Resolving the VO_{2} controversy: Mott mechanism dominates the insulator-to-metal transition

O. Nájera, M. Civelli, V. Dobrosavljević, and M. J. Rozenberg

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Resolving the chicken-and-egg problem in VO_2: a new paradigm for the Mott transition

O. Nájera,[1] M. Civelli,[1] V. Dobrosavljević,[2] and M. J. Rozenberg[1]

[1]*Laboratoire de Physique des Solides, CNRS-UMR8502, Université Paris-Sud, Orsay 91405, France*
[2]*Department of Physics and National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32306, USA*

We consider a minimal model to investigate the metal-insulator transition in VO_2. We adopt a Hubbard model with two orbital per unit cell, which captures the competition between Mott and singlet-dimer localization. We solve the model within Dynamical Mean Field Theory, characterizing in detail the metal-insulator transition and finding new features in the electronic states. We compare our results with available experimental data obtaining good agreement in the relevant model parameter range. Crucially, we can account for puzzling optical conductivity data obtained within the hysteresis region, which we associate to a novel metallic state characterized by a split heavy quasiparticle band. Our results show that the thermal-driven insulator-to-metal transition in VO_2 is compatible with a Mott electronic mechanism, providing fresh insight to a long standing "chicken-and-egg" debate and calling for further research of "Mottronics" applications of this system.

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Vanadium dioxide VO_2 and vanadium sesquioxide V_2O_3 remain at the center stage of condensed matter physics as they are prototypical examples of systems undergoing a strongly correlated metal-insulator transition (MIT)[1]. Their unusual electronic behavior makes them very attractive materials for novel electronic devices[2,3]. In fact, they are intensively investigated in the emerging field of "Mottronics", which aims to exploit the functionalities associated to the quantum Mott transitions. A key goal is to create fast and ultra-low power consumption transistors, which may be downsized to the atomic limit[4–6].

VO_2 and V_2O_3 have nominally partially filled bands, hence are expected to be metals. However, they undergo a first order metal to insulator transition upon cooling at $\sim$ 340K and 180K, respectively. This phenomenon has been often associated to a Mott MIT[1], namely a transition driven by the competition between kinetic energy and Coulomb repulsion[7]. Yet, that point of view has been questioned as often[1,8].

The case of VO_2, displaying a transition from a high-T rutile (R) metal to a low-T monoclinic (M_1) insulator, is emblematic[9–16]. The central issue is whether the transition is driven by a spin-Peierls structural instability, or by the electronic charge localization of the Mott-Hubbard type. This issue has been under scrutiny using electronic structure calculations[17–21] based on the combination of Density Functional Theory with Dynamical Mean Field Theory (LDA+DMFT)[22]. In the pioneering work of ref.[17], Biermann et al. argued that the insulator should be considered as a renormalized Peierls insulator. Namely, a band-insulator where the opening of the bonding-antibonding gap is driven by dimerization and renormalized down by interactions[17]. On the other hand, the calculations showed that within the metallic rutile phase, the Coulomb interaction failed to produce a MIT for reasonable values of the interaction. More recently, the problem was reconsidered by Brito et al.[19] and by Biermann et al. as well[20,23–25] providing a rather different scenario. Brito et al. found a MIT within a second monoclinic (M_2) phase of VO_2 that only has half the dimerization of the standard M_1, for the same value of the Coulomb interaction. Hence, they argued that Mott localization must play the leading role in both MITs. Nevertheless, they also noted that the Mott insulator adiabatically connects to the singlet dimer insulator state, and therefore the transition should be considered as a Mott-Hubbard in the presence of strong inter-site exchange[19,20,23].

While those LDA+DMFT works provided multiple useful insights, the issue whether the first order MIT at 340K in VO_2 is electronically or structurally driven, still remains. Here we shall try to shed new light on this classic "chicken-and-egg" problem by adopting a different strategy. We shall trade the complications of the realistic crystal structures and orbital degeneracy of VO_2 for a model Hamiltonian, the Dimer Hubbard Model (DHM), that captures the key competition between Mott localization due to Coulomb repulsion and singlet dimerization, i.e. Peierls localization. This permits a detailed systematic study that may clearly expose the physical mechanisms at play. Importantly, in our study the underlying lattice *stays put*. Therefore, we can directly address the issue whether a purely electronic transition, having a bearing on the physics of VO_2, exists in this model. The specific questions that we shall address are the following: (*i*) Does this purely electronic model predict a first order metal-insulator transition as a function of the temperature *within the relevant parameter region*? (*ii*) What is the physical nature of the different states? (*iii*) Can they be related to key available experiments? These issues are relevant, since if this basic model fails to predict an electronic MIT consistent with the one observed in VO_2, then it would be mandatory to include the lattice degrees of freedom. In the present study we shall provide explicit answers to these questions. We show that the solution of the DHM brings the equivalent physical insight for VO_2 as the single band Hubbard model for V_2O_3, which is one of the significant achievements of DMFT[26,27].

The dimer Hubbard model is defined as

$$H = [-t \sum_{\langle i,j\rangle \alpha\sigma} c^{\dagger}_{i\alpha\sigma} c_{j\alpha\sigma} + t_{\perp} \sum_{i\sigma} c^{\dagger}_{i1\sigma} c_{i2\sigma} + h.c.] + \sum_{i\alpha} U n_{i\alpha\uparrow} n_{i\alpha\downarrow} \quad (1)$$

where $\langle i,j\rangle$ denotes n.n. lattice sites, $\alpha = \{1,2\}$ denote the dimer orbitals, σ is the spin, t is the lattice hopping,

$t_\perp$ is the intra-dimer hopping, and U is the Coulomb repulsion. For simplicity, we adopt a semicircular density of states $\rho(\varepsilon) = \sqrt{4t^2-\varepsilon^2}/(2\pi t^2)$. The energy unit is set by t=1/2, which gives a full bandwidth of $4t$=$2D$=2, where D is the half-bandwidth. This interesting model has surprisingly received little attention, and only partial solutions have been obtained within DMFT[28–31]. The main results were the identification of the region of coexistent solutions at moderate U and small $t_\perp$ at T=0 using the IPT approximation[28] and at finite T=0.025 by quantum Monte Carlo[32,33] (QMC)[29]. Here we obtain the detailed solution of the problem paying special attention to the MIT and the nature of the coexistent solutions. We solve for the DMFT equations with hybridization-expansion continuous-time quantum Monte Carlo (CT-QMC)[34,35] and exact diagonalization[26], which provide (numerically) exact solutions. We also adopt the IPT approximation[28], which, remarkably, we find is (numerically) exact in the atomic limit $t = 0$, therefore provides reliable solutions of comparable quality as in the single-band Hubbard model[26]. Furthermore, IPT is extremely fast and efficient to explore the large parameter space of the model and provides accurate solutions on the real frequency axis. Extensive comparison between IPT and the CT-QMC is shown in the Supplemental Material. The DMFT equations provide for the exact solution of the DHM in the limit of large lattice coordination and have been derived elsewhere[28]. Here we quote the key self-consistency condition of the associated quantum dimer-impurity model,

$$\mathbf{G}^{-1}(i\omega_n) + \mathbf{\Sigma}(i\omega_n) = \begin{pmatrix} i\omega_n & -t_\perp \\ -t_\perp & i\omega_n \end{pmatrix} - t^2\mathbf{G}(i\omega_n), \qquad (2)$$

where $G_{\alpha,\beta}$ and $\Sigma_{\alpha,\beta}$ (with $\alpha,\beta = 1,2$) are respectively the dimer-impurity Green's function and self-energy. At the self consistent point these two quantities become the respective local quantities of the *lattice*[26]. An important point to emphasize is that this quantum dimer-impurity problem is *analogous* to that in the above mentioned LDA+DMFT studies[17,19,20,23]. Therefore, strictly speaking, our methodology is a Cluster-DMFT (CDMFT) calculation (cf Supplemental Material).

We start by establishing the detailed phase diagram, which we show in Fig. 1. We observe that at low T there is a large coexistent region at moderate U and $t_\perp$ below 0.6[28]. This region gradually shrinks as T is increased, and fully disappears at $T \approx 0.04$. The lower panel shows the phase diagram in the U-T plane at fixed $t_\perp$. At $t_\perp$=0 we recover the well known single-band Hubbard model result, where the coexistent region extends in a triangular region defined by the lines $U_{c1}(T)$ and $U_{c2}(T)$[26]. The triangle is tilted to the left, which indicates that upon warming the correlated metal undergoes a first order transition to a finite-T Mott insulator. This behavior was immediately associated to the famous 1st order MIT observed in *Cr-doped* V_2O_3[26,36], which has been long considered a prime example of a Mott Hubbard transition[1]. It is noteworthy that this physical feature has remained relevant even in recent LDA+DMFT studies, where the full complexity of the lattice and orbital degeneracy is considered[8,37]. This underlines the utility of sorting the detailed behavior of basic model Hamiltonians. Significantly, as $t_\perp$ is increased in the DHM, the tilt of the triangular region evolves towards the right. This signals

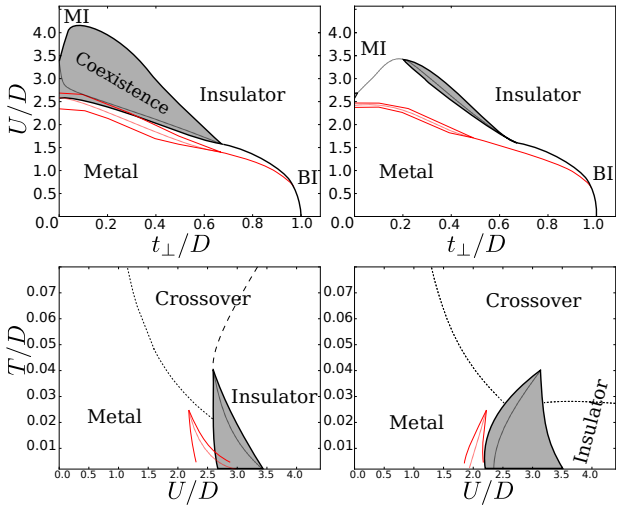

Figure 1. Phase diagram showing the coexistence (grayed) of metal and insulator states (black lines from IPT and red from QMC), where the approximate position of the 1st order lines is indicated. MI denotes Mott insulator and BI bond insulator, the crossover regions have bad metal behavior (see text and Ref.40). Top panels show $t_\perp$-U plane. Left one shows lower temperatures T=0.001 (IPT) and 1/200 (CT-QMC), and right one shows higher temperature T=0.03 (IPT) and 1/64 (CT-QMC). Lower panels show the U-T plane. Left one is for fixed $t_\perp$=0 (i.e. single-band Hubbard model), and right one for $t_\perp$=0.3 .

that $t_\perp$ fundamentally changes the stability of the groundstate. In fact, as shown in the lower right panel of Fig. 1, at $t_\perp$=0.3 we find that the MIT is *reversed* with respect to the previous case. Namely, upon warming, an insulator undergoes a 1st order transition to a (bad) correlated metal at finite-T. We may connect several features of this MIT to VO_2, both, qualitative and semi-quantitatively. We first consider the energy scales and compare the parameters of the DMH to those of electronic structure calculations. The LDA estimate of the bandwidth of the metallic state of VO_2 is $\sim$2eV[17], which corresponds in our model to $4t$, hence t=0.5eV. This is handy, since from our choice of t=0.5, we may simply read the numerical energy values of the figures directly in physical units (eV) and compare to experimental data of VO_2. We notice that the coexistence region (with a 1st order transition line) extends up to $T \approx 0.04$ (eV) $\approx$ 400K, consistent with the experimental value $\approx$ 340K. We then set the value of $t_\perp$=0.3eV, that approximately corresponds with LDA estimates for the (average) intra-dimer hopping amplitudes (cf Supplemental Material)[17,38,39]. Thus, the coexistence region is centered around $U \approx 2.5-3eV$, consistent with the values adopted in the LDA+DMFT studies[17,38].

We can make further interesting connections with experiments in VO_2. The metallic state is unusual and it can be characterized as a *bad metal*. Namely, a metal with an anomalously high scattering rate that approaches (or may violate) the Ioffe-Regel limit[41]. In Fig. 2 we show the imaginary part of the diagonal self-energy, whose y-axis intercept indicates the scattering rate (i.e. inverse scattering time). At $T \approx 0.04$ (i.e.$\sim$400K) we observe a large value of the intercept, of order $\sim$ t=1/2, which signals that the carriers are short lived

quasiparticles. In fact VO_2 has such an anomalous metallic state[12]. This anomalous scattering is likely the origin of the surprising observation that despite the fact that the lattice structure has 1D vanadium chains running along the c-axis, the resistivity is almost isotropic, within a mere factor of 2[11]. It is noteworthy that this lack of anisotropy observed in electronic transport experiments provides further justification for our simplified model of a lattice of dimers. This bad metal behavior is a hallmark of Mottness[40,42] and also indicates that the MIT in VO_2 should be characterized as a Mott transition[43]. Additional insights on the mechanism driving the transition can be obtained from the behavior of the off-diagonal (intra-dimer) self-energy $\Sigma_{12}(\omega_n)$. From Eq. (2), we observe that the intra-dimer hopping amplitude is effectively renormalized as $t_\perp{}^{eff} = t_\perp + \Re e[\Sigma_{12}](0)$. In Fig. 2 we show the behavior of this quantity across the transition. We see that in the metallic state it remains small, while it becomes large ($\gg t_\perp$) at low T in the insulator[19,20,23]. The physical interpretation is transparent. In the correlated metal, the two dimer sites are primarily Kondo screened by their lattice neighbors, as in the single band Hubbard model each one forms a heavy quasiparticle band. Then these two bands get split into a bonding and anti-bonding pair by the small $t_\perp$. Hence, the low energy electronic structure is qualitatively similar to the non-interacting one, with a larger effective mass. As T is lowered, the dramatic increase in $\Re e[\Sigma_{12}](0)$ when the Mott gap opens at the 1st order transition signals that the intra-dimer interaction is boosted by $t_\perp^{eff} \sim \Re e[\Sigma_{12}]$. Unlike the one-band Hubbard model, here the finite $t_\perp$ permits a large energy gain in the Mott insulator by quenching the degenerate entropy. This mechanism, already observed in other cluster-DMFT models[44–46], stabilizes the insulator within the coexistence region, leading to the change in the tilt seen in Fig.1. Another way of rationalizing the transition is that at a critical $U-$dependent $t_\perp$ the Kondo screening in the metal breaks down in favor of the local dimer-singlet formation in the insulator. In this view, the large gap opening may be interpreted as a $U-$driven enhanced band splitting $\propto 2t_\perp^{eff}(U)$.

Further detail is obtained from the comparison of the electronic structure of the metal and the insulator within the coexistence region[47]. In the correlated metallic state shown in Fig. 3 we find at high energies ($\sim \pm U/2$) the incoherent Hubbard bands, which are signatures of Mott physics. At lower energies, we also observe a pair of heavy quasiparticle bands crossing the Fermi energy at ω=0. Consistent with our previous discussion, this pair of quasiparticle bands can be though of as the renormalization of the non-interacting bandstructure. Significantly, as we shall discuss later on, this feature may explain the puzzling optical data of Qazilbash et al.[12] within the MIT region of VO_2, which has remained unaccounted for so far. Unlike the single-band Hubbard model, the effective mass of these metallic bands does not diverge at the MIT at the critical U, even at T=0. In fact, the finite $t_\perp$ cuts off the effective mass divergence as expected in a model that incorporates spin-fluctuations. In fact the DMH may be considered[28] the simplest non-trivial cluster DMFT model. It is interesting to note that the realistic values $U = 2.5$ and $t_\perp$ =0.3 lead to Hubbard bands at $\approx \pm 1.5$eV and a quasiparticle residue $Z \approx 0.4$,

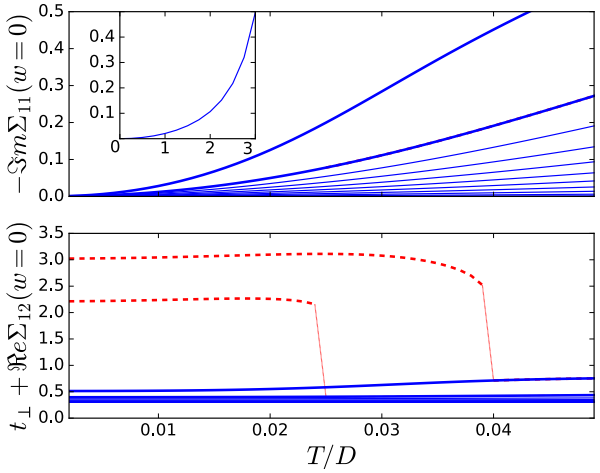

Figure 2. Top: The scattering rate Im$[\Sigma_{11}(\omega = 0)]$ for the metal (solid) at fixed $t_\perp$=0.3 values of U from 0 to 3 in steps of 0.5 (upwards). The experimentally relevant values U=2.5 and 3, are highlighted with thick lines. Inset shows the U dependence at fixed T=0.04. Bottom: The effective intra-dimer hopping $t_\perp{}^{eff}$= $t_\perp$+Re$[\Sigma_{12}](0)$ (bottom) as a function of T for the same parameters as the top panel. Metal states are in solid (blue) lines and the insulator in dashed (red) lines for U=2.5 and 3. The calculation are done with IPT.

both consistent with photoemission experiments of Koethe et al.[48].

In Fig. 3 we also show the results for insulator electronic dispersion at the same values of the parameters. The comparison of the insulator and the metal illustrate the significant changes that undergo at the 1st order MIT. We see that the metallic pair of quasiparticle bands suddenly open a large gap. More precisely, in contrast to the one-band case, here the Hubbard bands acquire a non-trivial structure, with sharp bands coexisting with incoherent ones. The coherent part dispersion can be traced to those of a lattice of singlet-dimers (see Sup. Mat.). Hence, the insulator can be characterized as a novel type of Mott-singlet state where the Hubbard bands have a mix character with both coherent and incoherent electronic-structure contributions. It is also interesting to note that the gap in the density of states is $\Delta \approx$0.6eV, again consistent with the photoemission experiments[48].

In order to gain further insight and make further contact with key experiments, we now consider the optical conductivity response $\sigma(\omega)$ within the MIT coexistence region. A set of remarkable data was obtained in this regime by Qazilbash et al.[12], bearing directly on the issue of the driving force behind the transition. They systematically investigated the $\sigma(\omega)$ as a function of T using nano-imaging spectroscopy. They clearly identified within the T range of the MIT the electronic coexistence of insulator and metallic regions, characteristic of a 1st order transition. A crucial observation was that upon warming the insulator in the M1 phase, metallic puddles emerge with a $\sigma(\omega)$ that was significantly different from the signal of the normal metallic R phase. Thus, the data provided a strong

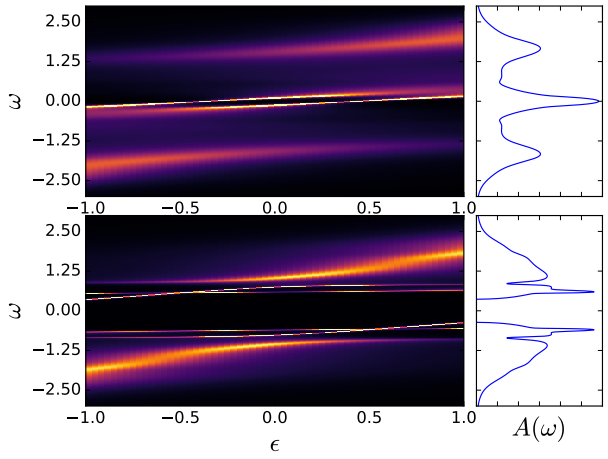

Figure 3. Electronic dispersion for the metal (left top) and insulator (left bottom) in the coexistence region for parameter values $t_\perp$=0.3, U=2.5 and T=0.01. Right panels show the respective DOS(ω). The calculations are done with IPT(cf. Sup. Mat.)

indication of a purely electronic driven transition. Regarding this point we would like to mention also the works of Arcangeletti et al.[15] and Laverock et al.[16] that reported the observation of metallic states within the monoclinic phase under pressure and strain, respectively. Coming back to the experiment of Qazilbash et al., a key point that we want to emphasize here is that $\sigma(\omega)$ in the putative M1-metallic state was characterized by a intriguing mid-infra-red (MIR) peak $\omega_{mir} \approx 1800$ cm$^{-1} = 0.22$ eV, whose origin was not understood. From our results on the electronic structure within the coexistence region, we find a natural interpretation for the puzzling MIR peak: It corresponds to excitations between the split metallic quasiparticle bands. Since they are parallel, they would produce a significant contribution to $\sigma(\omega)$, which enabled its detection. In Fig. 4 we show the calculated optical conductivity response (see Sup. Mat. section 7) that corresponds to the spectra of Fig. 3. In the metal we see that, in fact, a prominent MIR peak is present at $\omega_{mir} \approx 0.22$ eV, in excellent agreement with the experimental value. On the other hand, the optical conductivity of the insulator shows a maximum at $\omega_{ins} \approx 2$ eV in both, theory and experiment. Moreover, we also note the good agreement of the relative spectral strengths of the main features in the two phases.

In conclusion, we showed that the detailed solution of the dimer model treated within DMFT can account for a number of experimental features observed in VO_2. The minimal model has an impurity problem which is analogue to that of LDA+DMFT methods, yet the simplicity of this approach allowed for a detailed solution that permitted a transparent understanding of many physical aspects of the electronic first order transition in this problem. It exposes a dimer-Mott-transition mechanism, where the effective intra-dimer exchange is controlled by correlations, it is weakened in the metal and strongly enhanced in the Mott insulator. In the metal, this leads to a pair of split quasiparticle bands, which then in the insulator further separate, to join and coexist with

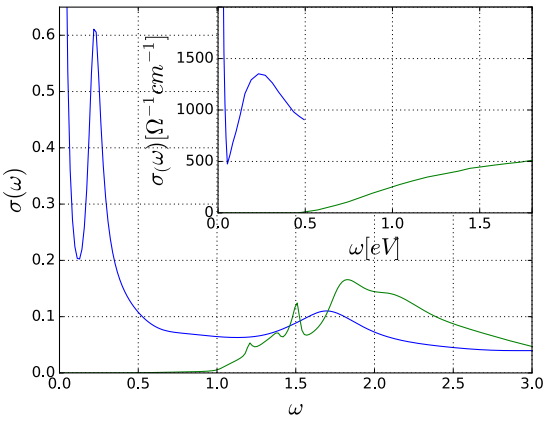

Figure 4. The optical conductivity $\sigma(\omega)$ of metal and insulator within the coexistence region for parameters $t_\perp$=0.3, U=2.5 and T=0.01. The calculations are done with IPT. Inset: The experimental optical conductivity adapted from Ref. 12.

the usual incoherent Hubbard bands. Despite the simplicity of our model, we made semi-quantitative connections to several experimental data in VO_2, including a crucial optical conductivity study within the 1st order transition, that remained unaccounted for. Our work, sheds light on the long-standing question of the driving force behind the metal-insulator transition of VO_2 highlighting the relevance of the Mott mechanism. The present approach may be considered the counterpart for VO_2, of the DMFT studies of the Mott transition in paramagnetic Cr-doped V_2O_3.

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