Electronic structure of tungsten-doped vanadium dioxide: from band to Mott insulator

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A common method of adjusting the metal-insulator transition temperature of $\text{M}_1\text{VO}_2$ is via disruption of the Peierls pairing by doping, or inputting stress or strain. However, since adding even small amounts of dopants will change the band structure, it is unclear how doped VO$_2$ retains its insulating character observed in experiments. While strong correlations may be responsible for maintaining a gap, theoretical evidence for this has been very difficult to obtain due to the complexity of the many-body problem involved. In this work we use GW calculations modified to include strong local $\mathbf{k}$-space interactions to investigate the changes in band structure from tungsten doping. We find that the combination of carrier doping and the experimentally observed structural defects introduced by inclusion of tungsten are consistent with a change from band insulating to Mott insulating behaviour.

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INTRODUCTION

Strongly correlated materials are an enormously active area of research as these systems exhibit many useful phenomena [1], with high temperature superconductivity being the most obvious example. However research into such compounds has suffered in comparison to devices based on weakly correlated materials due to the inapplicability of the rigid band model of electronic structure to such compounds [2, 3]. For weakly correlated materials, in which electron-electron interactions are a very small perturbation, band theoretical techniques such as Density Functional Theory (DFT) have proven to be accurate enough predictors of material behaviour to significantly facilitate device design [3]. In strongly correlated materials however, band theory fails spectacularly [2], such that even qualitative predictions are almost always inaccurate. For example, DFT characteristically predicts Mott insulators to be metallic [3, 4], a significant issue when designing materials to take advantage of their insulating behaviour.

Vanadium dioxide is considered a prototypical strongly correlated material, which undergoes a first order insulator metal transition at $\sim 340$ K from a low temperature monoclinic structure to a high temperature, metallic tetragonal structure [5]. In the last decade, advances in nanofabrication techniques have seen an explosion of interest in devices based on VO$_2$ nanobeams [6, 7], which show enormous potential for sensors [8] and even new transistor gates [9]. Dynamical Mean Field Theory [10] and GW calculations [11] suggest that pure VO$_2$ is a band insulator resulting from the three-dimensional Peierls pairings occurring in the transition from tetragonal to monoclinic, with strong correlations in the metallic form responsible for driving the transition to the insulating state [10].

However, many methods of controlling the critical temperature revolve around disrupting this Peierls pairing, such as the input of stress or strain [12], or doping [13]. Doping with tungsten has long been known to reduce $T_c$ by $\sim 23$ K per atomic percent [12]. However, when viewed through the lens of band theory, this presents something of a paradox, as doping carriers into pure VO$_2$ should result in a metallic structure. Experiments confirm however, VO$_2$ doped with < 10% tungsten remains insulating [13]. In addition, photoemission experiments reveal that tungsten assumes the place of a vanadium atom in the VO$_2$ lattice, but does not Peierls pair with neighbouring atoms [14], despite having the valence electrons to do so (unlike e.g. doping with Ti). Rather, the local environment of the tungsten is tetragonal.

Figure 1 compares the different geometries involved: Figure 1a illustrates the Peierls paired and antiferroelectrically distorted vanadium chain in the undoped compound. Figure 1b illustrates a substitutionally doped chain, in which the tungsten adopts the position of a vanadium atom. Figure 1c corresponds to the experimentally observed [13, 15] tungsten environment; the tungsten atom sits equidistant from the neighbouring vanadium atoms, and in the center of the oxygen octahedron, i.e. no Peierls pairing or antiferroelectric distortion. Given that the insulating state occurs via the vanadium atoms in the tetragonal structure forming pairs [6], disruption of this structural rearrangement as per Figure 1c, combined with the extra carriers would appear from a band theoretical view to transform tungsten-
doped VO$_2$ to a metallic structure. Unless of course the experimentally observed insulating behaviour in the doped structure arises due to strong correlations in the partially filled band.

The resolution of such a paradox from a computational perspective has been out of reach, due to the failure of \textit{ab initio} methods to reproduce Mott physics \cite{3}. Recently however, it was revealed that GW calculations can be modified to include strong local k-space correlations (the “Partially Screened GW” method or PS-GW \cite{16}), and can reproduce two significant characteristics of Mott physics: the splitting of partially filled bands into the upper and lower Hubbard bands, and the giant transfer of spectral weight upon carrier doping. The ability of this approach to reproduce these characteristics means that it is now possible to investigate systems in which the rigid band model fails, and in this work we apply it to the study of tungsten-doped VO$_2$. We find that the non-stoichiometric number of electrons results in a transition from band to Mott insulating behaviour.

**METHODS**

The M$_1$ VO$_2$ structure \cite{17} was first relaxed to the ground state using PBE-GGA \cite{18} DFT \cite{19} and the Brillouin zone integration method of Bloechl \textit{et al.} \cite{20}. 6 x 6 x 6, 4 x 6 x 6, 4 x 4 x 4 Monkhorst-Pack \cite{21} k-space grids were used for the 25 %, 12.5 % and 3.1 % structures, which were comprised of one, two and eight VO$_2$ unit cells in 1 x 1 x 1, 2 x 1 x 1, and 2 x 2 x 2 configurations respectively, with a single vanadium atom replaced with tungsten. The GW calculations were performed using the implementation of Shishkin and Kresse \cite{22, 23} as contained in the Vienna Ab Initio Simulation Package (VASP) \cite{24} after first calculating input wavefunctions using DFT with PBE \cite{18} functionals. The standard GW calculations were performed on a frequency grid of 30 points, using a cutoff energy of 200 eV. Strong correlations were included by setting the derivatives of the wavefunctions with respect to the k-point grid to zero (the PS-GW method, see Booth \textit{et al.} \cite{16}). Five self-consistency steps were used for the 12.5 % doped structures, while four and two steps were used for the 12.5 % and 3.1 % doped structures respectively, and all strongly correlated calculations were performed at a single frequency point, $\omega$=0 \cite{16}. In all calculations the Fermi level is set to zero energy.

**RESULTS AND DISCUSSION**

We investigate this problem by first examining the effect of substitutionally exchanging one vanadium atom for tungsten on the band structure and density of states (DOS) of VO$_2$, and then reduce the concentration to more experimentally accessible values. Figure 2a illustrates the results of unmodified G$_0$W$_0$ calculations on the M$_1$ structure of VO$_2$ (corresponding to the vanadium chain environment of Figure 1a). The GW band structure (black filled circles) clearly exhibits splitting of the valence and conduction bands at $E_F$ in contrast to the DFT bands (gray lines), which do split, however the gap is almost non-existent. The calculated GW gap is $\sim$ 0.70 eV, in excellent agreement with photoemission (also $\sim$ 0.70 eV) \cite{25}. Therefore, for M$_1$ VO$_2$, screening the Hartree-Fock interaction with the dielectric matrix resulting from non-interacting Green functions is sufficient to reproduce the experimental characteristics of the undoped structure.

However, Figure 2b indicates that for substitutional tungsten-doped VO$_2$ (Figure 1b) this is not the case. The red trace corresponds to the DOS of an unmodified G$_0$W$_0$ calculation of a VO$_2$ unit cell with one tungsten atom replacing one of the vanadiums. The DOS suggests that upon doping, the Fermi level shifts into the conduction band, which is dragged down slightly, reducing the gap between the original valence band and conduction band. The shift of the Fermi level results in a metallic structure, with a large number of empty states sitting at and just above $E_F$. This is directly contradicted by experimental data suggesting that tungsten-doped VO$_2$ is insulating in the monoclinic form \cite{14}.

This situation embodies the failure of the rigid band model for strongly correlated materials. Pure VO$_2$ has a filled valence band (Figure 2a). Therefore, any doped states will necessarily inhabit the conduction band. However the conduction states consist of a broad, continuous mix of bands. There are no gaps, and therefore shifting the Fermi level into it will create a metallic structure. Figure 2c illustrates the band structure corresponding to the G$_0$W$_0$ data of Figure 2b. Obviously, the “rigid” bands result in the Fermi level intersecting the conduction band minima at $\Gamma$, C, E and D. The good agreement between the G$_0$W$_0$ and DFT data of Figure 2c makes it apparent that there will be a continuum of states available above $E_F$, as the bands vary smoothly in k-space. Therefore, since pure VO$_2$ has a filled valence band, according to band theory, any amount of dopant, small or large, will result in a metallic structure due to the continuous nature of the states above $E_F$.

Given that tungsten-doped VO$_2$ is an insulator, and taking into account the existence of the Mott insulating M$_2$ structure of VO$_2$ which can be brought about by Cr doping \cite{26}, the most obvious place to look for an explanation is if the structure becomes a Mott insulator upon doping with tungsten. We can gain some idea of the plausibility of this by first transforming the doped structure into a Mott insulator, and then looking at the effects of the experimentally observed structural distortion in this context. Adding strong local k-space correlations generates the black trace of Figure 2b (PS-G$_2$W$_5$),
and the band structure of Figure 2d. Comparing the DOSs of Figure 2b reveals that strong correlations split the filled states below $E_F$ from the bulk of the conduction states, generating a broad low density region straddling the Fermi level. Comparing the band structures of Figures 2c-d indicates that this feature results from the filled conduction band minima at and around $\Gamma$, $C$, $E$ and $D$ shifting to lower energy, while the empty states are pushed upwards.

Figure 3 reveals the effect of increasing the dopant level. The DOS data of Figure 3a shows that adding another tungsten atom (black line) causes more states to cross the gap from the conduction band, adding to the small peak observed in the one atom doped structure (red line) at $\sim -1.0$ eV, revealing it to be the lower Hubbard band. Such an effect is consistent with the transfer of spectral weight expected in a Mott material [27], and observed in photoemission experiments on TiOCl [28], and in PS-GW data of CuO [16]. The band structure of Figure 3b indicates that these states again come from the conduction band minima, with more states from around the minima at $\Gamma$, $C$, $E$ and $D$ crossing the gap, and also one of the flat bands in the $A \rightarrow E$ region being filled. The magnitude of the DOS at $E_F$ is roughly unchanged by doping, and considerably smaller than the $G_0W_0$ structure (Figure 2c), suggesting that strong local correlations will result in a structure which is less metallic. However, experimentally, tungsten-doped VO$_2$ also exhibits a symmetrisation of the internuclear distances around the tungsten atom (Figure 1c). Figure 4 investigates the effect of this by comparing standard $G_0W_0$ data with a more strongly correlated PS-G$_5$W$_5$ calculation.

Figure 4a plots the DOS data of each calculation, and reveals that according to standard $G_0W_0$ calculations (red trace) the experimentally observed symmetrisation of the tungsten atom results in the original band gap closing completely, generating a metallic structure with an $\sim 3$ eV peak in the DOS straddling $E_F$. Thus, band theory suggests that rather than the structure rearranging to preserve an insulating state, it becomes even more metallic. In context this is unsurprising given that VO$_2$ is metallic above $T_c$ via the adoption of a tetragonal structure. Therefore, according to band theory, distorting the structure to reduce Peierls pairing takes the monoclinic form towards the tetragonal form, closing the gap. Including strong correlations in the ($G_5W_5\Gamma_0$) calculation however reveals very different behaviour. The original valence band and the doping-induced lower Hubbard band, corresponding to the band minima at $\Gamma$, $C$, $E$ and $D$, have been combined into a single valence band, split from the upper Hubbard band by a “gap” of $\sim 1.2$ eV.

This symmetrisation of the local environment of the tungsten dopant observed in photoemission experiments [14,15] (see Figure 1c) can be reconciled by starting from the Mott insulating ansatz. From Figures 2b-d, the most significant effect of introducing a tungsten dopant is to dope an electron into the conduction band. From figures 2a and 3a, it is apparent that undoped M$_1$ VO$_2$ already has a filled valence band, therefore doping introduces an unpaired electron into the system, creating a partially filled band. Substitutional doping of a tungsten atom into the crystal structure (as observed in photoemission) will result in an atom in one of the vanadium chains having an extra electron, therefore doping creates a partially filled band corresponding to an extra (unpaired) electron. If the tungsten atom Peierls pairs with a vanadium atom, the extra electron will interact with both electrons of the pairing, as the pairing will decrease the hopping energy by reduced the internuclear spacing, and creating potential overlap between the atoms. However if the structure symmetrises, the two valence electrons on the tungsten atom localise on it, and the single $d$-electron of the vanadium localises on the vanadium site, reducing correlations. In this respect, this symmetrisation is a classic Mott transition, increasing internuclear spacing giving rise to smaller correlations. The fact that this symmetrisation coincides with the environment observed in the high temperature tetragonal structure supports DMFT data which indicates that the metallic tetragonal structure is highly correlated [10].

However, the W$_{0.25}$V$_{0.75}$O$_2$ doped structure of Figure 4c corresponds to a dopant percentage of 25 %, which is higher than those commonly used to adjust $T_c$. The data of Figure 4a suggests that there still exist states interstitial to the Hubbard bands, and thus this structure may be a “bad metal” rather than an insulator [29]. Figure 4d explores the effect of reducing the dopant concentration from 25- through 12.5- to 3.1 % (scaled such that they integrate to the same total number of states). As the dopant percentage decreases, the density of states at $E_F$ decreases concurrently, suggesting that the structure becomes increasingly more insulating as the dopant amount tends to zero, consistent with the fact that fewer carriers are being doped into the structure. This data indicates that at dopant percentages designed to drop $T_c$ to approximately room temperature ($\sim 2$ %), tungsten doped VO$_2$ will exhibit insulating character.

**CONCLUSIONS**

In summary, by including strong correlations in GW calculations on tungsten-doped VO$_2$ it becomes evident that doping carriers into the band insulating VO$_2$ structure results in a switch to Mott insulating behaviour. The added electron inhabits the conduction band minima, and strong local correlations in k-space split these minima from the rest of the bands, while a concurrent disruption of the Peierls pairing created by the dopant atom results in them combining with the original valence band into a broad, mixed Peierls/Hubbard band. The data suggests that any modification of the pure VO$_2$ structure
which results in an increase in electron number will create a Mott insulating defect band in which the Peierls pairing is disrupted, and the structure seeks to minimise correlations by symmetrising the hopping distances around the defect. Therefore, non-stoichiometric structures of VO\(_2\) will exhibit a mixed band/Mott insulating character.

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\caption{FIG. 1: a) Undoped vanadium chain running along the monoclinic a-axis, b) substitutionally doped chain used in the calculations of Figures 2 and 3, and c) experimentally determined doped geometry used in the calculations of Figure 4.}
\end{figure}
FIG. 2: a) Left panel: $G_0W_0$ band structure of $M_1VO_2$ (black circles) and corresponding DFT bands (gray lines), Right panel: corresponding $G_0W_0$ density of states (DOS) b) DOSs of VO$_2$ doped with one tungsten atom using $G_0W_0$ (red) and PS-G$_5$W$_5$ (black), c) Left panel: $G_0W_0$ (black circles) and DFT (gray lines) band structures of tungsten doped VO$_2$, Right panel: corresponding $G_0W_0$ DOS, and d) Left panel: PS-G$_5$W$_5$ (black circles) and DFT (gray lines) band structures of tungsten doped VO$_2$, and Right panel: corresponding PS-G$_5$W$_5$ DOS.
FIG. 3: a) PS-G$_5$W$_5$ DOSs of VO$_2$ doped with one (red) and two (black) tungsten atoms, b) Left panel: PS-G$_5$W$_5$ (black circles) and DFT (gray lines) band structures of VO$_2$ doped with two tungsten atoms and Right panel: corresponding PS-G$_5$W$_5$ DOS.
FIG. 4: a) $G_0W_0$ (red) and PS-$G_5W_5$ (black) DOSs of tungsten doped VO$_2$ with internuclear symmetrisation around the dopant atom, b) Left panel: $G_0W_0$ (black circles) and DFT (gray lines) band structures of the symmetrised, doped structure, Right panel: corresponding $G_0W_0$ DOS, and c) Left panel: PS-$G_5W_5$ (black circles) and DFT (gray lines) band structures of this structure, Right panel: corresponding PS-$G_5W_5$ DOS, and d) comparison of the DOSs of VO$_2$ with dopant percentages of 25 % (red), 12.5 % (black) and 3.1 % (filled blue curve).