Density functional study of metal to half-metal transition in the rutile vanadium dioxide VO_2

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Abstract

First principles electronic structure calculations implemented in the density functional theory have been employed to investigate the electronic and magnetic properties of VO_2 in the high temperature rutile structure with tetragonal $P4_2/mnm$ symmetry. The system is a nonmagnetic metal in the absence of Hubbard- type Coulomb interaction U. It is revealed in this study that the three V-t_{2g} states are degenerate due to partial electron filling which is responsible for orbital fluctuations between them. Due to these orbital fluctuations and sharing of single 3d electron by V-t_{2g} states, no band gap opens in the close vicinity of Fermi level. Nevertheless, upon the application of U = 4 eV, the system encounters metal to half-metal transition without any structural phase transitions exhibiting ferromagnetic behaviour. In spin up channel, d_{yz} and d_{xz} states remain degenerate while $d_{x^2-y^2}$ state is more occupied but are strongly hybridized with O-2p orbitals resulting ferromagnetism. In spin down channel, Fermi level is suppressed below the V-t_{2g} bands while V- 4s state is shifted above the Fermi level causing opening of a band gap near the Fermi level. Copyright © 2018 VBRI Press.

Keywords: Metal insulator transition (MIT), half-metal, coulomb repulsion, crystal structure of VO_2", transition metal oxides.

Introduction

The problem of metal insulator transitions (MITs) in strongly correlated electron systems containing transition metals (TMs) has attracted strong attraction in recent years. Among the best studied of such systems, VO_2 and V_2O_3 **[1, 2]** are in the centre of interest due to strong electron correlation effects. The problem is acute for MIT in VO_2. This property makes them suitable for application in electronic devices, thermo chromic devices, optical and holographic devices, sensors, actuators and power meter or thermometer **[3-7]**. The vanadium dioxide is a nonmagnetic metal in the high temperature (HT) tetragonal structure with $P4_2/mnm$ symmetry. The HT phase has rutile (R) structure such as CrO_2. The rutile VO_2 encounters MIT at 340K with a structural phase change **[1, 8]**. The low temperature (LT) phase is monoclinic (M1). Several explanations have been offered to explain the origin of MIT in VO_2. Among them, some group reported that the MIT in VO_2 in the monoclinic phase is triggered due to Peierls distortions [**9-12]** whereas; some other group reported Mott-Hubbard transition **[13-15]** is responsible for the observed MIT. Although, another monoclinic phase (M2) has been reported **[2]** to be insulating but the scenario of MIT in these two phases (M1 and M2) are very different. In the former structure, zig-zag type of pairing of all V-sites are observed in the c-direction while in the later structure, half of the V-sites are paired and the rest half of the V-atoms forms evenly spaced chains and behave as magnetic insulators. Both of the low temperature phases are regarded as Mott-Hubbard insulators rather than Peierls insulators **[13, 14]**. A recent x-ray absorption spectroscopy experiment reported that due to orbital switching in the V-3d states across the MIT reduce effective band width and the system become more one dimensional which is more susceptible to a Peierls like transitions **[16]**. Perhaps in all the theoretical or experimental studies the rutile VO_2 is found to be metallic in HT phase but in this paper it has shown that metal to half-metal transition is observed in the rutile structure of VO_2 under the application of Coulomb repulsion of U = 4 eV with j value = 0.5 eV where Coulomb repulsion plays crucial role in metal to half-metal transition in VO_2.

A half-metal is a solid with an unusual electronic structure. Half- metals are metallic for electrons of one spins whereas, they are insulating (i.e. a gap at the Fermi level (E_F) for the opposite spins in the spin polarized densities of states (DOS) like semiconductors or insulators. In order to obtain only up spin (↑) or down spin (↓), one has to reorder the 3d and 4s bands by hybridization and by means of pushing of 4s bands up above (E_F) or depressing the Fermi level in the 3d band. As a result, a hybridization gap might be introduced at E_F for one kind of spin orientation. Two situations can be achieved by single electron orientation at E_F where there is a spin gap $\Delta_\uparrow$ for up spins or $\Delta_\downarrow$ down spins at E_F. Half metallic oxides for which 4s electrons are pushed above the Fermi level by hybridization with O-2p states are called I_A type when the number of d electrons are less than five and if the number of d- electrons are more than

five then it will be called I_B type half-metal, otherwise half metals tend to have *d-p* hybridization for which the d-states pushed below E_F (as in case of Sb). The metal to half-metal transition of rutile VO_2 is of I_A type with up spin electrons contribution from V-3dt_{2g} at E_F. In this compound, after application of Coulomb repulsion of U = 4 eV, the V- 4s states pushed above E_F and hybridization of V-3d and O-2p states takes place for up spin orientation but in case of down spin orientation the V- 4s states are shifted above E_F and the Fermi level is depressed below the V-t_{2g} states resulting a spin gap in the vicinity of E_F.

Methods of calculations

In the present study, first principles electronic structure calculations were performed those are implemented on the density functional theory (DFT) **[17]**. Local density approximation (LDA) **[17, 18]** and LDA with Coulomb repulsion U (LDA+U**) [19, 20]** approximation (where coulomb repulsion U is taken into consideration) were employed. The Hubbard-type repulsive interaction (LDA + U) is taken take 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 approximation (ASA) **[21, 22]** in which empty spheres were used in the open crystal structure of VO_2. 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 VO_2 in the rutile structure is tetragonal in the space group $P4_2/mnm$. The primitive unit cell consists of one V and O site each. The lattice parameters used are $a = 4.5546A^0$ and $c = 2.8514A^0$ with V in 2a sites (0, 0, 0) and oxygen in 4f sites (0.3001, 0.3001, 0) **[11]**. Self-consistence calculations were carried out in the LDA and LDA+U approximations. A standard value U = 4 eV, which reproduces the experimental semi-conducting band gap in the spin minority channel in the HT rutile structure is used. The spin-orbit interaction is not taken into account and the spin polarization is allowed when necessary. Gnuplot and *Xfig* were used for graphical purposes.

Results and discussion

Densities of states (DOS) calculations

The ongoing investigation of metal to half-metal transition in the rutile VO_2 has been carried out with the densities of states (DOS) calculations in the LDA and LDA+U approximations. In both LDA and LDA+U schemes spin polarizations is allowed for self-consistent calculations. In the paramagnetic calculations the system is found to be metallic with non-magnetic nature. There is a large peak in the paramagnetic density of states at E_F (not shown in **Fig.**) ensuring metallic character. In the LDA calculations the rutile VO_2 remains in the metallic state with ground state energy - 4392.11431 eV with zero net magnetic moment. The formal valence of V in VO_2 is 4+ (V^{4+}) i.e. the available electron in the V-3d orbital is 1 (V-$3d^1$). The number of electrons in both spin channels was found exactly the same. The total magnetic moments calculated is zero yielding individual magnetic moments of V and O atoms are also zero. So, the system is non-magnetic in the HT rutile structure. The total (black), V-3d (red) and O-2p (green) DOS for both spin channels are presented in **Fig. 1**.

It is evident from **Fig. 1** that DOS in the close vicinity of E_F is predominantly due to V-3d electrons. The number of V-3d and O-2p electrons at the E_F is 1.45 and 1.98 states/eV/f.u./spin respectively for both spin channels. Crystal field splitting expected from the fact that the metal atoms are located at the centers of slightly distorted VO_6 octahedra. The V-3d manifold splits into e_g doublet and t_{2g} triplet bands. The t_{2g} band consists of d_{yz}, d_{xz} and $d_{x^2-y^2}$ sub-bands whereas, e_g band comprises of d_{xy} and $d_{3z^2-r^2}$ sub-bands. The V-t_{2g} bands are found in the energy window -0.6 eV to 1.86 eV and e_g bands are located in between 1.92 eV and 5.62 eV having very small gap between t_{2g} and e_g states. The t_{2g} states have a small contribution below E_F and have major contributions above E_F, that means none of the three t_{2g} states are fully occupied rather than they are partially filled causing hybridization between them due to delocalized electrons in the t_{2g} orbitals causing orbital fluctuations between them which are expected due to weak static but strong dynamical correlation of d-electrons. Therefore, the system is metallic as no gap is observed at E_F.

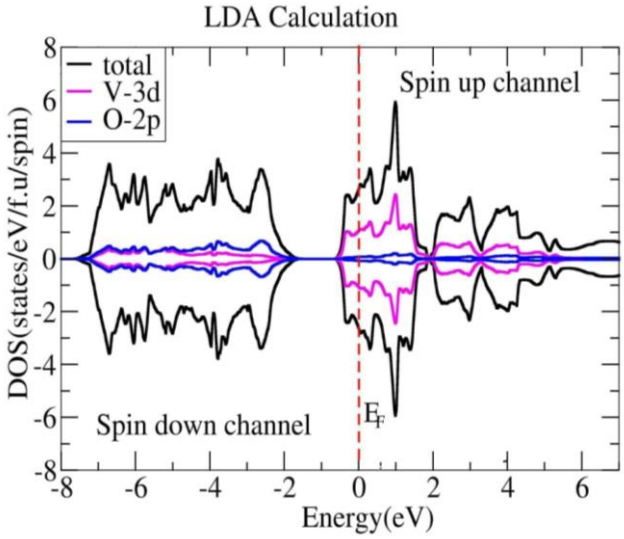

Fig. 1. Calculated total (black), V-3d (magenta) and O-2p (blue) densities of state (DOS) of VO_2 for LDA calculations. The system is metallic in both spin channels.

Table 1. The total ground state energy (eV) and magnetic moments (μ_B), magnetic moments per V and per O atom calculated in LDA and LDA+U (U = 4 eV) calculations.

Method	LDA	LDA+U
Ground State Energy	-4392.11431	-4391.69229
Total Mag. Mom.	0	-2.0
Avg. V-Mag. Mom.	0	-1.06
Avg. O-Mag. Mom.	0	+0.04

Next, DOS calculations have been performed by using Hubbard-type Coulomb repulsion U = 4eV with j value = 0.5 eV. The system is found to be metallic in the spin up channel whereas, it is insulating in the spin down channel i.e. metal to half-metal transition is observed on the application of U = 4 eV. The ground state energy calculated is -4391.69229 eV i.e. the application of U increases the ground state energy due to increase in correlation and hence repulsion between t_{2g} electrons. The total ground state magnetic moment calculated is -2.0 μ_B (see **Table 1**). So the half-metallic state is ferromagnetic. The individual magnetic moments calculated per V and O atoms are -1.06 μ_B and +0.04 μ_B respectively. Therefore, strong anti-coupling between V-3d and O-2p states are observed which is responsible for the ferromagnetic behaviour of VO_2.

The total (black), V-3d (red) and O-2p (green) DOS in the LDA+U calculations are shown in **Fig. 2**. The V-t_{2g} DOS dominate in the energy range -1.90 eV to 1.45 eV while e_g DOS is observed in the energy window 1.89 eV to 5.75 eV for spin up channel having a small energy gap ~ 0.45 eV between t_{2g} and e_g bands. Therefore, almost perfect energetically separation of the V-3dt_{2g} and e_g groups of bands is observed in spin up channel, which results from the octahedral crystal field splitting. The total numbers of V-3d, O-2p electrons at E_F are 1.89 and 1.98 states/eV/f.u./spin respectively (see **Table 2**). The number of V-d electrons increases due to hybridization between the occupied V-3d and O-2p bands resulting from octahedral crystal field splitting. The occupied O-2p states are located just below the Fermi level (–0.06 eV to -7.06 eV). From DOS calculations it is evident that none of the t_{2g} states is fully occupied by the single electron but orbital fluctuations between the t_{2g} bands decrease due to strong electron correlation. Further, strong hybridization between O-2p and V-3d orbitals is detected in the DOS calculations (**Fig.2**). This hybridization between O-2p and V-3d states are responsible for observed ferromagnetic behaviour of VO_2. The Fermi level is located almost in the deep valley of a pseudo gap from which one may anticipates that relatively minor changes in structure can push the occupied states down and empty states up, opening a gap in the spectrum and giving the gain in energy. This can be done by means of increasing of Coulomb repulsion U.

Further concentration is paid for the DOS calculations for spin down channel in the LDA+U calculations and a spin gap of $\Delta_\downarrow$ ~ 1.92 eV is observed in this channel. The calculated total V-3d (red) and O-2p (green) DOS at E_F are 0.89 and 2.04 states/eV/f.u./spin (see **Table 2**). Here hybridizations of V-t_{2g} and O-2p orbitals are not observed. The occupied O-2p bands are located in between -1.32 eV to -6.96 eV and the unoccupied V-t_{2g} and e_g bands are observed in the energy range 0.6eV to 8.0eV exhibiting small t_{2g}–e_g configuration mixing which implies slight distortions of the octahedra. The Fermi level in this case is depressed below the 3d-bands such that the t_{2g} bands lie above E_F whereas, the V-4s states are pushed above E_F causing a spin gap $\Delta_\downarrow$ ~1.92 eV at E_F. The e_g bands remain empty and shifted far above E_F. The $d_{x^2-y^2}$ states of V-t_{2g} bands are more occupied than d_{yz} and d_{xz} states.

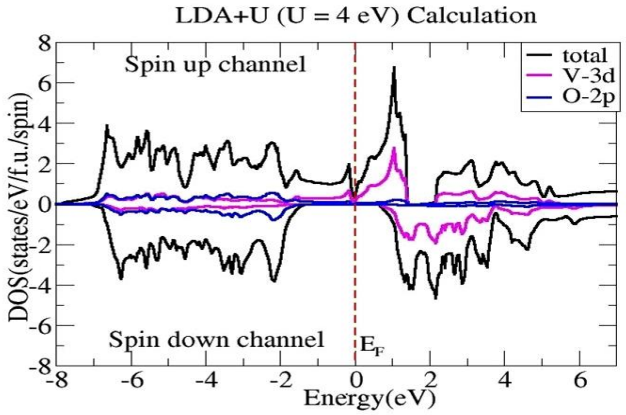

Fig. 2. Calculated total (black), V-3d (magenta) and O-2p (blue) densities of state (DOS) of VO_2 for LDA+U (U = 4 eV) calculations. In the spin up channel the system is metallic whereas insulating in the spin down channel.

Table 2. The calculate densities of statutes (DOS) in states/eV/f.u./spin in the LDA and LDA+U (U = 4 eV) calculations.

Method	LDA	LDA+U
	Total DOS for	
Up spin (↑)	13.05	13.86
Down Spin (↓)	13.05	12.05
	V-3d DOS for	
Up Spin (↑)	1.45	1.89
Down Spin (↓)	1.45	0.88
	O-2p DOS for	
Up Spin (↑)	1.98	1.98
Down Spin (↓)	1.98	2.05

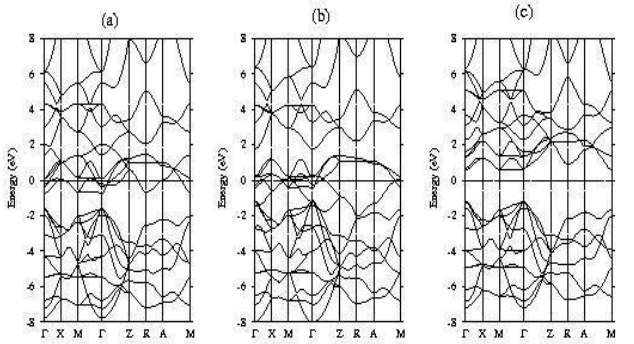

Fig. 3. Band dispersion structure of VO_2 in the LDA and LDA+U calculations for spin up and spin down channels. In the LDA calculations, both the channels are metallic (a). In the LDA+U calculations, the system is metallic in the spin up channel (a) and insulating in the spin down channel (b).

Band structure calculations

To elucidate the origin of metal to half-metal transition in the rutile VO_2 in HT phase, widespread band structure calculations were performed. In the LDA approach several groups of bands have been identified in the bands dispersion calculations (see **Fig. 1** and **Fig. 3**). In the energy range from -7.5 to -1.3 eV there observed 12 bands, which trace back mainly to O-2p bands but have a non-negligible contribution due to the V-3d bands. Thus

one can interpret the bands between -7.5 to -1.3 eV as the O-2p dominated. Bands are most easily counted along the direction Z-A where they are twofold degenerate. The next two groups, which extend from -0.6 to 1.86 eV and from 1.92 to 5.62 eV, contain six and four bands, respectively. They originate mainly from V-3d bands. The first six bands are originated from V-t_{2g} bands and the upper four bands are originated from V-e_g bands. The t_{2g} and e_g bands are separated by a very small gap in the LDA calculations. The scenario of band structure remains exactly the same in both spin channels. It is evident from the bands structure calculations that t_{2g} bands touch E_F which means there is no band gap at E_F; therefore VO_2 is metallic in this case. In the LDA+U approximations with U = 4 eV, the system remains metallic in the spin up channel but t_{2g} bands are shifted downwards but has finite contribution at E_F whereas unoccupied e_g bands are found well above E_F causing an energy separation of ~ 0.45 eV between t_{2g} and e_g bands. The scenario is different for spin down channel where the system is found insulating having a spin gap of $\Delta_\downarrow$ ~1.92 eV and the system encounters metal to half-metal transition due to the suppression of Fermi level below V-3d bands. In this case, no *p-d* hybridization is observed.

To understand the origin of metal to half-metal transition in VO_2 in the HT rutile structure preciously one has to investigate the orbital decomposed band dispersion calculations. In the LDA orbital decomposed band structure calculations, it has revealed that the two empty e_g states (d_{xy} and $d_{3z^2-r^2}$) are observed well above from E_F (not shown in **Fig. 4**) whereas the d_{yz} and d_{xz} states are exactly degenerate while the $d_{x^2-y^2}$ state has slightly higher electron filling (see **Fig. 4**). Hence none of the three t_{2g} states are fully occupied by the single electron (d^1) and hence the three t_{2g} states are almost degenerate resulting competition between them to be filled by the single electron (per V atom) indicating orbital fluctuations between the partially filled t_{2g} states at E_F. The d_{yz} and d_{xz} states are observed just above E_F while $d_{x^2-y^2}$ state has contribution both below and above E_F. However, all the three t_{2g} states touch the Fermi level which means there is no band gap at E_F and consequently VO_2 is metallic in this case.

Further, attention has been given for the orbital decomposed band structure calculations using U = 4eV. Here the picture is totally dissimilar for two spin channels (see **Fig. 5**). In the spin up channel the d_{yz} and d_{xz} states remain degenerate having very small hybridizations with O-2p orbitals. These states are found just above but still touching E_F. The occupancy of these states decrease by small amount causing upward shifting in the band structure. The occupancy of $d_{x^2-y^2}$ state is increased due to increase in electron correlations resulting raise in the number of electrons in the V-3d densities of states (**Table 2**). The $d_{x^2-y^2}$ state has higher contribution below the Fermi level comparing that above E_F. Nevertheless all of the t_{2g} states are still touching E_F. As an outcome, none of the three t_{2g} states are fully occupied and thus the system is metallic in spin up channel. The Fermi level is found almost in the deep valley of a pseudo gap (see **Fig. 2**).

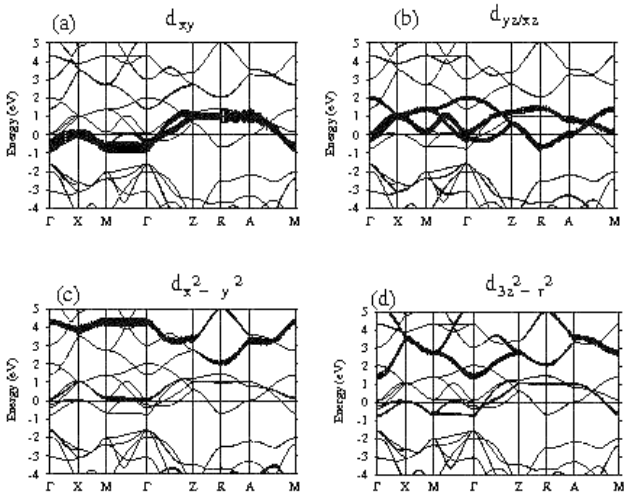

Fig. 4. Partial band structure of V-t_{2g} states in the LDA approximations. The d_{yz} and d_{xz} orbitals exactly degenerate (b) while d_{xy} state is slightly more occupied (a) in spin up/down channel. All the t_{2g} states are partially occupied and orbital fluctuation between them is observed. The material is thus metallic. All the e_g states ($d_{x^2-y^2}$ and $d_{3z^2-r^2}$) are found unoccupied (c and d).

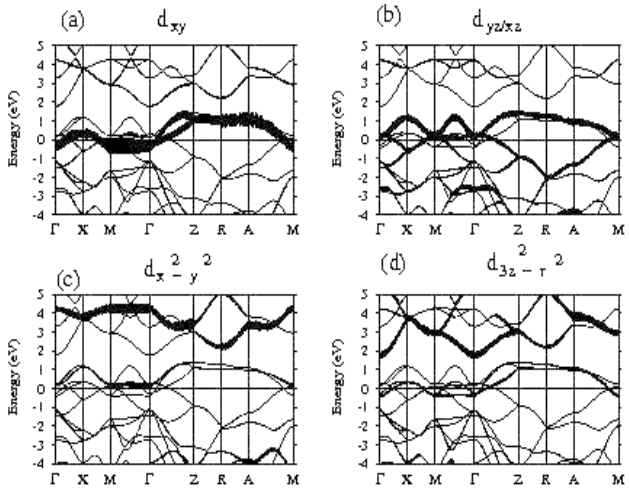

Fig. 5. Partial band structure of V-t_{2g} states in for spin up channel in the LDA+U (U = 4 eV) approximation. The d_{yz} and d_{xz} orbitals remain degenerate (a) and their occupancy increases slightly while occupancy of d_{xy} state remains almost the same (b). Hybridizations between V-t_{2g} and O-2p orbitals are observed. The two e_g states ($d_{x^2-y^2}$ and $d_{3z^2-r^2}$) are found unoccupied (c and d). The material is still metallic.

The empty e_g states are lifted upward from E_F, hence separation between t_{2g} and e_g bands is observed. Hybridizations between occupied V- $d_{x^2-y^2}$ and O-2p orbitals are detected. The *d-p* hybridization for $d_{x^2-y^2}$ state is higher comparing to d_{yz} or d_{xz} states. These *p-d* hybridizations imply strong anti-coupling between these states those are further responsible for ferromagnetic behavior of VO_2.

The optimization of t_{2g} states for down spin channel (**Fig. 6**) revealed that the Fermi level is suppressed downwards below the V-t_{2g} states. As a consequence, the partially filled degenerate d_{yz} and d_{xz} states are found above E_F. The components of $d_{x^2-y^2}$ states are also observed above E_F. The Fermi level is suppressed below

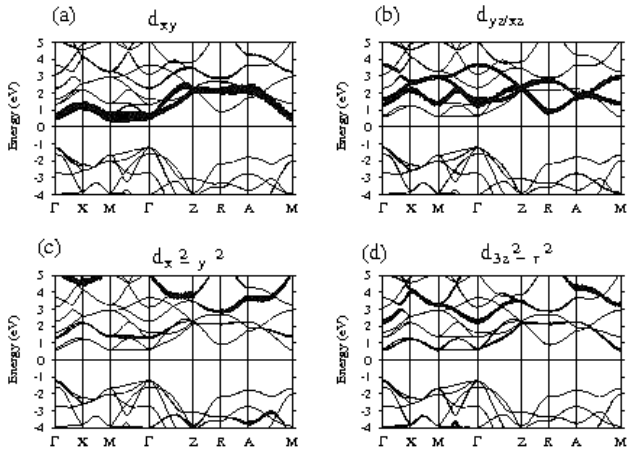

Fig. 6. Partial band structure of V-t_{2g} states in for spin down channel in the LDA+U (U = 4 eV) approximation. The Fermi level is suppressed below t_{2g}. As result, three V-t_{2g} (a and b) and two e_g (c and d) are found above E_F resulting opening of a spin gap ~ 1.92 eV. No hybridization between V-t_{2g} and O-2p orbitals is observed.

V-d states due to the octahedral crystal field splitting resulting from the strong electron correlations effect. The empty e_g states are pushed well above E_F. The t_{2g} states are now separated from the Fermi level due to suppression of E_F which results a spin energy gap in the close vicinity of E_F. Hybridizations between occupied t_{2g} and O-2p orbitals are absent here. Accordingly, the insulating state in the down spin channel indicates half-metallic character of VO_2**.** To make clear of this, the nature of V-4s band is also investigated further (see **Fig. 7**). In the non-polarized calculations (paramagnetic calculations) the Fermi level crosses the V-4s band that means contributions from both up spin and down spins are present there. In the LDA calculations, V-4s band is found near E_F which is touching E_F but having contributions both above and below E_F. In the LDA+U calculation the 4s band is found to move upward but still touching E_F for spin up channel. For spin down channel the scenario is completely different where 4s band is uplifted from E_F. Hence VO_2 exhibits metal to half-metal transition of I_A type (as the V-d electron is 1) in the HT rutile structure.

Conclusion

In conclusion, it has observed that the rutile VO_2 is metallic in HT phase having nonmagnetic nature. In the LDA calculation the oxide is observed metallic but upon the application of Coulomb repulsion U, it encounters metal to half-metal transition without structural transition. It has revealed in the present investigation that weak static but strong dynamical correlations between 3d electrons are responsible for orbital fluctuations between partially filled V-t_{2g} states. These orbital fluctuations between t_{2g} states and sharing of the single 3d electron by them results non opening of a gap at E_F. If Coulomb repulsion of U = 4 eV is applied then VO_2 encounters metal to half-metal transition due to downward suppression of E_F at which the less occupied d_{yz} and d_{xz} states up lifted from E_F. The components of $d_{x^2-y^2}$ state is also found above E_F. On the other hand, the V-4s states pushed above E_F causing opening a gap in the down spin channel. In the up spin channel the system is found metallic but strong *p-d* hybridization causes ferromagnetic behavior of VO_2.

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