ISSN: 2455-1848
International Journal of Innovative Research & Growth
A Peer Reviewed & Referred International Journal
Volume-3 Issue-9 July-2016
Impact Factor-2.58
www.iiirg.com, editor@iiirg.com

Metal To Half- Metal Transition In The Rutile Vanadium Oxide VO_2

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Abstract
The vanadium oxide VO_2 is a non magnetic metal in the high temperature rutile structure with tetragonal $I4_2/mnm$ symmetry. Using first principles electronic calculations implemented in the density functional theory it has revealed that, in the LDA calculations the three t_{2g} states are observed degenerate due to partial electron filling and orbital fluctuations between them is observed which is governed by the electron correlations. Due to these orbital fluctuations between the t_{2g} states no band gap opens at the Fermi level. Upon the application of Coulomb repulsion of U = 4 eV, the system encounters metal to half-metal transition without any structural transitions showing ferromagnetic behaviour. In the spin up channel, d_{yz} and d_{xz} states remain degenerate while d_x^2- $_y^2$ state is more occupied than the other two and are strongly hybridized with O-2p states resulting ferromagnetism whereas in the spin down channel the Fermi level is suppressed below the V-t_{2g} bands and V-4s states are shifted above the Fermi level causing opening of a spin gap at the Fermi level.

Keywords: Metal insulator transition (MIT), Half-metal, Coulomb repulsion, Crystal structure of VO_2.

1. INTRODUCTION

Metal insulator transitions (MITs) in strongly correlated electron systems containing transition metals (TMs) have 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 vanadium dioxide is a non magnetic metal in high temperature (HT) phase in the tetragonal structure with $I4_2/mnm$ 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, 3]. 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 [4-7] whereas; some other group reported Mott-Hubbard transition [8-10] 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 [8-9]. 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 been 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 repulsions play crucial role in metal to half-metal transition in VO_2. 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 the E_F and the Fermi level is depressed below the V-t_{2g} states resulting a gap at E_F. For up spin orientation the system remains in the metallic state as V-t_{2g} bands have finite contributions at E_F. This is probably the first example of metal to half- metal transition observed in the HT rutile structure of VO_2. The Metal to half-metal transition is dominated by strong V-3dt_{2g} electron correlations while the correlation effect in the absence of Coulomb repulsion is weak.

2. METHODS OF CALCULATIONS

In the present study, first principles electronic calculations were performed those are implemented on the density functional theory (DFT) [11], local density approximations (LDA) [11-12] and LDA with Coulomb repulsion U (LDA+U) [13] approximations where coulomb repulsion U is taken into consideration. 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) [14] in which empty spheres were used in the open crystal structure of VO_2. 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 $a = 4.5546\ A^0$ and $c = 2.8514\ A^0$ with V in 2a sites (0, 0, 0) and oxygen in 4f sites (0.3001, 0.3001, 0) [6]. 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. Coulomb repulsions of 4 eV or more with j value = 0.5 eV were tested in the LDA+U calculations to see the characters of the bands clearly. 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.

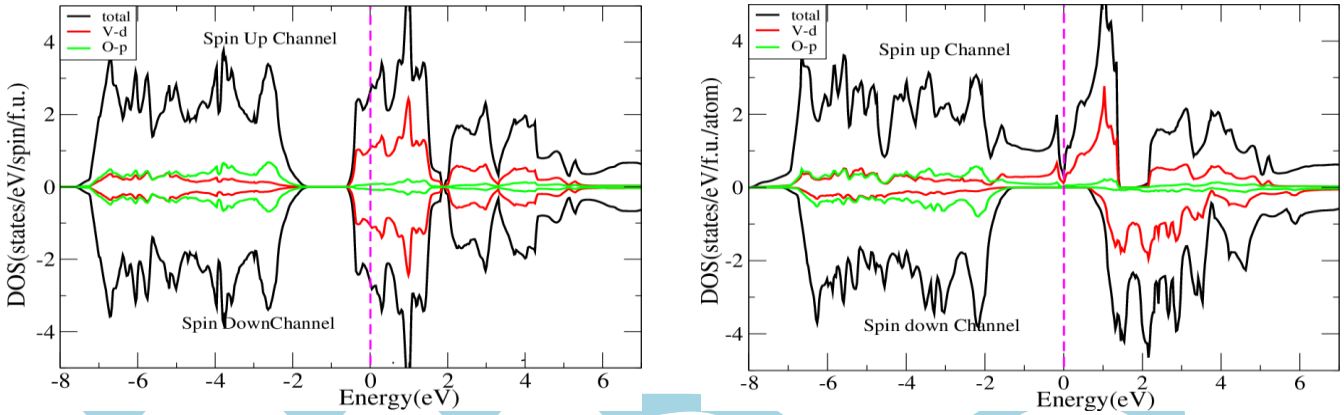
3. RESULTS AND DISCUSSION

3. 1 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 LDA calculations the rutile VO_2 is found metallic with ground state energy 4392.11431 eV. The V sites have average valence 4+ (V^{4+}) i.e. the available electron in the V-3d orbital is 1 (V-$3d^1$). The number of electrons in spin up and spin down channel were 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 up and spin down channels are presented in figure 1(a). The V-3d electrons have large contribution in the DOS. 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 each of spin up and spin down channel. The V-3d state splits into e_g doublet and t_{2g} triplet states. The t_{2g} state consists of d_{yz}, d_{xz} and d_x^2- $_y^2$ sub-bands whereas e_g state comprises d_{xy} and d_{3z}^2-$_r^2$ sub-bands. The V-t_{2g} bands are found in the energy range -0.6 eV to 1.86 eV and the 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} bands are fully occupied rather than they are partially filled causing

hybridization between them due to delocalized electrons in 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. The e_g states are practically empty and are located far above the Fermi level. The scenario remains exactly the same for both spin up and spin down channels.

Next, the DOS calculations have been performed by using 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.



(a) (b)

Figure 1: Calculated total (black), V-3d (red) and O-2p (green) densities of state (DOS) of VO_2 for LDA (a) and LDA+U (b) approximations.

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 t2g electrons. The total ground state magnetic moment calculated is -2.0μ_B. 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 figure 1(b). The V-t_{2g} DOS dominate in the energy range -1.90 eV to 1.45 eV while the e_g contribution to the DOS is observed in the energy range 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 3dt_{2g} and e_g groups of bands is observed for 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. The number of V-d electrons increases due to hybridization between the occupied V-d states and O-2p states 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 the DOS 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 states observed in the DOS calculation (see figure 1b). This hybridization between O-2p and V-3d states are responsible for observed ferromagnetic behaviour of VO_2. Further concentration is paid for the DOS 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 DOS of V-3d (red) and O-2p (green) bands at E_F are 0.89 and 2.04 states/eV/f.u./spin. Here hybridizations of

V- t_{2g} and O-2p states are not observed. The occupied O-2p states 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 0.6 eV to 8.0 eV exhibiting small $t_{2g} - e_g$ configuration mixing which implies slight distortions of the octahedra. The e_g states remains empty and far above E_F. The $d_{x^2-y^2}$ sub-bands of V-t_{2g} states are more occupied than d_{yz} and d_{xz} states.

3.2 BAND STRUCTURE CALCULATIONS

To elucidate the origin of metal to half-metal transition in the rutile VO_2 in HT phase, band structure calculations were performed. The scenario of band structure remains exactly the same in both spin channels for LDA approach. The 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} states are shifted downwards having finite contribution at E_F whereas unoccupied e_g states 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. In this case, none of the t_{2g} states are hybridized with O-2p states.

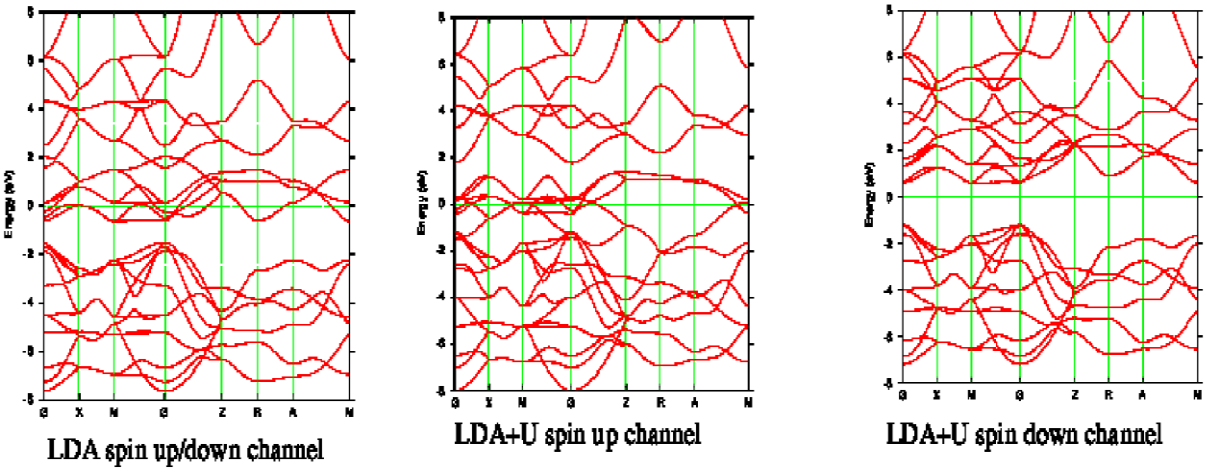


Figure 2: Band dispersion structure of VO_2 in the LDA and LDA+U calculations for spin up and spin down channels.

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 the Fermi level whereas the d_{yz} and d_{xz} states are exactly degenerate which have exactly the same occupation of electrons and the $d_{x^2-y^2}$ state has slightly higher electron filling. Hence none of the three t_{2g} states are fully filled by the single electron (d^1) and therefore the three t_{2g} states are almost degenerate resulting competition between them to be filled by the single electron (per V atom) causing 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} bands touch the Fermi level which means there is no band gap at E_F, therefore VO_2 is metallic in this case.

Further, concentration has been given for the orbital decomposed band structure calculations using U = 4eV. Here the picture is totally different for two spin

channels (see figure 3). In the spin up channel the d_{yz} and d_{xz} states remain degenerate having very small hybridizations with O-2p states. These states are found just above but 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 number of electrons in the V-d densities of states. The d_x^2-$_y^2$ state has higher contribution below the Fermi level comparing that above E_F (see figure 3). Nevertheless all of the t_{2g} states are still touching E_F. As a result 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 figure 2). The hybridizations between V-d and O-2p states imply strong anti-coupling between these states those are further responsible for ferromagnetic behaviour of VO_2. The optimization of t_{2g} states for down spin channel (figure 3) revealed that the Fermi level is suppressed downwards below the V- t_{2g} states.

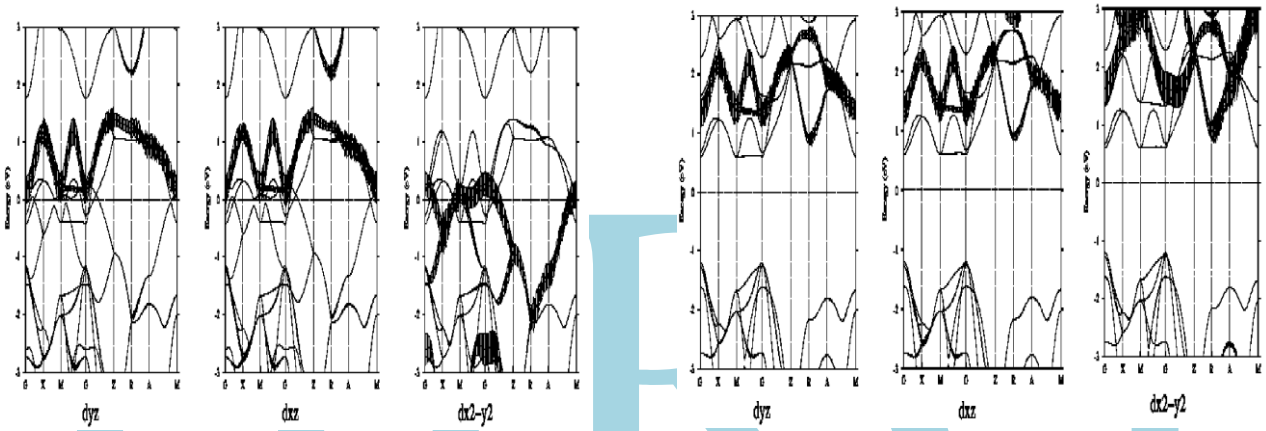


Figure 3: Partial band structure of V-t_{2g} states for spin up (1st figure) and down (2nd figure) channels in the LDA+U approximations.

As a result 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 V-d states due to the octahedral crystal field splitting resulting from the strong electron correlations. The empty e_g states are pushed well above E_F. The t_{2g} states are now separated from the Fermi level due to depression of Fermi level hence spin energy gap is observed at E_F. The hybridizations between occupied t_{2g} and O-2p states are absent here. Therefore the insulating state in the down spin channel indicates half-metallic character of VO_2.

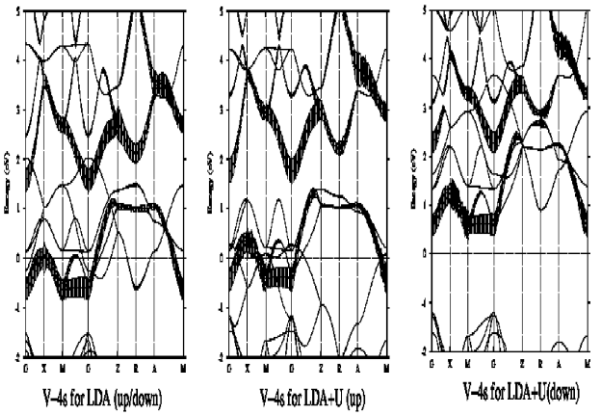


Figure4: Partial band structure of V-4s states in for LDA (1st pane) and LDA+U approximation for up/down (1st/2nd panel) spin channel.

To clarify this, the nature V-4s bands are investigated further (see figure 4). In the non polarized calculations (paramagnetic calculations) the Fermi level crosses the

V-4s bands that means contributions of both up spin and down spins are present there. In the LDA calculation the V-4s states are found near E_F which are touching E_F but having contributions both above and below E_F. In the LDA+U calculation the 4s sates are found to move upward but still touching E_F for spin up channel. For spin down channel the scenario is completely different where 4s states are uplifted from the Fermi level. Hence VO_2 exhibits metal to half-metal transition in the HT rutile structure.

4. CONCLUSION

In conclusion, it has observed that the rutile VO_2 is metallic in HT phase having non magnetic nature. In the LDA calculation the oxide is observed metallic but using Coulomb repulsion 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 do not allow opening a gap at the Fermi level. If Coulomb repulsion of U = 4 eV is applied then VO_2 encounters metal to half-metal transition due to suppression of Fermi level 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 due to the depression of Fermi level. 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 hybridization between V-3d and O-2p states causing ferromagnetic behaviour of VO_2.

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