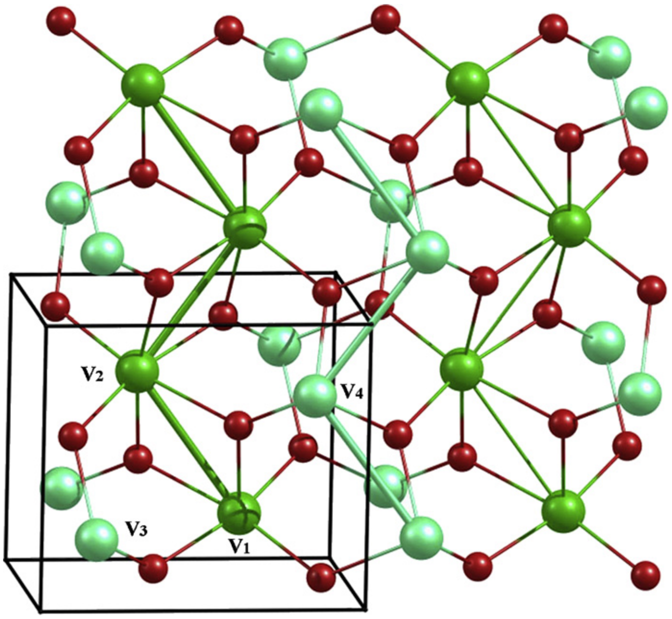

Fig. 1. (Color online.) The structure of VO_2 (D). The large and small balls represent the V and O ions, respectively. The parallelepiped enclosed by the black lines denotes the unit cell.

Table 1
The optimized equilibrium lattice constants, *a*, *b*, and *c* (in Å), the angle between lattice vectors $\vec{a}$ and $\vec{c}$ (β) of the compound VO_2 (D) in the AFM state. The experimental ones are also listed for comparison.

	a	*b*	*c*	β
This work	4.584	5.580	4.956	89.82
Expt. [12]	4.613	5.645	4.869	89.43

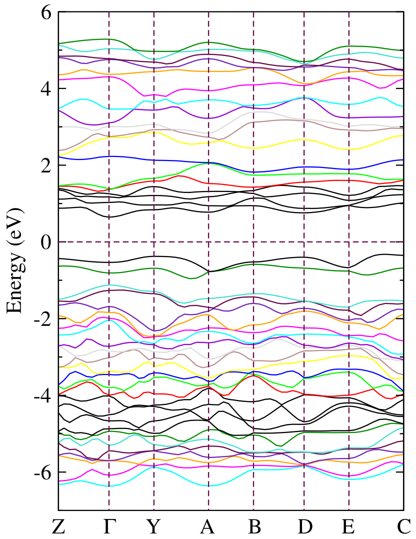

Fig. 2. (Color online.) The calculated band structure of VO_2 (D). The Fermi level is set at 0 eV.

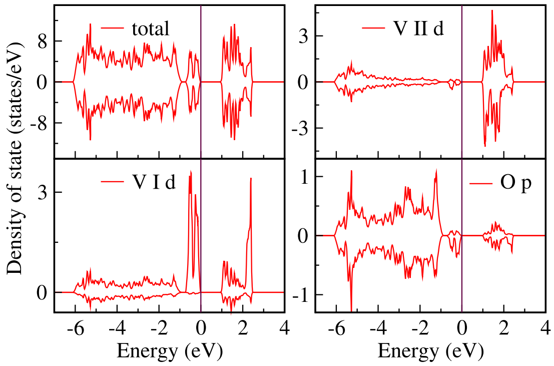

Fig. 3. (Color online.) The calculated TDOS and PDOS of VO_2 (D), where VId and VIId respectively represent the d states of V ions in chain-I and chain-II, and Op represents the p states of O ions. The vertical lines denote the Fermi level.

[16] is used, where the Coulomb parameters U and the exchange parameters J are introduced. After several attempts with different values of U and J, we find that, with using the values of 3.7 eV (U) and 0.8 eV (J), our calculated basic features such as the lattice constant, the bond lengths between ions and the band gap of the compound match from experiment. The electronic wavefunctions are described by a set of plane wave functions that are selected by an energy cutoff of 600 eV. The valence electrons and the local magnetic moments of the ions are determined by the Wigner Seitz radii chosen in the VASP code.

The Brillouin-zone integrations are performed using the Monkhorst–Pack grids, where the ($6 \times 6 \times 6$) grids are adopted for the unit cell of VO_2 (D) that is shown in Fig. 1. In Fig. 1, the V and O ions are denoted with the large and small balls, respectively, and the parallelepiped enclosed by the black lines denotes the unit cell. The optimized structure is used to perform phonon calculation at Γ-point using the frozen phonon method [17], by which the vibrational frequencies and the corresponding eigenmodes are obtained.

3. Structural feature and the electronic properties

As a theoretical study, the compound of VO_2 (D) in the antiferromagnetic (AFM) state and in the ferromagnetic (FM) state is respectively concerned. In our treatment, the directions of the local magnetic moments of V ions are initially arranged to be antiparallel for the antiferromagnetic state and to be parallel for the ferromagnetic state. Our calculations show that the resulting energy of the AFM state is slightly lower than that of the FM one. This implies that the ground state is an AFM state, in agreement with the observation in experiment [12]. To go further, careful examining the optimal structure indicates that the optimal lattice parameters are close to the related experimental values, as listed in Table 1. Meanwhile, we find that the V ions arrange in zigzag chains, as marked with the bold lines in Fig. 1. According to the local bonding features of the V ions, these zigzag chains can be divided into two groups, which are respectively notated as chain-I and chain-II. As shown in Fig. 1, the chain-I is comprised by the V_1 and V_2 ions, and the chain-II by the V_3 and V_4 ions. In the chain-I, the distance of the nearest neighboring V ions is about 3.04 Å, and that in the chain-II is about 3.08 Å. In addition, the bond lengths of V–O bonds around the both chains are also different. For example, the bond lengths of V–O around the chain-I are 1.98 Å, 2.06 Å and 2.07 Å, respectively, while the bond lengths of V–O around the chain-II are about 1.79 Å, 1.90 Å and 2.04 Å. Obviously, the averaged bond length of V–O in the former case is longer than that in the latter case.

Usually, the different bonding features as mentioned above will affect the electronic states around the Fermi level. Thus, we move our eyes on the electronic structures of the system. As displayed in Fig. 2, the conduction band minimum (CBM) occurs at Γ-point, but the valence band maximum (VBM) does not locate at the Γ-point yet. So, the compound of VO_2 (D) is an indirect band gap material, with a gap value of about 0.9 eV. As we know, VO_2 may exhibit diverse phases. This is essentially attributed to the intrigue couplings between the valence states of the ions. For the concerned VO_2 (D) compound in this work, our calculated total and partial density of states (Fig. 3) show that the V 3d orbital significantly

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