Tight-binding based modeling to demonstrate metal-insulator transition in VO₂ within Mott-Hubbard picture

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Abstract. The mechanism of metal-insulator transition (MIT) in vanadium dioxide (VO₂) is still under debate whether it is due to the structural phase transition or electron correlations. A previous study, indicating that MIT appears far below the critical temperature of \( T_c \approx 340 \) K when a small amount of oxygen is taken out from the system, suggested that oxygen screening and electronic correlations play a dominant role in MIT of VO₂. To demonstrate how the Mott-Hubbard picture works in this mechanism, we construct a Hamiltonian with a kinetic part constructed within tight-binding scheme and an interaction part treated within the mean-field approximation for the system mimicking the situation of VO₂ without and with oxygen deficiencies. Keeping the Hubbard repulsion parameter, \( U \), unchanged, we propose that the MIT is dominantly controlled by the changes of hopping parameters and the on-site energies due to possible orbital reorientations induced by correlation effects. We calculate the projected density of states (PDOS) using Green’s function technique and demonstrate the opening/closing of the insulating gap within the Mott-Hubbard picture. Our results qualitatively reproduce the band renormalization picture inferred from the experimental data suggested by literature. In addition, we find that ferromagnetic electron spin configuration is necessary for the overall MIT scenario to work.

1. Introduction
Vanadium dioxide (VO₂) is one of transition metal oxide materials getting so much attention from researchers since Morin [1] observed the metal-insulator transition (MIT) phenomena marked with the enhancement of resistivity up to four orders of magnitude and followed by the change of crystal structure from rutile to monoclinic when the material is cooled down below its critical temperature of \( T_c \approx 340 \) K, which is close to room temperature. Because of its MIT characteristic, VO₂ becomes a very promising material to be applied as heat and chemical sensors [2–5], electronic switch and insulator [6–9], optical devices [10–15], metamaterial [16, 17] and many more. Therefore, a clear understanding about the MIT mechanism in VO₂ is needed for optimizing its application in such devices.

MIT mechanism in VO₂ is still in debatable area whether its origin comes from structural distortion as suggested by Goodenough [18] or electronic correlations as proposed by Zylbersztejn and Mott [19]. Recently, Yeo et al. [20] reported the role of oxygen in the MIT mechanism of VO₂. They performed an experiment on two well-characterized films, namely VO₂⁺δ (\( \delta = 0.16 \)), which is in oxygen excesses condition, and VO₂₋ε (\( \epsilon = 0.06 \)), which is in oxygen deficiencies condition. While the former film showed a typical MIT characteristic of VO₂, i.e. it showed a strong MIT at 336 K, the latter film showed...
an intriguing behavior. By introducing a small amount of oxygen deficiencies, the MIT now is greatly suppressed below 10 K. This is due to the interplay of screening mechanism provided by electrons in $\pi^*$ band and electronic correlations between electrons in $O^p$ and $V^d$ orbitals.

Here, we propose a tight-binding based modeling to demonstrate the MIT in VO$_2$. Using Green’s function technique, we calculate the projected density of states (PDOS) of VO$_2$ for both systems without and with oxygen deficiencies. By including the electronic correlation effects in the calculation, we are able to demonstrate the opening/closing of the insulating gap of VO$_2$ system without oxygen deficiencies around $T_c$. Surprisingly, this condition does not occur in the system with oxygen deficiencies, suggesting the suppression of MIT, which is in agreement with literature [20]. Our results successfully reproduce qualitatively the band renormalization picture inferred from the experimental data suggested by literature [20].

2. Model

Based on a physical consideration that V-V dimerization, forming the $d^\perp$ band which contributes the most to the MIT, lies on the (110) plane of tetragonal rutile structure of VO$_2$, we model our effective unit cell as shown in figure 1(b). Using that unit cell, we propose a tight-binding based Hamiltonian as

$$
H = \sum_k \eta_k^\dagger [H_0(k)] \eta_k + U \sum_i n_{i\uparrow} n_{i\downarrow}. 
$$

(1)

Here, $k$ denotes $k$-point in the Brillouin zone and $i$ is index of V sites in a unit cell. The first term of the Hamiltonian represents the kinetic part with $\eta_k$ ($\eta_k^\dagger$) being a row (column) vector whose elements are the creation (annihilation) operators associated with the basis orbitals used in the calculation. The second term describes the local Coulomb repulsive interactions between two V electrons occupying the same $d$ orbitals.

Our model consists of two vanadium atoms (V$_A$ and V$_B$), each of which contributes two $d$ orbitals, namely $d_{x^2-y^2}$ orbital which forms the $d^\perp$ band, and $d_{xy}$ orbital, which hybridizes with $O^p$ orbital forming the $\pi^*$ band, and two oxygen atoms (O$_A$ and O$_B$), each of which contributes two $p$ orbitals, namely $p_x$ and $p_y$ orbitals, forming our Hilbert space. The basis states are ordered as follows: $\{|V_A d_{x^2-y^2}\rangle, |V_A d_{xy}\rangle, |V_B d_{x^2-y^2}\rangle, |V_B d_{xy}\rangle, |V_B d_{x^2-y^2}\rangle, |V_B d_{xy}\rangle, |O_A p_x\rangle, |O_A p_y\rangle, |O_A p_x\rangle, |O_A p_y\rangle, |O_B p_x\rangle, |O_B p_y\rangle, |O_B p_x\rangle, |O_B p_y\rangle\}$. These basis states form a $16 \times 16$ $[H_0(k)]$ matrix in momentum space, constructed through tight-binding approximation, whose structure is arranged into four $8 \times 8$

Figure 1. (a) Tetragonal rutile crystal structure of VO$_2$. Blue and red spheres indicate V and O atoms, respectively. The (110) plane is marked with black dashed line. (b) Detail of the model unit cell.
blocks corresponding to their spin direction as

\[
[H_0(k)] = \begin{bmatrix}
H_0(k)^\uparrow & O \\
O & H_0(k)^\downarrow
\end{bmatrix},
\]

where \(O\) is a \(8 \times 8\)-size zero matrix, and

\[
H_0(k)^{\uparrow(\downarrow)} = \begin{bmatrix}
d_{V,n}^{\uparrow(\downarrow)} & 0 & \alpha_k & 0 & 0 & 0 & 0 & 0 \\
0 & \varepsilon_{V,n}^{\alpha} & 0 & \beta_{k\sigma} & \beta_{k\sigma}^* & \beta_{k\pi}^* & 0 & 0 \\
\alpha_k & 0 & \varepsilon_{V,n}^{\sigma} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \varepsilon_{V,n}^{\sigma} & \beta_{k\sigma}^* & \beta_{k\sigma} & \beta_{k\pi} & 0 \\
0 & \beta_{k\sigma} & 0 & \beta_{k\sigma} & \varepsilon_{O,p}^\alpha - \gamma_k & 0 & 0 & 0 \\
0 & \beta_{k\sigma}^* & 0 & \beta_{k\sigma}^* & 0 & \varepsilon_{O,p}^\alpha - \gamma_k & 0 & 0 \\
0 & \beta_{k\pi} & 0 & \beta_{k\pi} & 0 & 0 & \delta_k & 0 \\
0 & \beta_{k\pi}^* & 0 & \beta_{k\pi}^* & 0 & 0 & \delta_k & \varepsilon_{O,p}^\sigma
\end{bmatrix},
\]

where \(\alpha_k = -2t_{VV}^{\alpha} \cos(k_xa)\), \(\beta_{k\sigma} = -2t_{VO}^{\alpha} \cos(k_xc)\), \(\beta_{k\sigma} = -2t_{VO}^{\beta} \cos(k_xc)\), \(\gamma_k = -2t_{OO}^{\beta} \cos(k_xc)\), and \(\delta_k = -2t_{OO}^{\beta} \cos(k_xc)\) with \(a = 2.87\ \text{Å}\) and \(c = 2.50\ \text{Å}\). Here, \(\varepsilon\) and \(t\) indicate the on-site energy and hopping parameter, respectively, while the superscripts and subscripts indicate the corresponding band and atom, respectively.

The second term of the Hamiltonian in equation (1) is the on-site Coulomb repulsive interaction between two electrons occupying the same \(V\) \(d\) orbitals. Here, \(n_{\sigma} = d_{\sigma}^\dagger d_{\sigma}\) is the occupation number operator corresponding to the \(V\) \(d\) orbital with spin \(\sigma\) and \(U\) is the corresponding Hubbard repulsive parameter. This term is treated within mean-field approximation by replacing the actual interaction term with the mean-field approximated version, that is

\[
U \sum_i d_{\sigma i}^\dagger d_{\sigma i}^\dagger d_{\sigma i} d_{\sigma i} \approx U \sum_i \left\{\langle n_{V\sigma,i}^d \rangle \langle d_{V\sigma,i}^\dagger d_{V\sigma,i}^\dagger \rangle + \langle n_{V\sigma,i}^\dagger \rangle \langle d_{V\sigma,i}^\dagger d_{V\sigma,i}^\dagger \rangle - \langle n_{V\sigma,i}^d \rangle \langle n_{V\sigma,i}^d \rangle \right\}
+ \left\{\langle n_{V\sigma,i}^{\alpha} \rangle \langle d_{V\sigma,i}^{\alpha} \rangle \langle d_{V\sigma,i}^{\alpha} \rangle + \langle n_{V\sigma,i}^{\alpha} \rangle \langle d_{V\sigma,i}^{\alpha} \rangle \langle d_{V\sigma,i}^{\alpha} \rangle - \langle n_{V\sigma,i}^{\alpha} \rangle \langle n_{V\sigma,i}^{\alpha} \rangle \right\}
+ \left\{\langle n_{V\sigma,i}^{\beta} \rangle \langle d_{V\sigma,i}^{\beta} \rangle \langle d_{V\sigma,i}^{\beta} \rangle + \langle n_{V\sigma,i}^{\beta} \rangle \langle d_{V\sigma,i}^{\beta} \rangle \langle d_{V\sigma,i}^{\beta} \rangle - \langle n_{V\sigma,i}^{\beta} \rangle \langle n_{V\sigma,i}^{\beta} \rangle \right\}
+ \left\{\langle n_{V\sigma,i}^{\gamma} \rangle \langle d_{V\sigma,i}^{\gamma} \rangle \langle d_{V\sigma,i}^{\gamma} \rangle + \langle n_{V\sigma,i}^{\gamma} \rangle \langle d_{V\sigma,i}^{\gamma} \rangle \langle d_{V\sigma,i}^{\gamma} \rangle - \langle n_{V\sigma,i}^{\gamma} \rangle \langle n_{V\sigma,i}^{\gamma} \rangle \right\}.
\]

Here, we choose ferromagnetic electron spin configuration to demonstrate the MIT in VO\(_2\) based on the consideration that in the ferromagnetic configuration, the insulating gap formed between the lower and the upper Hubbard bands is affected not only by the averaged occupation numbers of electrons occupying the Hubbard bands and the Hubbard repulsion parameter, but also by the change of the hopping parameter of electron. In VO\(_2\), this Mott-Hubbard theory in which electronic correlations dominate is supported indirectly by the magnetic susceptibility measurements [19, 21]. Hence, we set \(\langle n_{V\sigma,i}^{\alpha} \rangle = \langle n_{V\sigma,i}^{\beta} \rangle = \langle n_{V\sigma,i}^{\gamma} \rangle \neq 0\) and \(\langle n_{V\sigma,i}^{\alpha} \rangle = \langle n_{V\sigma,i}^{\beta} \rangle = \langle n_{V\sigma,i}^{\gamma} \rangle = 0\) to be our initial guessed values and those values are to be recalculated self-consistently.

3. Method
We solve our model using Green’s function technique. First, we define our Green’s matrix as

\[
[G(k,z)] = [zI - [H_0(k)] - \Sigma]^{-1},
\]
where $z = \omega + i0^+$ is a complex frequency variable and $[I]$ is a $16 \times 16$ identity matrix. Here, $[\Sigma]$ is a local, $k$- and frequency-independent self energy matrix whose elements are all zero, except for the elements

$$
\begin{align*}
\Sigma_{1.1} &= \langle n_{V_A}^d \rangle U, & \Sigma_{9.9} &= \langle n_{V_A}^d \rangle U, \\
\Sigma_{2.2} &= \langle n_{V_B}^d \rangle U, & \Sigma_{10,10} &= \langle n_{V_B}^d \rangle U, \\
\Sigma_{3.3} &= \langle n_{V_B}^d \rangle U, & \Sigma_{11,11} &= \langle n_{V_B}^d \rangle U, \\
\Sigma_{4,4} &= \langle n_{V_B}^d \rangle U, & \Sigma_{12,12} &= \langle n_{V_B}^d \rangle U.
\end{align*}
$$

Then, we coarse-grain the Green’s function matrix over all $k$-points in the Brillouin zone as

$$
[G(z)] = \frac{1}{N} \sum_k [G(k, z)].
$$

Next, we calculate the PDOS of the $j$-th orbital as

$$
\text{PDOS}_j(\omega) = -\frac{1}{\pi} \text{Im} G_{jj}(z)
$$

Using the calculated PDOS above, we calculate the averaged occupation numbers of electron occupying $j$-th orbital as

$$
\langle n_j \rangle = \int \text{PDOS}_j(\omega) f(\mu, T, \omega) d\omega,
$$

where $\mu$ is the chemical potential of the system. Note that since all calculations are done in ground state condition, we set $T = 0$ K. Then, we compare the calculated $\langle n_j \rangle$ with the initial guessed $\langle n_j \rangle$ and repeat the calculations until $\langle n_j \rangle$ converges.

4. Results and discussion

The parameter values used in our calculations are chosen based on typical tight-binding parameter values for transition metal oxides. These values are then re-tuned to be able to demonstrate the MIT in VO$_2$ system. For the system without oxygen deficiencies at $T > T_c$, we set the parameter values as follows: $\epsilon_{V_A}^{d_{z^2}} = \epsilon_{V_B}^{d_{z^2}} = 0$ eV, $\epsilon_{V_A}^{d_{x^2-y^2}} = 0.5$ eV, $\epsilon_{Ox}^{p_x} = \epsilon_{Ox}^{p_y} = \epsilon_{Ob}^{p_x} = \epsilon_{Ob}^{p_y} = -5$ eV, $t_{VV}^{d_{z^2}} = 1$ eV, $t_{VV}^{p_{x-y}} = 0.4$ eV, $t_{OVO}^z = 0.6$ eV and $t_{OVO}^{p_{x-y}} = 0.3$ eV. Whereas, at $T < T_c$, some of the parameter values are changed due to orbital reorientations induced by correlation effects. Hence, at $T < T_c$, we change $\epsilon_{V_A}^{d_{x^2-y^2}}$, $\epsilon_{V_B}^{d_{x^2-y^2}}$, $t_{VV}^{d_{z^2}}$, $t_{OVO}^z$ and $t_{OVO}^{p_{x-y}}$ values to be 2 eV, 2 eV, 0.4 eV, 0.6 eV and 0.8 eV, respectively. For the system with oxygen deficiencies, however, the situation is slightly different. As suggested by literature [20], the electrons in $d_{z^2}-d_{z^2}$ channel become more free to conduct when there is a small amount of oxygen deficiencies introduced to the system. Based on that consideration, for the system with oxygen deficiencies at $T > T_c$, we set $t_{VV}^{d_{z^2}} = 1.2$ eV, whereas at $T < T_c$, we set $t_{VV}^{d_{z^2}} = 0.72$ eV, while the other parameter values remain unchanged. For all calculations, we keep the Hubbard repulsion parameter, $U$, unchanged at 4 eV.

Figure 2 shows our calculated PDOS of VO$_2$ system without oxygen deficiencies at (a) $T > T_c$ and (b) $T < T_c$, respectively. The energy value is defined relative to the chemical potential ($\mu$) of the system. From figure 2(a), it can be seen that at $T > T_c$, the chemical potential is located where $d_{z^2}$ and $\pi^*$ bands are overlapping, making the system be a metal. Here, electrons occupying the $\pi^*$ band provide screening effect that decreases the electronic correlations between electrons in the $d_{z^2}$ band, resulting in those electrons to hop freely between $d_{z^2}-d_{z^2}$ channel. The screening effect induced by the $\pi^*$ electrons has an important role in characterizing the metallic state of the system. At $T < T_c$, as shown in figure 2(b), the $\pi^*$ band is shifted above the chemical potential due to the structural distortion. The $\pi^*$ band is now empty, making the screening mechanism no longer possible. Hence, the unscreened electrons coming
from the O $p$ and V $d_{||}$ bands hinder the electrons in the $d_{||}-d_{||}$ channel to hop freely, making them be effectively correlated. The correlation effects between the electrons in the $d_{||}-d_{||}$ channel then split the $d_{||}$ band, resulting in an opening of the gap around the chemical potential which turns the system to be an insulator. This MIT mechanism is in agreement with Zylbersztejn and Mott’s suggestion [19].

From our calculated PDOS of VO$_2$ system with oxygen deficiencies, it can be inferred that the system at $T > T_c$ is clearly a metal, shown in figure 3(a). Intriguingly, the metallic state still can be observed even at $T < T_c$ as shown in figure 3(b), i.e. there is no splitting of $d_{||}$ band around the chemical potential, in contrast with the system without oxygen deficiencies. Here, when a small amount of oxygen is taken out from the system, some of O $p$ orbitals vanish. This causes the electrons in the $d_{||}-d_{||}$ channel now to be able to hop more freely without any distraction from O $p$ orbitals, allowing the conduction of the electrons, even though the shifting of $\pi^*$ band reduces the screening effect, suggesting the suppression of MIT. This reveals the important role of O $p$ orbital in unscreening the electrons to produce the insulating state.

**Figure 2.** Calculated PDOS of VO$_2$ system without oxygen deficiencies at (a) $T > T_c$ and (b) $T < T_c$, respectively. At $T > T_c$, the system is a metal, while at $T < T_c$, the system shows an opening of the gap and behaves as an insulator.

**Figure 3.** Calculated PDOS of VO$_2$ system with oxygen deficiencies at (a) $T > T_c$ and (b) $T < T_c$, respectively. The system is in metallic state for both $T > T_c$ and $T < T_c$ conditions.
5. Conclusions
In conclusion, we have successfully demonstrated the MIT in VO$_2$ system without oxygen deficiencies. At $T > T_c$, the screening effect induced by $\pi^*$ electrons is a key ingredient that characterizes the metallic state of the system, while at $T < T_c$, the correlation effect between the electrons in $d_{||}$ channel plays an important role in splitting the $d_{||}$ band, making the system be in insulating state. Upon introducing a small amount of oxygen deficiencies, however, the system behaves as a metal even at $T < T_c$, suggesting the suppression of MIT. This is due to the exclusion of some of O $p$ orbitals that obstruct the electrons in the $d_{||}$ channel, resulting in conduction of electrons. This highlights the role of O $p$ orbital in MIT mechanism of the system.

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