Cooperative Effects of Strain and Electron Correlation in Epitaxial VO$_2$ and NbO$_2$

Wei-Cheng Lee,* Matthew J. Wahila, Tyler Eustance, Christopher N. Singh, and Louis F. J. Piper  
Department of Physics, Applied Physics, and Astronomy,  
Binghamton University, Binghamton, New York, 13902, USA

Shantanu Mukherjee  
Department of Physics, Indian Institute of Technology Madras, Chennai-600036, India

H. Paik and D. G. Schlom  
Department of Materials Science and Engineering,  
Cornell University, Ithaca, New York 14853-1501, USA

Fanny Rodolakis  
Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois, 60439, USA  
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We investigate the electronic structure of the epitaxial VO$_2$ films in the rutile phase using the density functional theory combined with the slave spin method (DFT+SS). In DFT-SS, the multiorbital Hubbard interactions are added to a DFT-fit tight-binding model, and we employ the slave-spin method to treat the electron correlation. We find that while stretching the system along the rutile c-axis results in a band structure favoring an anisotropic orbital fillings, the electron correlation favors an equal electron filling among $t_{2g}$ orbitals. These two distinct effects cooperatively induce interesting orbital-dependent redistributions of the electron occupations and the spectral weights, which pushes the strained VO$_2$ toward an orbital selective Mott transition (OSMT). The simulated single-particle spectral functions are directly compared to V L-edge resonant X-ray photoemission spectroscopy of epitaxial 10 nm VO$_2$/TiO$_2$ (001) and (100) strain orientations. Excellent agreement is observed between the simulations and experimental data regarding the strain-induced evolution of the lower Hubbard band. Simulations of rutile NbO$_2$ under similar strain conditions as VO$_2$ are performed, and we predict that OSMT will not occur in rutile NbO$_2$. Our results indicates that the electron correlation in VO$_2$ is important and can be modulated even in the rutile phase before the Peierls instability sets in.

I. INTRODUCTION

Enormous efforts have been made to understand the vanadium dioxide (VO$_2$), which exhibits a metal to insulator transition (MIT) near the room temperature.\cite{1} The MIT in VO$_2$ is accompanied by the structural transition from the rutile R (metallic) to the monoclinic (insulating) M$_1$ and it is understood that both Mott (electron correlation)\cite{2,3} and Peierls (structural distortion)\cite{4} physics play essential roles in the physical properties of VO$_2$. A large number of theoretical research has been performed to investigate the electronic structures of VO$_2$ using the local density approximation (LDA), LDA + U, LDA + DMFT, quantum Monte Carlo, etc... However, the role of the electron correlation in driving the MIT is still under debates due to the fact that the insulating phase can not be disentangled from the Peierls instability.\cite{5–11}

Recent progress in strain-engineering VO$_2$ grown by molecular beam epitaxy on TiO$_2$ substrates has shed a new light on the possibility of modulating electron correlation effects by the large strains before the Peierls instability sets in.\cite{12–16} Since TiO$_2$ remains in the rutile crystal structure at all temperatures and has a c-axis lattice constant $\sim 3.8\%$ longer than that of the bulk VO$_2$, the strain can be engineered by choosing the growth direction. If the growth direction is along the rutile c-axis, denoted as VO$_2$ (001), the strain is small and the corresponding VO$_2$ thin film behaves like a bulk one.\cite{7} On the other hand, a large strain can be induced in the ultra thin epitaxial VO$_2$ grown on TiO$_2$ along directions perpendicular to the rutile c-axis, e.g., (100) and (110), due to the significant elongation of the c-axis lattice constant. Recent evidence of a strain-induced orbital selective Mott state (OMST) phase was reported from hard X-ray photoelectron spectroscopy (HAXPES) and X-ray absorption spectroscopy (XAS) experiments in epitaxial VO$_2$ (100) and (110) by\cite{14,15} The reports revealed how electron correlation can be strain-enhanced in VO$_2$ thin films but a full theoretical description of the interplay between the strain and the electron correlation remained incomplete.

In this paper, we employ the density functional theory implemented with the slave spin method (DFT+SS) to investigate the electronic structure of VO$_2$ thin film under the strain. We focus on the rutile phase and study the phase diagram as a function of doping, strain, and the correlation strength. We find that while the band structure modified by the strain-induced elongation of the c-axis tends to drive more electrons into the $d_{\parallel}$ band, the electron correlation has the opposite effect to distribute the electrons more evenly among the three $t_{2g}$
In the single band case, the transition from the metallic band interactions that describe the extra Coulomb energy $H$ structure calculation, and is the kinetic energy typically obtainable from the band non-interacting generic two-orbital system with the orbital selective Mott state. (a) The Fermi surface of a FIG. 1. Schematic illustrations of the Mott insulator and the orbital selective Mott state. (a) The Fermi surface of a non-interacting generic two-orbital system with $d_{xz}$ and $d_{yz}$. The red (black) color represents larger $d_{xz}$ ($d_{yz}$) component at these momenta. (b) At the half-filling ($n = 2$), the Fermi surface completely vanishes in the Mott insulating state. (c) In the orbital selective Mott state, only parts of the Fermi surface associated with one particular orbital vanish, exhibiting an interesting ‘Fermi arc’ profile. This can be achieved by the strain engineering even at non-integer fillings.

The interplay between these two effects results in the orbital-dependent redistributions of the electron occupations and the spectral weights, which pushes the strained VO$_2$ toward an orbital selective Mott transition (OSMT). Our theoretical models are in excellent agreement with V L-edge resonant X-ray photoemission spectroscopy of epitaxial 10 nm VO$_2$/TiO$_2$ (001) and (100) strain orientations, highlighting the evolution of the lower Hubbard band modulated by strain. We have further employed the same theoretical approach to study the rutile NbO$_2$ under the similar strain condition, and conclude that no OSMT can be tuned in this system for comparable strain regimes. Our results demonstrate that the electron correlation has significant effects on the physical properties of VO$_2$ even in the rutile phase and can be modified dramatically by the strain engineering.

II. GENERAL DISCUSSION

The Mott physics can be generally described by a Hamiltonian containing two terms: $H = H_t + H_U$. $H_t$ is the kinetic energy typically obtainable from the band structure calculation, and $H_U$ is the multiorbital Hubbard interactions that describe the extra Coulomb energy whenever two conduction electrons are on the same atom. In the single band case, the transition from the metallic to the Mott insulating states can be tuned by varying the ratio of $U/W$, where $U$ is the Hubbard on-site Coulomb energy and $W$ is the bandwidth, if the system is at the ‘half-filling’ which refers to the electron density being 1 electron per site ($n = 1$).

The physics of Mottness is even richer in a multiorbital system. The half-filling condition for the Mott insulating state becomes $n = N_0$, where $N_0$ is the number of orbitals, but there could exist new state beyond the standard Mott insulator. Let’s consider a generic two-orbital system with $d_{xz}$ and $d_{yz}$ whose typical Fermi surface is plotted in Fig. 1(a). At half-filling ($n = 2$), the Mott insulating state can occur with large enough on-site Coulomb interaction, and the Fermi surface will be completely gapped out, as shown in Fig. 1(b). As the electron density is away from the half-filling, the correlation effect becomes weaker, and it is generally expected that the Mott physics becomes much less important. However, strain engineering facilitates the OSMT mechanism explained below.

Let’s assume that $n_{xz,yz}$ and $W_{xz,yz}$ are the electron density and the bandwidth of orbitals $d_{xz}$ and $d_{yz}$. The total electron density is just $n = n_{xz} + n_{yz}$, and the correlation effect on each orbital can roughly be characterized by the ratio of $U/W_{xz,yz}$. The key part of this mechanism is that the orbital wavefunctions are highly anisotropic in real space, thus the bandwidths can be modulated quite differently in different orbitals under the same tensile strain. In this example of the two-orbital system, the $d_{xz}$ ($d_{yz}$) orbital has a much larger wavefunction overlap along the $x$ ($y$) direction. If the tensile strain is applied along the $x$ direction, the lattice constant along $x$ direction will be elongated, which reduces $W_{xz}$ more significantly than $W_{yz}$. This orbital-dependent bandwidth reduction due to the tensile strain leads to two important consequences. Firstly, it is entirely possible to put more electrons in the $d_{xz}$ orbital. Secondly, the correlation effect can be increased only in the $d_{xz}$ orbital due to the increase of the ratio of $U/W_{xz}$. As a result, even if the system is not strictly half-filled originally, the application of the strain along $x$ direction could drive the system to a state in which only the $d_{xz}$ orbital is Mott insulating ($n_{xz} \sim 1$ with larger $U/W_{xz}$) while the $d_{yz}$ orbital remains weakly-correlated ($n_{yz}$ away from 1 with smaller $U/W_{yz}$). In this new state of matters, namely the orbital selective Mott state, the Fermi surfaces will be disconnected, exhibiting an interesting ‘Fermi arc’ profile shown in Fig. 1(c).

The mechanism described above is quite general for a system with multiple orbitals near the Fermi surface together with strong local Hubbard interactions. In the following sections, we will present our theoretical study and supporting experimental data on the case of VO$_2$ thin films. We also perform the same calculations for rutile NbO$_2$ under similar strain condition. Our results show that the OSMT occurs in VO$_2$ thin films but not in NbO$_2$, which can be attributed to the fact that NbO$_2$ has much larger bandwidths in general compared to VO$_2$. 
III. THEORETICAL METHODOLOGY

We solve the Hamiltonian expressed as

\[ H = H_{TB} + H_U. \]  

(1)

\( H_{TB} \) is the tight-binding model composed of the \( d \) orbitals of the \( V \) atom as well as the \( p \) orbitals of the \( O \) atom, and the hopping parameters are determined by fitting the band structure calculated by the density functional theory (DFT) using the Wannier90.\textsuperscript{18} The DFT calculations are performed by full potential linear augmented plane waves plus local orbital (FP-LAPW+lo) and the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) provided in the WIEN2k code.\textsuperscript{19} The electron correlation is represented by the standard multiorbital Hubbard interactions \( H_U \) on the \( d \) orbitals of the \( V \) atom defined as

\[
H_U = U \sum_{i, \alpha} \hat{n}_{i\alpha\uparrow} \hat{n}_{i\alpha\downarrow} + \frac{U'}{2} \sum_{i, \alpha \neq \beta} \sum_{\sigma} \hat{n}_{i\alpha\sigma} \hat{n}_{i\beta, \bar{\sigma}} \\
+ \frac{U' - J}{2} \sum_{i, \alpha \neq \beta} \sum_{\sigma} \hat{n}_{i\alpha\sigma} \hat{n}_{i\beta, \sigma} + H_{\text{pair}} + H_{\mu_d},
\]  

(2)

where \( \alpha (\beta) \) is the orbital index referring to the five \( d \) orbitals of \( V \) atom, \( \sigma \) is the spin index, \( \bar{\sigma} = -\sigma \), \( \hat{n}_{i\alpha\sigma} = c_{i\alpha\sigma}^\dagger c_{i\alpha\sigma} \) creates an electron in the orbital \( \alpha \) with the spin \( \sigma \) at site \( i \), \( J \) is the Hund’s coupling, \( U' = U - 2J \), and \( H_{\text{pair}} \) is the pair hopping term defined as

\[
H_{\text{pair}} = -\frac{J}{2} \sum_{i, \alpha \neq \beta} \left[ c_{i\alpha\uparrow}^\dagger c_{i\alpha\downarrow} c_{i\beta\downarrow}^\dagger c_{i\beta\uparrow} + c_{i\alpha\downarrow}^\dagger c_{i\alpha\uparrow} c_{i\beta\uparrow}^\dagger c_{i\beta\downarrow} \right] + \text{h.c.}
\]  

(3)

Lastly,

\[
H_{\mu_d} = -\mu_d \sum_{i, \alpha \sigma} \hat{n}_{i\alpha\sigma},
\]  

(4)

is the chemical potential shift introduced to make \( H_U = 0 \) at the half-filling condition.\textsuperscript{20} It is easy to show that for a five orbital model, \( \mu_d^U = (9U - 20J)/4 \) if we adopt the form of the Hubbard interactions defined in Eq. \( \text{2} \). We will use the values of \( U = 6 \) eV and \( J = 1 \) eV for \( \text{VO}_2 \) and \( \text{NbO}_2 \) throughout the paper.

The slave spin method\textsuperscript{14,20–33} will be employed to treat \( H = H_{TB} + H_U \). It is worth mentioning that the slave spin formalism\textsuperscript{21,23} has been shown to capture the key features of the quasiparticle weight \( Z \rightarrow 2x/(1 + x) \), where \( x \) is the doping away from the half-filling, in the large \( U \) limit.\textsuperscript{14,23,26} We adopt the \( U(1) \) version of the slave spin method described in Ref. \[26\] and focus only on the rutile phase of \( \text{VO}_2 \) in the normal state without any spontaneous symmetry-breaking order in this study.

The strained case of \( \text{VO}_2 \) thin film grown on the TiO\textsubscript{2} substrate with the growth direction along the rutile \( a \)-axis, denoted as \( \text{VO}_2(100) \), is schematically illustrated in Fig. \text{2}.

**TABLE I.** Lattice constants of the bulk \( \text{VO}_2 \) and \( \text{VO}_2(100) \) in rutile phase

| System     | \( a_R \)   | \( b_R \)   | \( c_R \)   |
|------------|-------------|-------------|-------------|
| Bulk \( \text{VO}_2 \) | 4.554Å     | 4.554Å     | 2.851Å     |
| \( \text{VO}_2(100) \) | 4.47Å      | 4.594Å     | 2.958Å     |

Fig. \text{2}. In this case the lattice constants of \( b \)- and \( c \)-axis of the \( \text{VO}_2 \) match those of the \( \text{TiO}_2 \) substrate and the \( a \)-axis lattice constant shrinks. Table \text{I} summarizes the lattice constants used in the present study. We will make a comparison between the unstrained (bulk) \( \text{VO}_2 \) and \( \text{VO}_2(100) \) to highlight the interplay between bandstructures and electron correlations.

IV. RESULTS

A. Non-interacting limit

First of all, we present our results without \( H_U \) as a reference to highlight the effects of the strain on the band structures. We follow the local coordinate system introduced by Eyert, in which the \( t_2g \) orbitals are \( d_{x^2-r^2} (d_{||}) \), \( d_{xz} \), and \( d_{yz} \), (\( d_{z^2} \) bands), and the \( e_g \) orbitals are \( d_{3z^2-r^2} \) and \( d_{xy} \).\textsuperscript{5} Fig. \text{3}(a) summarize our results of the DOS from \( H_{TB} \) for the unstrained \( \text{VO}_2 \), which reproduces the previous DFT calculations accurately.\textsuperscript{5} One remark is that the total electron fillings in the vanadium \( d \) orbitals
and the oxygen $p$ orbitals has been found to deviate significantly from in the ionic picture that predicts the full occupation of the oxygen $p$ orbitals and 1 electron in vanadium $d$ orbitals. While the DFT calculations obtain the total electron filling in $V \, d$ and $O \, p$ orbitals per unit cell, denoted as $n_{tot}$, to be thirteen as expected, the electron filling in the vanadium $d$ orbitals ($n_d$) is significantly larger than 1 due to the strong hybridizations between $V \, d$ and $O \, p$ orbitals. Previous calculations have obtained $n_d$ ranging from 1.0 to 3.1. Since in DFT-SS we employ a tight-binding model and total electron filling can be varied freely by changing the chemical potential $\mu$, we studied the general trend in the range of $13 < n_{tot} < 14$, which covers the range of $n_d$ of the experimental interest.

Figs. 3(c) and (d) plot the electron filling in each $d$ orbital as a function of $n_{tot}$ for the unstrained VO$_2$ and VO$_2$ (100). Clearly, in both cases the electron fillings in $e_g$ orbitals remain almost the same as $n_{tot}$ increases while those in $t_{2g}$ orbitals increase significantly as $n_{tot}$ increases. This result indicates that only $t_{2g}$ orbitals are important near the Fermi energy, and consequently the correlation effects will be primarily on $t_{2g}$ orbitals.

Now we discuss the effects of the (100) strain on the band structures. Comparing Fig. 3(a) and (b), it can be seen that under the strain the bandwidth of the $d_{x^2-y^2}$ ($d_{ij}$) near the Fermi energy is significantly reduced while those of the $d_{xz}$ and $d_{yz}$ ($d_{k}$ bands) remain roughly the same. This orbital-dependent reduction of the bandwidth is one of the crucial ingredients for the occurrence

![Figure 3](image-url)

**FIG. 3.** Results of $U = J = 0$ for both unstrained (bulk) VO$_2$ and VO$_2$ (100). The density of states on $V \, d$ and $O \, p$ orbitals obtained from $H_{TB}$ are plotted for (a) unstrained VO$_2$ and (b) VO$_2$ (100), and the corresponding electron fillings in $d$ orbitals are plotted in (c) and (d) respectively. The figure legends are $d_{x^2-y^2}$ (red, circle), $d_{xz}$ (blue, square), $d_{yz}$ (yellow, up-pointing triangle), $d_{3z^2-r^2}$ (green, down-pointing triangle), $d_{xy}$ (black, diamond). The pink lines in (a) and (b) represent the DOS of the oxygen $p$ orbitals.

![Figure 4](image-url)

**FIG. 4.** The electron fillings of $d$ orbitals with $U = 6$ eV and $J = 1$ eV are calculated using the slave-spin method for (a) unstrained VO$_2$ and (b) VO$_2$ (100), and the corresponding quasiparticle weights are plotted in (c) and (d) respectively. The figure legends are the same as Fig. 3.

of the orbital selective Mott state driven by the strain.

**B. Effects of $H_U$ in unstrained VO$_2$**

Before we turn on the Hubbard interactions $H_U$, it is helpful to discuss the general effects of $H_U$. Firstly, it costs energy to put two electrons on the same site so the electron hopping is suppressed resulting in the reduction of the quasiparticle weight $Z$. Secondly, $H_U$ could produce orbital-dependent effective on-site potentials that lead to the redistribution of the orbital occupation numbers. To see why this happens, we analyze $H_U$ given in Eq. 2. If $J$ is nonzero, $U' = U - 2J < U$. This means that if two electrons are at the same site, the interaction energy will be lower for them to stay in different orbitals than in the same orbital. As a result, $H_U$ favors an equal orbital filling and this tendency is reflected in the orbital-dependent effective on-site potentials generated by $H_U$. Such an orbital-dependent on-site potential can be ignored only if the Hund’s coupling $J$ is negligible, which does not seem to be the case for VO$_2$. The slave-spin method can capture both effects from $H_U$, as demonstrated in previous works. The orbital occupation numbers and the quasiparticle weights as a function of the total electron filling $n_{tot}$ with $U = 6$ eV and $J = 1$ eV for the unstrained VO$_2$ are plotted in Figs. 4(a) and (c). It can be seen clearly that the Hubbard interactions make the electron occupations in $t_{2g}$ bands more symmetrical. Moreover, the quasiparticle weights of $t_{2g}$ bands are much smaller than those of $e_g$ bands. These observations are consistent with the discussions given above. It is also interesting to note that the correlation effects are more and more pronounced as $n_{tot}$
approaches 14. As mentioned above, since \( e_g \) bands are away from the Fermi energy, they are not affected by \( H_U \) and most extra electrons will go into \( t_{2g} \) bands. Consequently, the electron filling in \( t_{2g} \) bands increases with the \( n_{tot} \). If the electron filling in \( t_{2g} \) bands \((n_{t2g})\) approaches 3, the ‘half filling’ for a three-orbital \((t_{2g})\) model, the correlation effects in \( t_{2g} \) bands will be enhanced significantly. From Fig. 4(a), it can be seen that \( n_{t2g} \) increases from 1.88 to 2.38 as \( n_{tot} \) increases from 13 to 14, which explains the rapid reduction of the quasiparticle weights in \( t_{2g} \) bands.

C. Orbital Selective Mott State in VO\(_2\) (100)

Here, we discuss the strained case of VO\(_2\) (100) with the Hubbard interactions. As mentioned above, the strain results in an orbital-dependent reduction of the bandwidth, and turning on the interaction \( H_U \) leads to even more non-trivial effects as shown in Figs. 4(b) and (d). An intriguing difference in the behaviors of the quasiparticle weights can be seen from the comparison between the strained to the unstrained cases. As \( n_{tot} \) is fixed, the quasiparticle weights of \( d_{\alpha} \) bands remain roughly the same but that of the \( d_{\parallel} \) band decreases significantly in the strained system, which suggests that only the \( d_{\parallel} \) band is driven to be more correlated under the strain. Moreover, we also find that the electron filling in \( d_{\parallel} \) band increases while that in \( d_{\alpha} \) bands decreases in VO\(_2\) (100). These two behaviors strongly indicate that the strained VO\(_2\) is approaching an orbital selective Mott transition (OSMT), consistent with our previous reports.\(^{14,15}\)

Fig. 5 plots the differences in the electron fillings and the quasiparticle weights between VO\(_2\) (100) and the unstrained VO\(_2\). In the non-interacting limit shown in Fig. 5(a), we find that \( \Delta n \) in the \( d_{\parallel} \) (red dots) changes signs as \( n_{tot} \) increases from 13 to 14. With the interactions, it can be seen in Figs. 5(b) and (c) that \( \Delta n \) (\( \Delta Z \)) in the \( d_{\parallel} \) increases (decreases) monotonically in all the ranges of \( n_{tot} \). This observation proves that the electron correlation plays a crucial role here, and the mechanism for OSMT relies on the cooperative interplay between the strain-modulated bandstructures and the electron correlation. In VO\(_2\) (100), because \( c \)-axis is elongated due to the strain and the \( d_{\parallel} \) band has a large wavefunction overlap along \( c \)-axis, the bandwidth of the the \( d_{\parallel} \) band is significantly reduced compared to the \( d_{\alpha} \) bands. Since the correlation effect is usually characterized by the ratio of the Hubbard interaction to the bandwidth \((U/W)\), the \( d_{\parallel} \) band becomes effectively more correlated if the Hubbard interactions exist. These two effects due to the strain cooperatively induce the intriguing OSMT in VO\(_2\) (100).

D. Single particle spectral function and HAXPES

Another important feature of the Mott physics is the emergence of the incoherent spectra, known as upper and lower Hubbard bands (LHB and UHB), in the single particle spectral function.\(^{35,36}\) We adopt the formalism of the single particle Green’s function in the slave-spin method derived in Ref. [25], and the spectral function can be calculated directly by

\[
A(\omega) = \frac{-2}{V} \sum_{\vec{k}} \sum_{\alpha} \text{Im} G_{\alpha}^{ret}(\vec{k}, \omega),
\]

where \( G_{\alpha}^{ret}(\vec{k}, \omega) \) is the retarded Green’s function in orbital \( \alpha \).\(^{25}\) With the spectral function, we can simulate the photoemission (PES) and inverse photoemission (IPES) spectra by

\[
A^{PES}(\omega) = n_F(\omega)A(\omega),
A^{IPES}(\omega) = [1 - n_F(\omega)]A(\omega).
\]

\( n_F(\omega) \) is the Fermi Dirac function at room temperature \( T = 25 \text{ meV} \), which is added to reflect the fact that PES (IPES) only measures the spectral weights of occupied (unoccupied) states. Fig. 6 presents the simulated spectra for cases of unstrained and (100) samples with several different total electron filling numbers. At smaller \( n_{tot} \), the incoherent spectrum (green line) due to LHB at energy around 1 eV can be clearly seen, and it becomes more pronounced in the strained sample. This is another strong evidence of stronger correlation effects in the strained sample, consistent with the OSMT scenario. At larger \( n_{tot} \), the incoherent spectrum is pushed to more
negative energy, and both bulk and strained samples have pronounced LHB. This is not surprising since as $n_{tot}$ approaches 14, the electron filling in $t_{2g}$ orbitals approach 3, which is the 'half-filling' for a three-orbital model. In this case, the system is already close to the Mott limit even for the unstrained case. As a result, the physical properties do not change dramatically under the strain.

V. COMPARISON WITH RESONANT PHOTOEMISSION DATA OF STRAINED VO$_2$

We previously presented evidence of a strain-induced OSMT for epitaxial VO$_2$/TiO$_2$ films in the high temperature phase using a combination of HAXPES and V $L_3$-edge XAS. Evidence for the preferential orbital filling was determined from the XAS dichroism and the loss of quasiparticle weight was observed from the HAXPES. In addition, $c$ axis elongation also increased spectral weight away from the Fermi energy (i.e. at $\sim 1.5$ eV). Our simulations presented in Fig. 6 suggest that the lower Hubbard band contributes to this region and is dependent on the strain orientation. In order to interrogate these features further, we have employed resonant X-ray photoemission spectroscopy (RPES) at the V $L_3$-edge to enhance our sensitivity of the occupied V 3d orbital region. The 10 nm epitaxial films were grown by reactive molecular beam epitaxy at Cornell University, further details are provided by Paik et al.\textsuperscript{12} Fresh samples were prepared ahead of the RPES experiments at the 29-ID beamline at Argonne Photon Source on the soft X-ray ARPES endstation. The samples were measured in their respective high temperature phases (in (001) at room temperature and (100) at 398K), and energy calibrated using a combination of Au foil and reference VO$_2$ films. When at resonance, the direct recombination of the decay process emits 3d electrons when excited at the L-edge resulting in enhanced 3d contributions in the measured X-ray photoemission spectra. Eguchi \textit{et al.} previously employed V $L_3$-edge RPES to measure the insulating and metallic phases of 10 nm thin VO$_2$ (001) films, where they were able to enhance sensitivity to the quasiparticle peak and incoherent feature.\textsuperscript{37} For the VO$_2$ (001) case we reproduced V $L_3$-edge RPES to measure the insulating and metallic phases of 10 nm thin VO$_2$ (001) films, where they were able to enhance sensitivity to the quasiparticle peak and incoherent feature.\textsuperscript{37} The VO$_2$ (100) is shown to display a weaker quasiparticle peak intensity compared to the (001) case for all energies, along with a more intense incoherent peak at $\sim 1.5$ eV. These data agree with simulated spectral functions for the same strain orientations of VO$_2$ presented in Fig. 6. As a result we can assign this feature as the lower Hubbard band and con-
include that VO$_2$ can be strain-engineered as predicted by our modeling of the OSMT.

VI. STRAIN EFFECT ON NBO$_2$ IN RUTILE PHASE

As a comparison, in this section we study the strain effect on NbO$_2$ in rutile phase. NbO$_2$ undergoes a metal-to-insulator transition at a temperature around 810 °C simultaneously with the crystal structure change from the undistored rutile to a body-center tetragonal distored rutile phases.$^{38}$ Although the strain engineering on NbO$_2$ in rutile phase has not been achieved experimentally, here we investigate the change of quasiparticle weights in rutile NbO$_2$ under the same strain condition as the VO$_2$ case. For the bulk NbO$_2$, we adopt the LDA-optimized lattice parameters, $(a_R, b_R, c_R) = (4.93\,\text{Å}, 4.93\,\text{Å}, 2.94\,\text{Å})$.$^{38}$ For NbO$_2$ (100), we choose the lattice parameters of $(a'_L, b'_L, c'_L) = (4.74\,\text{Å}, 4.93\,\text{Å}, 3.016\,\text{Å})$, which is in the same strain condition of VO$_2$ (100) studied in previous sections. Fig. 8(a) and (b) plot the non-interacting DOS obtained from the DFT-fitted $H_{TB}$ for bulk and (100) respectively, and the orbital-dependent quasiparticle weights calculated from our DFT-SS method with $U = 6$ eV and $J = 1$ are plotted in (c) and (d) respectively. The figure legends are the same as Fig. 3.

![DOS plots](image)

**FIG. 8.** The non-interacting DOS of $d$ and $p$ orbitals for (a) unstrained NbO$_2$ and (b) NbO$_2$ (100) in rutile phase. The orbital-dependent quasiparticle weights with $U = 6$ eV and $J = 1$ are plotted in (c) and (d) respectively. The figure legends are the same as Fig. 3.

that NbO$_2$ has a weaker correlation and consequently is not an ideal material for modulating the Mott physics by the strain.

VII. CONCLUSION

Fig. 9 summarizes the general trends of the redistribution of electron occupations due to the interplay between strain and Hubbard interactions in the epitaxial VO$_2$/TiO$_2$ systems. Since $e_g$ bands are far away from the Fermi energy, the correlation effect will be related mainly to the $t_{2g}$ bands. We find that the stronger Hubbard interaction tends to make the electron fillings in $t_{2g}$ orbitals more even, which is a general trend for a non-zero Hund’s coupling $J$. Moreover, because most extra electrons will go into $t_{2g}$ orbitals as $n_{tot}$ increases, increasing $n_{tot}$ will push the system closer to the half-filling condition which is $n = 3$ for a three-orbital $t_{2g}$ system. This consequently enhances the correlation effect, resulting in the reduction of quasiparticle weights in the $t_{2g}$ orbitals and the emergence of the incoherent spectrum as shown in our calculations. Finally, the strain in VO$_2$ (100) causes an elongation of the rutile $c$-axis that produces a significant reduction of the bandwidth particularly on the $d_{\parallel}$ band but not on the $d_{\perp}$ bands. This orbital-dependent reduction of the bandwidth leads to an intriguing ‘orbital-selective’ Mott transition (OSMT) in which only one of the orbitals is pushed much closer to the Mott insulating state. Based on our results, we conclude that in the epitaxial VO$_2$/TiO$_2$ (100) and (110),$^{14}$ because the $c$-axis is elongated by the strain from the lattice matching with TiO$_2$, the system moves toward the OSMT, as indicated by the green arrow in Fig. 9.
In summary, we have employed the density functional theory combined with the slave spin method (DFT+SS) to study the electronic structures of the epitaxial VO$_2$ films under the strain in the rutile phase. We have found that while asymmetrical orbital occupation numbers are favored due to the band structure effects in the strained systems with an elongated c-axis, the strong electron-electron correlation drives orbital-dependent modifications of the quasiparticle weights as well as the incoherent spectra in the single particle Green’s function. The interplay between these two distinct effects pushes the epitaxial VO$_2$ films toward an orbital selective Mott transition (OSMT) in the rutile phase without a Peierls instability. Our results indicates that the Mott physics is important and can be significantly modulated even in the rutile phase of VO$_2$ by appropriate strain-engineering.

VIII. ACKNOWLEDGEMENT

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