

Correlation assisted metal-insulator transition in the high temperature tetragonal rutile vanadium dioxide

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Vanadium dioxide is a nonmagnetic metal in high temperature rutile phase and undergoes metal-insulator transition (MIT) upon the application of Coulomb interaction $U = 5$ eV. The insulating phase is ferromagnetic. By employing first principle electronic structure calculations implemented in the density functional theory, it has been found in the LDA approximations that d_{xy} , d_{yz} and $d_{x^2-y^2}$ states are almost degenerate and responsible for non opening of a gap in the close vicinity of Fermi level (E_F). In the LDA+U approximations, strong Coulomb interactions play crucial role in the MIT of VO₂ in the high temperature rutile phase. Application of Coulomb interactions increases orbital polarizations and hence static electron correlations for which $d_{x^2-y^2}$ state becomes completely occupied and shifted below E_F whereas, d_{yz} and d_{xz} states become empty and shifted above E_F resulting opening of a band gap near E_F . The hybridizations between occupied V- $3d_{x^2-y^2}$ and O-2p orbitals are responsible for observed ferromagnetic behavior of VO₂ in the insulating phase.

Keywords: Metal insulator transition (MIT), Rutile structure, Coulomb repulsion, Crystal structure of VO₂

1 Introduction

Vanadium oxides are important in the oxide electronic devices. Among all vanadium oxides, vanadium dioxide (VO₂) has been highly investigated^{1,2} as it shows a metal-insulator transition (MIT) near room temperature ($T_{MI} = 341$ K) accompanied by structural phase transition (SPT) from high temperature (HT) rutile phase to low temperature (LT) monoclinic phase. The properties arising from MIT in VO₂ have made it suitable for electrical, optical, thermal sensing and memory based electronics devices³. An abrupt increase in electrical resistivity over several orders of magnitude is observed even in a small decrease in temperature from T_{MI} . This large coefficient of electrical resistivity of VO₂ is compatible with device fabrication processes.

This material is a nonmagnetic metal in the HT rutile phase with tetragonal P4₂/mnm symmetry. The LT phase has monoclinic M1 (space group P2₁/c) and M2 (space group C2/m) structures those are insulating. The problem of MIT is acute for VO₂. The scenario of MIT in VO₂ was described either as predominantly a Peierls transition⁴ or as a Mott-Hubbard transition⁵.

A fascinating aspect that has largely been neglected in the discussions of MITs in transition metal oxides (TMOs) is the possible role of magnetic correlations

and especially the orbital structure of constituent TM ions⁶. However, the mechanisms of MITs in LT phases are very different. Formation of zig-zag type pairing of V-V atoms running in the c -direction is responsible for the observed MIT in M1 phase. The situation is different in M2 phase, where half of the V atoms form zig-zag pairs and the rest half form evenly spaced chains and behave as magnetic insulators. Both of the low temperature phases are regarded as Mott-Hubbard insulators rather than Peierls insulators^{7,8}. Although in all theoretical or experimental studies, the rutile VO₂ is observed metallic. This material encounters a transition from nonmagnetic metal to ferromagnetic half-metal upon the application of Coulomb interaction $U = 4$ eV with J value = 0.5 eV. This metal to half-metal transition in rutile VO₂ is of I_A type⁹.

The system is metallic in the up spin channel due to finite electron occupancy of V-3d bands at E_F . The hybridizations of V-3d and O-2p orbitals are responsible for ferromagnetic behaviour. Nevertheless the system is insulating in the down spin channel due to suppression of E_F below V-3d bands. In this study, MIT is observed even in the HT rutile structure upon the application of Coulomb repulsion $U = 5$ eV with J value = 0.5 eV. Coulomb repulsion plays crucial role in this MIT which pronounces due to V-3d_{2g} electron correlation effect. Application of $U = 5$ eV enables to open a gap $E_g \approx 0.17$ eV. Higher values of U

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broaden the gap. In this paper the origin of MIT in the HT rutile phase of VO₂ has been investigated and it has shown that Coulomb interaction plays crucial role in the observed MIT.

2 Method of Calculations

In the present study, first principles electronic structure calculations have been carried out those are implemented in the density functional theory¹⁰ (DFT). Local density approximations^{10,11} (LDA) and LDA with the inclusion of Hubbard-type Coulomb repulsion¹² U (LDA+ U) is taken into consideration. The Hubbard-type repulsive interaction (LDA + U) is taken into account to improve the description of electron correlations in the V-3d orbitals. Augmented spherical plane wave (ASW) is also employed which uses atomic sphere approximations¹³ (ASA). In the ASA scheme empty spheres were used in the open crystal structure of VO₂. The empty spheres are spheres those have no nucleus. The number of empty spheres used in this study is two such that the overlap between any pair of physical and empty spheres is less than 16%. The primitive unit cell of VO₂ in the rutile P4₂/mmn structure consists of one V and O site each. The lattice parameters used are $a = 4.5546 \text{ \AA}$ and $c = 2.8514 \text{ \AA}$ with V at $2a$ site (0, 0, 0) and oxygen at $4f$ site (0.3001, 0.3001, 0)¹⁴.

Self-consistent calculations were carried out both in LDA and LDA+ U approximations. A standard value $U = 4 \text{ eV}$ which reproduces the experimental semi-conducting band gap in the spin minority channel was used. Coulomb repulsions of 4 eV or more with J value = 0.5 eV were tested in the LDA+ U calculations to understand the characters of the bands clearly. Application of $U = 5 \text{ eV}$ enables to open a band gap of 0.17 eV while higher U values broaden the gap. The spin-orbit interactions are not taken into account while spin polarizations are allowed when necessary. Gnuplot and Xfig were used for graphical purposes.

3 Results and Discussion

3.1 Densities of states (DOS) calculation

The ongoing investigation of MIT in HT rutile VO₂ has been carried out with the densities of states (DOS) calculations in the LDA approximations. In this treatment, spin polarization is allowed for self-consistent calculations. The ground state energy calculated is -4392.1143 eV with zero effective magnetic moments. The individual magnetic moments per V and O atoms are also zero. So the material is

nonmagnetic in the absent of Coulomb interaction. In this case, orbital polarizations are negligible hence the static correlations are also negligible causing contribution of DOS both above and below E_F . The average valence of V atoms in the present compound is $4+$ (V^{4+}), i.e., the occupancy of the V-3d manifold is d^1 .

Figure 1 represents the total (black), V-3d (red) and O-2p (green) DOS in the LDA treatment for both spin channels. A peak at 1 eV and another near E_F (0.3 eV) are observed in this case. The number of electrons in both spin channels was found exactly the same. The DOS near E_F is predominantly due to V-3d character. Due to octahedral crystal symmetry, the states near E_F have t_{2g} character ($3d^1$), while the unoccupied E_g bands have higher energy and shifted above the Fermi level. The t_{2g} bands are separated by a small gap from E_g bands and from O-2p bands by an energy gap of about 1 eV. Total calculated DOS of 3d bands per V-atom at E_F is 1.45 (states/eV/f.u./spin) for both spin channels.

The t_{2g} bands have a small contribution below E_F and have major contributions above E_F , but have finite contribution at E_F , which means none of the three t_{2g} orbitals is fully occupied rather than they are partially filled causing hybridization between them. This hybridization arises from the delocalized electrons in t_{2g} orbitals causing orbital fluctuations at E_F . Due to these orbital fluctuations, three t_{2g} orbitals become degenerate. These orbital fluctuations are expected from weak static but strong dynamical correlations of 3d-electrons. Therefore, the system is metallic as no gap is observed at E_F . The E_g bands are practically

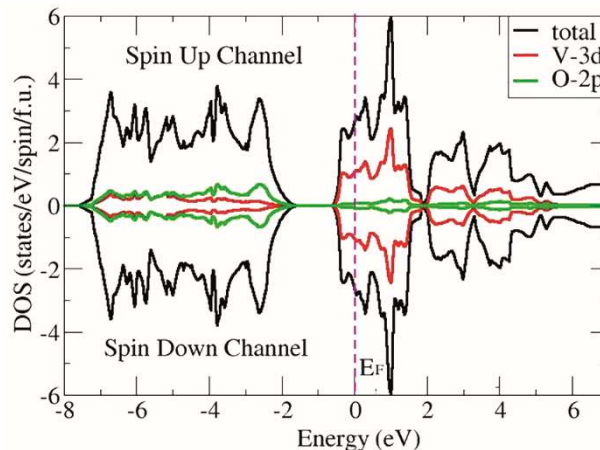


Fig. 1 — Calculated total (black), V-3d (red) and O-2p (green) densities of states (DOS) of VO₂ for LDA approximations. The system is metallic in both spin channels.

empty and are located far above E_F . The scenario remains exactly the same for both spin channels.

Next, let us concentrate on the LDA+U approach for the spin up channel using $U = 6$ eV. The total ground state energy calculated for $U = 6$ eV is -4391.4927 eV. Thus the total ground state energy increases which indicates the rise in static correlation effect. The total ground state magnetic moment calculated is $-2.0 \mu_B$ per f.u. and that calculated for V and O atoms are $-1.03 \mu_B$ (per V-atom) and $+0.03 \mu_B$ (per O-atom), respectively (see Table 1). Therefore, O-2p orbitals are strongly anti-coupled with V-3d orbitals. This anti-coupling gives rise to $p-d$ hybridization and is responsible for the ferromagnetic behaviour of VO₂ in the HT insulating phase.

The total (black), V-3d (red) and O-2p (green) DOS in the LDA+U scheme for both spin channels are represented in Fig. 2. It is obvious from Fig. 2 that DOS at E_F disappears and two peaks are observed at 1.93 and 1.33 eV, respectively. In this treatment different occupation of t_{2g} orbitals give rise to orbital dependent potential terms which shift different t_{2g} bands in opposite direction. The unoccupied E_g and t_{2g} bands are shifted above E_F while the occupied t_{2g} bands are shifted downward causing opening of a band gap of 0.59 eV. The total V-3d DOS calculated at E_F for each V atom is 1.82 (states/eV/f.u./spin) (Table 1). So, no evidence of charge ordering/separation between V atoms is observed. Therefore, charge ordering/separation is not responsible for the MIT in rutile VO₂. Hybridizations between O-2p and V-3d orbitals are also observed in the DOS (Fig. 2) calculations. The system remains insulating in the spin down channel. Band gaps observed for applications of different Coulomb interactions are listed in Table 1. It is evident from Table 1 that the ground state energy increases with the increase of Coulomb interaction

which enhances static correlations and hence orbital polarizations. The increase in static correlations is further responsible for the widening of the band gap.

3.2 Band structure calculations

To investigate the origin of metal MIT in the HT rutile VO₂ precisely, band structure calculations were performed both in the LDA and LDA+U (applying Coulomb interaction U) treatments. In the LDA scheme, the material is found metallic. It is evident from the orbital decomposed band structure calculations that d_{yz} and d_{xz} states are exactly degenerate due to equal electron contribution at E_F (Fig. 3(a)). On the other hand, the $d_{x^2-y^2}$ state has slightly higher electron filling at E_F (Fig. 3(b)). As a result, orbital fluctuations were observed between the partially filled d_{yz} and d_{xz} states. The empty d_{xy} and $d_{3z^2-r^2}$ states having higher energy are observed

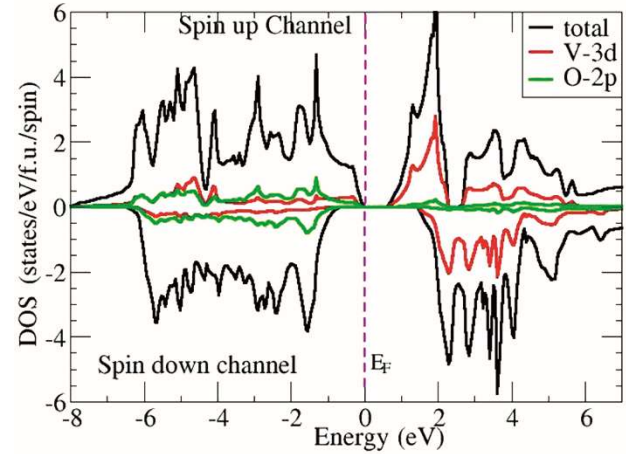


Fig. 2 — Calculated total (black), V-3d (red) and O-2p (green) densities of states (DOS) of VO₂ in the LDA+U approximations with $U=6$ eV. The system is insulating in both spin channels. The band gap observed is 0.59 eV. In this case $p-d$ hybridizations observed which are responsible for the ferromagnetic behaviour of VO₂.

Table 1 — Calculated ground state energies (eV), magnetic moments (μ_B) per V and O atom, total V-3d-DOS (states/eV/spin/f.u.) at E_F for up spin channel and band gaps (eV) using different Coulomb interactions U (eV). The total DOS for V-3d bands increases due to increase in electron occupation in the $d_{x^2-y^2}$ orbital.

Value of U	Ground state energy	Magnetic moment		Total V-3d DOS at E_F	Band gap	Conductivity
		μ_V	μ_O			
0	-4392.1143	0.0	0.0	1.45	0.0	Metallic
4	-4391.6923	-1.06	+0.04	1.88	0.0	Half-metallic
5	-4391.6018	-1.04	+0.03	1.85	0.17	Insulating
6	-4391.4927	-1.03	+0.03	1.82	0.59	Insulating
7.5	-4391.4100	-1.05	+0.03	1.82	0.98	Insulating

Note: f.u. = formula unit, μ_V = magnetic moments per V-atom, μ_O = magnetic moments per O-atom.

well above E_F . The situation remains exactly the same for both spin channels. So, no band gap is observed in the vicinity of E_F and the material is thereby metallic.

In the spin down channel, the system remains insulating as it was in case of $U = 0$ (LDA calculations). In the LDA+ U orbital decomposed band structure calculations for the spin up channel, it is revealed that the two empty states (d_{xy} and $d_{3z^2-r^2}$) are observed well above the Fermi level (not shown in figure). The d_{yz} and d_{xz} orbitals become completely empty and are uplifted from E_F (Fig. 4 (a)). The $d_{x^2-y^2}$ orbital is completely filled by the single $3d$ electron and pushed below E_F (as shown in Fig. 4 (b)). Therefore, a band gap is observed near the Fermi level. The band gaps calculated for $U = 5, 6$ and 7.5 eV are 0.17, 0.59 and 0.98 eV, respectively (Table 1).

The system, therefore, undergoes metal insulator transition for Coulomb interaction $U = 5$ eV. Orbital polarization increases with the raise in Coulomb interaction which is further responsible for increase in static correlation. Therefore, MIT in rutile VO_2

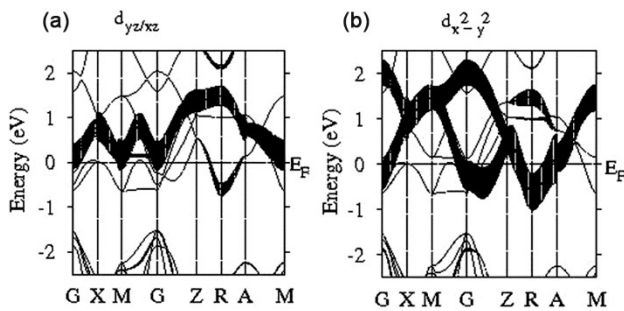


Fig. 3 — Partial band structure of $V-t_{2g}$ orbitals in LDA approximations. In this scheme, three t_{2g} bands almost degenerate and touch E_F causing non opening of band gap at E_F . The system is metallic in this case

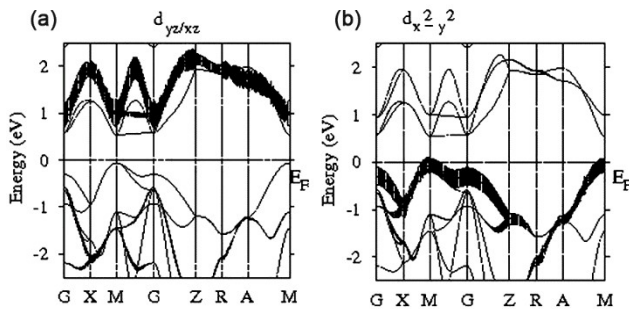


Fig. 4 — Partial band structure of $V-t_{2g}$ orbitals in LDA+ U approximations using $U = 6$ eV. In this case, the d_{yz} and d_{xz} states are exactly degenerate but they are empty and shifted upwards (a). The occupied $d_{x^2-y^2}$ states are shifted below E_F causing opening of the band gap. Further occupied $d_{x^2-y^2}$ states are strongly hybridized with $O-2p$ states which are responsible for ferromagnetic of VO_2 .

originates from electron correlations arising from Coulomb interaction. In the orbital decomposed band structure calculations, it is also observed that the occupied $d_{x^2-y^2}$ orbitals are hybridized with $O-2p$ orbitals resulting ferromagnetic behaviour of VO_2 in the insulating phase.

3.3 Structural analysis

Finally, structural studies have been performed, but no structural transition is observed in the MIT of rutile VO_2 even upon application of Coulomb interactions. It is emerged from both LDA and LDA+ U calculations, that four neighboring VO_6 octahedra form V-V rectangular four chain columns in the ab plane in which V atoms in the opposite diagonal positions ($z = 1$ or $z = 0$) lie in the same mirror plane, i.e., every mirror symmetry is preserved by V-atoms at the opposite diagonal positions (as shown in Figs 5 (a, b)). The calculated V-O distances in the VO_6 octahedra for all V-atoms in the opposite diagonal positions are 1.9211 Å for four equatorial oxygens and 1.9330 Å for two apical oxygens.

All V-atoms of the upper plane ($z = 1$) are connected to V-atoms of lower plane ($z = 0$) via an oxygen atom with $\langle \text{V-O-V} \text{ angle} = 95.828^\circ$. As a consequence, no tilting in the $\langle \text{V-O-V} \text{ angle}$ is observed resulting uniform V-V distances (2.8514 Å) running in the c -direction. Because of uniform V-V distances, no dimerization is observed. All V atoms of the upper plane is connected to V atoms of the lower plane by an equatorial oxygen with uniform V-O distance = 1.9211 Å. In the V-V rectangular four chain column, all the V-V atoms have uniform distance = 3.5220 Å, consequently, no tetramer forms in the insulating state of rutile VO_2 . Therefore, no structural transition is detected in the MIT of rutile VO_2 .

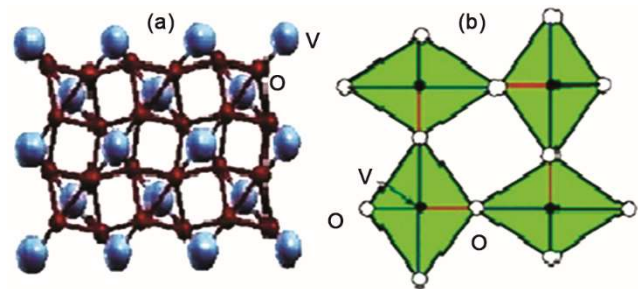


Fig. 5 — Crystal structure of VO_2 viewed from c -axis (a). The four neighboring V atoms form a V-V rectangular four-chain column and each V is surrounded by four equatorial oxygen and two apical oxygen. Schematic illustrations of four-chain columns for VO_2 are also shown (b) All V-atoms in opposite diagonal positions preserve mirror symmetries. As a result, all V-V distances are uniform, indicating no lattice dimerization within the crystal.

4 Conclusions

In conclusion, VO₂ is observed metallic in HT phase having nonmagnetic nature in the LDA treatment. The electron occupancies of $d_{yz/xz}$ and $d_{x^2-y^2}$ states are almost same and therefore they are exactly degenerate. The contributions of these states at E_F results non opening of a band gap. Orbital polarization and hence static correlation effect is weak in absence of Coulomb interaction. But the application of Coulomb interaction $U = 5$ eV increases the orbital polarization hence static correlation for which the $d_{x^2-y^2}$ state becomes completely occupied and shifted below while the unoccupied d_{yz} and d_{xz} states become empty and shifted above E_F resulting opening of a band gap near E_F . In the insulating state the occupied $d_{x^2-y^2}$ orbitals are hybridized with O-2p orbitals causing the ferromagnetic behaviour of VO₂.

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